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Nuclear Fuels – III. Raw Materials

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EXPLANATORY NOTE

The Proceedings of the Third International Conference on the Peaceful Uses of Atomic Energy comprise a single, multilingual publication of sixteen volumes. This form was prescribed by the General Assembly of the United Nations in approving the Conference budget.

Papers accepted for consideration at the Conference are accordingly printed herein only in the original language of submission, each being followed by its abstract in the other three languages of the Conference.*

The budgetary arrangements for the Conference required also that Governments provide abstracts and papers in two of the Conference languages. One of the three abstracts following each paper is, therefore, in a translation provided by the Government concerned. The abstracts were translated into the other two languages either by the Division of Language Services, International Atomic Energy Agency (IAEA) in Vienna, or, with its assistance, through the intermediary of the national atomic energy authorities in London, Paris, Moscow and Madrid.

The Foreword by the Secretary-General of the United Nations, the Preface by the Director General of IAEA, and this Explanatory Note, together with the records of discussion at each of the six scientific general sessions and thirty-six technical sessions of the Conference, are published in all four languages. All other material, which is largely of a formal nature and is confined to Volumes 1 and 16, is published in the language of submission or delivery, followed in the case of French, Russian and Spanish originals by the English translation.

Governments whose national tongue is not one of the four Conference languages were consulted as to their preference for the language in which their papers should appear in these Proceedings.

The Table of Contents in each volume gives the titles of papers in the original language, or language of choice, followed in the case of French, Russian and Spanish titles by the English translation.

Starting from the 992 abstracts submitted by Governments, specialized agencies and IAEA, the Scientific Secretariat, working under the guidance of the United Nations Scientific Advisory Committee, finally chose 747 papers for inclusion in the Programme of the Conference; of these, 358 were selected for oral presentation at the 42 working sessions.

In arranging the programme, the Scientific Secretariat aimed at achieving a balanced schedule, providing for the oral presentation of as many papers as possible at each session while still leaving adequate time for discussion of the material presented. Two afternoons were left entirely free, to enable informal groups to discuss matters arising out of discussions at the formal sessions of the Conference. No records were taken of such informal meetings.

Wherever possible, the author, or authors, of papers were consulted during the Conference by members of the Scientific Secretariat, who acted as secretaries of session, or by the team of editors made available for the purpose by IAEA,** to ensure maximum accuracy.

The records of discussion at the various sessions, based on notes taken in the meetings by IAEA records officers,** and checked where necessary against the sound recordings made of all sessions, were prepared by the Division of Language Services of IAEA in English, and subsequently translated into French, Russian and Spanish through the intermediary of the atomic energy authorities in the three countries concerned (see third paragraph of the present note).

The editing of the English, French and Spanish papers was carried out at the United Nations Office at Geneva under United Nations supervision by a team of editors, whose services, also, were made available by the atomic energy authorities of their respective countries, with some help from outside consultants. The editing of the Russian papers was done in Moscow in similar circumstances. The following served as editors: Mr. A. de Calmès, Dr. C. E. Granados, Mr. D. H. Hill, Mr. V. F. Kalinin, Cand. Tech. Sc., Dr. R. Lapage, Mr. E. T. Marles, Dr. J. D. C. Mole, Mr. C. Ségot, Mr. J. J. Stobbs, Mr. C. R. Symons and Mr. J. Williamson.

The task of printing this large collection of scientific information has been shared by printers in

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* The languages of the Conference were English, French, Russian and Spanish.

** The names of the scientific secretaries, editors and records officers will be found in the list of the Conference Secretariat in Annex 1, Volume 1, of this series.

Belgium, Canada, France, Switzerland, the Union of Soviet Socialist Republics and the United Kingdom.

Full titles of the sixteen volumes of these Proceedings, together with the sessions covered by each volume, are as follows:

Volume No.		*Sessions included*
1	Progress in Atomic Energy	A, B, 1.6, C, H
2	Reactor Physics	3.1
3	Reactor Studies and Performance	3.2, 3.3
4	Reactor Control	3.4, 3.5
5	Nuclear Reactors — I. Gas-cooled and Water-cooled Reactors	1.1, 1.2, 1.3
6	Nuclear Reactors — II. Fast Reactors and Advanced Concepts	1.4, 1.5, 1.7
7	Research and Testing Reactors	D, 1.9, 1.8
8	Reactor Engineering and Equipment	1.10, 1.11, 3.7
9	Reactor Materials	2.8, 2.9, 2.4
10	Nuclear Fuels — I. Fabrication and Reprocessing	2.3, 2.6, 2.7
11	Nuclear Fuels — II. Types and Economics	2.5, 2.1, 2.2
12	Nuclear Fuels — III. Raw Materials	2.11, 2.12, 2.10
13	Nuclear Safety	3.9, 3.8 3.6
14	Environmental Aspects of Atomic Energy and Waste Management	3.10, 3.11
15	Special Aspects of Nuclear Energy and Isotope Applications	E, 4.1, F, G, 4.2
16	List of Papers and Indexes	

NOTE EXPLICATIVE

Les Actes de la troisième Conférence internationale sur l'utilisation de l'énergie atomique à des fins pacifiques sont publiés ici sous la forme d'une édition unique, multilingue, en seize volumes. Cette présentation a été décidée par l'Assemblée générale lorsqu'elle a approuvé le budget de la Conférence.

En conséquence, les mémoires qui ont été acceptés pour la Conférence sont reproduits ici dans la langue originale dans laquelle ils ont été soumis et sont suivis d'un résumé dans les trois autres langues de la Conférence *.

Aux termes des dispositions budgétaires prises en vue de la Conférence, les gouvernements devaient fournir les résumés et les mémoires dans deux des langues de la Conférence. Ainsi, sur les trois résumés qui suivent chaque mémoire, un est une traduction fournie par le gouvernement intéressé. La traduction des résumés dans les deux autres langues a été faite soit par la Division des services linguistiques de l'Agence internationale de l'énergie atomique (AIEA), à Vienne, soit avec son concours, par les soins des organismes nationaux compétents en matière d'énergie atomique à Londres, Paris, Moscou et Madrid.

L'avant-propos du Secrétaire général de l'Organisation des Nations Unies, la préface du Directeur général de l'AIEA et la présente note explicative, ainsi que les comptes rendus de chacune des six séances scientifiques générales et des trente-six séances techniques de la Conférence, sont publiés dans les quatre langues. Tous les autres textes, qui pour la plupart sont d'un caractère non technique et figurent dans les volumes 1 et 16, sont publiés dans la langue dans laquelle ils ont été présentés par écrit ou oralement et sont suivis, lorsque cette langue est l'espagnol, le français ou le russe, d'une traduction en anglais.

Les gouvernements des pays dont la langue officielle n'est pas l'une des quatre langues utilisées à la Conférence ont été consultés pour savoir dans quelle langue ils préféraient voir paraître leurs mémoires.

La table des matières de chaque volume donne les titres des mémoires dans la langue originale ou dans la langue choisie; ces indications sont suivies, pour les titres en espagnol, en français et en russe, de la traduction en anglais.

Sur les 992 résumés présentés par les gouvernements, les institutions spécialisées et l'AIEA, le Secrétariat scientifique, travaillant sous la direction du Comité consultatif scientifique des Nations Unies, en a finalement retenu 747 pour les inscrire au programme de la Conférence; sur ce nombre, 358 ont été présentés oralement aux 42 séances de travail.

En établissant le programme de la Conférence, le Secrétariat scientifique a cherché à réaliser un équilibre: il s'est efforcé de ménager un temps suffisant pour la présentation du plus grand nombre possible de mémoires tout en laissant du temps pour leur discussion. Deux après-midi avaient été laissés entièrement libres afin de permettre aux participants d'organiser des réunions non officielles et de discuter en petits groupes des questions qui se posaient à la suite des séances officielles de la Conférence. Ces réunions n'ont pas fait l'objet de comptes rendus.

Toutes les fois que cela a été possible, l'auteur ou les auteurs des mémoires ont été consultés pendant la Conférence par les membres du Secrétariat scientifique, qui ont assuré le secrétariat des séances, ou par l'équipe d'« éditeurs » que l'AIEA ** avait mis à cet effet à la disposition de la Conférence, afin d'assurer l'exactitude la plus grande.

Les comptes rendus des discussions aux réunions, établis d'après les notes prises en séance par les rédacteurs de comptes rendus de l'AIEA** et comparés toutes les fois qu'il le fallait avec les enregistrements sonores, ont été rédigés en anglais par la Division des services linguistiques de l'AIEA, puis traduits en espagnol, en français et en russe par les soins des organismes compétents en matière d'énergie atomique des trois pays intéressés (voir le troisième alinéa de la présente note).

Les mémoires rédigés en anglais, en espagnol et en français ont été mis au point pour l'impression à l'Office européen des Nations Unies à Genève, sous le contrôle de l'ONU, par une équipe de rédac-

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* Les langues de la Conférence étaient l'anglais, l'espagnol, le français et le russe.

** On trouvera les noms des secrétaires scientifiques, des « éditeurs » et des rédacteurs de comptes rendus dans la liste des membres du secrétariat de la Conférence à l'annexe 1 du volume 1.

teurs mis à la disposition de la Conférence par les organismes compétents en matière d'énergie atomiques des pays intéressés, avec l'aide de quelques consultants extérieurs. La mise au point définitive des mémoires rédigés en russe a été faite à Moscou dans les mêmes conditions. Voici les noms des rédacteurs qui ont assuré la mise au point des mémoires: M. A. de Calmès, M. C. E. Granados, M. D. H. Hill, M. V. F. Kalinin, Mlle R. Lapage, M. E. T. Marles, Mlle J. D. C. Mole, M. C. Ségot, M. J. J. Stobbs, M. C. R. Symons et M. J. Williamson.

Des entreprises de Belgique, du Canada, de France, du Royaume-Uni, de Suisse et de l'Union des Républiques socialistes soviétiques se sont partagé la tâche que représentait l'impression de cette masse importante de documents scientifiques.

Les titres complets des seize volumes des Actes de la Conférence, ainsi que les numéros des séances sur lesquelles porte chaque volume, figurent ci-après:

Numéro du volume		*Séances*
1	Progrès accomplis dans le domaine atomique	A, B, 1.6, C, H
2	Physique des réacteurs	3.1
3	Etude des réseaux et performance des réacteurs	3.2, 3.3
4	Contrôle des réacteurs..	3.4, 3.5
5	Réacteurs nucléaires — I. Réacteurs refroidis par un gaz et réacteurs refroidis à l'eau	1.1, 1.2, 1.3
6	Réacteurs nucléaires — II. Réacteurs à neutrons rapides et réacteurs d'avant-garde	1.4, 1.5, 1.7
7	Réacteurs de recherche et réacteurs d'essai de matériaux..................	D, 1.9, 1.8
8	Technologie et équipement des réacteurs	1.10, 1.11, 3.7
9	Matériaux pour réacteurs	2.8, 2.9, 2.4
10	Combustibles nucléaires — I. Fabrication et retraitement	2.3, 2.6, 2.7
11	Combustibles nucléaires — II. Caractéristiques et aspects économiques	2.5, 2.1, 2.2
12	Combustibles nucléaires — III. Matières premières	2.11, 2.12, 2.10
13	Sûreté nucléaire	3.9, 3.8, 3.6
14	Influence sur le milieu de l'emploi de l'énergie nucléaire. Traitement et élimination des déchets	3.10, 3.11
15	Aspects particuliers de l'énergie nucléaire et applications des radioéléments..	E, 4.1, F, G, 4.2
16	Liste des mémoires et index	

ПОЯСНИТЕЛЬНАЯ ЗАПИСКА

Труды третьей Международной конференции по использованию атомной энергии в мирных целях представляют собой единое многоязычное издание из шестнадцати томов. Такая форма была предусмотрена Генеральной Ассамблеей Организации Объединенных Наций при одобрении ею бюджета Конференции.

Принятые к рассмотрению Конференцией доклады соответственно опубликованы здесь лишь на языке оригинала; при этом каждый доклад сопровождается аннотацией на других трех языках Конференции*.

Бюджетные постановления в отношении проведения Конференции также предусматривали, что правительства представят аннотации и доклады на двух языках Конференции. Поэтому одна из трех аннотаций, сопровождающих каждый доклад, является переводом, представленным соответствующим правительством. Аннотации были переведены на другие два языка либо Отделом переводов Международного агентства по атомной энергии (МАГАТЭ) в Вене, либо с его помощью при сотрудничестве национальных органов, ведающих вопросами атомной энергии, в Лондоне, Париже, Москве и Мадриде.

Введение и предисловие Генерального Секретаря Организации Объединенных Наций и Генерального директора МАГАТЭ, соответственно, и настоящая пояснительная записка, наряду с протоколами каждого из шести научных пленарных заседаний и тридцати шести секционных заседаний Конференции, публикуются на всех четырех языках. Все другие материалы, которые по своему характеру в основном относятся к числу официальных и содержатся в томах 1 и 16, публикуются на языке оригинала; и когда речь идет о французских, русских и испанских оригиналах, то к ним приложен английский перевод.

С правительствами стран, язык которых не относится к числу четырех языков Конференции, были проведены консультации по поводу того, на каком языке было бы желательно, по их мнению, опубликовать в настоящих трудах представленные ими доклады.

В содержании каждого тома указаны заглавия докладов на языке оригинала либо на другом избранном языке, и в том случае, когда речь идет о французских, русских и испанских заглавиях, их сопровождает английский перевод.

Из 992 аннотаций, представленных правительствами, специализированными учреждениями, а также МАГАТЭ, Ученый секретариат, работая под руководством Научного консультативного комитета Организации Объединенных Наций, в итоге отобрал 747 докладов для включения их в программу Конференции; из них 358 были отобраны для представления в устной форме на 42 рабочих заседаниях.

При составлении программы Ученый секретариат ставил целью добиться сбалансированного расписания, которое дало бы возможность представить в устной форме максимальное количество докладов на каждом заседании при обеспечении достаточного времени для проведения дискуссии по поводу представленного материала. В двух случаях имеющееся во второй половине дня время оставили нераспределенным, с тем чтобы дать возможность неофициальным группам обсудить вопросы, возникшие в ходе дискуссии на официальных заседаниях Конференции. На таких неофициальных заседаниях протоколы не составлялись.

По мере возможности, с автором или авторами докладов консультировались в ходе Конференции члены Ученого секретариата, которые выполняли функции секретарей заседаний, либо такие консультации проводились группой редакторов, которые были выделены МАГАТЭ** для этой цели, с тем чтобы обеспечить максимальную точность.

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* Языками Конференции являлись: английский, французский, русский и испанский.

** Фамилии ученых секретарей, редакторов и протоколистов приведены в перечне сотрудников секретариата Конференции в приложении 1-ом к тому 1-му настоящей серии.

Протоколы дискуссии на различных заседаниях, составленные на основе записей, сделанных в ходе заседаний протоколистами МАГАТЭ*, и проверенные, по мере необходимости, путем сравнения со звуковой записью, которая велась на всех заседаниях, были подготовлены Отделом переводов МАГАТЭ на английском языке и впоследствии переведены на французский, русский и испанский языки при сотрудничестве национальных органов, ведающих вопросами атомной энергии, в трех заинтересованных странах (смотри третий абзац пояснительной записки).

Работа по редактированию документов на английском, французском и испанском языках была проведена в Европейском отделении Организации Объединенных Наций, в Женеве, под руководством Организации Объединенных Наций группой редакторов, услуги которых были также предоставлены по линии органов, ведающих вопросами атомной энергии в соответствующих странах, с использованием в некоторой степени помощи приглашенных со стороны консультантов. Русские документы редактировались в Москве в таких же условиях. Нижеследующие лица осуществляли работу в качестве редакторов: д-р К. Э. Гранадос, кандидат технических наук В. Ф. Калинин, г-н А. де Кальмэс, д-р Р. Лепейдж, г-н Э. Т. Марлз, д-р Дж. Д. К. Моул, г-н Ч. Р. Саймонс, г-н Дж. Дж. Стобз, г-н Ш. Сэго, г-н Дж. Уильямсон, г-н Д. Х. Хилл.

В выполнении задачи по печатанию этой обширной научной информации принимали участие типографии в Бельгии, Канаде, Соединенном Королевстве, Союзе Советских Социалистических Республик, Франции и Швейцарии.

Ниже приводятся полные заглавия шестнадцати томов настоящих Трудов, а также указывается, какие сессии охватываются каждым томом:

Номер Тома		Заседания, включенные в том
1	Прогресс в работах по атомной энергии	A, B, 1.6, C, H
2	Физика реакторов	3.1
3	Изучение реакторов и их характеристики	3.2, 3.3
4	Регулирование реакторов	3.4, 3.5
5	Ядерные реакторы — I. Реакторы с водяным и газовым охлаждением	1.1, 1.2, 1.3
6	Ядерные реакторы — II. Реакторы на быстрых нейтронах и усовершенствованные реакторы	1.4, 1.5, 1.7
7	Исследовательские и испытательные реакторы	D, 1.9, 1.8
8	Технология и оборудование реакторов	1.10, 1.11. 3.7
9	Реакторные материалы	2.8, 2.9, 2.4
10	Ядерное топливо — I. Изготовление и переработка	2.3, 2.6, 2.7
11	Ядерное топливо — II. Типы и экономика	2.5, 2.1, 2.2
12	Ядерное топливо — III. Сырьевые материалы	2.11, 2.12, 2.10
13	Ядерная безопасность	3.9, 3.8, 3.6
14	Исследование окружающей среды и удаление радиоактивных отходов	3.10, 3.11
15	Специальные аспекты применения ядерной энергии и изотопов	E, 4.1, F, G, 4.2
16	Список докладов и указатели	

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* Фамилии ученых секретарей, редакторов и протоколистов приведены в перечне сотрудников секретариата Конференции в приложении 1-ом к тому 1-му настоящей серии.

NOTA EXPLICATIVA

Las Actas de la tercera Conferencia Internacional sobre la Utilización de la Energía Atómica con Fines Pacíficos están constituidas por una publicación única y plurilingüe compuesta de dieciséis volúmenes, en conformidad con lo dispuesto por la Asamblea General de las Naciones Unidas al aprobar el presupuesto de la Conferencia.

Por consiguiente, las memorias aceptadas para ser examinadas en la Conferencia sólo figuran impresas en el idioma original en que se presentaron, y cada una de ellas va seguida de un resumen de la misma en los otros tres idiomas de la Conferencia *.

En los arreglos presupuestarios para la Conferencia se dispuso también que los gobiernos tenían asimismo que presentar resúmenes y memorias en dos de los idiomas de la Conferencia. En consecuencia, uno de los tres resúmenes que siguen a cada memoria es una traducción facilitada por el gobierno interesado. Los resúmenes fueron traducidos a los otros dos idiomas, ya por la División de Idiomas del Organismo Internacional de Energía Atómica (OIEA) de Viena, o, con su asistencia, por conducto de las autoridades nacionales de energía atómica de Londres, París, Moscú y Madrid.

La introducción del Secretario General de las Naciones Unidas, el prefacio del Director General del OIEA y la presente nota explicativa, junto con las actas de los debates celebrados en cada una de las seis sesiones científicas generales y las treinta y seis sesiones técnicas de la Conferencia, se publican en los cuatro idiomas. El resto del material, que reviste en su mayoría un carácter oficial y está contenido exclusivamente en los volúmenes 1 y 16, se publica en el idioma en que fue presentado o entregado, seguido para los originales en español, francés y ruso, de la traducción en inglés.

Se consultó a los gobiernos cuyo idioma nacional no es uno de los cuatro idiomas de la Conferencia para saber en cuál de ellos preferían que se publicaran sus memorias en estas Actas.

El índice de cada volumen contiene los títulos de las memorias en el idioma original, o en el idioma elegido, seguidos, cuando se trata de títulos en español, francés y ruso, de la traducción en inglés.

De los 992 resúmenes presentados por gobiernos, organismos especializados y el OIEA, la Secretaría Científica, bajo la dirección del Comité Científico Consultivo de las Naciones Unidas, escogió por último 747 memorias que debían ser incluidas en el programa de la Conferencia; de éstas, 358 fueron seleccionadas para ser presentadas oralmente en las 42 sesiones de trabajo.

Al preparar el programa de actividades, la Secretaría Científica trató de conseguir un justo equilibrio, y así se previó la presentación oral del mayor número posible de memorias en cada sesión, pero dejando todavía tiempo suficiente para examinar la información presentada. Se dejaron dos tardes totalmente libres, a fin de que los grupos oficiosos pudieran examinar las cuestiones que surgieran en las sesiones oficiales de la Conferencia. No se levantó acta de tales reuniones.

Siempre que fue posible, el autor, o los autores, de las memorias fueron consultados en el curso de la Conferencia por miembros de la Secretaría Científica, que actuaron de secretarios de sesión, o por un grupo de editores facilitado a dicho efecto por el OIEA**, a fin de asegurar la máxima exactitud.

Las actas de los debates celebrados en las diversas sesiones, basadas en notas tomadas en las reuniones por redactores de actas del OIEA**, y verificadas siempre que fue necesario mediante las grabaciones efectuadas en todas las sesiones, fueron preparadas por la División de Idiomas del Organismo Internacional de Energía Atómica (OIEA) en inglés, y traducidas después al español, el francés y el ruso por conducto de las autoridades de energía atómica de los tres países interesados (véase el tercer párrafo de la presente nota).

La preparación para la publicación del texto de los documentos en español, francés e inglés se efectuó en la Oficina de Ginebra de las Naciones Unidas, bajo la fiscalización de las Naciones Unidas, por un equipo de editores cuyos servicios fueron también proporcionados por las autoridades de energía atómica de sus respectivos países, con alguna ayuda de consultores del exterior. La preparación para la publicación de los documentos en ruso se efectuó en Moscú en circunstancias análogas. Actuaron de editores las personas siguientes: Sr. A. de Calmès, Dr. C. E. Granados, Sr. D. H. Hill,

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* Los idiomas de la Conferencia fueron el español, el francés, el inglés y el ruso.

** Los nombres de los secretarios científicos, editores y redactores de actas figuran en la lista de la Secretaría de la Conferencia, en el anexo 1, volumen 1, de esta serie.

Sr. V. F. Kalinin, Dra. R. Lapage, Sr. E. T. Marles, Dra. J. D. C. Mole, Sr. C. Ségot, Sr. J. J. Stobbs, Sr. C. R. Symons y Sr. J. Williamson.

En la impresión de esta gran recopilación de información científica han participado impresores de Bélgica, el Canadá, Francia, el Reino Unido, Suiza y la Unión de Repúblicas Socialistas Soviéticas.

Los títulos completos de los dieciséis volúmenes de estas Actas, junto con las sesiones comprendidas en cada volumen, son los siguientes:

Número del volumen		*Sesiones*
1	Progresos realizados en el dominio atómico	A, B, 1.6, C, H
2	Física de los reactores	3.1
3	Estudios sobre reticulados. Funcionamiento de reactores	3.2, 3.3
4	Control de los reactores	3.4, 3.5
5	Reactores nucleares — I. Reactores refrigerados por gas y por agua	1.1, 1.2, 1.3
6	Reactores nucleares — II. Reactores rápidos y conceptos más avanzados	1.4, 1.5, 1.7
7	Reactores de investigación y de ensayo	D, 1.9, 1.8
8	Tecnología y equipo de los reactores	1.10, 1.11, 3.7
9	Materiales de los reactores	2.8, 2.9, 2.4
10	Combustibles nucleares — I. Fabricación y tratamiento	2.3, 2.6, 2.7
11	Combustibles nucleares — II. Características y estudios económicos	2.5, 2.1, 2.2
12	Combustibles nucleares — III. Primeras materias	2.11, 2.12, 2.10
13	Seguridad nuclear	3.9, 3.8, 3.6
14	Influencia del empleo de la energía nuclear sobre el ambiente. Evacuación de residuos	3.10, 3.11
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Session 2.11

URANIUM AND THORIUM RESOURCES AND REQUIREMENTS

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Pourquoi continuer à chercher de l'uranium

par J. Mabile et A. Gangloff*

Parmi les puissances atomiques dont les programmes sont connus, la France est probablement la seule à soutenir un important programme de prospection de l'uranium. Cependant, le phénomène de surproduction qui a atteint tous les producteurs mondiaux ne l'épargne pas.

Il semble intéressant d'analyser les raisons qui justifient, de notre point de vue, cette persistance dans la recherche et de tirer de cet examen quelques conclusions valables pour le développement à très long terme de l'énergie atomique, considérée essentiellement sous l'angle de la production de l'électricité.

RAPPEL DE LA SITUATION DE L'APPROVISIONNEMENT FRANÇAIS

Actuellement, le programme français est alimenté en uranium pour les trois quarts par les mines de la métropole, et pour un quart par des achats à l'étranger : Madagascar et Gabon.

Il n'y a pas eu de modifications importantes apportées à l'outil de production tel qu'il fut conçu il y a de nombreuses années et dont le projet alors en cours de réalisation fut largement décrit dans une communication présentée à la deuxième Conférence internationale des Nations Unies sur l'utilisation de l'énergie atomique à des fins pacifiques [1].

Mines métropolitaines

Les trois divisions minières du CEA et quelques mines privées livrent un peu plus de 1 000 t/an, sous forme d'uranate de magnésie à 60 % ou de nitrate d'uranyle en solution à 400 g/l, produits dans trois usines de traitement**.

Les productions des différentes mines et usines et les capacités de ces dernières sont indiquées dans le tableau 1.

Le développement modeste des exploitations privées reflète mal les résultats de la prospection effectuée par celles-ci : d'importants gisements ont été découverts, loin des usines actuelles, si bien que leur mise en valeur exigera la création d'une ou deux usines régionales nouvelles, création que le Commissariat ne peut susciter actuellement.

Achats outre-mer

Les deux sources essentielles d'approvisionnement français sont à Madagascar et au Gabon.

Madagascar

Les mines d'uranothorianite sont toujours exploitées; le peu d'intérêt présent du thorium a fait évoluer ces productions vers la recherche de thorianites à hautes teneurs en uranium (dans les diverses espèces d'uranothorianite, la somme des teneurs en uranium et en thorium est pratiquement constante).

Tableau 1. Productions de minerais et concentrés[a] métropolitains

Région	Mines Désignation	Production Minerai (t)	 U contenu (t)
Vendée . .	CEA Vendée.	294 000	252,100
	Privés Bretagne . . .	13 700	56,300
	Total Vendée . . .	307 700	308,400
Limousin .	CEA La Crouzille . .	299 100	366,200
	Privés Massif Central .	43 700	143,700
	Total Limousin . .	342 800	509,900
Forez . . .	CEA Bois-Noirs . . .	141 700	255,700
TOTAL		792 200	1 074

Usines Désignation	Capacité Minerai (t)	 U livrable (t)	Production 1963 Minerai (t)	 U (t)
Vendée :				
Écarpière-en-Gétigné[b] . . .	300 000	300	312 800	293,8
Limousin :				
Bessines[b]	600 000	900	337 500	475,4
Forez :				
Bois-Noirs[c] . . .	180 000	330	152 000	253,0
TOTAL.	1 080 000	1 530	802 300	1 022,2

[a] Toutes les données chiffrées sont évaluées en uranium élément (et non en oxyde U_3O_8).

[b] Usines de la Société industrielle des Minerais de l'Ouest, filiale 50-50 entre les Établissements Kuhlmann et l'État (SIMO).

[c] Usine CEA, gérée par SIMO.

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* Commissariat à l'Énergie atomique.

** Usines gérées et partiellement possédées par la Société industrielle des minerais de l'Ouest, filiale 50-50 entre les Établissements Kuhlmann et l'État.

En 1964, 125 t d'uranium seront achetées ou produites directement par les mines du CEA dans la Grande-Ile. La production concomitante de thorium sera de 312 t.

D'une économie difficile, les gisements d'uranothorianite ne peuvent être exploités qu'à ciel ouvert. Les ressources disponibles sont aussi très limitées et l'épuisement des réserves économiques est à craindre d'ici quelques années.

Gabon

Le gisement de Mounana, découvert fin 1956, a pu rapidement être mis en valeur malgré les difficultés géographiques locales. Il produit régulièrement 400 t/an depuis 1962, livrées sous forme de préconcentrés à 30-40 %.

Ces produits d'outre-mer sont traités en France afin d'en tirer des concentrés habituels : l'usine du Bouchet raffine l'uranothorianite; l'usine de Gueugnon (Saône-et-Loire), autrefois construite pour traiter des minerais pauvres locaux, mais arrêtée en raison de sa trop petite taille (30 000 t/an) et du procédé périmé qui y était employé, fut transformée en usine de concentration des préconcentrés gabonais et livre du nitrate d'uranyle.

Raffinage

Les concentrés à 60 % et le nitrate d'uranyle sont raffinés dans deux usines : l'une exploitée par le CEA au Bouchet (Seine-et-Oise), l'autre par la Société de raffinage d'uranium*, à Malvési, près de Narbonne.

Les productions et achats totaux ont atteint 1 600 t/an en 1961 et 1962 et furent réduits à 1 500 t/an depuis 1963. Cette réduction traduit en fait un effort de compression rigoureux (diminution de 40 % des effectifs miniers), car les programmes initiaux visaient 2 000 t/an.

Le coût moyen est de 115 F/kg d'uranium**.

RESSOURCES FRANÇAISES

La recherche de gisements d'uranium en France a été entreprise en 1946 par le CEA, aux travaux duquel sont venus s'ajouter, à partir de 1954, ceux de l'industrie privée.

Cet effort de prospection a été soutenu sans interruption jusqu'à présent, c'est-à-dire pendant près de 18 ans. Les sommes investies pendant cette période, en prospection de surface, en sondages et en travaux miniers de reconnaissance, peuvent être évaluées à 350 MF, dont un peu plus du quart correspond aux dépenses du secteur privé. L'effort maximum a eu lieu dans les années 1957 à 1959.

Nous indiquerons ici sommairement les résultats acquis jusqu'à présent, c'est-à-dire les ressources dont nous disposons aujourd'hui pour assurer la production à venir, et nous évoquerons ensuite les perspectives qui subsistent encore et qui justifient la poursuite de nos travaux.

Ressources actuelles

Les ressources françaises actuellement connues, exploitables sur la base du prix de l'uranium dans les concentrés, fixé à 115 F/kg, sont de 28 000 t de métal***, dont un peu plus de la moitié se trouve répartie entre les trois districts de *La Crouzille* (Haute-Vienne), du *Forez* et de *Vendée*, que nous avons déjà cités [1, 2] lors de la Conférence de Genève de 1958.

Le district de La Crouzille, avec ses trois sièges miniers en exploitation (Bessines, Margnac et Fanay) aux réserves desquels il convient d'ajouter celles de gisements voisins encore très partiellement reconnus, vient en tête avec environ 6 000 t de métal actuellement inventoriées (teneur moyenne : 1,28 ‰).

Le district du Forez, où les réserves s'élèvent à 5 400 t, dont la plus grande part (4 300 t) sont contenues dans un seul gisement (Bois-Noirs) (teneur moyenne : 1,80 ‰).

Le district de Vendée, avec 3 700 t, dont l'essentiel est réparti en cinq gisements (Écarpière, Commanderie, Chapelle-Largeau, Chardon et Dorgissière) (teneur moyenne : 1,02 ‰).

Les descriptions de chacun de ces gisements ont déjà été publiées [3-5]. Nous rappellerons simplement qu'il s'agit en général de gisements de type filonien, encaissés dans des granites, notamment dans des granites à deux micas, et localisés dans des structures tectoniques (failles, zones broyées) dont la géométrie peut être, dans le détail, fort complexe et parfois donner naissance à des amas.

Il est intéressant d'évaluer les réserves disponibles en fonction des « teneurs de coupure ». Le graphique de la figure 1 indique schématiquement cette évolution pour chacune des divisions minières du CEA (seuls les principaux gisements ont été pris en considération), et pour l'ensemble de ces trois divisions (courbe 4 du graphique). Ces différentes courbes mettent en évidence l'importante quantité de métal contenue dans des minerais dont la teneur est comprise entre 0,8 et 1,2 ‰; c'est dire la grande sensibilité des réserves vis-à-vis du prix de l'uranium. La teneur de coupure en mine (avant travaux préparatoires d'exploitation) est actuellement de l'ordre de 0,5 à 0,7 ‰. Compte tenu de l'existence des zones à teneurs plus élevées, une telle teneur de coupure confère à l'ensemble des réserves une teneur moyenne compatible avec les critères économiques d'exploitabilité de ces gisements.

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* Société d'économie mixte entre CEA (30 %), Saint-Gobain (40 %) et Potasse & Engrais chimiques (30 %).

** Soit $ 8/lb U_3O_8 en tenant compte de l'incidence des taxes.

*** Ce chiffre est la somme des tonnages répartis en trois catégories de certitude : réserves mesurées, réserves probables, réserves possibles, intervenant dans le total pour respectivement : 54 %, 28 %, 18 %.

A ce même type filonien ou en amas appartiennent les gisements de Lozère (Le Cellier, les Pierres-Plantées) de la Compagnie française des Minerais d'Uranium, et ceux de Bretagne (Morbihan) de la Société industrielle et minière de l'Uranium.

Les deux gisements de Lozère représentent, dans l'état actuel des reconnaissances, des réserves globales de 4 200 t de métal. Leur production est limitée à un niveau bas pour les raisons indiquées au précédent chapitre. Il est évident que le chiffre des réserves s'en trouve influencé, et que des tonnages importants supplémentaires pourront être pris en compte le jour où, à ces mines, sera associée une usine de traitement.

Les gisements de Bretagne représentent actuellement un millier de tonnes de réserves; mais il faut noter que les reconnaissances ne sont pas terminées et que des ressources supplémentaires pourront apparaître.

Pour terminer ce tour d'horizon sur les gisements actuellement en exploitation, il faut citer le gisement de Saint-Pierre-du-Cantal, de la Société centrale de l'Uranium et des Minerais radioactifs, dont les réserves sont encore de 700 t environ. Rappelons qu'il s'agit d'un gîte sédimentaire, dans une formation détritique.

Enfin, des réserves supplémentaires se trouvent dans des gisements qui ne sont pas aujourd'hui en exploitation. Parmi eux citons notamment les schistes noirs du massif des *Vosges* (gisement de *Saint-Hippolyte*, Bas-Rhin) dont les réserves sont estimées à 2 000 t; les gisements de *Lodève* (Hérault), dans des formations permiennes, où les travaux de reconnaissance par sondages et travaux miniers ont jusqu'à présent mis en évidence 4 300 t de métal; les gisements de type filonien actuellement en cours de reconnaissance par la Compagnie minière et métallurgique d'Indochine, dans le nord du Limousin, où apparaissent d'ores et déjà quelques centaines de tonnes de métal.

Nous terminerons cette évocation rapide de nos ressources actuelles en indiquant que, si l'on rapporte le montant global des investissements de recherches (prospection, sondages, reconnaissance minière) au potentiel global actuel (ressources à exploiter + tonnage déjà exploité) le coût de la recherche ressort à 9 F par kilo de métal. Il convient cependant de préciser qu'à ce chiffre correspondent des ressources qui sont à des stades de reconnaissance plus ou moins avancés et que, pour les amener toutes à la catégorie des réserves mesurées prêtes à être exploitées, ce coût des recherches par kilo de métal passe généralement de 9 à 15 F/kg d'uranium.

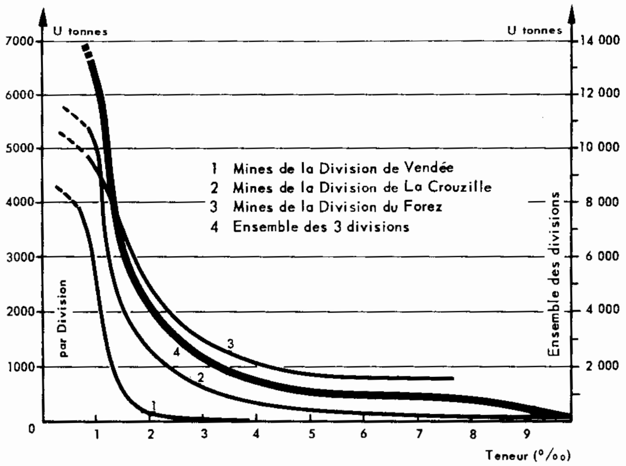

Figure 1. Réserves d'uranium en fonction de la teneur de coupure dans les principaux gisements ouverts des Divisions minières du CEA

Perspectives

Malgré 18 années bientôt d'une prospection systématique à laquelle sont venus s'ajouter dès 1948 des travaux de reconnaissances minières et d'exploitation, il est permis d'attendre encore un certain accroissement de nos ressources.

Jusqu'à ces dernières années, la cadence et les méthodes de la prospection, orientés surtout vers les formations cristallines, ont été déterminées par un compromis entre le souci de découvrir les zones qui semblaient *a priori* les plus favorables et la nécessité de créer rapidement des structures de production. De ce fait, pendant de nombreuses années, seules les minéralisations qui en surface paraissaient les plus symptomatiques de gisements importants ont été retenues, étudiées et mises en valeur : ainsi sont nés, tant au CEA que dans le secteur de l'industrie privée, les sièges miniers aujourd'hui en production. Or, nous n'estimons pas avoir de critères géologiques ou métallogéniques suffisamment précis et sûrs pour admettre qu'à de nombreux indices superficiels, sans doute moins beaux ou moins évidents que les précédents, ne correspondent pas, dans certains cas, des gisements d'importance industrielle. En outre, aux techniques de la radiométrie classique sont venues s'ajouter les méthodes géophysiques, émanométriques et géochimiques.

De nouvelles ressources peuvent apparaître dans des formations sédimentaires, où se tient pour le moment le quart environ de nos ressources.

Enfin, un accroissement notable de ressources doit être attendu de la reconnaissance en extension latérale et en aval-pendage dans la plupart des gisements aujourd'hui en exploitation. L'exploitation, par les guides nouveaux qu'elle met en évidence, permet d'augmenter d'année en année le potentiel de la plupart de nos gisements. Le graphique de la figure 2 met en évidence cet accroissement pour quelques gisements du CEA. Pour donner à chacune de ces courbes toute sa signification, il faudrait bien sûr indiquer corrélativement la cadence des travaux de reconnaissance; nous n'entrerons pas ici dans ces détails : le fait important qui apparaît est l'allure encore ascendante des courbes propres à la plupart de ces gisements. Compte tenu des programmes de reconnais-

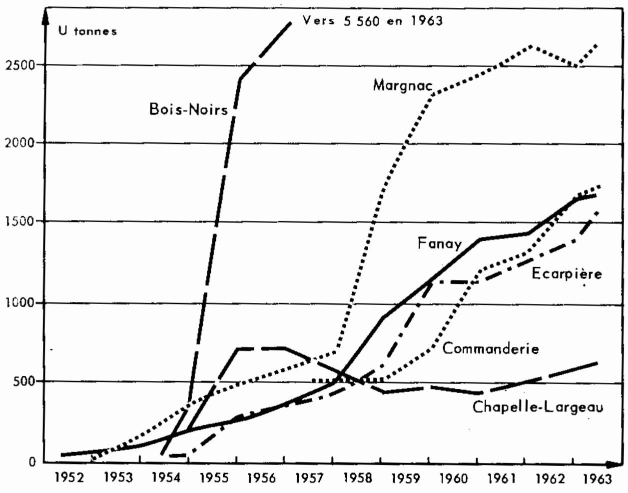

Figure 2. Évolution annuelle du potentiel (réserves + exploité) de quelques gisements

sance qui restent à réaliser tant dans les extensions latérales que vers l'aval, il est vraisemblable que le phénomène que nous constatons aujourd'hui se poursuivra pendant quelques années encore.

Il est certes fort délicat de préjuger des résultats que pourront nous apporter dans l'avenir l'ensemble de ces travaux de prospection et de développement. Dans le cadre d'une économie d'exploitation fondée sur un prix de 115 F/kg d'uranium et, compte tenu de l'état actuel des techniques de prospection, il serait certainement peu réaliste — et ce sera là notre conclusion — d'espérer porter nos ressources actuelles (28 000 t) à un ordre de grandeur supérieur à environ 50 000 t.

BESOINS FRANÇAIS

On sait qu'actuellement cinq centrales électriques nucléaires [en plus de celle de Marcoule : 80 MW(e)] sont, soit en début d'exploitation : EDF1, EDF2, soit en construction : EDF3, EL4 et EDF4. A la mise en service de cette dernière en 1968, la puissance électrique nucléaire installée atteindra 1 200 MW(e) dans la filière graphite-gaz-uranium naturel, auxquels il faudra ajouter la part française de la centrale francobelge de Chooz [120 MW(e)] et la centrale prototype à eau lourde EL4 [70 MW(e)], ces deux dernières étant alimentées en uranium enrichi.

Si le programme définitif des centrales ultérieures n'est pas encore totalement précisé, on peut tenir pour certain qu'à partir de l'année 1970 entreront en service 500 MW(e) nouveaux par an.

La compétitivité plus ou moins grande qu'aura alors atteint l'énergie nucléaire permet d'envisager que, dès 1974, le nombre de groupes de 500 MW(e) mis en service chaque année augmenterait d'une unité, dans le cas le plus favorable.

Ainsi, en 1980, la puissance nulcéaire installée variera, selon les hypothèses, de 8 500 à 16 000 MW(e), couvrant les besoins électriques à raison de 15 à 30 %, l'accroissement annuel étant assuré par le nucléaire à raison de 30 à 90 %.

Il est supposé pour l'instant que presque toutes ces centrales appartiendront à la filière actuelle uranium naturel-graphite-gaz.

Le calcul des consommations dépend de plusieurs facteurs :

a) *Économiques :* Traduits par la large fourchette des prévisions ci-dessus;

b) *Nucléaires :* On espère porter le taux de combustion de 3 500 à 5 000 MWj/t. Sur une aussi longue période, des changements de filière sont certes possibles : l'introduction de l'uranium enrichi n'apporte pas de modification sensible, les taux de combustion plus élevés étant compensés par les pertes des usines de séparation isotopique; les réacteurs à uranium naturel et eau lourde diminueraient fortement les besoins en uranium, d'un facteur 2 à 3 pense-t-on, mais il est probable que l'avance prise actuellement par les réacteurs graphite-gaz limitera l'incidence sur la consommation en 1980 de l'introduction, forcément tardive, d'une filière aussi nouvelle.

Les calculs faits dans les deux hypothèses extrêmes du développement de la filière graphite-gaz donnent les résultats rapportés dans le tableau 2. Les ordres de grandeur des consommations sont peu différents dans leur valeur élevée : 6 600 à 8 600 t/an en 1985*.

Tableau 2. Consommations annuelles d'uranium naturel

Programme nucléaire	Consommations en tonnes U par an		
	1975	1980	1985
Développement rapide (5 000 MWj/t)	1 800	4 800	8 600
Développement lent (3 500 MWj/t) .	1 400	2 600	6 600

Or, comme il a été dit ci-dessus, on estime qu'il serait imprudent d'évaluer les ressources métropolitaines actuellement à plus de 50 000 t, dont l'épuisement à cadence raisonnable, 30 à 50 ans, correspond à une production de 1 200 t/an.

La France ne peut donc compter sur son seul territoire métropolitain pour assurer l'alimentation de ses futures centrales électriques et elle doit rechercher des ressources extérieures nouvelles importantes pour faire face à une valeur élevée toujours croissante de sa demande.

EXTENSION EUROPÉENNE

Un document fort important fut publié en 1963 par la Communauté européenne de l'énergie ato-

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* Y compris les premières charges, mais exclu l'uranium naturel nécessaire à l'enrichissement pour les deux réacteurs à uranium enrichi (Chooz, EL4).

mique [6]. Un travail commun entrepris dans le cadre de l'Agence d'approvisionnement chercha à définir quelles pourraient être les tendances à long terme de la consommation mondiale face aux ressources connues. Il fit apparaître essentiellement des possibilités d'un déséquilibre mondial entre demandes et offres sur lesquelles nous reviendrons.

L'Europe est certainement la zone d'élection pour le développement de l'énergie électrique atomique, en raison de la cherté relative de l'énergie classique, de la raréfaction des sources d'approvisionnement traditionnelles (essentiellement charbon *), de l'importance de son réseau de distribution électrique qui peut supporter sans difficulté l'insertion des très grosses unités de production [500-1 000 MW(e)] généralement exigées pour la compétitivité du nucléaire.

Cependant, les ressources en uranium de notre petit continent sont certainement limitées : 50 000 t aujourd'hui en France, des possibilités en Allemagne et en Italie, sans oublier la péninsule Ibérique, qui fut de tout temps un producteur d'uranium.

Ces ressources ne sauraient alimenter les puissants programmes d'énergie nucléaire considérés en Europe, qui sera ainsi un client des fournisseurs et producteurs du reste du monde : sa consommation atteindra sans doute la moitié de la demande internationale, évaluée à 35 000 à 50 000 t/an vers 1980.

Un autre document important, publié par la United States Atomic Energy Commission [7], conclut à la nécessité à long terme de la surgénération; dans les conditions actuelles de leur utilisation, les ressources en uranium du monde accessibles aux prix actuels de l'ordre de 115 F/kg d'uranium ou \$ 8/lb U_3O_8 permettent la compétitivité du nucléaire classique mais ne constituent qu'un appoint : évaluées en énergie récupérable, elles représentent seulement une fraction des ressources contenues dans les combustibles fossiles : charbon, hydrocarbures.

Cependant, on sait que l'insertion de la surgénération dans l'énergie atomique sera très progressive et intéressera assez peu notre génération :

a) D'une part, seulement vers 1980, les divers prototypes de surgénérateurs auront-ils atteint un stade de développement tel que leur réplique en un grand nombre d'unités industrielles de puissance sera possible;

b) D'autre part, il faut, à l'évidence, des quantités importantes de plutonium pour alimenter ces réacteurs. Or, M. Gibrat l'a démontré dans une communication récente [8], la simple considération de l'équation traduisant l'égalité des quantités de plutonium chargé dans les surgénérateurs et produit dans les réacteurs primaires montre que le taux de pénétration de la surgénération atteindrait dans les meilleurs cas 50 %.

Ce résultat, satisfaisant dans l'abstraction des chiffres, s'insère concrètement dans un cadre moins plaisant : si l'on admet qu'à l'époque où la surgénération aura atteint cette limite industrielle, vers la fin du siècle, la consommation en énergie électrique continuera de doubler tous les 10 ans, les réacteurs primaires atteindront, en l'an 2010, la puissance installée qu'ils auraient dû atteindre en l'an 2000 sans surgénération.

Celle-ci ne supprime pas le problème difficile de l'approvisionnement en uranium des centrales nucléaires : elle apporte seulement un sursis d'au plus une dizaine d'années d'ici 40 ans.

Le rapport du Président de la United States Atomic Energy Commission déjà cité démontre la nécessité pour les seuls États-Unis de disposer d'ici la fin du siècle de 1 100 000 t de U_3O_8 en réserve (800 000 t U). Une extrapolation facile au monde « occidental » évalue ses besoins à plusieurs millions de tonnes d'uranium à trouver dans les gisements à mettre en exploitation avant la fin du siècle.

Ce chiffre est corroboré par les calculs que l'on peut faire dans le cas de la France : nous arrivons pour notre pays à la conclusion que les consommations cumulées de l'énergie atomique électrique, augmentées des réserves nécessaires en l'an 2000 pour assurer l'approvisionnement des centrales alors existantes, devraient être, suivant les hypothèses de développement de l'énergie nucléaire, de 150 000 à 300 000 t d'uranium.

Sauf faits nouveaux que fera apparaître cette Conférence, les réserves totales du monde libre semblent être actuellement de l'ordre d'un demi-million de tonnes d'uranium, comme indiqué dans le tableau 3, extrait du rapport déjà cité de l'Euratom, établi à partir de documents publiés par les pays intéressés.

Tableau 3. Réserves contenues d'uranium au 1er janvier 1962

(extrait du rapport EURATOM cité sous référence [6])

	Minerai (millions de tonnes)	U métal (t métriques)
États-Unis d'Amérique	64	130 000
Canada	143	145 000
Afrique du Sud	680	115 000
Autres pays	—	60 000
TOTAL		450 000

Ces évaluations sont faites, à notre connaissance, pour de l'uranium livrable en concentrés à \$ 8/lb U_3O_8.

Il est évident qu'une réévaluation faisant appel à de plus hauts prix, donc à de plus basses teneurs, se traduirait par une augmentation massive des réserves que l'on connaît mal : sauf quelques cas particuliers,

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* Les incidences réelles des découvertes récentes du gaz naturel de Hollande ne peuvent encore être mesurées; il n'apparaît pas toutefois qu'elles puissent changer les dimensions du problème énergétique européen.

les gisements à plus faible teneur n'ont pas été étudiés sérieusement *.

Cependant, encore à ce jour, les projets de développement de l'énergie électrique nucléaire sont souvent basés sur des coûts plus faibles. Nombreuses par exemple sont les études qui prennent en considération un uranium à \$5/lb ou \$6/lb U_3O_8. Sont-elles bien réalistes?

CONCLUSION

Sans jouer au devin, il est prudent, mais difficile, de chercher à prévoir l'avenir.

A l'époque présente de surproduction, d'extraction limitée aux réserves riches, de fermeture des mines, succédera dès 1970-75 l'augmentation nécessaire des productions annuelles. D'abord il suffira de rouvrir les mines abandonnées, mais bien avant 1980 il aura fallu mettre en exploitation de nouveaux gisements, construire de nouvelles mines et usines puisque la demande du monde occidental excédera la capacité des installations actuelles atteinte en 1960-61.

Les prix se stabiliseront, écartelés entre la situation facile des mines restées en exploitation et totalement amorties et les exigences économiques de l'ouverture des nouvelles mines. Il est trop tôt pour être pessimiste, mais \$ 8/lb U_3O_8 est certainement l'optimum espérable pour le producteur d'énergie électrique nucléaire.

Au delà, l'incertitude la plus complète règne : fera-t-on des découvertes minières extraordinaires, ou plus simplement les mécanismes d'équilibre propres au nucléaire (choix des filières, recyclage du plutonium) joueront-ils? et surtout le monde sera-t-il capable de doubler, tripler ou quintupler dans des régions vierges les réserves actuelles dont la mise en évidence exigea 10 ans d'efforts soutenus, partant d'indices connus?

Nous devons être optimistes, mais avec vigilance, et une vision claire de la situation future s'impose à la France, aux pays européens aussi, qui ne pourront plus guère compter sur les ventes des gros producteurs nord-américains, sans doute accaparés alors par la demande énorme de leur propre continent.

Nous plaçant dans cette optique, il nous paraît donc indispensable de participer dès maintenant à la découverte de nouvelles provinces uranifères, à l'extérieur du continent européen, et notamment en Afrique, pays immense et mal connu.

L'action du CEA sur ce continent remonte à sa création en 1946. La précision progressive des guides géologiques permit successivement les découvertes de l'uranothorianite malgache et de l'uranium gabonais, mais jusqu'à ce jour aucune province uranifère véritable n'a été trouvée. Nos efforts furent renforcés dès 1954, et orientés spécialement vers les séries précambriennes ou les formations continentales largement représentées sur ce continent.

Aujourd'hui des indices dans la République Centrafricaine et dans la République du Niger prouvent la justesse des vues géologiques, mais il reste encore à prouver l'existence de ressources économiques, très dépendantes de la situation géographico-économique.

Cependant, nous sommes suffisamment encouragés pour continuer, en souhaitant que notre effort pour dégager des ressources nouvelles ne sera pas unique dans le monde. Nous savons d'ailleurs que des efforts parallèles se manifestent sur d'autres continents.

Mais en fait, nous devons bien avouer notre grande anxiété devant l'énormité du programme nucléaire mondial et devant la confiance sans doute inconsciente faite aux géologues et mineurs : ne leur demande-t-on pas d'assurer dans les prochaines décennies un programme d'approvisionnement d'une ampleur jamais approchée, même de loin, par aucune industrie minière métallique, en un aussi court laps de temps.

Cette Conférence devra être celle de la prise de conscience de cette réalité.

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* Sauf quelques gros gisements, gisements d'ailleurs très différents de ceux actuellement exploités, avec des teneurs de quelques centaines de ppm d'uranium, entraînant des prix 3 à 5 fois plus élevés que les prix actuels.

ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/72 France

Why exploration for uranium must go on

By J. Mabile and A. Gangloff

At the Second United Nations International Conference on the Peaceful Uses of Atomic Energy (Geneva, 1958), an account was given of the hopes placed in French uranium resources, and of the work in hand on projects for mines and concentration plants. But even though the French soil kept its promises, production has been restricted because of the risk of massive over-production. Moreover, worldwide production surpluses allay any immediate worries about the continuity of supplies.

Even so, at the rate of exploitation that can be reasonably foreseen, France's uranium potential seems to be limited, guaranteeing only a few decades of production.

The situation is even more serious for Europe as a whole, at the very time when the use of atomic energy is beginning to expand rapidly.

On the world basis, it is to be expected that, as a result of the closing down of mines, a balance between production and demand will be reached within ten years, after which it will be an easy matter to increase production by reopening temporarily shut-down mines. But by 1980 demand will exceed the maximum production capacity installed in 1960-1961. Finally, towards the end of the twentieth century, a gap will open between the uranium reserves required at that time and those which have been discovered in the world so far by virtue of the considerable efforts in prospecting made between the years 1948 and 1958.

It follows that there is no time to be lost in endeavouring to discover new resources either in countries not yet prospected, or by the use of more sensitive methods of detection. Failing this, the uranium market, badly shaken by current over-production, will undergo new crises if the mining industry is not fully prepared, and well in advance at that, for a rapid exponential expansion after 1975-1980.

A/72 Франция

Почему нужно продолжать поиски урана

Ж. Мабиль, А. Ганглоф

На второй Женевской конференции в 1958 году были высказаны большие надежды на французские сырьевые ресурсы урана и на французские рудники и заводы. Однако опасность большого перепроизводства привела к сокращению промышленного производства, несмотря на то что французские месторождения урановых руд подтвердили самые оптимистические предположения. Между тем, мировые излишки производства позволяют решать насущные задачи обеспечения потребностей в уране.

Однако запасы урана во Франции по самым реальным предположениям представляются ограниченными и могут обеспечить производство только на несколько десятков лет. Такое положение представляется еще более серьезным для всей Европы даже сейчас, когда мы являемся свидетелями быстрого развития атомной промышленности.

В мировом масштабе можно ожидать, что в результате закрытия рудников равновесие между производством и потреблением будет установлено через десять лет, поскольку к тому времени рост производства будет осуществляться за счет открытия рудников, законсервированных в настоящее время. Однако с 1980 года спрос будет опережать максимальное производство урана, установленное в 1960—1961 годах. И, наконец, к концу столетия возникнет диспропорция между необходимыми ресурсами урана и запасами, уже открытыми во всем мире ценой значительных усилий за 1948—1958 годы.

Пока еще не очень поздно заняться поисками новых месторождений как в еще неразведанных районах, так и усовершенствованием методов разведки в старых районах, без чего рынок урана, потрясаемый нынешним перепроизводством, снова окажется в трудном положении, если горнорудная промышленность заранее не подготовится к быстрому прогрессу после 1975—1980 годов.

A/72 Francia

Por qué continuar buscando uranio

por J. Mabile y A. Gangloff

En la Conferencia de Ginebra de 1958 se manifestó que se tenían depositadas las esperanzas en los recursos franceses de uranio, y en la producción de las minas y de las fábricas en explotación. El riesgo de una superproducción masiva ha obligado a limitar la producción, mientras que el subsuelo francés confirmaba sus promesas. Por otra parte, los excedentes de la producción mundial disipan las preocupaciones por el abastecimiento a corto plazo.

Sin embargo, las reservas de uranio francesas parecen limitadas, no asegurando la producción más que para algunos decenios.

Este desequilibrio es más grave todavía para el conjunto europeo, en el mismo momento en que comienza la rápida expansión de la energía atómica.

En un plano mundial se puede considerar que, como consecuencia del cierre de algunas minas, se alcanzará en diez años el equilibrio entre la producción y el consumo; después se podrá aumentar la producción fácilmente reanudando la explotación de las minas cerradas provisionalmente. Pero desde 1980, la demanda sobrepasará la capacidad de producción máxima instalada en 1960-1961. Finalmente, hacia finales de siglo, existirá una desproporción entre las reservas de uranio necesarias y las que se han descubierto en el mundo hasta el momento, como consecuencia de los esfuerzos considerables de los años 1948-1958.

Ya es hora de preocuparse por descubrir nuevas reservas : ya sea en países en los que todavía no se han efectuado prospecciones, ya sea mediante la utilización de métodos más finos. De lo contrario, el mercada del uranio, sobre el que repercute la superproducción actual, tropezará con nuevas dificultades si la industria minera no se prepara con bastante antelación a una progresión exponencial rápida después de 1975-1980.

Fuel resources and availability for civilian nuclear power, 1964-2000

By R. L. Faulkner and W. H. McVey*

This conference comes at an opportune time to assess the expected availability of nuclear fuel to meet projected requirements. Military needs are no longer governing, and the rate of development of civilian nuclear power is now of dominant importance in determining future requirements for uranium. The sudden and dramatic decrease in the capital cost of nuclear electric plants employing light water reactors and the resultant drop in total estimated nuclear power costs have probably made most earlier nuclear power growth forecasts obsolete. The decrease in cost makes large nuclear power stations competitive with those using conventional fuels in many additional areas in the United States and throughout the world. Recognizind that the cost of producing power is only one of a number of factors in making a choice now between conventional and nuclear fuel, and between types of nuclear reactors, it nevertheless seems evident that in the long run the choice will be dictated by economics. Planners everywhere must take note of these developments.

Many changes have taken place since the first Conference on Peaceful Uses of Atomic Energy held in Geneva nearly ten years ago. In a paper presented in 1955 [1], the United States described the success of the western nations in finding uranium deposits and developing uranium production. Since that time many new uranium deposits have been brought into production throughout the world. Metallurgical processes have been refined to reduce costs and improve extraction. Extensive studies of the geology and mineralogy of uranium deposits have led to new concepts which already have proven their worth and promise to aid in the discovery of new deposits to meet future needs [2].

On the basis of developments to 1955, and geological evidence then available, resources of the producing nations of the West were estimated to be between 1.10^6 and 2.10^6 tons [1]. [All tons are short tons of 2 000 pounds (907.2 kg) U_3O_8.] Developed reserves at that time were estimated at 500 000 tons; known United States reserves were less than 70 000 tons. These figures related to uranium ores from which high-grade concentrates could be produced at a cost of about $10 per pound of U_3O_8 or less. The review indicated that there were extensive deposits of uranium throughout the world, that production already developed was adequate for a major nuclear power program and that additional production could be obtained when needed. The observation was also made that when the vast low-grade resources were required, more efficient use of nuclear fuel through improved conversion or "breeding" might offset the higher uranium cost.

By 1958, annual production rates of the major producers, the United States, Canada and South Africa, had reached about 15 000, 13 000, and 6 000 tons respectively. Australia, the Congo and France had a combined production of about 3 000 tons per year. Although total world production was expected to increase moderately and level off at 40 000 tons U_3O_8 annually, several of the uranium producing countries were concerned over the probable short term problem of production in excess of requirements; some of these countries were already considering plans to limit production.

Nevertheless, production continued to expand under previously planned programs. It reached its peak of about 43 000 tons U_3O_8 in 1959 and since 1960 has been trending downward. Because of the temporary shrinkage in markets, exploration and development of new deposits has been at a virtual standstill in the United States and in most of the other major producing countries. As a result, less uranium has been discovered in the past few years than has been mined. This fact alone would have sufficed to bring about a reduction in world reserves, estimates of which reached a maximum of somewhat more than one million tons in 1958. Of greater importance, however, a number of countries have reviewed their ore reserves and have refined their estimates or reduced them to conform to the economics of producing uranium to sell at $8 a pound. Consequently, estimated world reserves had declined to about 600 000 tons at the beginning of 1964. A further decline in reserves over the short term future is in prospect. Few companies have been inclined to use their financial resources to search for new deposits until they can see more clearly when the uranium will be needed.

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World uranium production is expected to continue to decline from the present level of about 20 000 tons U_3O_8 per year to about 14 000 tons annually by 1970. From that date forward production must rise sharply to meet projected nuclear fuel requirements. Thus, we find ourselves in a paradoxical situation in which it is evident that a vigorous search for new deposits should not be long delayed but, notwithstanding this, active exploration is being restrained by the existence of over-capacity in the uranium mining and milling industry. The nuclear power growth projections given in this paper clearly herald a spectacular growth for the nuclear industry and in requirements for new uranium production. It follows that new deposits will be needed in the 1970s to sustain uranium production at adequate levels.

Current forecasts of nuclear power installation in the next few years show little change over previous studies. However, longer range projections are much more optimistic than those previously made. This optimism, we believe, is fully justified and stems from the promise of competitive power costs using large light water reactors fuelled with enriched uranium such as the plant ordered earlier this year by Jersey Central Power and Light Company from General Electric Company. General Electric will build the 515-640 electrical megawatt [MW(e)] plant at Oyster Creek, New Jersey, at a cost of a little less than $105 per kilowatt of installed electrical generating capacity if the maximum estimated output of 640 megawatts can be obtained. Jersey Central estimates that the total cost of generating electricity will be in the neighborhood of 4 mills/kwh. The new, optimistic estimates of lower costs are due at least in part to the larger size equipment (especially pressure vessels) which can now be manufactured and hence the larger size stations which can be constructed and integrated into interconnecting systems.

In applying economics such as these outside the United States, consideration has been given to the fact that European power systems, with less extensive interconnections, have more limited opportunities for plants in the 500-600 megawatt range. However, even small reactors using enriched uranium are now of interest. For example, the 150-160 MW(e) reactor expected to be sold by Westinghouse to Spain for $30 million is comparable in economic importance in its size class to the Oyster Creek reactor. Such costs allow the extension of optimism outside the United States and have been reflected in the range of the forecasts. Since there has been relatively little time to assess fully the possibilities outside the United States, our projections of enriched uranium usage still may be low.

Table 1. Installed electric utility generating capacity (thermal capacity only in 1 000 MW(e)[a]

	1962	1970	1975	1980
USA	154	257	354	472
Western Europe (including UK)	111	180	230	300
Other non-communist countries	61	117	171	240
Total	326	554	755	1 012

[a] Installed capacity, including hydroelectric, obtained from references [3-5] has been adjusted to eliminate hydroelectric installation, based on information obtained from the Bureau of Power, Federal Power Commission [18, 19, 20].

Through 1980 most of the nuclear power stations built will probably be thermal converter reactors using, primarily, enriched uranium and plutonium recycle, while after 1980 fast reactors utilizing plutonium recycle may well become dominant. Thermal thorium breeders also should become increasingly important. Although breeder reactors may appear before 1980, their impact on uranium requirements to that date is not expected to be significant.

Table 1 shows projected installed electric generating capacity in the non-communist world through 1980. The estimates for the United States are Federal Power Commission figures published in its 1963 Annual Report [3]. Figures for the rest of the world are by Adams [4] and by the United Nations Economic Commission for Europe [5]. It will be seen that very large additions to generating capacity are forecast throughout the world, particularly in those nations already highly industrialized.

Table 2 shows projected nuclear generating capacities for various areas of the non-communist world and the basis on which the projections were prepared, namely:

(*a*) Data obtained from the US Federal Power Commission staff in June 1962, from the US FPC Advisory Committee Report No. 13 of June 1963,

Table 2. Installed nuclear generating capacity in MW(e)

	Calendar year			
	1964	1970	1975	1980
USA	940	6 000- 7 000	21 000-37 000	60 000- 90 000
Other non-communist world	3 250	14 000-15 000	35 000-50 000	80 000-110 000
Total non-communist world	4 190	20 000-22 000	56 000-87 000	140 000-200 000

and from the US FPC Annual Report for 1963 [3] have been used to estimate growth of power from large steam-electric plants in 48 power supply areas of the United States. Judgments have been made for the two periods 1970 to 1975 and 1965 to 1980 as to the likelihood of nuclear plants being installed in these areas, leading to the range of megawatts given in Table 2.

(*b*) For the rest of the non-communist world, references cited [7-15] and other recent studies indicate a growth of nuclear power from 1970 to 1980 at about the same rate as that predicted for the United States. However, this growth starts from a higher level abroad in 1970, estimated to include about 9 000 MW(e) of normal uranium reactors and 5 000-6 000 MW(e) of enriched-uranium reactors.

(*c*) In order to translate these power growths to U_3O_8 requirements, it has been assumed that all US plants and all plants installed abroad after 1975 will utilize enriched uranium. It has also been assumed that all enriched uranium plants will recycle plutonium after mid-1972. We believe, however, that the range in the estimated requirements is broad enough to accommodate other likely types of reactors.

Because the differential between conventional and nuclear power costs is small in many areas, small changes in the cost of either may result in rather large changes in the rate of growth of nuclear power. The broad range in Table 2 reflects this fact. The figures for the United States may be compared with the forecast in the 1962 *Report to the President by the Atomic Commission* [6] of 16 000 MW(e) by 1975 and 40 000 by 1980.

Estimates for the United States were made on the basis of an area-by-area examination. Forecasts for the rest of the world, exclusive of communist nations, drew upon data from several published sources [7-15]. When available, published information was used to estimate the split in the future between reactors using slightly enriched uranium and reactors using normal uranium. In matter of fact, however, the more important variable is the neutron moderation used; that is, heavy water moderation can significantly reduce uranium requirements over light water or graphite moderation, as discussed later. In general, it was assumed that a large proportion of the power generation from nuclear plants would come from those using slightly enriched uranium with light water moderation. The uncertainty in the choice of reactors is much less significant in estimating requirements for virgin uranium than the uncertainty regarding the nuclear share of the total power market.

The estimate of nuclear capacity for the non-communist world given in the Euratom report [7] for 1980 was 117 000 megawatts. Although the figures for installed nuclear capacity in Table 2 cover a wide range, we believe that the lower figure is conservative and that in the absence of unforeseen adverse developments, nuclear growth and uranium requirements to supply new reactors may approach and possibly exceed the high figure. Estimates by the General Electric Company and Westinghouse Electric Corporation of the growth of nuclear power in the United States as reported in the press [16] are comparable to or higher than any of the figures given for 1980 in Table 2. General Electric has predicted installed nuclear generating capacity in the US for various periods between 1968 and 1980 which indicate a total installed nuclear capacity by 1980 of about 82 000 MW(e), while Westinghouse's figure based on 60% of installed capacity beginning in 1969 equates to more than 100 000 MW(e).

Megawatts of installed capacity can be translated into needs for uranium once reactor characteristics have been assumed. We have assumed that reactors using enriched uranium will be light water cooled and moderated, pressurized or boiling, using fuel clad with zirconium or its alloys. Reactors using natural uranium are assumed to be either graphite moderated, gas cooled, or heavy water cooled and moderated. The approximate uranium requirement per megawatt of installed capacity for inventory and burn up is given in Table 3 for these types of reactors; the inventory contains allowances for spare fuel and for material in process, both new and irradiated, that is, material in the "pipeline". Although other types of reactors undoubtedly will be used also, the resulting variation in uranium requirements is expected to be within the degree of precision of the estimates. In estimating requirements in this paper a fuel withdrawal and return schedule was set up for each type of reactor. In this way the pipeline is taken into account automatically and realistically with regard to time. It will be noted from Table 3 that enriched uranium reactors and gas cooled normal uranium reactors require somewhat more U_3O_8 per megawatt than those using heavy water moderation. In spite of the larger amounts of uranium required, and hence higher cost of inventory, reductions

Table 3. Approximate uranium usage in reactors per unit power[a]

	Water cooled and moderated, zirconium clad [b]	D_2O cooled and moderated [c]	Gas cooled graphite moderated [d]
Inventory (short tons U_3O_8/MW(e))	1.0	0.3	1.1
Burn-up (short tons U_3O_8/MW(e) yr). . . .	0.2	0.2	0.3

[a] The average uranium usage has been reduced in the 1970-1980 period to reflect plutonium recycle.

[b] Using enriched uranium and based on tails from isotope separation plant at 0.253% ^{235}U.

[c] Using normal uranium or slightly enriched uranium.

[d] Using normal uranium, relatively low burn-up in MWd/ton.

Table 4. Estimated uranium requirements (short tons U_3O_8)

		1970	1975	1980
USA	Annual	1 600- 4 200	8 900- 14 000	19 000- 27 000
	Cumulative[a]	9 400-14 000	37 000- 64 000	110 000-170 000
Other non-communist countries	Annual	6 200- 9 000	14 000- 19 000	24 000- 32 000
	Cumulative[a]	28 000-33 000	80 000-110 000	180 000-240 000
Total	Annual	7 800-13 000	23 000- 33 000	43 000- 59 000
	Cumulative[a]	37 000-47 000	120 000-170 000	290 000-410 000

[a] Beginning with 1965.

in the capital costs of the plant may more than offset the larger investment in uranium. The evidence now seems to favor reactors using slightly enriched uranium.

Table 4 shows U_3O_8 requirements expressed as ranges. Perhaps more significant than the total cumulative requirement through 1980 is the annual production rate which will be needed to support an expanding nuclear industry at that time. Even larger demands will be made on the uranium mining industry in succeeding years.

Table 5 shows the ore reserve estimates published by the principal producing countries. The second column of the table shows expected production from 1 January 1964, through 31 December 1970, pursuant to present Government procurement or production arrangements. The last column shows an ore reserve balance at 1 January 1971, excluding possible new discoveries. New discoveries, however, certainly will be made. The figures in column three therefore should be regarded as base figures to which new discoveries will be added.

The United States has reduced its weapons materials production and expects to have substantial stocks of normal uranium on hand by the end of 1970. These anticipated stocks could well be large enough to meet all foreseeable enriched uranium requirements for several years beyond 1970. The U. K. Atomic Energy Authority in its 1962-63 Annual Report [17] has stated that production from its gaseous diffusion plant at Capenhurst is no longer needed for defense purposes. Thus, it seems reasonable to assume that the known reserves plus above-ground inventories of normal uranium available for projected civilian requirements will be closer to 600 000 tons U_3O_8 than to the approximately 500 000 shown as 1971 reserves in Table 5.

Table 5. Available uranium reserves, 1964-1970 (short tons U_3O_8)

	Estimated reserves at 1 Jan. 1964	Estimated production in 1970 on government contracts	Reserves at 1 Jan. 1971 excluding new discoveries
USA	160 000	64 000	96 000
Canada	207 000	19 000	188 000
South Africa	147 000	13 000	134 000
Others	75 000	19 000	56 000
Total	589 000	115 000	474 000

One might conclude that 600 000 tons would be sufficient to meet total requirements through 1980, even if the higher estimate of requirements proves correct. However, known deposits are not capable of supplying low-cost uranium ($8.00/lb U_3O_8) at the continually increasing rates called for between 1975 and 1980. Production rates could be temporarily expanded in some mines, but all have physical limitations. Furthermore, the heaviest demands will be made as currently known reserves approach exhaustion. In this situation production would tend to decline rather than increase. Mines recovering uranium as a by-product, as in South Africa, are limited by the economics of producing gold and, unless the price for uranium is materially increased, output would not be greatly affected by uranium demand.

Although there is little exploration in progress in the United States, newly discovered ore has offset in part the depletion of reserves resulting from mining. Production in 1963 was about 14 000 tons of U_3O_8, whereas the net decrease in reserves was only 7 000 tons due to the addition of about 7 000 tons to known reserves. Most of this ore has been found in or adjacent to known deposits. In the absence of renewed incentives for exploration, this rate of addition to reserves would tend to decrease. We believe, however, that the rapidly increasing requirements now forecast will supply the necessary incentive for exploration and that estimated United States civilian requirements through 1980 (Table 4) can be met by domestic production from reserves of the types that have supplied production in the past. Nevertheless, substantial additions to ore reserves must be made in the US and elsewhere within the next ten years in order to supply adequately the nuclear industry with fuel at reasonable costs.

Uranium sales have been reported in small lots at prices as low as $3.00 a pound, and a number of sizable sales have been made at prices in the $4.00 to $5.00 range. Assuming requirements of the magnitude (either high or low) indicated by Table 4, it is unrealistic to assume that uranium prices will continue to be depressed for more than a few years. One would look for prices becoming firm soon after 1970. There is a reasonable possibility that prices can be held at $8.00 or less throughout the decade, but this will depend in large measure on when large-scale exploration activity is undertaken and the results of these efforts.

There are many favorable areas throughout the world which have yet to be intensively explored. In the United States, for example, geologists of the Atomic Energy Commission have been studying both the long-term and short-term availability of uranium. A short-term ore reserve potential has been defined as that quantity which could be developed by intensive activity over a five-year period. This short-term potential is in the areas from which most of the production is now coming and in close proximity to existing ore deposits. With an $8.00 price, we have estimated this short-term potential at about 65 000 tons of U_3O_8.

Renewed exploration and prospecting in Canada and Australia would doubtless result in extensions to known reserves. Other countries with small current production potential may also be able to develop important reserves by further prospecting. There is no reason, therefore, to fear that shortages of uranium will occur between now and 1980 assuming, of course, that active prospecting will be resumed in the next few years.

We feel confident that vigorous search will uncover substantial new uranium reserves which can be mined as cheaply, or nearly as cheaply, as those now being exploited. Past production plus developed ore reserves total about 900 000 tons. While no one can predict with any certainty the size of uranium ore reserves which remain undiscovered, it does not seem unreasonable to assume that discoveries in the next twenty years will be at least equal to those of the last twenty years, and they may be much larger.

Before considering requirements after 1980, mention should be made of the position of thorium. Several power reactors in the United States are operating on cores containing thorium. In addition, a substantial Thorium Utilization Program is under way at Oak Ridge National Laboratory, which is expected to point to solutions to some of the technical problems inherent in the thorium ^{233}U cycle. Notwithstanding the research programs of the United States and other countries designed to develop thorium technology, it is unlikely that use of thorium prior to 1980 will cause any significant reduction in the estimated uranium requirements shown in Table 4. It is likely that increasing amounts of thorium will be used after 1980 but there is no basis at present on which to predict what effect this may have on uranium requirements.

Projections of supply and demand for nuclear fuels for the years 1981 to 2000 involve many uncertainties. Contingencies presently unknown could have an important effect on the rate of growth of nuclear power during that period and, consequently, projections of requirements over the last two decades of the century have not been developed in detail.

In considering the situation in the United States, some observations made in the US Atomic Energy Commission's *Report to the President*, issued in November 1962 [6], are of interest. This report included a review of United States energy resources and probable long-term requirements and projections of the economics of nuclear power. It concluded that if a long-term benefit were to be realized from nuclear power, more emphasis should be placed on the difficult problem of developing breeder reactors in order to achieve greater utilization of available resources of nuclear fuels through effective use of the fertile materials uranium-238 and thorium. This would permit the eventual use of much higher cost nuclear fuels than can be economically used in the present generation of converter reactors and expand available resources many times.

Table 6 shows estimated nuclear capacity in the United States through the year 2000, together with estimated uranium requirements for the period 1980-2000. The quantities shown represent the tons of uranium which it is estimated will have to be mined to provide initial inventory and make-up requirements during the periods indicated. Breeder reactors, however, may become important during the last half of the period and the total requirements might thus be reduced to about 500 000 to 600 000 tons. Nevertheless, this would exceed our present estimate of US low-cost resources (Table 7). Therefore, unless this estimate is unduly pessimistic, which is possible, reserves in the next higher category or foreign supplies would have to be drawn on to meet US requirements through the year 2000.

The growth rate of electrical generating capacity in the United States projected in the *Report to the President* (1962) [6] closely parallels the growth of total world electrical generating capacity given by Adams [4] for the period through 1975. If this relation-

Table 6. Installed nuclear generating capacity in the US and natural uranium requirements (plutonium recycle mode of operation)

Year ending	Nuclear MW(e)	Cumulative additions (short tons U_3O_8)
1980	75 000[a]	
1985	150 000	150 000
1990	280 000	380 000
2000	730 000	900 000

[a] Average figure for 1980 taken from Table 2.

ship is extrapolated to the year 2000, total world additions of electrical generating capacity in the period 1981-2000 would approximate to 4 million MW(e). If the nuclear portion of this additional capacity projected for the United States, 64%, is applied to the world as a whole, additions to nuclear power throughout the world, including the communist countries, would represent about 2 500 000 MW(e) during this period. That the proportion of nuclear additions in other countries will approximate to that in the US is believed to be a reasonable assumption because, by 1980, the relative economics of nuclear vs. conventional power are expected to govern power installation decisions in all areas including those in which, prior to that time, other considerations may have favored conventional power. Total uranium requirements, including the United States, during 1981-2000 would be about 3 200 000 tons if this capacity were to be provided by converter reactors using plutonium recycle. If, however, one assumes, as we have assumed for the United States, extensive use of breeders, particularly in the 1990s, world uranium requirements would be substantially below this figure.

Thus, if installation of nuclear electrical generating capacity in the remainder of the world should follow the pattern projected for the United States during the period 1980-2000, the demand on world resources of nuclear fuels may be 1 500 000 to 2 000 000 tons compared with the 900 000 to 1 000 000 tons represented by total discoveries to date. Deposits not now known must be relied upon to satisfy these requirements if they are to be met with low-cost uranium.

Tables 7 and 8 give estimates of US resources of uranium and thorium available at costs that fall within five ranges. The resources in each price category are separated into those known with reasonable assurance and possible additional resources which are less certain with respect to their existence or economics.

The $5 to $10 category represents reserves of uranium and thorium in deposits of the type now being mined in the western United States. It is expected that by the end of 1980 most of the presently known uranium reserves in this category will have been depleted but that the short-range potential in the producing areas will have been realized. It is also expected that additional resources in deposits of the type presently exploited will remain to be discovered as indicated in the middle column. Thorium resources in the $5 to $10 range are not expected to be appreciably reduced by production before 1980.

Table 7. US uranium resources, 1981 (thousand short tons U_3O_8)

Price range per pound U_3O_8	Reasonably assured resources	Possible additional resources	Total resources
$			
5- 10	50-100[a]	250[b]	300-350
10- 30	400	300[b]	700
30- 50	5 000	3 000[c]	8 000
50-100	6 000	9 000[c]	15 000
100-500	500 000	1 500 000[c]	2 000 000

[a] Reflects the approximately 50 000-ton range in estimated US U_3O_8 consumption, 1970-1980.

[b] Depends on new discoveries which may yield smaller or larger reserves than indicated.

[c] Extensions of known uraniferous (thoraniferous) formations.

Table 8. US thorium resources 1981 (thousand short tons ThO_2)

Price range per pound Tho_2	Reasonably assured resources	Possible additional resources	Total resources
$			
5- 10	100	300[a]	400
10- 30	100	100[a]	200
30- 50	3 000	7 000[b]	10 000
50-100	8 000	17 000[b]	25 000
100-500	1 000 000	2 000 000[b]	3 000 000

[a] Depends on new discoveries which may yield smaller or larger reserves than indicated.

[b] Extensions of known uraniferous (thoraniferous) formations.

The $10 to $30 category includes presently uneconomic uraniferous material peripheral to and in the same western mining districts as the low-cost reserves plus the higher grade and more easily minable portions of extensive sedimentary deposits such as Florida phosphate rock formations. In the case of thorium, some of the reserves in this range consist of placers in which thorium is continuously disseminated over wide areas. The estimates in this cost category for both uranium and thorium are considered conservative because of the lack of any significant exploration effort expended so far to find such deposits.

In the $30 to $50 category, uranium reserves are contained primarily in the Chattanooga shale located in southeastern United States and in phosphate deposits situated in southeastern and western states. Most of the thorium and a minor portion of the uranium occurs in the Conway granite of New Hampshire.

The very high-cost resources estimated to be available at prices of $50 or more per pound include uranium and thorium from extensive granite bodies located in Colorado, Idaho, Minnesota, Wisconsin, and in New England. Portions of extensive sedimentary formations containing less than 50 ppm uranium are also included.

The results of past exploration efforts would seem to indicate the likelihood that a substantial portion of the large world requirements projected in this paper can be developed in new deposits of relatively low-cost uranium in North America. However, it is probable that at least half will have to come from areas of the world which until now have provided only relatively small production.

A number of countries have geologic settings similar to the uranium producing areas of the United States and may have undiscovered resources of uranium of similar type and magnitude. The uraniferous conglomerates of South Africa and Canada, a type of deposit not found in the United States, are the most extensive low-cost deposits presently known in the world. Uranium resources in conglomerate should be competitive in the future US market and will figure prominently in the world market. Sweden has large reserves of uraniferous shales which could become a significant source of uranium in the $10 to $20 price range before the end of the century, if lower cost reserves prove inadequate.

To the extent it can be effectively used, low-cost thorium should be amply available during the next 35 years. Major deposits in India, Canada, and the United States should be capable of supplying 1 000 000 tons, and a number of other areas also have known or potential resources.

Because of the relatively high energy content of uranium and thorium as nuclear fuels, the geographical location of their ores is not of major economic importance. Consequently, the existence of supplies of these materials should be viewed on a world-wide basis with transportation costs a minor consideration. Utilization of nuclear resources on a world-wide basis should assure their availability at reasonable costs to meet expected requirements well into the next century.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/256 États-Unis d'Amérique

Ressources en combustible et quantités disponibles pour l'énergie d'origine nucléaire civile, 1964-2000

par R. L. Faulkner et W. H. McVey

Lors de la première Conférence de Genève sur l'utilisation de l'énergie atomique à des fins pacifiques tenue en 1955, le monde a eu l'occasion de passer en revue pour la première fois l'état des ressources en matières premières nucléaires. De grands programmes de production d'uranium commençaient à prendre forme et on a mis en relief les efforts passés et les espoirs de succès futurs. Ces espoirs étaient amplement satisfaits au moment où s'est réunie la deuxième Conférence de Genève en 1958. Des mesures étaient déjà envisagées dans les principaux pays producteurs pour limiter l'expansion future de la production. Bien que l'achèvement des projets de prospection déjà entrepris, l'exploration des réserves et l'accroissement des capacités de production aient été poursuivis pendant un an ou deux, l'effort avait déjà atteint son maximum et une diminution de cet effort était prévu, sauf dans les pays qui n'avaient pas encore établi de base solide d'exploration des ressources et de production et qui désiraient être assurés de disposer au moins de réserves suffisantes pour satisfaire leurs besoins.

Une baisse de l'optimisme du point de vue du temps qu'il faudra pour mettre au point des centrales nucléaires compétitives a accentué l'impression de surproduction et a ramené à l'arrière-plan les pro-

blèmes de disponibilité de matières premières. La production mondiale d'uranium a atteint un maximum en 1959 et est maintenant très peu au-dessus de la moitié de ce maximum. Les évaluations des réserves mondiales d'uranium à bon marché ont atteint également un maximum d'un peu plus d'un million de tonnes, mais ces évaluations des réserves sont depuis lors tombées de 700 000 à 600 000 tonnes (chiffres exprimés en tonnes courtes (907,20 kg) de U_3O_8). Les additions à ces réserves sont inférieures à la production, même à allure réduite, et les ré-évaluations économiques liées à la chute des prix mondiaux réduisent ces réserves encore davantage.

Paradoxalement, le niveau actuel relativement bas de la production et des réserves d'uranium coïncide, au moment où se tient la troisième Conférence, avec un optimisme renouvelé au sujet de l'étendue prochaine des utilisations de l'énergie nucléaire à des fins civiles. La production continuera à diminuer, mais des besoins en uranium rapidement croissants sont maintenant prévus pour le proche avenir. Les besoins croissants pour les années 1970, après une longue période de déclin dans la production et la prospection de l'uranium, pourraient mettre à l'épreuve nos capacités à découvrir, exploiter et produire de l'uranium en quantité suffisante.

L'extrapolation à l'échelle mondiale des besoins en uranium n'a pas été poussée en détail au-delà de 1980, mais le total des besoins des États-Unis peut varier de 600 000 tonnes à un million de tonnes ou même davantage d'ici l'an 2000, ceci comparé à des réserves à bon marché connues d'à peu près 160 000 tonnes, avec l'addition possible, mais non certaine, de 400 000 tonnes supplémentaires dans les régions minières de l'ouest où l'uranium peut être présent en quantités comparables. Les informations concernant de l'uranium plus coûteux qui pourrait être disponible à des prix atteignant 20 dollars la livre sont peu nombreuses, mais les quantités totales disponibles pourraient fort bien être considérablement moins du double des réserves à bon marché.

L'utilisation du thorium dans des réacteurs convertisseurs ou surgénérateurs thermiques avancés pourrait ralentir l'épuisement des ressources en uranium, lorsque ces systèmes entreront en fonctionnement. Les États-Unis sont bien pourvus en réserves de thorium disponibles à bas prix. Des progrès dans les processus hydrométallurgiques pourraient retarder l'utilisation de l'uranium ou du thorium à prix élevé, ou réduire le coût estimé de l'extraction à partir de matériaux très pauvres, à la fois directement et par l'utilisation économique des sous-produits.

La situation géographique des ressources en combustible nucléaire est de faible importance du point de vue économique à cause de la grande quantité d'énergie qu'ils renferment. Les quantités disponibles de combustibles nucléaires peuvent par conséquent être considérées sur une base mondiale, ce qui pourrait prolonger la durée pendant laquelle on pourra les obtenir à des prix raisonnables.

A/256 США

Запасы топлива и их доступность для ядерной энергетики (1964—2000)

Р. Л. Фолкнер, У. Г. Мак-Вей

На Первой международной конференции по мирному использованию атомной энергии в 1955 году мир впервые узнал о запасах ядерного топлива. Начали оформляться основные программы производства урана, возлагались надежды на успехи в будущем, которые были осуществлены к моменту начала Второй международной конференции по мирному использованию атомной энергии в 1958 году. К этому времени в важнейших уранодобывающих странах уже обсуждались меры к ограничению дальнейшего расширения производства. Хотя завершение начатых работ по разведке урана и дальнейшая разработка запасов и повышение производственных способностей продолжалось еще год-два, стимул уже достиг своей высшей точки и предпринимались шаги к снижению производства, за исключением тех стран, которые еще не создали у себя значительных запасов и базы производства и которые хотели убедиться по крайней мере в наличии источников сырья, необходимых для удовлетворения своих собственных потребностей.

Спад энтузиазма, отмечаемый по шкале зависимости времени от степени развития рентабельной ядерной энергетики, подтверждал мнение об избытке сырья и способствовал уменьшению значения проблемы наличия сырья. Мировое производство урана достигло максимума в 1959 году и в настоящее время находится на уровне, немного превышающем половину максимальной величины. Оценка запасов дешевого урана в мировом масштабе также достигла наивысшего значения в 1959 году; она составила несколько больше одного миллиона тонн. Теперь мировое количество запасов дешевого урана составляет около 600—700 тыс. *т* в пересчете на U_3O_8 (все данные указаны в коротких тоннах, 1 кор. *т* = 907,2 *кг*). Прирост запасов ниже прироста производства урана даже в условиях замедленных темпов; кроме того, экономические переоценки, связанные с падением мировых цен, еще больше уменьшают запасы.

Этот сравнительно низкий уровень производства и запасов урана совпадает на конференции с выражением оптимизма относительно широкого применения ядерной энергии в гражданских целях. Производство урана будет и дальше сокращаться, однако полагают, что в недалеком будущем потребность в уране быстро возрастет. Увеличение спроса на уран в 70-х годах вслед за периодом длительного упадка добычи и разведки урана легко может превысить наши возможности на поиск, разработку и производство достаточного количества урана.

Мировые потребности в уране детально разработаны не дальше 1980 года. В США общая потребность в уране до 2000 года колеблется от 600 тыс. до 1 млн. *т* и более. В настоящее время запасы дешевого урана в США составляют примерно 160 тыс. *т* и, возможно, но не наверное, еще 400 тыс. *т* в западных ураноносных провинциях. Сведения о более дорогостоящих запасах ядерного топлива (приблизительно 44 *долл/кг*) скудны, но доступные количества этих запасов могут оказаться значительно меньше количества, необходимого для пополнения ресурсов дешевого топлива.

Использование тория в усовершенствованных реакторах-конвертерах и реакторах-размножителях на тепловых нейтронах может уменьшить расход урана, когда эти системы войдут в эксплуатацию. США хорошо обеспечены торием, доступным по низкой цене. Успехи гидрометаллургических процессов смогут отдалить то время, когда потребуется использовать дорогостоящий уран или торий, или смогут сократить предполагаемую стоимость извлечения урана из очень низкосортных источников либо непосредственно, либо путем экономически выгодного извлечения побочных продуктов.

Ввиду высокого энергосодержания ядерного топлива географическое расположение запасов этого топлива с экономической точки зрения не имеет важного значения. Поэтому наличие запасов ядерного топлива может рассматриваться во всемирном масштабе, что должно увеличить ресурсы такого топлива по умеренной цене.

A/256 Estados Unidos de América

Fuentes de combustible y disponibilidad de la energía nuclear para usos civiles entre 1964 y 2000

por R. L. Faulkner y W. H. McVey

En la Primera Conferencia de Ginebra sobre la Utilización de la Energía Atómica con Fines Pacíficos, celebrada en 1955, el mundo tuvo da oportunidad de considerar por primera vez el estado de las reservas de materias primas nucleares. Comenzaban a desarrollarse grandes proyectos para la producción de uranio y se hizo hincapié en los esfuerzos pasados y en la esperanza de futuros éxitos. Estas esperanzas se vieron cumplidas en su mayoría en 1958, año de la Segunda Conferencia de Ginebra. Ya en ese año se estaban adoptando medidas en los principales países productores para prevenir una mayor expansión de la producción. A pesar de que se terminaron proyectos de exploración que ya habían sido comenzados y de que la explotación de reservas y el aumento de la capacidad de producción, se continuó por uno o dos años, el estímulo habia alcanzado su punto culminante, y se estaban ya proyectando menores esfuerzos; excepto en los países que todavía no habían establecido una base de reservas y producción importante y que querían tener al menos una fuente segura de suministro para cubrir sus propias necesidades.

La disminución del entusiasmo en lo que respecta al tiempo de desarrollo de una potencia nuclear competitiva sirvió para hacer más aparente la superproducción y quitar importancia al problema de la disponibilidad de materias primas. La producción mundial de uranio alcanzó el máximo en 1959, y ahora es solamente un poco mayor que la mitad de ese máximo. Se estima que las reservas mundiales de uranio de bajo costo también alcanzaron un máximo de algo más de un millón de toneladas, pero estas reservas han decredico hasta unas 600 000 o 700 000 t de uranio en la forma de U_3O_8. Todos estos datos se dan en toneladas cortas (907,2 kg). Los aumentos en la reserva son menores que la producción incluso a ritmo reducido y las reevaluaciones económicas relacionadas con los decrecientes precios en el mercado mundial están reduciendo aún más las reservas.

Paradójicamente, este estado relativamente bajo de la producción y reservas de uranio coincide en esta Conferencia con un nuevo optimismo con respecto a los usos extensos de la energía nuclear para fines no militares. La producción continuará decreciendo, pero se espera que la demanda de uranio aumentará rápidamente en un futuro próximo. La creciente demanda de uranio durante el decenio de 1970-1980 que habrá seguido a un largo período de decadencia de la producción y exploración del uranio, aumentará las dificultades para explorar y producir suficiente uranio.

La pósible demanda mundial de uranio no ha sido calculada detalladamente después de 1980, pero las crecientes necesidades de los Estados Unidos pueden variar de 600 000 t a 1 000 000 de t o más para el año 2 000. Compárense estas cantidades con la presente reserva de uranio de bajo costo de cerca de 160 000 t y posiblemente unas 400 000 t adicionales que pueden existir en nacimientos de las regiones mineras del oeste. La información acerca del uranio de precio alto del que podría disponerse a precios hasta de 20 dólares la libra es inadecuada, pero las cantidades disponibles están lejos de doblar la reserva de uranio de bajo costo.

La utilización del torio en los reactores convertidores avanzados y en los reactores reproductores térmicos puede hacer más lento el agotamiento de las reservas de uranio cuando estos sistemas empiecen a ser prácticos. Los Estados Unidos son un país bien provisto de reservas de torio a bajo costo. Los adelantos en procesos hidrometalúrgicos pueden retardar el día en que se necesite usar uranio o torio de precio alto o pueden reducir el costo de recuperación usando fuentes de bajo contenido, directamente y utilizando económicamente los productos secundarios.

La situación geográfica de las reservas de combustible nuclear tiene poca importancia económica debido a su gran contenido de energía. La disponibilidad de combustibles nucleares puede por lo tanto ser considerada bajo un punto de vista mundial. De esta manera, esta disponibilidad puede prolongarse a precios razonables.

The development of nuclear energy in relation to the resources of nuclear materials

By J. C. van Staveren and J. J. Went *

For the economic evaluation of nuclear energy, studies have been made of the construction cost of nuclear installations as well as the cost of the fuel cycle. Although it is generally accepted that, at least for a long time to come, the capital investments for nuclear plants will remain high compared with those for conventional thermal power stations, a low fuel cycle cost is essential for competitive nuclear power. Fuel cycle costs are of primary importance for world economy when fossil energy sources are running out and a large scale use of nuclear energy will be necessary. The price of uranium and thorium, although not very important for the present day fuel cycle cost, depends on the availability of these materials.

In this paper the relation between the magnitude of the resources, the consumption and the future cost of uranium and thorium and the price of nuclear energy is discussed. Two different aspects are important—namely, the influence of raw material price on the start-up of a nuclear programme and on a running nuclear energy production.

RESOURCES OF NUCLEAR MATERIALS

The data used in the following discussion of uranium and thorium resources are taken from two sources. The first is a compilation of the nuclear resources given by the U.S. Atomic Energy Commission in its report *Civilian Nuclear Power : a Report to the President, 1962*, and more specially in Appendices I and II of this report. The second source is EURATOM Report 414 *The Problem of Uranium Resources and the Longterm Supply Position* prepared by the Consultative Committee of the Supply Agency of EURATOM (September 1963).

Attention is drawn to the fact that EURATOM gives the amount of uranium ore available in 1963 at a price up to $10/lb U_3O_8, while the USAEC adds to this the cumulative amount of uranium already delivered up to 1962. The figures for the USAEC reserves available at $10/lb U_3O_8 have therefore been corrected so that they may be compared with the EURATOM data. Thereby, the USAEC estimates for reasonably assured resources of U_3O_8 at a cost up to $10/lb are reduced by half.

Only the needs of nuclear materials for the production of electricity in the Western world, to which the two estimates of reserves relate, are discussed here. General conclusions cannot be drawn unless comparable estimates for the whole world are obtained.

CONSUMPTION AND INVESTMENT OF NUCLEAR MATERIALS

Three aspects of the consumption or investment of nuclear materials in four different reactor concepts are discussed :

(*a*) The percentage of heavy atoms present in the primary material, natural uranium or thorium, that can be fissioned either with or without recycling of the fuel;

(*b*) The capacity of different reactor types to produce new fissile material and its isolation for use in a different reactor than the one in which it is made;

(*c*) The amount of natural uranium or thorium to be invested per MW(e) installed.

Questions related to the costs of fuel enrichment, fuel element fabrication and reprocessing will not be discussed here as they are independent of the cost of the original material.

REACTOR TYPES

The three aspects mentioned above are discussed for two present day reactor types (converters) and two types of breeder reactors.

Natural uranium gas-cooled graphite reactor (GCR)

The Latina reactor in Italy is taken as an example but with a higher burn-up than guaranteed by the fuel element manufacturer (3 000 MWd/t instead of 2 500 MWd/t).

Light-water moderated and cooled reactor

An example is the boiling water reactor (BWR) near Garigliano in Italy. Here, slightly enriched uranium is used, but the amount of natural uranium required for the production of the enriched uranium in a diffusion installation is given. It is assumed that

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* N.V. SEP (Co-operating Electricity Producing Companies), Arnhem.

the depleted uranium of this diffusion process still contains 0.25% ^{235}U and that the ^{235}U content of the fuel at the end of the fuel cycle is still higher than in depleted uranium and even higher than in natural uranium. Credit proper to these potentially available amounts of ^{235}U is given.

Fast breeder reactor (FBR)

The Enrico Fermi reactor is an example. This is fuelled with ^{235}U, but in future fast breeder reactors the fuel will be mainly plutonium to increase the breeding ratio. As investments in nuclear material for each MW(e) installed have to be given, computations cover two different cases, one using ^{235}U as the fissile material at start-up, the other with plutonium, that is :

(*a*) The amount of natural uranium necessary to produce the highly enriched ^{235}U in a diffusion installation;

(*b*) The amount of natural uranium required to produce the necessary amount of plutonium in a GCR or in a BWR.

The isotopic composition of plutonium found after a burn-up of 3 000-4 000 MWd/ton natural uranium is such that about the same weight of either ^{235}U or plutonium is required.

Thermal breeder reactor (TBR)

Since no large scale working example yet exists, a conceptual design of a heavy-water homogeneous suspension reactor is chosen as an example. The following data relevant to the conceptual design is used :

Total thermal power.	800 MW(th)
Net electrical power	200 MW(e)
Fuel concentration (ThO_2-$^{235}UO_2$ in D_2O)	400 g/l
$^{235}UO_2$ concentration in ThO_2 . . .	1.5%
Moderator.	D_2O
Ratio reactor vessel volume to total reactor volume	1 : 2
Power density in reactor vessel . .	40 kW/l

In order to reach the breeding state in a thermal thorium reactor which starts by burning ^{235}U or a mixture of plutonium isotopes in the first cycle, an additional amount of ^{235}U or plutonium is needed to produce sufficient ^{233}U. These additional amounts of ^{235}U or plutonium are incorporated in the conceptual design data for the thermal breeder.

In Table 1 are given the nuclear materials investment and consumption for the four reactor types. It is assumed that only 25% of the original atoms (^{238}U in the FBR and ^{232}Th in the TBR) will be fissioned in the breeder reactors. This amount is about equivalent to 250 000 MWd/ton. Although slightly different values may be obtained for other comparable reactor conceptions, the general picture will be the same.

Table 1. Nuclear material requirement for different reactor types expressed in terms of natural uranium

	Reactor type			
	GCR	BWR	FBR[a]	TBR[b]
Investment	Ton U(nat)/MW(e)			
^{235}U	1.5	1.35	1.0	0.35
Pu from GCR . . .	—	—	1.75	0.7
Pu from BWR . . .	—	—	2.55	1.2
Consumption	MWd/ton U(nat)			
Without recycle . .	3 000	4 000		
and Pu credit (kg/ton U(nat)) . .	2.7	1.8		
With recycle	4 800	6 000	250 000 + Pu	250 000

[a] U-Pu cycle breeding factor > 1.
[b] Th-^{233}U cycle breeding factor = 1.

From Table 1 it is obvious that, as regards materials investment, it is better to start breeders with ^{235}U produced in a diffusion installation than with a mixture of plutonium isotopes produced in present day power reactors. This picture may change completely, however, if a neutron saving near-breeder reactor can be constructed for plutonium production to replace the present day converters. Several conceptions of the heavy-water moderated reactors offer possibility of this. If the conversion factor of such a reactor were considerably higher than that of the GCR or the BWR, more plutonium could be produced than the equivalent amount of ^{235}U obtained from natural uranium in a diffusion installation (4.6 kg ^{235}U/ton natural uranium). The use of these near-breeders would thus result in a smaller investment of natural uranium in breeder reactors compared with the use of ^{235}U extracted from natural uranium.

ENERGY CONTENT OF THE RESERVES

In Table 2 the energy content of the nuclear material resources is given as a function of their price per unit weight for both converter and breeder reactors.

The burn-up values of the two converter reactors (CGR and BWR) are between 3 000 and 6 000 MWd/ton natural uranium depending on whether plutonium is burned in the same reactor in which it is produced or extracted for other purposes. These values are equivalent to a burn-up of about 0.3 to 0.6% of the original amount of uranium atoms. In Table 2 an average value of 0.5% burn-up is used for these reactors.

In a breeder reactor 25% of the atoms can be used, which gives a burn-up value 50 times the burn-up in a converter reactor.

Table 2. Energy content of reserves

	Price	USAEC		EURATOM	
		Q values [a]		Tonnes metallic uranium	
		USA		USA	Western world
Fossil fuel	\$ 5/25 × 10^6 Btu	6			
Burn-up		0.5%	25%		
	\$/lb				
	-10	0.05	2.5	130 000	450 000
	10-30	0.12	6	—	—
U_3O_8	30-100	3.5	175	—	—
	100-500	150	7 500	—	—
	\$/lb				
	-10	—	1.6	—	—
	10-30	—	1.6	—	—
ThO_2	30-100	—	175	—	—
	100-500	—	16 000	—	—

[a] $Q = 10^{18}$ Btu.

The following conclusions can be drawn from Table 2 :

(*a*) Up to \$30/lb U_3O_8, only a very small amount of nuclear materials and thus of nuclear energy (0.17 Q, where $Q = 10^{18}$ Btu) is available if the uranium is used in the converter reactors mentioned above. Taking into account that the present world market price for uranium is only \$5/lb U_3O_8, further development of present day power reactors is not very attractive. It should be kept in mind that the total annual energy consumption in the USA is about 0.05 Q and in the whole world 0.15 Q.

(*b*) Using breeder reactors, fifty times more energy can be produced from the same amount of uranium. This means that no objection should exist to paying fifty times a given price for the same amount of natural uranium (e.g., \$500/lb U_3O_8 instead of \$10/lb U_3O_8). Under such conditions the raw materials problem will cease to exist in the large scale application of nuclear energy even in the unforeseeable future. The uranium reserves of the USA will then present an energy content of 7 500 Q.

This calculation does not apply, however, to the nuclear material investment for the start-up of the reactor. For this, cheap uranium is essential.

(*c*) When the energy content of the material reserves is calculated, assuming the use of neutron-saving near-breeders, it stands to reason that the figures are intermediate between those derived from present-day converters and from future breeders. When uranium is used in such reactors, three or four times the burn-up values of the converter reactors may be reached. Even higher burn-up values are possible with thorium.

In general these conclusions are now accepted and give rise to the financial consequences (which however are not yet generally accepted) concerning the start-up investment of a large nuclear programme.

THE COST OF NUCLEAR ELECTRICITY

From Table 1 it can be seen that the nuclear material investment of the different reactor types is of the same order of magnitude (0.3-2.6 ton U(nat)/MW(e); but that the nuclear material consumption differs by orders of magnitude (3 000-250 000 MWd/ton U(nat)). At the present low prices of uranium, the raw material cost does not play an important role in the costs of nuclear energy. If, however, it becomes necessary to pay \$30/lb U_3O_8 instead of \$5/lb U_3O_8, the raw material costs could be limiting.

Table 3. The influence of price of natural uranium on nuclear material cost per kWh produced and per kW(e) installed[a]

Reactor	\$ 5/lb U_3O_8		\$ 30/lb U_3O_8	
	Mill/kWh produced	\$/kW(e) installed	Mill/kWh produced	\$/kW(e) installed
GCR . .	0.4	19.5	2.4	115
BWR . .	0.32	17.5	1.9	105
FBR . . .	< 0.001	13	0.005	80
TBR . . .	< 0.001	4.5	0.005	27

[a] Only the contribution of U_3O_8 to the total costs of generating electricity is given.

In Table 3 the pure raw material price per kWh(e) produced and per kW(e) installed is given for each of the four reactor types. It should be kept in mind that, even if the specific power density of a particular reactor could be increased in the future, the estimates for the investment in nuclear materials are still rather low. For operational reasons it is necessary to have about 10% spare fuel elements in stock. Furthermore, investment of nuclear material must be larger than the amount necessary for just one fuel cycle, because the different fuel cycles overlap during fabrication, cooling and reprocessing of the fuel elements. These facts are neglected in the calculations.

From the data given in Table 3 it is concluded that an increase in the price of the raw material by a factor of 6 will completely eliminate the applicability of converter reactors, with respect both to the kWh price and to the investment per kW installed.

MATERIALS CONSUMPTION IN A LARGE POWER PROGRAMME

To determine how long the known nuclear material reserves could last in a future large scale nuclear power programme, the consumption of raw materials can be calculated using Table 1 and Table 2 and by making assumptions about the scale of the programme. The following assumptions are made only in illustration and do not include any suggestions as it is not known when breeder reactors will be available on a technical scale; certainly this stage will not be reached within the next ten years.

The total electricity production capacity at the end of 1962 in the Western world was 350 000 MW. It is assumed that this capacity will be doubled in twelve years, which is a rather conservative estimate, because the present doubling time is about 10 years.

The nuclear material consumption can be calculated assuming that a large scale nuclear power programme will start in 1970 and that from then on 50% of the new installed electric capacity will be nuclear with a load factor of 75%, it is also assumed that the doubling time of the fissile material in the FBR is 10 years, that the TBR will not produce an excess of ^{233}U (breeding factor = 1) and that plutonium and ^{233}U are burned in the reactors in which they were produced.

The quantity of nuclear materials needed for the effectuation of such a programme can then be calculated for a given number of years. It is also possible to calculate the number of years in which a certain amount of material is consumed.

In Table 4 the results of some calculations of the consumption of nuclear material in a large scale nuclear power programme are given.

Table 4. Nuclear material consumption in a world-wide nuclear power programme[a]

Reactor type	Years to use up 450 000 ton U_3O_8 World reserve up to $ 10/lb	Capacity of breeder reactors, fuelled with Pu from different reactor types MW (e)		Quantity of nuclear material needed up to year 2000 ton U (nat)
		FBR	TBR	
GCR . .	7	65 000	160 000	7 500 000
BWR . .	8	35 000	75 000	6 000 000
FBR . . .	17	280 000	800 000	1 300 000
TBR . . .	32	—	—	450 000

[a] The programme starts in 1970 with 50% of the new installed capacity as nuclear energy and runs at a load factor of 75%.

In Table 2 the known reserves of uranium available at \$10/lb U_3O_8 are given as 450 000 metric tons. If the ratio of the amount of uranium available up to \$30/lb U_3O_8 to the amount available up to \$10/lb were the same in the USA as in other parts of the world, 1 650 000 metric tons of natural uranium at a price up to \$30/lb would be available in the Western world.

The values for the estimated nuclear material consumption in a large scale nuclear power programme as given in Table 4 are high compared with the known reserves. If a breeder programme should be started for the production of electricity, it will nevertheless be necessary to watch the uranium reserves rather carefully. The later such a programme starts, the more urgent this will be, owing to the previous use of fissile material by the converter reactors and the larger capacity to be installed. If it will be long before a breeder programme can start, an intermediate stage of near breeder reactors would ease the situation, but with the limited uranium reserves in mind, it seems advisable to start a breeder programme as soon as possible.

Thermal breeders seem favourable for a fast growing programme. It is a pity, therefore, that notwithstanding the interesting results obtained with the Homogeneous Reactor Experiment at Oak Ridge, USA, and the development work on a homogeneous suspension reactor at Arnhem in the Netherlands, the technical feasibility of such a reactor has not yet been demonstrated.

If large new reserves of uranium ores are found, the whole raw material situation with respect to a future large scale nuclear power programme might change. For this reason prospecting for unknown reserves would seem to be urgent. In view of these facts, however, it is obvious that a doubling of the reserves might be important but will certainly not be decisive.

CONCLUSIONS

The following conclusions are drawn from the facts discussed in this paper :

(*a*) Prospecting for cheap uranium resources is urgent;

(*b*) Rapid development of breeder reactors is essential for the future of nuclear energy which may have to meet the energy needs of the world;

(*c*) Large scale application of present day power reactors is undesirable;

(*d*) High conversion near-breeder reactors can be accepted for an intermediate period whilst breeder reactors are not sufficiently developed.

ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/366 Pays-Bas

Le développement de l'énergie nucléaire comparé aux réserves de matériaux nucléaires

par J. C. van Staveren et J. J. Went

Le prix de revient de l'énergie nucléaire a fait l'objet de plusieurs études détaillées. Les coûts du cycle de combustible nucléaire, notamment, ont été souvent discutés en détail. Cependant l'influence du prix de revient des matériaux nucléaires, qu'il s'agisse d'uranium naturel ou de thorium, est rarement prise en considération en fonction de la quantité disponible à ce prix. De plus, bien que la nécessité de disposer de réacteurs surgénérateurs en vue de la production future d'énergie nucléaire à grande échelle soit souvent soulignée, l'influence du prix de revient de la première charge fissile est fréquemment négligée.

Le mémoire traite des conditions matérielles pour la mise en œuvre initiale et l'exécution d'un programme nucléaire futur à grande échelle de construction de centrales nucléaires productrices d'électricité, en se fondant sur les hypothèses suivantes :

a) De 1970 à 2000, environ 50 % de la capacité de production d'électricité nouvellement installée sera nucléaire;

b) Pendant la période 1962-2000, la capacité installée sera doublée tous les 12 ans;

c) Le facteur de charge des centrales nucléaires sera 75 %.

En se fondant sur les réserves de matériaux nucléaires bruts, telles qu'elles ont été évaluées par l'USAEC et l'EURATOM, l'exposé traite de l'investissement et de la consommation de matières fissiles pour les réacteurs nucléaires actuels, les réacteurs à rapports de conversion élevé et les réacteurs surgénérateurs, rapides ou thermiques.

Les résultats indiqués ci-après détermineront le développement futur et l'application de l'énergie nucléaire.

a) La consommation des matières nucléaires dans les types actuels de centrales nucléaires, que le combustible soit enrichi ou non, se fait avec un si faible rendement que si l'on utilise seulement ces réacteurs, les réserves connues d'uranium naturel à des prix allant jusqu'à cinq fois le prix actuel seront épuisées vers 1983;

b) La production d'énergie dans les réacteurs surgénérateurs à uranium et thorium se fait avec un rendement tel que même les matériaux nucléaires très coûteux peuvent être utilisés si on en dispose abondamment;

c) Si le plutonium est produit par les centrales nucléaires actuelles comme première charge des réacteurs surgénérateurs, il faudra deux ou trois fois plus d'uranium naturel pour cette production de plutonium qu'en utilisant comme première charge l'uranium 235 séparé par une usine à diffusion;

d) Il sera nécessaire d'utiliser comme matière première pour la première charge des réacteurs surgénérateurs de l'uranium naturel relativement peu coûteux, pour éviter des investissements excessifs;

e) La première charge de matières fissiles des réacteurs surgénérateurs rapides est double ou triple de celle des réacteurs surgénérateurs homogènes thermiques;

f) Dans les réacteurs à eau lourde à rapport de conversion élevé, il est possible de produire au moins une quantité de plutonium équivalant aux quantités d'uranium 235 qu'on peut extraire de la même quantité d'uranium naturel.

Les résultats conduisent aux conclusions suivantes :

a) La prospection des ressources d'uranium à bon marché est urgente;

b) Le développement des réacteurs surgénérateurs est indispensable pour l'avenir de l'énergie nucléaire;

c) L'utilisation à grande échelle des centrales nucléaires actuelles n'est pas désirable;

d) Si les réacteurs surgénérateurs ne sont pas encore suffisamment développés, l'utilisation des réacteurs à eau lourde à rapport de conversion élevé sera acceptable pendant une période transitoire.

A/636 Нидерланды

Использование атомной энергии в связи с запасами ядерных материалов

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Проведено много детальных исследований стоимости атомной энергии. Особенно часто и тщательно рассматривалась проблема стоимости топливного цикла. Однако очень редко изучалось изменение стоимости ядерных материалов (природного урана или тория) в зависимости от количества этих материалов, имеющихся в продаже по этой цене. Кроме того, хотя часто подчеркивается необходимость создания реакторов-размножителей в целях производства атомной энергии в промышленном масштабе в будущем, однако оценкой влияния стоимости начальной топливной загрузки часто пренебрегают.

В данном докладе потребности в материалах, необходимых для начала и осуществления будущей программы строительства промышленных атомных электростанций в целях производства электроэнергии в крупных масштабах, рассматриваются на основе следующих предположений.

a) в период 1970—2000 гг. около 50% новой установленной электрической мощности будет приходиться на атомные электростанции;

b) время удвоения установленной электрической мощности составит 12 лет в период 1962—2000 гг.;

c) коэффициент нагрузки атомных электростанций будет равен 75%.

Основываясь на оценках запасов сырьевых ядерных материалов, сделанных Комиссией по атомной энергиии США и Евратомом, проблема производства и потребления ядерных материалов обсуждается в докладе применительно к существующим в настоящее время энергетическим реакторам, реакторам-конвертерам с высоким коэффициентом воспроизводства и реакторам-размножителям на быстрых или тепловых нейтронах.

Следующие полученные результаты требуют определения будущего развития и использования атомной энергии.

a) потребление ядерных материалов (обогащенных и необогащенных) в существующих энергетических реакторах настолько неэффективно, что при использовании этих реакторов существующие поставки природного урана по ценам, в пять раз превышающим ныне действующие цены, истощатся к 1983 году;

b) получение энергии в урановых и ториевых реакторах-размножителях настолько эффективны, что в них можно использовать даже очень дорогие ядерные материалы, имеющиеся в достаточном количестве;

c) если в существующих энергетических реакторах производить плутоний для использования в качестве запального материала в реакторах-размножителях, то для этого потребуется в два-три раза больше природного урана, чем при использовании в качестве запального топлива U^{235}, производимого на диффузионной установке;

d) чтобы избежать чрезмерных капиталовложений для производства первых запальных материалов для реакторов-размножителей, придется использовать в качестве исходного материала довольно дешевый природный уран;

e) в реакторах-размножителях на быстрых нейтронах запальная загрузка делящихся материалов в два-три раза выше, чем в гомогенных реакторах-размножителях на тепловых нейтронах;

f) в тяжеловодных реакторах с высоким коэффициентом воспроизводства из одинакового количества природного урана можно получить ядерный эквивалент плутония, по крайней мере такой же, как и для U^{235}.

На основе вышеуказанных результатов можно сделать следующие выводы:

a) необходимы поиски дешевых месторождений урана;

b) будущее использования атомной энергии требует разработки реакторов-размножителей;

c) широкое использование существующих энергетических реакторов нежелательно;

d) тяжеловодные реакторы с высоким коэффициентом воспроизводства могут быть использованы в промежуточный период при условии, если не будут еще достаточно разработаны реакторы-размножители.

A/636 Países Bajos

Desarrollo de la energía nuclear en relación con las reservas de materiales nucleares

por J. C. van Staveren y J. J. Went

Se han hecho muchos estudios detallados acerca del precio de coste de la energía nuclear. En particular, se han discutido frecuentemente con detalle los costes del ciclo de combustible. Sin embargo, rara vez se tiene en cuenta en aquel precio la influencia del precio de coste de los materiales nucleares, uranio natural o torio, en función de la cantidad disponible. Además, aunque se suele poner de relieve la necesidad de los reactores reproductores para una futura producción de energía nuclear a gran escala, se desprecia muchas veces la influencia del precio de coste de la primera carga nuclear.

En esta memoria se discuten las necesidades de material para la puesta en marcha y explotación de un futuro programa a gran escala de centrales nucleares para producción de energía eléctrica, partiendo de los siguientes, supuestos:

a) Desde 1970 al 2000 aproximadamente el 50 % de la capacidad de producción de energía eléctrica que se instale será nuclear;

b) El tiempo necesario para duplicar la capacidad instalada será de 12 años en el período 1962-2000;

c) El factor de utilización de las centrales nucleares será del 75 %.

Apoyándose en los datos sobre las reservas de materia prima nuclear calculados por la USAEC y EURATOM, se discute la inversión y consumo de materiales nucleares para reactores de potencia actuales, reactores de alta conversión y reactores reproductores rápidos y térmicos.

Los siguientes resultados sirven para determinar el desarrollo y aplicación futura de la energía nuclear:

a) El consumo de materiales nucleares en los actuales reactores de potencia, enriquecidos o no, tiene tan bajo rendimiento, que con estos reactores las reservas actualmente conocidas de uranio natural a precios incluso cinco veces el precio normal en la actualidad, estarán agotadas para 1983.

b) La producción de energía en reactores reproductores de uranio y torio es de tan alto rendimiento que se pueden emplear incluso materiales nucleares muy caros, disponibles en abundancia.

c) Si el plutonio que se produce en los reactores de potencia actuales se utiliza como carga de puesta en marcha de reactores reproductores, se necesitará dos o tres veces más uranio natural para producir plutonio, que empleando como carga de puesta en marcha ^{235}U, que puede producirse en una instalación de difusión.

d) Para la primera carga de puesta en marcha de reactores reproductores será necesario el empleo de uranio natural barato, como materia prima, para evitar una inversión de capital excesiva.

e) En reactores reproductores rápidos la carga de puesta en marcha de materiales fisibles es dos o tres veces mayor que en reactores reproductores homogéneos térmicos.

f) En los reactores de agua pesada de alta conversión al menos se puede producir una cantidad de plutonio nuclearmente equivalente a la cantidad de ^{235}U que se extrae de la misma cantidad de uranio natural.

Las conclusiones a que se llega a partir de estos resultados son:

a) Es urgente la prospección de recursos de uranio baratos;

b) Es esencial el desarrollo de reactores reproductores para el futuro de la energía nuclear;

c) No es aconsejable emplear los reactores de potencia de los tipos actuales en gran número;

d) Para un período intermedio se pueden aceptar reactores de agua pesada de alta conversión, si los reactores reproductores no se encuentran aún suficientemente desarrollados.

Uranium and thorium ore reserves and potential

by S. H. U. Bowie*

DEFINITIONS

Several estimates of uranium and thorium ore reserves have been made in recent years, but these have not always been meaningful since the term "reserves" has not been defined. Published figures have ranged from hundreds of thousands of tons of oxide to several millions of tons and this has resulted in uncertainty among non-geologists as to what can be regarded as an acceptable figure. The use of the term "ore" implies that the material can be mined and treated and the contained uranium or thorium recovered as a commercial proposition.

Ore reserves are defined by professional geologists in fairly precise terms, but in reports to non-geologists it is not always possible to make the three categories of "measured ore", "indicated ore" and "inferred ore" clearly understood. It is probably for this reason that the Council of the British Institution of Mining and Metallurgy has recently recommended to members that the term "ore reserves" should be restricted "to ore of which the quantity and grade have been established with reasonable assurance by a responsible professionally qualified person"[1]. It is generally accepted, for the purpose of classifying uranium resources, that material from which uranium can be recovered at a cost of less than $10 per pound of oxide can be classed as "ore". Therefore "ore reserves" should refer only to uranium that is recoverable at less than $10 per pound of oxide and of which the quantity and grade have been established with reasonable assurance by a responsible person with the necessary professional qualifications.

Ore reserves are estimated on such measurements and analyses of samples as are feasible as well as on geological knowledge of the character of the ore bodies. Hence figures are not precise. On the basis of our knowledge of metalliferous ore bodies that have been worked, it can be stated that the margin of error in estimating "measured ore" is about 20 per cent, and 50 per cent for reserves of all categories.

"Potential ore" can be defined as material which is not known sufficiently well to class as "reserves", or which cannot be worked profitably at the present time. Hence potential ore may be included in reserves only after it has been delineated with the required certainty or when technological improvements make it possible to recover the uranium below the ruling market price.

"Resources" of uranium and thorium include ore reserves and potential ore as well as material available in low-grade rocks such as granites or shales for which there seems little likelihood of economic recovery even at 10 times present extraction costs. However, resources may be drawn upon in times of emergency or may be regarded as a long-term safeguard against shortage of more conventional fuels.

URANIUM ORE RESERVES

Since the 1958 Geneva Conference, uranium reserves have been loosely quoted as being between 1 and 2 million tons of oxide. Yet in a recently published report [2] the "free-world" total is given as 450 000 metric tons of uranium metal (equivalent to 584 500 short tons U_3O_8). It seems necessary to examine the reasons for this apparent decrease and to consider what degree of certainty can be attached to published figures. Official estimates of reserves by the major producing countries at the end of 1958 are given in Table 1, together with figures for the end of 1961. During this interval output for the main producing countries was approximately 119 500 short tons U_3O_8, derived as shown in Table 2, which also includes production for the years 1958 and 1962. Production by Canada, the USA and the Republic of South Africa during 1959-1961, inclusive, amounted to 108 182 short tons U_3O_8, which should be added to the 1961 reserves when calculating the

Table 1. Uranium reserves in short tons[a] U_3O_8

Country	Year ending		
	1958	1961	1971[c]
Canada	414 577	277 968[b]	245 000[b]
USA	220 750	175 000	85 000
Republic of South Africa	370 000	150 000	128 000
Other countries	60 000	80 000	40 000
TOTALS	1 065 327	682 968	498 000

[a] Short tons times 0.77 gives metric tons uranium metal.

[b] Includes 1080 00 short tons additional "inferred" U_3O_8 estimated by Department of Mines and Technical Surveys.

[c] Estimate assuming no major discoveries in interim period.

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* Atomic Energy Division, Geological Survey of Great Britain.

Table 2. Production of uranium since 1957

Short tons U_3O_8

Country	1958	1959	1960	1961	1962
Canada	13 403	15 892	12 748	9 641	8 431
USA	12 570	16 420	17 760	17 399	17 010
France[a]	755	1 110	1 185	1 767	1 656
Republic of the Congo	2 300	2 300	1 200	—	—
Republic of South Africa	6 245	6 445	6 409	5 468	5 024
Australia	700	1 100	1 100	1 500	1 300
Totals	35 973	43 267	40 402	35 775	33 421

[a] Includes production from Malagasy Republic and Gabon.

Small tonnages of uranium were also produced in Portugal, Spain, Sweden, Finland, India, Japan, Italy, Western Germany, Southern Rhodesia and Colombia.

percentage reduction in reserves due to the revision. However, this tonnage is almost exactly equivalent to that of the additional "inferred" ore referred to in Table 1, hence the revision downwards has been 35 per cent, or 25 per cent if the additional ore, not estimated by the mining companies holding the properties, is included.

The main reasons for the revision downwards of USA reserves, other than production, are that the earlier estimates were based on drilling which in some cases was inadequate to delineate the ore bodies with sufficient accuracy, and on gamma-ray logs of the holes which overestimated the grade. The earlier Canadian figures were mainly based on borehole data that were insufficient to take account of the loss of ore due to faulting, lateral thinning of the ore horizons and the additional complication of dykes intersecting the ore bodies. In the Republic of South Africa, the main causes for revision downwards are that the average grade of the ore has proved to be less than was originally estimated (0.4 lb U_3O_8 per short ton as compared with 0.66 lb per short ton) and that unpredicted faulting has been encountered as mining has progressed.

This revision of ore reserve estimates is understandable when one considers that only a small proportion of uranium in the major ore-fields of the world has been "measured". To take Canada as an example, only about 2.5 per cent of the ore reserves fall into the "measured" class. The bulk of the ore (about 75 per cent) is inferred, that is, the quantitative estimates are based largely on knowledge of the geological character of the deposit and there are few available samples or measurements to confirm them. Similarly, in the Republic of South Africa only 18 500 short tons of oxide fall into the "measured" category. The remaining 131 500 short tons are known with a lesser degree of certainty. It should be clear from this that ore reserves are estimates made with differing degrees of certainty and that too much reliance should not be placed on quantitative estimates of "indicated" or "inferred" ore. However, because of geological knowledge of the distribution of uranium in the three main ore-fields, there seems to be a reasonable certainty that ore reserves available in countries that have published data amount to about 500 000 tons of recoverable oxide.

URANIUM ORE POTENTIAL

Although ore reserves are assessed to be of the order of 500 000 tons of oxide, this does not mean that no more uranium is available. To estimate uranium ore potential we have to rely on geological knowledge of the distribution of abnormal concentrations of uranium in the earth's crust and on the past history of uranium discovery.

An analysis of discoveries over the past fifteen years has shown that few important uranium fields have been found by prospectors. Three of the most important fields in the world, which together contain over 90 per cent of the estimated reserves, were all discovered as a result of basic geological research. Studies carried out on the carnotite occurrences of the USA early in the century resulted in the discovery after the Second World War of the primary uranium deposits of the Colorado Plateau which are estimated to contain more than 90 per cent of the total USA reserves. Likewise, research carried out in the early 1920s led, in 1945, to the recognition of the vast potential of the Witwatersrand as a uranium producer; and the discovery of the third major field, Elliot Lake, Canada, was a product of geological deduction based on the similarity of the host rocks to those of the Witwatersrand and on studies of the natural leaching of uranium ores. No major ore field is known to have been discovered since 1955, despite the widespread search effort maintained up to 1958 and more localized prospecting continuing up to the present time in many parts of the world. This indicates that a high proportion of outcropping deposits has already been located and that additional reserves will prove more difficult to find than those presently known. However, this can to some extent be offset by the assimilation of the vast amount of empirical data on uranium ore bodies that has accumulated over the past decade, by undertaking further fundamental studies directed at increasing our knowledge of where uranium is likely to be found, and by developing geophysical and geochemical methods of locating hidden ore deposits that cannot be detected by surface radiation methods.

The potential of uranium likely to cost less than $10 per pound of oxide to produce seems, on the basis of past discovery and on current geological knowledge, to be of the same order as reserves. This means there is a reasonable chance of finding twice as much ore as is estimated to exist. Added to this is ore from which uranium cannot yet be extracted economically, but which might be treated more cheaply by improved beneficiation methods. The most obvious way of substantially increasing uranium reserves would be the perfection of a process or processes for recovering uranium from black shales and phosphate rocks. Vast tonnages of these rocks, containing between 0.005 and 0.03 per cent U_3O_8, occur in the USA, North Africa, Sweden, Great Britain and the Near East, and could yield 10 million tons or more uranium. However, the cost of producing uranium from these sources (by-product uranium from phosphate excepted) is likely to be more than $20 per pound of oxide, and, so long as there are reasonable prospects of discovering more uranium that can be recovered at less than $10 per pound of oxide, it will be expedient to explore for more deposits of the type now being worked.

On present geological knowledge, it seems probable that potential ore in the Colorado Plateau province is of the same order as recently-estimated reserves. The same can be said of the Canadian Shield, but it is doubtful if the Witwatersrand Basin has a large potential; and to date there have been no indications of another uranium field in the Republic of South Africa. Outside these three main producing areas, possibilities exist of discovering fairly large tonnages of uranium, for example, in the Singhbhum copper belt of India, where low-grade ore has been proved and is presently being worked at the Jaduguda mine. In Pakistan there is a possibility of appreciable tonnages of ore being proved in the Sulaiman Range, where a uranium mineral akin to tyuyamunite, $Ca(UO_2)_2(VO_4)_2.10\,H_2O$, has recently been discovered. No important discovery of uranium has been made in Australia in recent years, but the Australian Shield is undoubtedly favourable for the occurrence of uranium, particularly in the environment of unconformities in pre-Cambrian rocks. The most favourable area in Africa would appear to be the Copper Belt arc which stretches from Northern Rhodesia, through the Republic of the Congo and into Angola. In addition to the Congo deposits, numerous occurrences of uranium have been recorded in this province and it is to be expected that further economic deposits will eventually be discovered. More detailed geological information is required to help assess the potential of South America, though, on the basis of what is already known, there would seem to be a good chance of more uranium being found in both the South American Cordillera and the Brazilian Shield. Other countries such as Mexico, Finland, Italy, Spain, Portugal and Japan clearly have a potential as uranium producers, but output from these may not be large.

AVAILABILITY OF URANIUM

In considering the long-term requirements of uranium, not only do the reserves have to be considered, but the rate at which they can be mined must be taken into account. If it is assumed that production in Canada, USA, the Republic of South Africa and other countries is determined by the contracts currently agreed, then reserves at the end of 1971 will be approximately as shown in Table 1. It is apparent from this table that only Canada and the Republic of South Africa will be in a position to export substantial quantities of uranium after 1971, assuming no new major discoveries are made in the USA or elsewhere during the intervening period. However, since uranium is mined as a by-product of gold in the Republic of South Africa, it is unlikely that the annual output of uranium costing less than $10 per pound of oxide could exceed 6 000 to 7 000 short tons. Thus if the annual requirement of uranium is about 22 000 metric tons (equivalent to 28 600 short tons U_3O_8) by 1975, as is indicated in the Euratom report [2], then about three-quarters of the requirement would have to come from Canada and other countries. But, as nearly half of the presently estimated reserves of Canada are in the property of Denison Mines Ltd., production may be restricted because of the limited output possible from a relatively small area.

Also, it must be noted that by 1965 it is probable that only one uranium plant will be in operation in Canada, while in the Republic of South Africa only five out of the peak number of twenty-two will be in production. Several plants in both countries will then be on a care and maintenance basis and their effectiveness as producers of uranium concentrate will depend on how long they are kept in this way. It is assumed that most existing plants will be in operation in the USA, but by 1975 presently-estimated ore reserves will be seriously depleted. Even if the annual requirements by 1975 prove to be appreciably less than Euratom have forecast and the figure of 22 000 metric tons is only reached some years later, there will still be a need for new deposits of uranium to be found and exploited.

THORIUM ORE RESERVES

Little prospecting has been carried out for thorium in post-war years and most discoveries have been associated with the search for uranium. Both the disseminated uranium deposits of the Elliot Lake district and the pegmatitic granite dykes of the Bancroft contain appreciable thorium which can be recovered as a by-product. Thus by 1962 Canada was able to capture a considerable share of the world's thorium market in competition with that produced from concentrates of monazite and thorite.

Traditional resources of thorium occur mainly in India, Brazil, Australia and Nyasaland in the form of placer deposits [3]. Thorium vein deposits occur in Cape Province, Republic of South Africa, and in Idaho and Montana. In Nigeria, thorite, in addition to occurring in placer deposits, is obtained as a by-product of the mining of weathered granite for pyrochlore.

Tentative figures for reserves of thorium are given in Table 3.

Table 3. Tentative estimate of thorium reserves

Country	Reserves tons ThO_2
India	300 000
Canada	200 000
Brazil	200 000
USA	150 000
Australia	50 000
Republic of South Africa	15 000
Nigeria	15 000
Nyasaland	15 000
Total	945 000

ASSESSMENT OF PRESENT POSITION

On available estimates of uranium requirements it is probable that there will be no difficulty in meeting demands until 1975. However, reserves are small compared with those of the two other main fuels, oil and coal, and it would therefore seem prudent to devote more energy to research in the field of radiogeology. We should increase our knowledge of where economic concentrations of uranium and thorium are likely to occur in the earth's crust and develop geophysical and geochemical methods of locating hidden deposits that cannot be detected at surface by radiometric techniques.

The cost of prospecting will increase as deposits that outcrop are discovered and worked out, but it still seems reasonable to assume that it will prove more economic to prospect for low-cost sources of uranium than to concentrate on devising new methods of recovering high-cost uranium (i.e., material costing more than $20-30 per pound of oxide to produce). It cannot be assumed than an important new ore field will be discovered in less than five years and as it may take another five years to bring a major field into production, the time is not far distant when reconnaissance surveys and prospecting for uranium should be recommenced. Prospecting by the methods practised from 1945-1955 is not likely to be as remunerative in, say, the period 1965-1975. Hence, if we are to ensure that there will be adequate supplies of fissionable raw materials for future generations, research into new discovery methods should be increased and, as a safeguard against a failure to discover new fields comparable with the Witwatersrand, Elliot Lake or the Colorado Plateau, research should be encouraged on both physical and chemical methods of upgrading ore that, at present, is of too low a grade to be worked economically.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/164 Royaume-Uni

Réserves et potentiel en minerais d'uranium et de thorium

par S. H. U. Bowie

La confusion existant à l'heure actuelle sur les estimations des réserves d'uranium et de thorium provient en grande partie de l'utilisation abusive du terme « réserves ». On définit donc les termes « réserves », « potentiel » et « ressources » et on établit le degré de confiance que l'on peut accorder aux chiffres et données publiés concernant les réserves.

On donne un bref historique de la découverte des principaux gisements d'uranium et l'augmentation des réserves de minerais au cours de la période 1945-55. On discute les valeurs et le « potentiel » des gisements connus ainsi que la possibilité de trouver d'autres régions avec des tonnages comparables de minerais. Il est noté qu'aucun gisement important de minerai n'a été trouvé depuis 1955 et que les estimations des réserves d'uranium à la fin de 1961 sont en diminution de plus de 30 pour 100 par rapport aux chiffres retenus en fin de 1958. La cause de cette révision est que les réserves de minerais avaient été principalement estimées d'après des données recueillies en surface et des sondages qui donnaient une idée incomplète de la situation dans le sous-sol.

La disponibilité du minerai est d'une importance égale aux réserves si l'on considère le point de vue de

l'utilisation à long terme. On relève que si aucune découverte importante d'uranium n'a lieu et que la production actuelle se maintienne, en 1975 les réserves des États-Unis seront fortement entamées et, par la suite, la production devrait principalement être le fait de l'Afrique du Sud et du Canada. Cependant la production de l'Afrique du Sud ne dépassera vraisemblablement pas 6 000 à 7 000 tonnes de U_3O_8 par an et celle du Canada peut ne pas représenter un pourcentage normal par rapport à ses réserves totales, car approximativement la moitié des gisements de minerai connus est entre les mains d'une seule firme.

On examine les changements qu'il faudra apporter aux techniques de prospection pour découvrir des dépôts cachés d'uranium et de thorium. On donne également une indication sur les recherches de base nécessaires pour diminuer le coût de la prospection de nouveaux gisements lorsque le besoin s'en fera sentir. Les réserves de thorium ne sont pas connues avec le même degré de certitude que pour l'uranium, mais des chiffres approximatifs indiquent qu'elles sont du même ordre que pour l'uranium.

A/164 Соединенное Королевство

Действительные и предполагаемые запасы урановой и ториевой руд

С. Г. Ю. Бауи

Существующая путаница в отношении исчисленных к настоящему времени запасов урана и тория происходит во многом из-за неправильного употребления термина «запасы». Поэтому в данном докладе дается определение терминов «запасы», «предполагаемые запасы» и «ресурсы» и указывается, в какой степени можно полагаться на опубликованные данные о запасах руд.

Дается краткий исторический обзор открытия крупных урановых месторождений и определения запасов руды в период 1945—1955 годов. Рассматриваются данные, касающиеся запасов руды, и обсуждаются предполагаемые запасы известных месторождений, а также возможности поиска дополнительных районов, располагающих аналогичными запасами руды. Следует заметить, что с 1955 года не было обнаружено никакого крупного месторождения и что в конце 1961 года в результате пересмотра запасы урана оказались примерно на 30% меньше, чем было оценено на конец 1958 года. Это обусловливается тем, что запасы урановой руды оценивались на основе данных поверхностных и буровых исследований, которые недостаточно отражали картину изменений, происходящих на глубине.

Одинаковую важность для запасов с точки зрения перспектив имеет также доступность урановой руды. Отметим, что если не будут открыты новые крупные месторождения урана и в то же время сохранится нынешний уровень добычи, к 1975 году запасы урана в США значительно истощатся и можно ожидать, что в последующие годы основными поставщиками урановой руды будут Южно-Африканская Республика и Канада. Однако производство урана в Южно-Африканской Республике не будет, вероятно, превышать 6000—7000 *т* U_3O_8 в год, а в Канаде производство может не соответствовать общим запасам, поскольку приблизительно половина известных запасов урановой руды принадлежит одному владельцу.

Обсуждаются изменения в методике разведки, которые будут необходимы для обнаружения скрытых залежей урана и тория. Указывается также, что для максимального снижения стоимости разведки месторождений, если понадобятся дополнительные поиски руды, потребуется проведение фундаментальных исследований. Запасы тория неизвестны с такой степенью точности, как запасы урана, однако предварительные данные показывают, что запасы урана и тория приблизительно одинаковы.

A/164 Reino Unido

Reservas y perspectivas de minerales de uranio y torio

por S. H. U. Bowie

La confusión que existe acerca de las estimaciones actuales sobre reservas de uranio y torio procede, en gran parte, del uso un tanto vago que se hace del término « reservas ». Por consiguiente, se definen los términos « reservas », « perspectivas » y « recursos » y se da una indicación del grado de confianza que puede ponerse en los datos publicados sobre reservas.

Se hace un breve relato de la historia del descubrimiento de las minas de uranio más importantes y del incremento de las reservas de mineral durante el período de 1945-55. Se discuten los datos sobre reservas y se comentan las perspectivas de las zonas mineras, así como la posibilidad de hallar otras regiones con un tonelaje de mineral comparable. Se hace notar que no se ha encontrado ningún yacimiento importante desde 1955 y que las reservas de uranio, en la evaluación hecha a finales de 1961, se redujeron en más de un 30 % respecto a las cifras dadas a finales de 1958. La causa de tal reducción proviene de que las reservas de mineral se estimaron, principalmente, con datos de superficie y sondeos que dieron una visión poco exacta de los cambios que ocurren en profundidad.

De tanta importancia como las reservas, considerando la situación a largo plazo, es la disponibilidad del mineral. Se pone de manifiesto que si no se hacen descubrimientos importantes de uranio y se mantiene la producción actual, las reservas de los Estados Unidos de América estarán prácticamente agotadas en 1975 y puede esperarse que en los años siguientes la producción proceda principalmente de Sudáfrica y de Canadá. Sin embargo, no es probable que la producción del primer país citado, exceda de 6 000-7 000 t de U_3O_8 al año y en cuanto a la producción del segundo, es posible que no se desarrolle en proporción normal a sus reservas totales, puesto que aproximadamente la mitad del mineral de uranio conocido se encuentra en un solo yacimiento.

Se comentan las variaciones que será necesario introducir en la técnica de prospección para localizar depósitos ocultos de uranio y torio. También se hace una indicación sobre la investigación básica necesaria para reducir al mínimo el coste de la prospección, cuando sea necessaria, para obtener más mineral. No se conocen las reservas de torio con el mismo grado de certeza que las de uranio, pero cifras provisionales indican que son del mísmo orden que las de éste.

Canadian resources of uranium and thorium

By J. W. Griffith and S. M. Roscoe *

Canada has been one of the world's leading producers of uranium since the metal became important as a raw material in the development and production of atomic energy. One of the largest known deposits in the world is in Canada, where present reserves represent about 37% of the total among those countries that have published reserve statistics. The production of uranium has been characterized by features which are unique in Canadian mining, because the industry was created by the government at a time of emergency and, unlike other minerals, the sale of its product is controlled by the State. The rapid growth of the uranium-mining industry since World War II has been a remarkable achievement. In 1958, Canada was the world's leading producer of uranium and the value of U_3O_8 produced in both 1958 and 1959 exceeded the value of any other Canadian-produced metal. As an export commodity, uranium ranked fourth in value in 1959, following newsprint, wheat and lumber. Production from 25 mines in that year was 14 462 tonnes of U_3O_8 valued at $318 million.** Since 1959, however, the decline in production, resulting from declining export markets, has been almost as rapid as the spectacular rise from 1953 to 1959. At the end of 1963, only seven mines were in production, and by the end of 1965 only two mines are expected to remain in operation.

Contracts and sales

The present surplus of uranium in the United States and Britain, the major consuming countries to which Canada has been shipping, makes it unlikely that the demand will rise again before the 1970s. Practically all of Canada's uranium was sold under contract to the United States Atomic Energy Commission (USAEC) and the United Kingdom Atomic Energy Authority (UKAEA). The United States, Canada's largest customer, announced in 1959 that it would not exercise its option to purchase additional uranium from Canada. To prevent a collapse of the industry in 1962 and 1963, when the USAEC contracts would expire, the Government of Canada, through Eldorado Mining and Refining Limited (a Crown agency), negotiated a delivery stretch-out for the uranium already under contract with the USAEC and the UKAEA. This plan also permitted the transfer of contracts between companies. By September 1968, when the stretch-out period ends, most companies will have fulfilled their original contracts and any additional ones that they may have acquired through transfers from other companies.

In 1962, a contract was signed with the UKAEA for the delivery of 10 920 tonnes of U_3O_8 over a period extending until late 1971. This contract permitted each of the seven mining companies, which were still operating in 1962, to extend its operating life approximately 16.7 months past the completion date of its previous commitments. However, only one mine will be able to stretch out its production into 1971.

PRICES AND MARKETING

The prices paid to the Canadian producers for the sale of mill concentrates (yellow cake) under government contract varied with each company, having been originally calculated to provide a profit after allowances for amortization of the major estimated capital costs and the estimated operating costs. Under most contracts, however, the maximum price paid was $23 a kilogram of U_3O_8 contained in the yellow cake. Before the announcement of the stretch-out plan, a few contracts were extended from 31 March 1962 to 31 March 1963; the price under these was either the original contract price or $17.60 per kg plus the amortization factor, whichever was the lower.

Procurement and marketing of most of the uranium produced in Canada is the responsibility of the Crown corporation, Eldorado Mining and Refining Limited. Canadian producers are permitted, however, to make small sales of surplus uranium (U_3O_8) to countries that do not hold agreements with Canada for co-operation in the peaceful uses of atomic energy. The maximum amount any such country may receive in total from Canada is 1 125 kg. Producers may also sell larger amounts, under permit from the Atomic Energy Control Board, directly to countries that hold bilateral agreements with Canada, but sales of this nature have been small.

Future prices

It is probably too early to discuss future prices in a free uranium market. Some small individual transac-

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** All monetary values are in US dollars.

tions, which have taken place in recent years, have been at prices as low as \$8 per kg U_3O_8 although such prices cannot be considered as realistic in view of published cost figures. In any case, it is doubtful if large sales would be made by Canadian mines at such low prices. The average price received by Canadian producers under a contract signed with the UKAEA in 1962 was \$10.25 per kg. In the writers' view, if a free market is established before 1970, the price will be in the \$11 to \$14 range and in the post-1970 period this price trend will continue to climb unless large new deposits of high-grade ore are discovered.

PRODUCTION COSTS

The reduction of operating costs at the mines, treatment plants and refinery through new equipment, automation and process improvements is a continuing one and further cost reductions are expected in the future. Generally, costs reported by most Canadian uranium mines cover mine operating costs only, which include underground development, mining, milling and general mine expense; usually, they do not include prospecting and exploration, amortization, head office administration expenses, interest, taxes and royalties. In some cases the latter items would increase mine operating costs substantially, largely because of an unusually short amortization period. Mine operating costs in the Elliot Lake camp have ranged from \$7.50 to \$12 per tonne of ore, or \$8.30 to \$12 per kg U_3O_8. Mining and development costs have averaged about \$5 per tonne of ore, and milling costs have been slightly less. The average costs at Bancroft and Beaverlodge have been slightly higher than that for the Elliot Lake camp. Some producers have been understandably reluctant to divulge operating costs so that more precise figures cannot be given.

PRESENT RESERVES OF URANIUM AND THORIUM

Despite the present surplus of uranium, there is a growing concern about long-term supplies for a market that some authorities believe will reach major proportions by 1980. The main reason for this concern is that the cost of nuclear power in certain areas of the world is becoming competitive with the cost of power from conventionally fuelled thermal plants, and it is expected that by 1975, or earlier, nuclear power will show economic advantages in comparison with conventional thermal power in many countries. The Consultative Committee of Euratom Supply Agency has estimated [1] that uranium requirements between 1970 and 1980 for nuclear power plants alone will amount to 190 000 tonnes of uranium (Table 1).

The concern about the long-term supply of nuclear fuel has become more manifest as a result of recent downward revisions of ore reserves by the major producers. For example, the revision by the USAEC was from 209 300 t U_3O_8 in late 1960 to 151 970 t in January 1963 [2]. French reserve estimates have been reduced from an excess of 50 000 t U_3O_8 in 1960 [3] to 30 000 t in 1962 [1]. South African reserves were re-assessed from 337 000 t U_3O_8 in 1958 [4] to 137 000 t in 1963 [1]. Australia's reserves are considered to be low and the Republic of the Congo (Leopoldville) ceased treating ores in 1961 [5]. Canada's reserves have also been revised downward from approximately 350 000 t U_3O_8 in 1958 [6] to 188 000 t in January 1964. The earlier figure did not allow for unrecoverable uranium and included some material which we consider should now be reported as potential ore. In addition, 62 000 t have been produced since the beginning of 1958.

Table 1. Requirements of uranium between 1970 and 1980 estimated by the Consultative Committee of Euratom Supply Agency [1]

	Annual requirements In 1970 (tonnes U)	Annual requirements In 1980 (tonnes U)	Cumulated requirements 1970-1980 (tonnes U)
Europe	4 000	20 000	100 000
North America	3 000	14 000	70 000
Other countries	1 000	4 000	20 000
Total	8 000	38 000	190 000

The tabulation of present reserves (Table 2) includes developed ore in underground workings and ore indicated in drill holes. These constitute tonnages which can be exploited under present technology at a profit to the operator at prices ranging from \$11 to \$22 a kilogram for U_3O_8 (1963 US dollars). Reserves in the conglomeratic deposits in the Blind River–Elliot Lake area of Ontario constitute 93% of the total in Canada. Reserves in pitchblende-bearing vein type deposits in the Beaverlodge Lake area of Saskatchewan comprise 6% and the pegmatitic deposits in the Bancroft area of Ontario make up about one per cent.

In calculating recoverable U_3O_8 (Table 2), allowance has been made for percentage recovery through chemical treatment and the percentage of ore extraction in the mines, particularly those of the Elliot Lake district where about 80% is recovered by the room-and-pillar method of mining. Average recovery and extraction percentages for 1961 were used for calculation, although it is known that ore extraction percentages have increased since then; recovery in ore treatment processes has remained steady at about 95%.

Despite the severe contraction in production as a result of the depressed market situation, established ore reserves in mines that have closed or that expect to close in the near future, will not be lost through caving or flooding.

Scheduled deliveries of U_3O_8 to the USAEC and

Table 2. Canadian reserves of uranium and thorium

(as of 1 January 1964)

Type and location of principal deposits	Ore 10^6 tonnes	Grade		Recoverable	
		U_3O_8 %	ThO_2 %	U_3O_8 10^3 tonnes	ThO_2 10^3 tonnes
Conglomeratic (Elliot Lake, Ontario)					
Past and present producers. . . .	196	0.12	0.05	176	74
Veins and related types (Beaverlodge Lake, Saskatchewan)					
Past and present producers. . . .	6	0.20	nil	9	nil
Other deposits	2	0.15	nil	2	nil
Pegmatitic (Bancroft, Ontario)					
Past and present producers. . . .	1	0.10	0.07±	0.6	0.5±
Other deposits	1	0.10	0.1 ±	0.6	6±
Totals and averages	206	0.12	0.05	188	75

UKAEA from 1964 to 1971 inclusive total 15 334 t. Thus, by the end of 1971 Canada's reserves will be approximately 173 000 t of recoverable U_3O_8 if no further exploration is undertaken before then. Domestic requirements of uranium for nuclear power purposes will not appreciably affect Canada's ability to export uranium in the future. However, total production capacity at that time will be reduced unless new deposits are discovered or unless the lower-grade material, which is described later, is required.

FUTURE SOURCES OF URANIUM AND THORIUM

Radioactive conglomerates

General description of Elliot Lake deposits. The conglomeratic deposits in Huronian strata near Elliot Lake underlie two separate areas about 10 km apart. One, about 23 km² in extent, is on the north flank of the Quirke Lake syncline; the other, about 8 km² in area is on the south flank of the syncline. Both zones outcrop and extend down dip to depths of as much as 1 100 m below surface. The bedded and relatively uniform character of the deposits make them remarkably amenable to drill hole exploration. About 275 million tonnes of ore and similar amounts of marginal and submarginal conglomeratic material discussed below were outlined during a period of only three years of intensive deep drilling. Approximately 1 200 holes aggregating some 300 000 m were drilled. The average exploration cost would amount to only about 2 cents per kg of uranium in the ore discovered. With one or two exceptions, estimates of tonnages and grade based on drill hole data have been satisfactorily borne out by underground work.

The ore occurs within conglomerate-bearing units up to 30 m thick in the southern ore zone and up to 75 m thick in the northern part of the northern zone, where there are two persistent conglomerate-rich layers about 45 m apart. The ore reserve calculations include only one section of mineable thickness in any one area although parts of a second band are mined in a few places. The remainder of the thick radioactive units contain more than 0.01% U_3O_8 with the bulk of this in distinct conglomerate beds, many of which are sufficiently closely spaced to permit mining of one to three separate sections if this were technically and economically feasible.

Potential ore. With a cut-off grade of about 0.03%, some 180 million additional tonnes of ore containing about 120 000 t U_3O_8 and 90 000 t ThO_2 could be added to ore reserves at prices of \$22 to \$33 per kg for U_3O_8. This includes material at the fringes of ore zones, accessible from extensions of present workings, and material obtainable by increasing thicknesses mined in the main ore sections, as well as zones above and below the main ore zones.

An area of about 25 km² extending 13 km east of the southern ore zone evidently contains almost continuous conglomerate layers carrying 0.03 to 0.06%, and locally nearly 0.1%, U_3O_8 through mineable thicknesses. Thicknesses of as much as 6 m are present locally. In places, a second potential ore zone occurs above or below the main zone.

A second area of potential ore occurs along the east side of the northern ore zone. This area is about 8 km² in extent and contains material with 0.03 to 0.07% U_3O_8 and about 0.1% ThO_2. It has not been delineated towards the east; grades decrease in this direction but radioactive conglomerate beds may extend 13 km southeasterly to an area on the nose of the syncline where material with a grade of about 0.02% U_3O_8 and 0.04% ThO_2 has been discovered. Significant thicknesses of radioactive conglomerate have also been intersected in drill holes south of the northern ore zone but exploration possibilities in this area are limited as the conglomerate beds are separated from the southern conglomeratic zones by an intervening barren unit, and are probably also truncated locally by a disconformity. A total of about 180 million tonnes containing 90 000 t U_3O_8 and 90 000 t ThO_2

may be present in these areas. Some of this could be mined at a price of $22 per kg for uranium but its full exploitation would probably require uranium prices of more than $33 per kg.

The total potential ore indicated by drilling in the Elliot Lake area is estimated to be about 365 million tonnes, containing about 210 000 t U_3O_8 and 180 000 t ThO_2 mineable at prices less than $45 per kg. About half of this could be mined at prices less than $33 per kg. Small amounts of potential ore are also known in Huronian rocks outside of the Elliot Lake area.

Conglomeratic material containing 0.01 to 0.03% U_3O_8 is abundant in the Elliot Lake area and in Huronian rocks elsewhere in the region. This might ultimately be valuable if prices rose to $45 and more per kg U_3O_8, but our data is inadequate for estimates of amounts of such material present in Huronian rocks, amounts recoverable, and recovery costs. A tentative opinion concerning the relative abundance of this material may nevertheless be of interest here. At present, we have no reason to believe that tonnages of recoverable uranium in this type of material are greater or even comparable with tonnages in conglomerates containing more than 0.03% U_3O_8. About 400 million tonnes, containing 100 000 t U_3O_8 and 200 000 t ThO_2, may still be available in the Elliot Lake area after higher-grade ores are mined. Greater amounts at slightly lower grade are present throughout other parts of the region.

Future discoveries. All the ore and potential ore in the Elliot Lake area occurs in a lithostratigraphic unit which Roscoe has called the Matinenda Formation [7]. The formation outcrops in a few limited areas outside of the Elliot Lake-Blind River area but all of these contain radioactive conglomerate beds. Numerous occurrences of highly radioactive conglomerates have been found in a structurally complex area 70 km east of Elliot Lake. The most extensively explored of these has been reported [8] to contain an indicated 6 000 t per vertical metre of potential ore containing 0.09% U_3O_8 and 0.3% ThO_2. Sixty to 130 km west of Elliot Lake, radioactive conglomerate beds containing up to 0.1% U_3O_8 have been found within volcanic strata.

Figure 1. Regional distribution of radioactive conglomerates

The extent and depth of the Matinenda Formation (or equivalent strata) largely control our exploration possibilities. The formation is believed to underlie areas totalling at least 1 800 km² at depths less than 2 000 m. Surface prospecting and drilling, of course, have eliminated possibilites of occurrences of large deposits throughout part of this area but about 1 300 km² can be considered as unexplored. Certain sections aggregating about 260 km² can be considered as prime exploration targets because of geological considerations such as location with respect to known deposits or to conglomerate beds that are likely to be more abundant and richer further up the paleoslope, the probable character and paleotopography of underlying basement rocks, and projected positions of facies changes, wedge outs and overlaps of stratigraphic units. If highly radioactive conglomerates are one-third as abundant in unexplored sections of the Matinenda Formation as they are in the prospected sections, we are likely to find as much ore and submarginal material in the future as we have in the past.

Several Huronian formations above the Matinenda Formation also contain radioactive pebble beds in places (Fig. 1). Conglomerate beds are particularly abundant in the northernmost outcrops of the Mississagi Formation. Some exploration and sampling has been done on such beds 30 km northwest, 70 km east and 150 km east of Elliot Lake. Drill core sections with as much as 0.08% U_3O_8 through 2.4 m have been reported [8]. Thin, radioactive pebble beds have been discovered near the base of the Gowganda Formation in a number of places. None of these appears to average more than 0.01% U_3O_8 but the most easterly occurrence, 210 km east of Elliot Lake, reportedly yielded some erratic analyses of as much as 0.05% U_3O_8 and 14 parts per million gold [8]. Extensive monazite-rich, hematitic conglomerates occur in gently-dipping arkosic beds in the Lorrain Formation along a belt 50 km long, 30 km north of Elliot Lake. Surface samples collected by Roscoe ranged between 0.01% and 0.12% ThO_2 and had ThO_2: U_3O_8 ratios between 8 and 43. Thorium probably could not be as readily recovered from this type of material as it can from pyritic conglomerates. The total area wherein higher radioactive horizons might be tested by drilling is about 5 000 km².

The Witwatersrand conglomeratic deposits and the relatively few similar occurrences known elsewhere in the world all occur in pre-Cambrian sedimentary rocks similar to the Huronian rocks. Possibilities of discovering important deposits of this class may be restricted to sedimentary rocks that were deposited under unusual conditions during pre-Cambrian time. If abundance of belts of pre-Cambrian sedimentary rocks is a valid criterion, chances of discoveries of new areas containing conglomeratic deposits should be greater in Canada than in most regions of equivalent size elsewhere in the world.

Pitchblende veins and related deposits

It is rarely possible to develop ore reserves in vein-type deposits far in advance of mining operations. We have no data on tonnages of mineralized rock that might be promoted to the ore reserve category at uranium prices above \$22 per kg U_3O_8. Exploration of any given radioactive zone is normally discontinued if it becomes apparent that chances of finding ore (at prevailing prices) are slight. However, it is likely that additional ore could be discovered in the Beaverlodge area at an adequate rate to maintain a substantial rate of production of relatively low cost uranium for many years.

The area of abundant pitchblende occurrences at Beaverlodge Lake is about 1 300 km^2 in extent but less numerous occurrences are found throughout a belt 320 km long along the north shore of Lake Athabasca (Fig. 2). This mineralogenic province, incidentally, is superimposed upon a larger mineralogenic province characterized by pegmatitic radioactive occurrences. Other extensive areas of pitchblende occurrences are found in the Northwest Territories and smaller areas and isolated occurrences are known in Manitoba, western Ontario, eastern Ontario, near Sault Ste. Marie and near Cobalt, on the Labrador coast, in the Cordilleran region of British Columbia and the Yukon Territory and in the Appalachian region of the Atlantic provinces. More will be found in less accessible areas. One extensively developed deposit on the Labrador coast could produce uranium at a relatively low cost. Under more favourable market conditions further prospecting and more detailed exploration would be warranted in all the known pitchblende-bearing areas.

Pegmatitic and related deposits

Radioactive pegmatites and the many other radioactive concentrations that are essentially consanguineous with their igneous and metamorphic host rocks

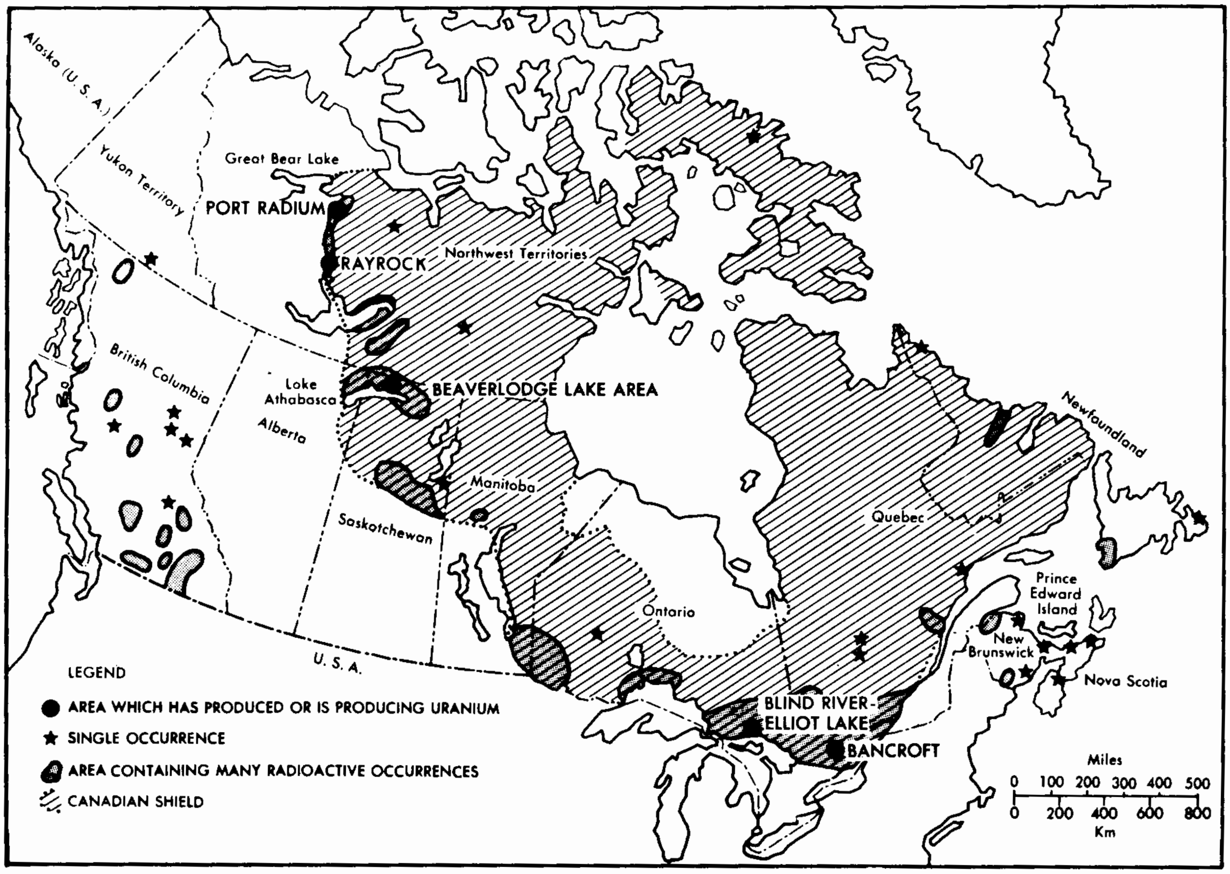

Figure 2. Map of Canada showing distribution of uranium and thorium

are considered together for purposes of this study. Such primary deposits occur in pegmatitic and other facies of granites and syenites, in zoned pegmatites, in skarns and other metamorphic rocks, in alkalic syenites and in granophyric phases of basic intrusives. Thorium, uranium, rare-earth elements, titanium and zirconium are intimately associated in most of these types of deposits. Concentrations of such elements as molybdenum, beryllium, niobium, tantalum, tin, iron, fluorine and phosphorus are also commonly present in a variety of other types which offer possibilities of multi-product operations.

The bulk of radioactive occurrences that have yielded U_3O_8 equivalent radiometric analyses greater than 0.05% belong to these classes. Known occurrences are most abundant in the Grenville region along the southeastern edge of the Canadian Shield. They are also abundant throughout extensive areas in Saskatchewan, Manitoba and western Ontario; many are also known in more remote sections of the Shield and in the Cordilleran and Appalachian regions.

Despite the abundance of pegmatitic deposits, few were extensively explored and sampled during the period of active search for uranium. Most of the available exploration funds were directed to pitchblende and conglomeratic deposits which were rightly regarded as most apt to yield low-cost uranium. Exceptions were the Bancroft deposits which were brought into production, deposits near Birch Island, British Columbia, which were extensively developed but not brought into production, and numerous deposits in the Charlebois Lake area in Saskatchewan where drilling has demonstrated that extensive reserves of potential ore could be developed.

A number of deposits explored primarily for other elements could probably yield by-product uranium and thorium at moderate cost. These include niobium deposits at Oka near Montreal and near North Bay and Chapleau, Ontario. Combined production of uranium and fluorspar is a possibility in some deposits near Bancroft, Ontario, and Birch Island, British Columbia.

It is fairly obvious that world abundances and sizes of primary deposits with various different uranium contents will control the price of uranium at some future date when we are no longer able to discover reserves of richer secondary deposits at rates equal to consumption. Canadian reserves and production of uranium and thorium in pegmatitic deposits would increase rapidly with increasing uranium prices. Material containing 0.005 to 0.05% U_3O_8 appears to be relatively abundant in Canada, but we have no data that would enable us to make estimates of resources at various radioelement price levels.

Table 3. Canadian resources of nuclear fuels

Price $/kg U_3O_8	U_3O_8 10^6 tonnes		By-product ThO_2 10^6 tonnes	
(a) Present and potential reserves				
11-22	0.19		0.07	
22-33	0.12		0.09	
		0.31[a]		0.16[a]
33-45	0.09		0.09	
		0.40		0.25
(b) Reserves plus geologically prognosticated resources				
11-22	0.4		0.2	
22-33	0.3		0.2	
		0.7		0.4
33-45	0.3		0.3	
		1.0		0.7

[a] Cumulative totals.

SUMMARY

Table 3 (*a*) and (*b*) summarizes estimates of Canadian resources of uranium and thorium discussed in the text. Table 3 (*a*) shows reserves and potential reserves for which some measurements are available. Table 3 (*b*) shows reserves and potential reserves plus an additional allowance for geologically probable future discoveries. Canadian uranium mines, efficient by any standards, have gradually reduced operating costs. Further improvements would place larger amounts of uranium in lower price categories. All the thorium shown in the tables could be produced as a low-cost by-product. If there were a large market for thorium at a price comparable with that of uranium, the average cost chargeable against the recovery of U_3O_8 from present reserves would be reduced appreciably and large amounts of U_3O_8 in potential reserves would be promoted to lower price categories. The reserves are almost entirely in conglomeratic material. If it had been possible to estimate ultimate resources in all types of deposits, the estimates would probably have shown successively higher U_3O_8 tonnages in successively higher U_3O_8 price categories.

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Grateful acknowledgment is made to company engineers, geologists and mine managers who supplied much of the data presented in this paper. Information on ore reserves was obtained partly from published company reports and partly from unpublished information on the Blind River–Elliot Lake deposits collected by S. M. Roscoe. Special thanks are due to D. D. Bell, of Eldorado Mining and Refining Limited, for his helpful suggestions.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/24 Canada

Ressources canadiennes d'uranium et de thorium

par J. W. Griffith et S. M. Roscoe

Depuis 1953, le Canada a extrait et traité en tout 57 000 000 de tonnes de minerai contenant 74 000 tonnes de U_3O_8. La production annuelle maximale (14 462 t) a été atteinte en 1959, quand 25 mines et 19 usines de traitement étaient actives. Depuis lors, la plupart ont fermé et, à moins de trouver de nouveaux débouchés, il est douteux que plus de deux mines et usines soient encore en service après 1965. On estime que les réserves pouvant être exploitées à des prix variant entre $ 11 et $ 22 par kilogramme d'U_3O_8 (devises des États-Unis en 1963) s'établissent à 206 000 000 de tonnes de minerai titrant 188 000 tonnes d'U_3O_8 et environ 75 000 tonnes de ThO_2.

La plus grande partie des réserves d'uranium et de thorium se trouvent sous la forme de minerai conglomératique, près d'Elliot Lake. Les carnets de forages laissent supposer la présence de gros tonnages de conglomérats à minerais radioactifs, qui, croit-on, seraient exploitables si les prix du U_3O_8 étaient plus élevés. On peut prévoir d'importantes découvertes en certains endroits.

Les réserves actuelles contenues dans les gîtes de pechblende de type filonien de la région de Beaverlodge forment 6 % des réserves canadiennes, et celles des gîtes de type pegmatitique de la région de Bancroft environ 1 %. On devrait cependant finir par découvrir, dans les gîtes précités et dans divers autres gîtes de types non stratifiés, des réserves plusieurs fois supérieures à celles dont on peut raisonnablement déduire l'existence à présent.

Les ressources du pays en combustibles nucléaires suffiront pendant bien des années à alimenter les centrales nucléaires. Le total des réserves potentielles (y compris les réserves actuelles), exploitables si l'U_3O_8 se vend à des prix inférieurs à $ 45 par kilogramme sont de l'ordre de 1×10^6 tonnes d'uranium et de $0{,}7 \times 10^6$ tonnes de thorium. D'autres grosses réserves, non mesurées, de minerai à moindre teneur pourraient être exploitées si les taux de consommation mondiale parvenaient à dépasser ceux de la découverte de minerais à plus fortes teneurs.

A/24 Канада

Запасы урана и тория в Канаде

Дж. У. Гриффит, С. М. Роскоу

С 1953 г. в Канаде было добыто и переработано 57 млн. тонн руды, содержавшей 74 тыс. *т* U_3O_8. Максимальное годовое производство 14 462 *т* было достигнуто в 1959 г., когда работало 25 рудников и 19 обогатительных фабрик. С тех пор их большая часть была закрыта и сомнительно, чтобы после 1965 г. все еще работали бы более двух рудников и обогатительных фабрик. По оценке запасы, которые можно разрабатывать со стоимостью от 11 до 22 долл. за 1 *кг* U_3O_8 (в валюте США 1963 года), составляют 206 млн. *т* руды, содержащей 188 тыс. *т* U_3O_8 и около 75 тыс. *т* ThO_2.

Большая часть запасов урана и тория залегает в виде кварцевых конгломератов в районе оз. Эллиот. Разведочное бурение позволяет предположить наличие большого количества конгломератов радиоактивных руд, которые разрабатывались бы при более высокой цене на U_3O_8. Возможно, что в некоторых районах могут быть открыты в будущем большие рудные залежи.

Существующие запасы урановых руд представляют собой жильные месторождения урановой смолки у оз. Биверлодж, составляющие 6% всех канадских запасов, а запасы пегматитовых гранитных дайках в районе Банкрофт — около 1%. В результате дальнейшей разведки осадочных месторождений и других месторождений нестратифицированного типа могут быть открыты во много раз бóльшие запасы, чем известные в настоящее время.

Ресурсы ядерного топлива в Канаде достаточны для снабжения топливом атомных электростанций страны в течение многих лет. Общие потенциальные запасы (включая сюда современные разведанные запасы, которые будут

разрабатываться при продажной цене на U_3O_8 менее 45 *долл/кг)* составят для урана порядка 1 млн. *т* и 700 тыс. *т* для тория. Другие неоцененные запасы бедных руд могут разрабатываться, если объем мирного потребления начнет превышать объем запасов более богатых руд.

A/24 Canadá

Recursos canadienses de uranio y torio

por J. W. Griffith y S. M. Roscoe

Desde 1953 el Canadá ha extraído y sometido a tratamiento un total de 57 000 000 de t de mineral que contienen 74 000 t de U_3O_8. Se alcanzó la producción anual máxima (14 462 t) en 1959, fecha en la que había 25 minas en explotación y funcionaban 19 fábricas de tratamiento. Desde entonces han cesado las actividades en casi todas esas instalaciones y, a menos que se encuentren nuevos mercados, es poco probable que haya más de dos minas y fábricas en explotación después de 1965. Se estima que las reservas que pueden explotarse a precios comprendidos entre 11 y 22 dólares por kilogramo de U_3O_8 (divisas de los Estados Unidos en 1963) se cifran en 206 000 000 de t de minerales de las que se pueden extraer 188 000 t de U_3O_8 y cerca de 75 000 t de ThO_2.

La mayor parte de las reservas de uranio y de torio se hallan en forma de mineral conglomerádico, cerca del lago Elliot. Los registros de perforación indican la presencia probable de grandes cantidades de conglomerados de minerales radiactivos que, al parecer, podrían explotarse si subieran los precios del U_3O_8. Cabe prever que en ciertos lugares se efectuarán importantes descubrimientos de minerales.

Las reservas actuales contenidas en los yacimientos de pechblenda de tipo filoniano de la región de Beaverlodge forman el 6 % de las reservas canadienses y las de los depósitos de tipo pegmatítico de la región de Bancroft aproximadamente el 1 %. Sin embango, en los yacimientos citados y en otros de tipo no estratificado se tendrá que descubrir reservas varias veces superiores a las que con bastante probabilidad cabe suponer que existen actualmente.

Las reservas del país en combustibles nucleares bastarán durante muchos años para alimentar las centrales nucleares. El total de reservas potenciales (comprendidas las reservas actuales), explotables si el U_3O_8 se vende a precios inferiores a 45 dólares por kilogramo, son del orden de 1×10^6 t de uranio y de $0{,}7 \times 10^6$ t de torio. Podrían explotarse otras importantes reservas, cuya cuantía no se ha calculado, de minerales de menos riqueza si el ritmo de consumo mundial llegase a superar el de descubrimiento de minerales de mayor riqueza.

Recursos y posibilidades uraníferas en Argentina

por C. T. Friz, F. Rodrigo y P. N. Stipanicic *

Los primeros estudios sobre yacimientos uraníferos argentinos se iniciaron en 1945, por cuenta de la Dirección General de Fabricaciones Militares y tuvieron como finalidad revisar las pegmatitas radiactivas de las sierras de Córdoba y San Luis.

Después de dicho intento, orientado hacia depósitos sin interés económico, la Universidad Nacional de Cuyo tomó a su cargo la exploración limitada de algunos yacimientos de discreto interés, para pasar luego a colaborar con la entonces Dirección Nacional de la Energía Atómica (Comisión Nacional de Energía Atómica a partir de 1956), institución que desde 1950 se constituyó en el organismo regulador de las actividades nucleares en la Argentina.

Los trabajos de prospección y exploración se siguieron cumpliendo en escala reducida hasta 1956, año en que se decidió intensificarlos, para lo cual se organizó en la CNEA un sector geológico-minero encargado de tales tareas.

Durante los años 1957 y 1958 se integró el plantel de profesionales y técnicos y se adquirieron los equipos y el instrumental básico. A partir de 1958 se inició la etapa de perfeccionamiento avanzado en el exterior de los geólogos e ingenieros de minas, que se intensificó desde 1961, incorporándose también un buen número de electrónicos, químicos, ingenieros químicos e hidrometalurgistas, a los efectos de constituir un grupo homogéneo de técnicos afectados a la industria del uranio.

Puede decirse que 1961 señala en la Argentina el comienzo de los trabajos orgánicos de prospección, exploración y evaluación, realizados con criterio económico, teniendo fundamentalmente en cuenta el costo del concentrado que produciría cada yacimiento [1].

Las actividades destinadas a la prospección, evaluación y producción de minerales nucleares se concentran en el Departamento de Recursos Minerales, que junto con el de Elaboración integran la Gerencia de Materias Primas.

En el presente trabajo las cifras dadas como « mineral » son las que se obtuvieron mediante trabajos de exploración y evaluación (labores mineras, perforaciones, etc.), aplicando métodos de cálculos ortodoxos o estadísticos. Las indicadas como « posibilidades razonables de desarrollo » son las que se estima que podrían alcanzarse con bastante seguridad, especialmente para el caso de yacimientos con control sedimentario, mediante la ejecución de un plan intensivo de trabajos, teniendo en cuenta las características de los mismos, sobre todo la extensión de algunos de sus parámetros (corrida, profundidad, etc.), la continuidad, homogeneidad o distribución de la mineralización, etc. Bajo el título de « posibilidades potenciales » se indican valores a los que razonablemente podría llegarse, tomando en cuenta no sólo factores como los anteriores, sino también el número de anomalías o de manifestaciones conocidas en el distrito pero aún no exploradas, las características geológicas del ambiente que las contiene, etc.

AREAS CON POSIBILIDADES URANÍFERAS

Un análisis crítico basado en la composición geológica de la Argentina y en los modernos conceptos que rigen sobre génesis de yacimientos uraníferos, permitió definir que de los 3 000 000 de km^2 del territorio continental del país, más de la tercera parte presenta posibilidades de albergar acumulaciones de minerales radiactivos, quedando desechadas, en principio, las extensas planicies centrales y mesopotámicas (figura 1) [2].

Dentro de la superficie señalada, superior a 1 000 000 de km^2, se estimó que distintas zonas, integrando 400 000 km^2, ofrecían interés inmediato y con mejores perspectivas, sea por sus características geológicas como por sus ubicaciónes geográficas más favorables o por poseer indicios o yacimientos uraníferos ya conocidos.

Prácticamente toda la actividad de la CNEA se concentró en esas áreas de « interés inmediato », habiéndose reconocido a la fecha una superficie de 125 000 km^2, de los cuales 75 000 km^2 fueron cubiertos con prospección aérea semi-regular.

Los trabajos exploratorios cumplidos por la CNEA y por empresas privadas permitieron localizar más de 150 zonas con manifestaciones uraníferas de variada importancia. Prácticamente la totalidad de ellas quedan incluídas en las áreas de « interés inmediato » (figura 2).

De acuerdo con los programas nucleares argentinos y los fondos disponibles, los trabajos de exploración

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* Comisión Nacional de Energía Atómica.

y evaluación se limitaron a un número muy reducido de manifestaciones y anomalías, que ofrecían posibilidades y condiciones operativas más favorables.

Tipos de yacimientos uraníferos argentinos

Dentro de la gran variedad de manifestaciones y depósitos conocidos, se distinguen tres tipos principales: pegmatíticos, vetiformes, con control sedimentario.

Los primeros prácticamente carecen de valor económico y sólo de algunas pegmatitas se recuperan pequeños volúmenes de mineral de uranio, como subproducto de las explotaciones de mica, berilo, feldespatos, etc.

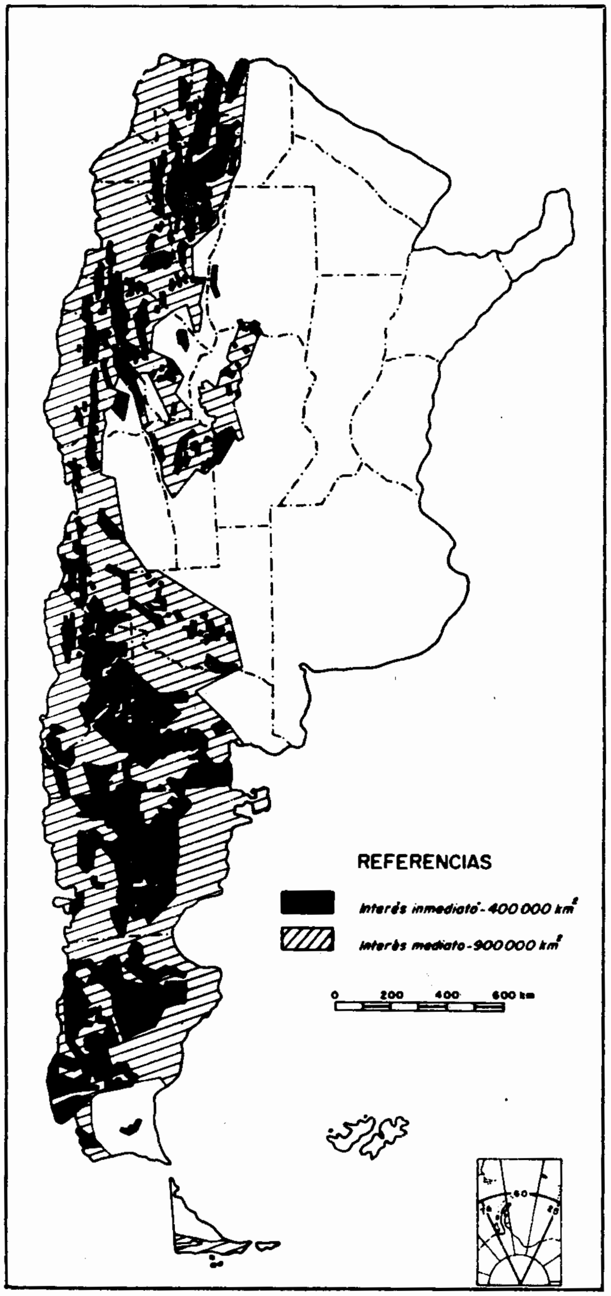

Figura 1. Áreas con posibilidades uraníferas en la República Argentina

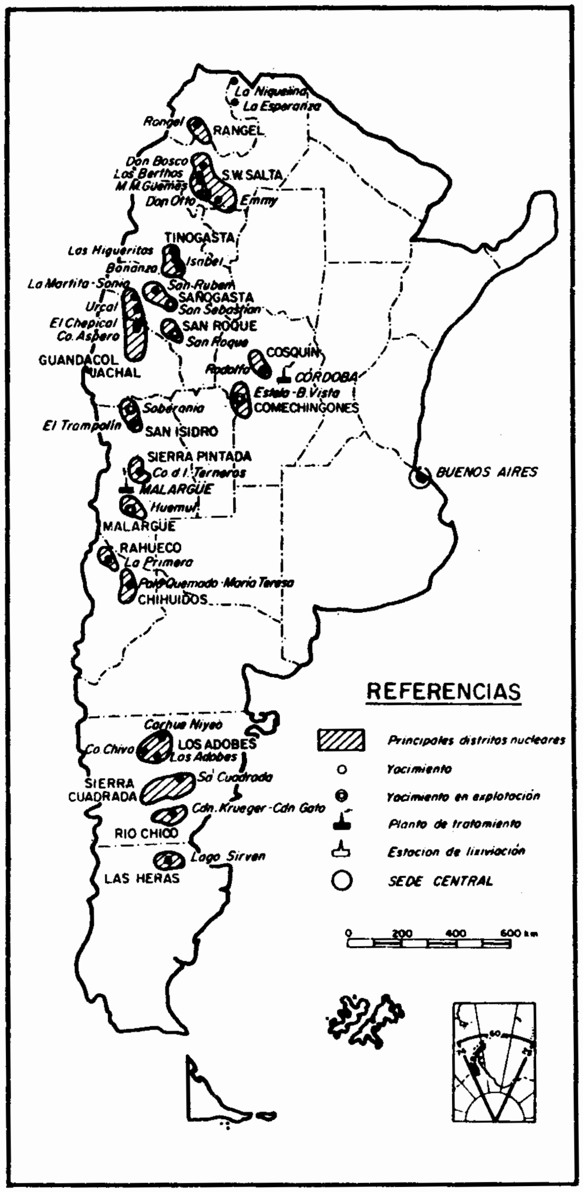

Figura 2. Distritos y yacimientos uraníferos en la República Argentina

Los yacimientos de tipo vetiforme adquirieron preponderancia, tanto en número como en volumen, hasta el año 1958. A partir de dicha fecha fueron desplazados por el descubrimiento y/o desarrollo de aquellos que presentaban control sedimentario, como es el caso de « Huemul », « Agua Botada », « Rodolfo », « Sierra Cuadrada », etc., que a partir de 1960 pasaron a dominar por entero el panorama uranífero argentino, gracias al descubrimiento, mediante prospección aérea, de numerosos depósitos con interesantes perspectivas (« Los Adobes », « M. M. de Güemes », « Don Otto », « Los Berthos », « Pedro Nicolás », « Emmy », etc.).

Existen otras acumulaciones uraníferas, de volúmenes considerables pero con bajas leyes, y que no serán descritas porque no se cuentan entre las de interés económico actual. Las mismas se incluyen en el cuadro de recursos, por su posible interés mediato, a partir del año 1970. Son ellas: las areniscas de Alemanía (Salta), con 200 a 400 g U_3O_8/t; las areniscas petrolíferas de La Brea (Salta), con 100 a 300 g U_3O_8/t; los esquistos de San Juan [3], con 20 a 100 g U_3O_8/t y con potentes sectores de hasta 300 g; los esquistos bituminosos de Mendoza y San Juan, con 100 a 400 g U_3O_8/t y las Tobas Amarillas de Chubut, con 50 a 200 g U_3O_8/t, con espesos niveles hasta 400 g U_3O_8/t.

YACIMIENTOS Y DISTRITOS URANIFEROS

Pegmatitas uraníferas

Dentro del ambiente antecámbrico de las Sierras Pampeanas, que abarca una superficie de 120 000 km^2, son frecuentes las manifestaciones uraníferas alojadas en cuerpos pegmatíticos profusamente distribuídos en áreas graníticas, en especial en la zona de contacto con las metamorfitas circundantes.

Las de mayor interés desde el punto de vista uranífero son las de las Sierras de Comechingones [4] y Grandes, de las provincias de Córdoba y San Luis, que presentan « bolsones » de mineral con muy alta ley (hasta 50 % U_3O_8), orlados por zonas de impregnación variable, con tenores que oscilan entre 0,25 y 0,50 % U_3O_8. En los primeros, por lo general aparece uraninita en nódulos de hasta varios kilogramos, a la vez que en las zonas marginales domina la autunita y variedades de « ocres de uranio ».

De la información disponible al presente, se infiere que de estos depósitos pegmatíticos puede esperarse la producción de varios miles de toneladas de mineral de impregnación, con ley media de 0,35 % U_3O_8 y cantidades variables de nódulos de alta ley. Sin embargo, la recuperación de los mismos sólo resulta económica bajo la forma de subproductos de la explotación de las pegmatitas por otros minerales como berilo, micas, feldespatos y cuarzo, de modo que la magnitud de este aporte uranífero queda condicionado a las variaciones del mercado de los otros minerales.

El potencial mínimo para estos depósitos, en todas las Sierras Pampeanas, se estima en el orden de 50 t U_3O_8.

Yacimientos vetiformes

Distrito Comechingones (Provincias de Córdoba y San Luis).

Dentro del ambiente granítico antecámbrico de la vertiente occidental de la Sierra de Comechingones se alojan varias manifestaciones y depósitos uraníferos de tipo vetiforme o *stockwerk*. La más importante de ellas es la mina « Estela », sita en Villa Larca (San Luis), que presenta un grueso *stockwerk* fluorítico-uranífero de hasta 11 metros de potencia, alojado en un granito porfiroide, del cual se desprenden ramificaciones vetiformes. Tanto aquél como éstos estan rodeados por halos de impregnación de uranio. El mineral dominante es el *uranofano*, apareciendo en profundidad pechblenda alterada en gummita [5]. De este yacimiento, con una explotación esporádica e incipiente, ya se extrajeron más de 3 000 t de mena con tenor medio de 0,5 % U_3O_8.

Otro depósito similar es el de « Bella Vista » [6], en el que dominan los fosfatos de uranio, no apareciendo la fluorita fétida. El tenor medio de los minerales es algo superior a 0,2 % U_3O_8.

En la vertiente oriental de la Sierra de Comechingones se presentan asimismo numerosas vetas fluoríticas, brechosas, en las que el uranio aparece finamente diseminado en calcedonia, que cementa el conjunto. Las brechas pueden alcanzar varios metros de potencia y extensiones de algunos kilómetros, siendo la mineralización uranífera de baja ley, salvo en algunos sectores en los que presenta enriquecimientos de hasta 0,3 % U_3O_8.

Se estima que las posibilidades uraníferas del distrito superan las 115 t U_3O_8.

Distrito Sañogasta (Provincia de La Rioja).

Comprende varios depósitos (« San Sebastián », « Santa Brígida », etc.) alojados en metamorfitas paleozoicas, en los que la mineralización uranífera aparece en forma de *stocks*, en mayor o menor grado cupríferos, rodeados por gruesos halos de impregnación [7].

Explotaciones espóradicas de algunos cuerpos permitieron la producción de 2 500 t de mineral, con ley media de 0,85 % U_3O_8, estimándose que aún permanecen reservas del orden de las 25 t U_3O_8 y que el potencial mínimo del distrito puede alcanzar la cifra de 165 t U_3O_8.

Distrito San Isidro (Provincia de Mendoza).

A 20 km al oeste de la ciudad de Mendoza se localizan algunos depósitos uraníferos, de los cuales los más importantes son los de las minas « Soberanía », « Independencia » y « Papagayos » [8-10]. La mineralización de uranio se aloja en fracturas brechosas, dentro de sedimentos triásicos.

Estos yacimientos, que sólo operaron corto tiempo, produjeron más de 1 200 t de mena con ley de 0,25 % U_3O_8, estimándose que el potencial del distrito es reducido, del orden de 50-70 t U_3O_8.

Distrito Guandacol, Sector Urcal (Provincia de La Rioja).

Recientemente en este distrito, que alberga depósitos con control sedimentario, se descubrieron una serie de cuerpos uraníferos alojados a lo largo de una

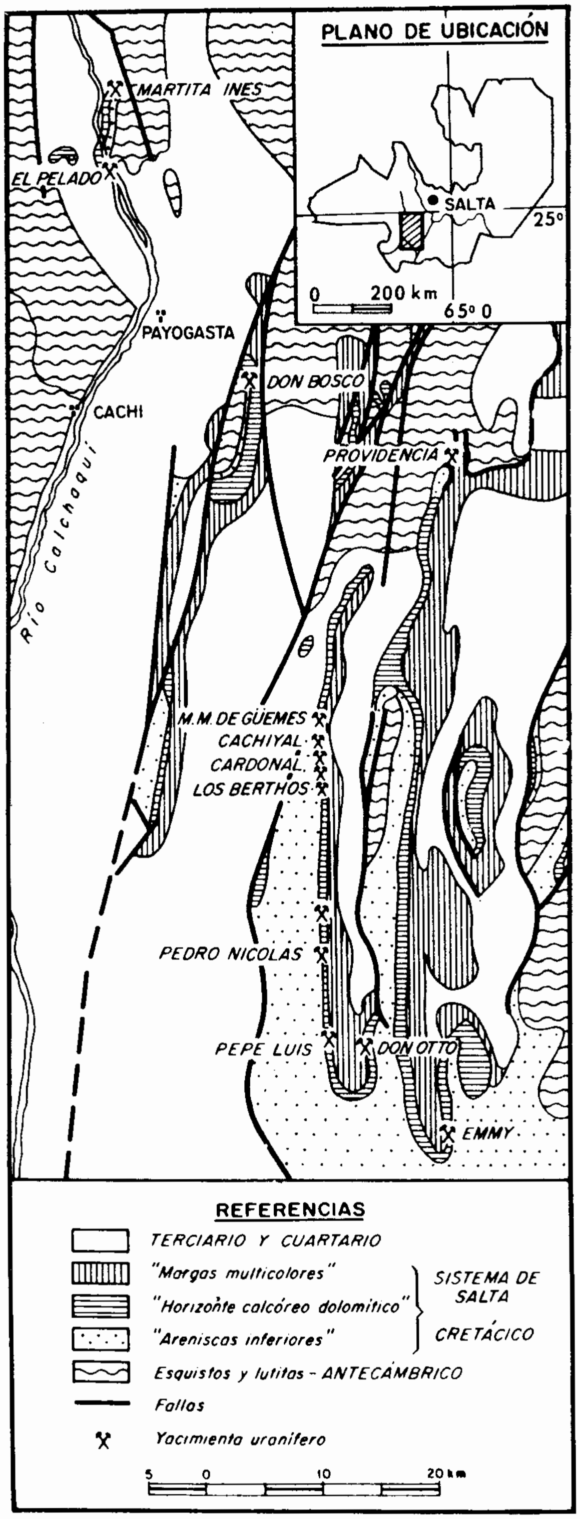

Figura 3. Principales yacimientos uraníferos del distrito La Poma-San Carlos, provincia de Salta (según levantamiento de YPF)

línea de fractura, cercana al contacto de calizas ordovícicas con areniscas carbónicas (yacimiento Urcal). Si bien su estudio recién se inicia, se estima que los mismos pueden adquirir interés económico, habiéndose recuperado de los trabajos exploratorios más de 200 t de mineral seleccionado, con ley media de 1,50 % U_3O_8. Las posibilidades razonables de desarrollo del distrito se estiman en 450 t U_3O_8 y su potencial en 950 t U_3O_8.

Otros yacimientos vetiformes menores o poco conocidos

Existe un número discreto de yacimientos de este tipo cuya real importancia no se conoce al presente, por no contarse con suficientes trabajos exploratorios, casi siempre limitados por la ubicación geográfica o topográfica no favorable de los mismos. Entre ellos se destacan los de las minas « San Santiago », « La Niquelina » y « La Esperanza », con menas complejas de uranio y níquel en las dos primeras, y uranio, cobre, plomo y cinc en la última [11].

Yacimientos con control sedimentario

Distrito La Poma — San Carlos (Provincia de Salta).

Comprende una serie de cuerpos uraníferos alojados en distintos niveles (preferentemente arenosos), de la serie mesocretácica del norte argentino, distribuídos en una zona de 90 km de extensión NS y 60 km EO (figura 3).

En su casi totalidad, los depósitos con interés económico fueron descubiertos con trabajos de prospección aérea en 1959 [12], localizándose en el sector Tonco-Amblayo. El mayor de ellos es el de « Don Otto » [13], que presenta una mineralización continua en superficie a lo largo de 2 500 m, con potencia útil de 1 m y ley media de 0,15 % U_3O_8. Los trabajos de desarrollo se cumplen sobre la mitad austral del depósito, hasta 100 m de profundidad (nivel 0), con más de 2 000 m de labores subterráneas. Actualmente la exploración ya alcanzó el nivel — 40 (figura 4).

El yacimiento « Martín M. de Güemes » tiene un desarrollo en superficie de 300 m, potencia útil de 1 m y leyes medias de 0,13 % U_3O_8 y 0,5 % V_2O_5, habiendo sido explorado hasta 40 m de profundidad.

El cuerpo de « Los Berthos » presenta mineralización algo irregular a lo largo de 300 m y posee leyes de 0,5 % U_3O_8 y 1 % V_2O_5 para espesores medios de 1 m. Las labores subterráneas se extienden hasta —32 m.

El depósito « Pedro Nicolás » presenta en superficie una mineralización continua sobre 700 m, habiéndose certificado recientemente la extensión de la misma hasta 180 m por debajo del afloramiento, con un desarrollo de aproximadamente 300 m sobre banco. El cuerpo « Cachiyal », también aflorante, muestra la continuidad del mismo hasta el nivel —35 m.

Otros depósitos del distrito, con características semejantes a los anteriores, sólo fueron reconocidos en superficie, presentando « Pepe Luis », mineralización sobre 400 m; « Emmy », sobre 200 m, etc., con

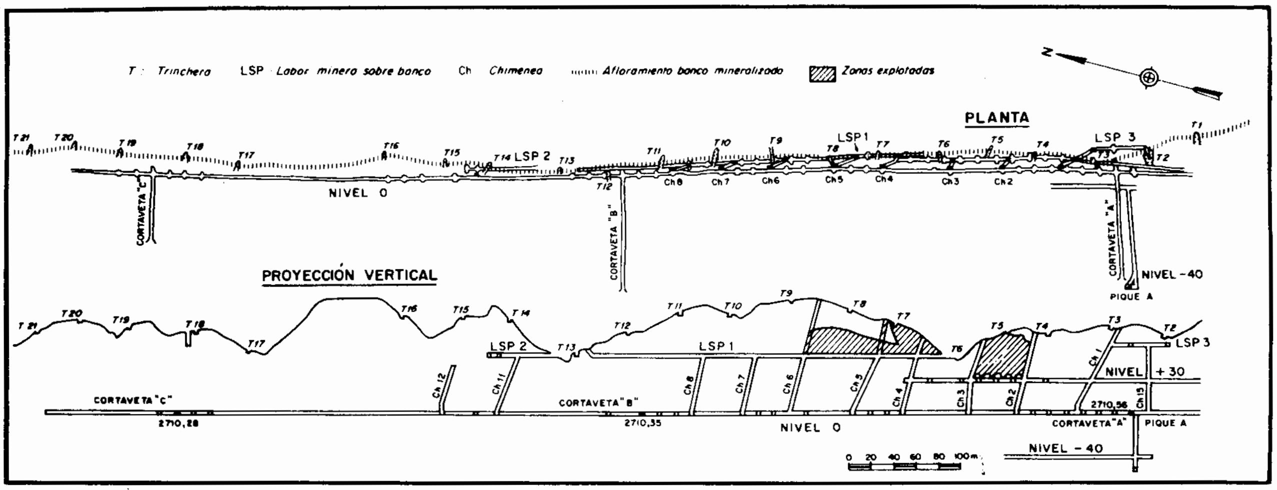

Figura 4. Yacimiento « Don Otto », Salta. Estado del laboreo minero en marzo de 1964

potencias útiles que oscilan entre 0,60 y 1 m y tenores medios entre 0,1 y 0,2 % U_3O_8.

Sobre otros cuerpos (« Don Bosco », « El Pelado », « Providencia », etc.) se ejecutaron trabajos menores de reconocimiento, los que evidenciaron que los mismos son de menor importancia que los anteriores.

Las reservas (mineral « medido », « indicado » e « inferido »), alcanzan a 2 000 t U_3O_8 (recuperables a menos de 8 $US/lb U_3O_8), más otras 300 t U_3O_8 que se obtendrían a costos comprendidos entre 8 y 10 $US/lb U_3O_8.

La extensión y continuidad de la mineralización en superficie y en profundidad de los depósitos « Don Otto », « Pedro Nicolás », « Los Berthos », « Cachiyal », etc., y las características semejantes de los cuerpos aún no explorados, permite inferir que las posibilidades razonables de desarrollo del distrito son del orden de 14 000 t U_3O_8 [14].

Hasta el presente, el mineral dominante es la tyuyamunita en « Don Otto », y « Martín M. de Güemes », y carnotita en « Los Berthos » y « Emmy » [15]. Las menas del distrito son económicamente concentrables por lixiviación ácida, operando ya una estación cargada con 20 000 t, cifra que se elevará en los próximos meses a 36 000 t. El preconcentrado cálcico que se obtiene, con ley variable entre 5 y 8 % U_3O_8, se envía para su refinación final a Planta Córdoba [16].

Distrito Tinogasta (Provincia de Catamarca).

Comprende una serie de manifestaciones uraníferas (yacimientos: « Helios », « La Flecha », « Las Higueritas », « Bonanza », etc.) que se alojan en sedimentos continentales finos, lutíticos, de posible edad triásica.

Las acumulaciones no son continuas, raramente sobrepasan los 100 m de extensión y si bien los espesores con impregnaciones de baja ley pueden llegar a varios metros, las potencias útiles se confinan a 1 – 1,50 m, con leyes medias de 0,04 % U_3O_8 registrándose sectores de enriquecimiento con hasta 0,3 % U_3O_8.

La reducida ley del mineral y las dificultades que presenta su tratamiento no confiere al distrito un interés inmediato, aunque recientes exploraciones evidenciaron posibilidades promisorias.

Distrito Guandacol — Jáchal (Provincias de La Rioja y San Juan).

En el borde oriental de la Precordillera de San Juan y La Rioja se extiende una ancha faja de sedimentos paleozoicos, la que contiene un elevado número de manifestaciones uraníferas, casi siempre de volúmen reducido pero con elevados tenores en U_3O_8 (yacimientos: « Sonia », « La Martita », « Cerro Aspero », « La Cuesta », etc.) [17, 18].

La mineralización aparece como lentes, guías o nódulos de uraninita dentro de sectores arenosos de sedimentos continentales permo-carbónicos y está finamente ligada al material carbonoso. El volumen de los cuerpos raramente excede algunas decenas de toneladas de mineral, con leyes que oscilan entre 0,15 y 1,5 % U_3O_8, registrándose casos con tenores de 27 % y 68 % U_3O_8 para partidas de 2 y 1 t, respectivamente.

Distrito Cosquín (Provincia de Córdoba).

Comprende los yacimientos: « Rodolfo », « Año Dos Mil », etc. Una sucesión sedimentaria eocénica aflora por más de 30 km en el Valle de Punilla, con *facies* continental, quedando limitada hacia el oriente, mediante falla, por gneises antecámbricos, a la vez que hacia el oeste se apoya sobre granitos y dioritas de la misma edad (figura 5), los que acusan un contenido elevado de uranio (6-9 ppm) y son atravesados por abundantes pegmatitas, algunas de ellas también uraníferas [19].

Dentro de dicho paquete de sedimentos, un sector

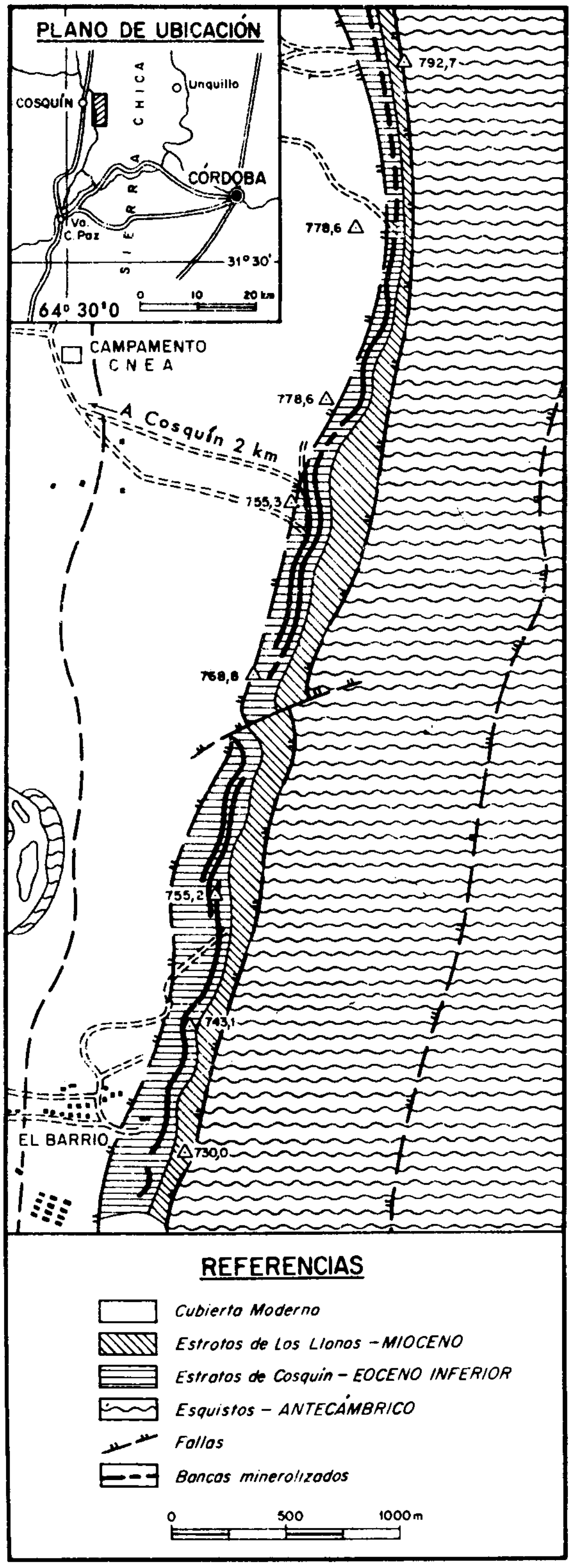

Figura 5. Yacimiento « Rodolfo », en Cosquín, Córdoba (adaptado de Timonieri y Linares)

arenoso-limoso, con alto contenido de carbonato de calcio, de 9 a 12 m de espesor, incluye 3 niveles mineralizados con uranio, de los cuales el del medio es el de mayor interés por su continuidad. Hasta principios de 1964, el depósito había sido estudiado sobre una extensión superficial de 2 000 m y hasta 60 m de profundidad, comprobándose que el sector uranífero tenía una potencia variable entre 5 y 7 m y tenor medio para la misma de 0,04 % U_3O_8. Un intensivo plan exploratorio que se viene cumpliendo en los últimos meses mediante perforaciones, certificó que la mineralización continúa hasta —130 m, dentro de la cual puede delimitarse un sector de 1,5 a 2 m, cuyas leyes oscilan entre 0,1 - 0,15 % U_3O_8 y que el cuerpo se uranífero repite en profundidad por efectos de un tectonismo cuartario.

Hacia el norte, el yacimiento fué reconocido en menor detalle sobre otros 4 km, hasta 30 m de profundidad y muestra características semejantes al sector austral.

La prospección radimétrica y emanométrica, como así también reducidas labores mineras, permitieron evidenciar la continuidad de la mineralización a lo largo de algunas decenas de kilómetros. Hasta el momento sólo se encontraron minerales amarillos, dominando la carnotita y tyuyamunita [15].

En vista de los actuales resultados exploratorios, se estima que fácil y rápidamente podrá integrarse una reserva superior a 11 000 t U_3O_8, de las cuales más de 3 000 t permitirán obtener concentrados a costos del orden de 8 $US/lb U_3O_8.

La presente constituye una de las mayores acumulaciones uraníferas de la Argentina. Si bien la misma es de baja ley, el mineral, muy friable, puede ser fácilmente preconcentrado deslamándolo, con lo que su ley original se eleva hasta 3 veces, reduciendo su volumen al 20 - 37 %.

Estudios previos indican que del mineral con leyes de 400-500 g U_3O_8/t, podría obtenerse torta amarilla a un costo comprendido entre 9,5 y 10 $US/lb U_3O_8 [20].

Distrito Malargüe (Provincia de Mendoza).

En un área de 150 km² [14, 21, 22], situada a 45 km al SO de Malargüe, se ubican varios depósitos cuprouraníferos, de volumen variable, alojados en distintos niveles arenoso-conglomerádicos del Cretácico medio-superior (figura 6).

El cuerpo mineralizado de « Huemul » [23] posee una extensión que varía entre 60 y 100 m según el rumbo de las capas, 310 m en dirección del buzamiento y potencia media de 1,15 m (figura 7), aunque recientes trabajos lo extienden tanto al sur como en profundidad.

En el sector « Arroyo Seco » se presentan dos cuerpos, de los cuales el mayor tiene 300 m de largo, 100 m en el sentido del buzamiento y potencia útil de 0,80 m.

En « Agua Botada » hay 5 niveles mineralizados, de importancia variable, de los cuales se destacan el

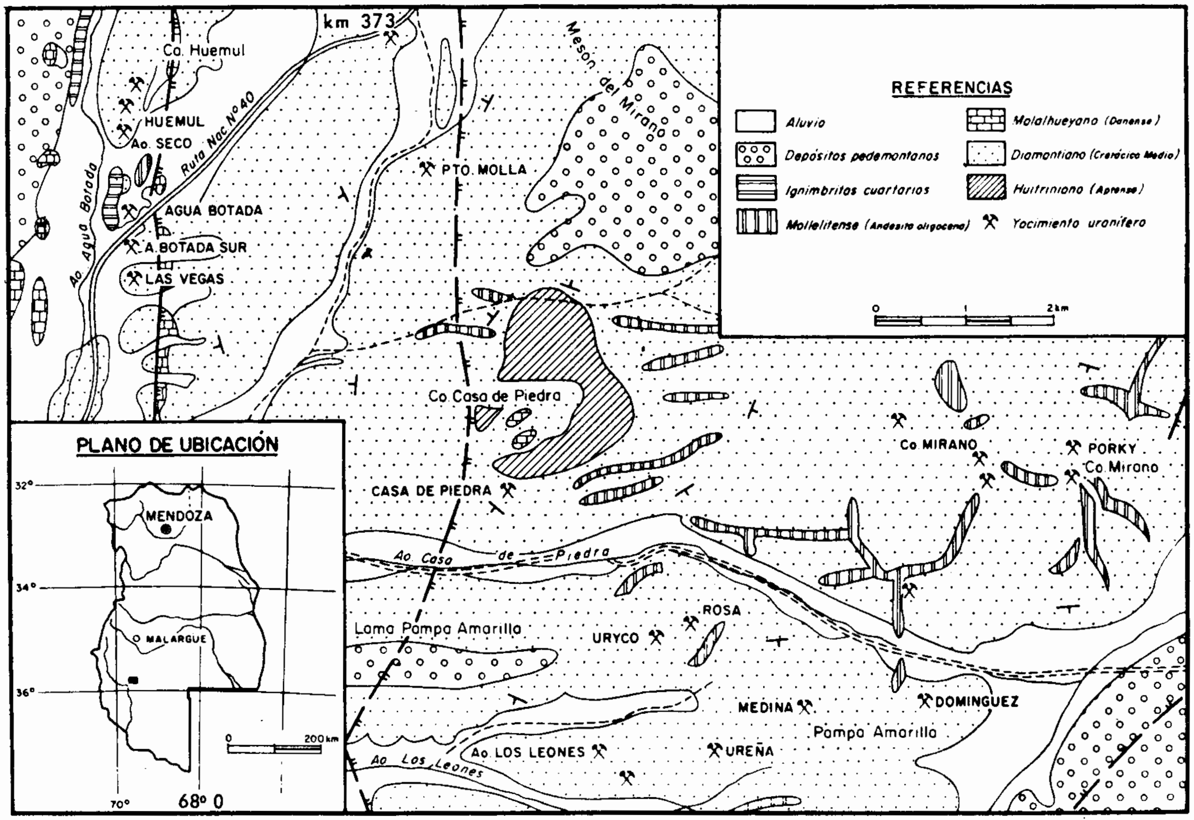

Figura 6. Yacimientos uraníferos del distrito Malargüe, provincia de Mendoza

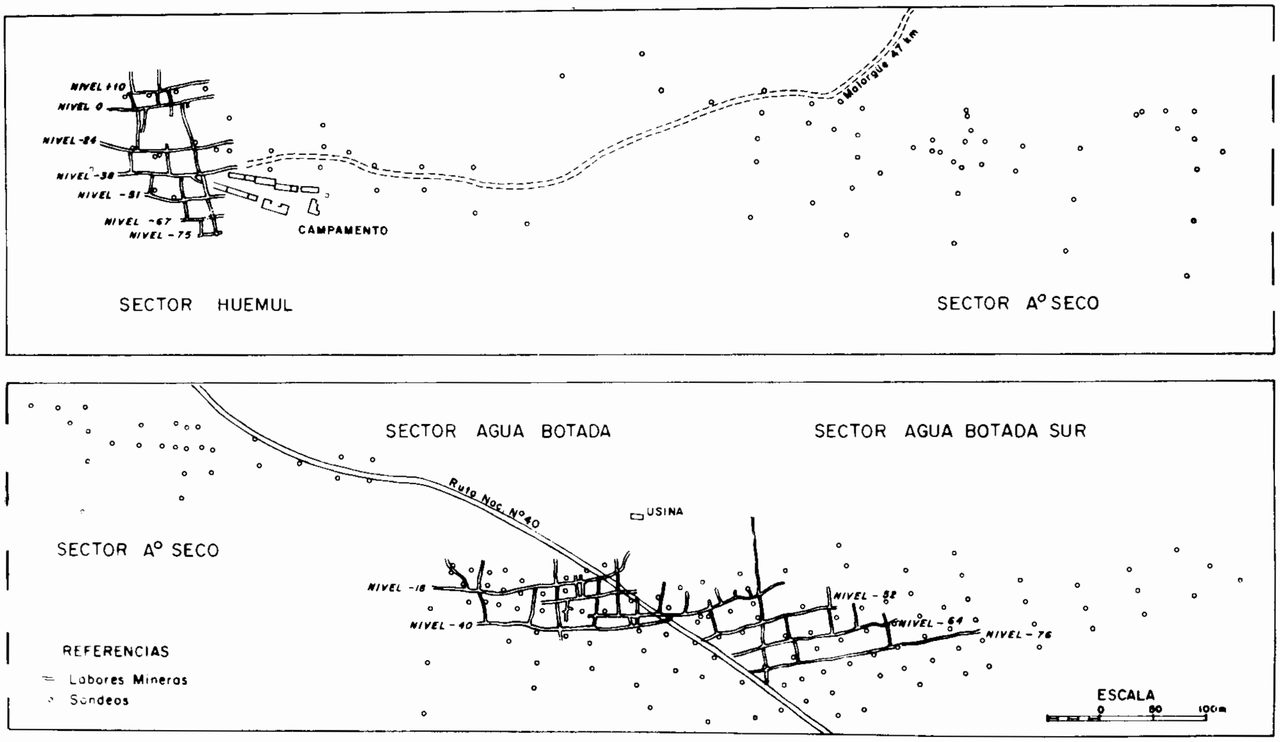

Figura 7. Mina « Huemul », Mendoza. Estado del laboreo minero y sondeos de exploración en marzo de 1964

1.º (superior), el 3.º y 4.º, los que muestran un desarrollo NS de 300, 500 y 600 m, y EO de 140, 100 y 130 m, respectivamente. La mineralización consiste en uraninita, asociada con material asfáltico y calcopirita, predominando en los niveles superiores carnotita, tyuyamunita, azurita y malaquita [24].

Las reservas totales de los cuerpos citados alcanzan a 300 t U_3O_8, concentrables a costos inferiores a 8 $US/lb U_3O_8 en Planta Malargüe, más 50 t U_3O_8 adicionales, que no podrán ser enviadas a esta última y que posiblemente sean tratados por lixiviación en pilas. Las reservas en cobre ascienden a 1 230 t Cu.

Otros depósitos del distrito, pertenecientes a firmas privadas, son poco conocidos y cuentan con escasos trabajos de exploración.

Las características de los cuerpos mineralizados hacen presumir que las posibilidades de mayor desarrollo económico son limitadas, estimándose que con el avance de los trabajos sólo se podrían incrementar reservas, en forma más o menos inmediata, en el orden de 200 y 300 t U_3O_8 (para concentrados a costos inferiores y superiores a 8 $US/lb U_3O_8, respectivamente). Además se considera que el potencial total del área difícilmente supere las 1 000 t U_3O_8.

Distrito Chos Malal (Provincia de Neuquén).

Una serie de manifestaciones cupro-uraníferas (yacimientos: « La Primera », « La Segunda », « Cajón de Tierras Azules », etc.), de reducidas dimensiones, se alojan en sedimentos jurásicos en el área de Rahuécó, a 30 km al OSO de Chos Malal [25]. La importancia de las mismas es muy reducida, considerándose, por el momento, que el potencial total del distrito no supera las 100 t U_3O_8. El único interés reside en el tratamiento local del mineral por el método de lixiviación, mediante el cual se puede recuperar el 70 % aproximadamente del uranio y del cobre, los que se encuentran con tenores de 0,2 % U_3O_8 y 5 % Cu [16].

Distrito los Chihuidos (Provincia de Neuquén).

A 75 km al ESE de Chos Malal (yacimientos: « Palo Quemado », « María Teresa », etc.) se encuentran varios pequeños cuerpos lenticulares mineralizados, de 2 a 4 m de largo y ancho (excepcionalmente alcanzan a 10 m), con potencias que oscilan entre 0,10 y 0,30 m, comprendidos entre lentes de entrecruzamiento de areniscas continentales supracretácicas. Los mismos aparecen en superficie o a escasa profundidad (hasta 10 m) y sus leyes oscilan entre 0,08 y 2,5 % U_3O_8 (media 0,3 % U_3O_8); 4 % Cu y 3 % V_2O_5 [26]. El mineral dominante es la carnotita, asociada con calcopirita, malaquita, volbortita y hematita. El distrito reviste una importancia limitada, estimándose que el potencial del mismo difícilmente supere las 100-150 t U_3O_8.

Si bien el volumen de las reservas no alcanza significación, el beneficio de las menas presenta interés económico, pues las mismas pueden ser procesadas por lixiviación, demostrando los ensayos rendimientos de extracción del 75 % para el uranio y cobre y del 25 % para el vanadio.

Ambiente de Chubut Central

En una extensa área del centro de Chubut, que cubre 30 000 km^2 y en la que participan formaciones jurásicas, cretácicas y terciarias (pórfiros y porfiritas con sus tobas, areniscas, conglomerados, lutitas, etc.) se localizaron, sea por prospección aérea o terrestre, un buen número de manifestaciones uraníferas, las que pueden reunirse en tres grupos [27-29]: *a*) alojadas en areniscas y conglomerados cretácicos; *b*) alojadas en tobas y tobas lutíticas jurásicas; *c*) en relación con diatremas y sedimentos contactantes.

A las primeras pertenecen los depósitos « Los Adobes » y « Sierra Cuadrada ». En « Los Adobes » hay varios cuerpos mineralizados, pero hasta el momento sólo uno reviste interés por su desarrollo. Consiste en un depósito lenticular, alojado en un espeso banco arenoso-conglomerádico sub-horizontal, que presenta una extensión de 150 × 100 m, con potencias que varían entre 3 m en los bordes hasta 10 m en su parte central, con una ley media de 0,18 % U_3O_8 [29]. Las reservas, a la fecha, alcanzan a 250 t U_3O_8 recuperables a 8 $US/lb, estimándose que las otras manifestaciones vecinas carecen de importancia económica en relación a los precios actuales.

En « Sierra Cuadrada » hay varios cuerpos uraníferos alojados en bancos arenosos y lutíticos subhorizontales, de edad cretácica, relacionándose la mineralización con el contenido en material orgánico de los estratos. Las dimensiones de los cuerpos varían entre 50 y 100 m, oscilando las leyes entre 0,04 y 0,18 % U_3O_8. El área fué estudiada en forma preliminar, debiéndose continuar la exploración mediante perforaciones [30].

Otro grupo de manifestaciones y cuerpos uraníferos que se alojan en tobas y lutitas tobáceas del Jurásico, como « Cerro de los Chivos », « Carhué Niyeu », « Manganeso », etc., son aún poco conocidos.

En « Cerro de los Chivos », los bancos mineralizados, que buzan entre 10 y 15° NE, afloran a lo largo de 700 m, presentando acumulaciones uraníferas continuas con potencias que varían entre 0,50 y 1,5 m y tenores oscilantes entre 0,06 y 0,3 % U_3O_8.

Cercana a esta manifestación hay otra, « Manganeso », que muestra una corrida en superficie de 150 m, en la que el uranio se asocia con abundante manganeso (manganita), pareciendo primar el control estructural sobre el sedimentario.

En « Carhué Niyeu », la mineralización ocurre bajo dos formas. En una de ellas, potentes bancos de tobas compactas, en parte silicificadas, que a veces sobrepasan los 10 m de espesor y que afloran por más de 1 000 m, son portadores de acumulaciones uraníferas constantes pero de baja ley, del orden de 0,05 % U_3O_8. En otro sector, se registran incrementos en las leyes (hasta 0,3 % U_3O_8), en relación con factores estructurales, cuando las tobas líticas están afectadas por tectonismo.

Otras manifestaciones, en terrenos jurásicos, fueron localizadas en « Cañadón Sauzal », « Cuchilla Blanca », « Laguna del Molle », etc., pero las mismas no parecen revestir mayor interés por sus bajas leyes.

En el tercer grupo de depósitos de Chubut Central se incluyen los yacimientos « Cañadón Gato » y « Cañadón Krueger » (distrito Río Chico). En el primero, la mineralización se relaciona con una diatrema, la que presenta varios ensanchamientos (bulbos), apareciendo meta-autunita y meta-torbernita tanto en las paredes de la grieta como en el material de relleno de los bulbos y en algunos sectores arenosos de los bancos que los contactan. El desarrollo del cuerpo es de 340 m y su extensión en profundidad fué certificada hasta 35 m. Las potencias útiles varían entre uno y varios metros (en los bulbos) y la ley media del yacimiento es de 0,14 % U_3O_8. Nuevos cuerpos han sido puestos recientemente en evidencia por ionometría y perforaciones.

Los minerales presentes en « Los Adobes » son: uranofano, schroeckingerita y fosfuranilita; en « Cerro de los Chivos »: uraninita y schroeckingerita; en « Sierra Cuadrada »: carnotita schroeckingerita y autunita y en « Cañadón Gato » y « Cañadón Krueger »: fosfatos de uranio.

La extensión del área con interés uranífero de Chubut, la que aún no fué revisada ni explorada en detalle, el número de manifestaciones conocidas en la misma y el carácter de algunos de sus depósitos, permiten inferir que en forma inmediata podrán desarrollarse reservas superiores a 1 200 t U_3O_8 para valores menores a 15 $US/lb U_3O_8.

Distritos y ambientes aún no reconocidos

Quedan aún extensas áreas de la Argentina con posibilidades uraníferas, sobre las que todavía no se realizaron trabajos de prospeción o de reconocimiento. Entre ellas se destacan:

Ambiente extraandino de Santa Cruz

En el mismo, 15 000 km² presentan afloramientos de formaciones sedimentarias cretácicas y terciarias con *facies* favorables, en las cuales mediante rápidos reconocimientos aéreos se ubicaron varias anomalías, las que se corresponden con depósitos uraníferos alojados en areniscas cretácicas (« Baqueró »). Además, en vetas cupríferas contenidas en el cuerpo granodiorítico de « Tres Cerros », se constató la presencia de uranio, con leyes de hasta 0,1 % U_3O_8.

Se estima que el potencial de este ambiente, dada su similitud geológica y el carácter de la mineralización conocida, puede llegar a ser del mismo orden que el distrito Paso de Indios – Sierra Cuadrada, de Chubut.

Area cordillerana de la Patagonia

Participan de la misma terrenos de variada edad, desde antecámbricos hasta recientes y de carácter ígneo y sedimentario. Por su posible interés uranífero se destacan los complejos sedimentarios jurásicos, cretácicos y terciarios, poseedores de numerosos niveles carbonosos, los que se presentan intruídos por rocas ácidas, mesosilícicas y básicas.

En rápidos reconocimientos, se certificó la existencia de acumulaciones uraníferas en el Valle de Pinturas, las que ocurren en relación con niveles carbonosos y poseen tenores de 0,04 y 0,05 % U_3O_8.

Por el momento no es posible abrir juicio sobre las posibilidades del área.

Ambiente de Rio Negro

Participan en el mismo rocas ígneas y metamórficas de variada edad y composición. Sobre el macizo de Río Negro, que comprende más de 25 000 km², prácticamente no se efectuaron trabajos de prospección regular capaces de definir el interés uranífero del mismo. Rápidos reconocimientos en su borde septentrional, certificaron la presencia de manifestaciones radiactivas de escaso valor, alojadas en granitos, a la vez que se citó la presencia de minerales de uranio en basaltos amigdaloides de Somuncurá.

En el borde sur del macizo, reconocimientos de prospección aérea localizaron áreas anómalas en las cercanías de Gastre, las que serán objeto de próximas revisiones.

Ambiente de la Alta Cordillera

Este ambiente se desarrolla desde la latitud de 37° S hacia el norte del país, comprendiendo 200 000 km². Participan en el mismo variadas formaciones, tanto ígneas como metamórficas y sedimentarias, de distintas edades.

Su topografía abrupta y la elevada cota media, han hecho que este ambiente fuera considerado como de importancia no inmediata, a pesar que presenta interés uranífero pues en él se conocen algunos depósitos radiactivos, al igual que numerosos yacimientos paragenéticos con los minerales de uranio.

Ambiente de las Sierras Pampeanas

El macizo antecámbrico de las Sierras Pampeanas, que cubre una superficie aflorante de 120 000 km² en el centro del país, sólo fué prospectado en forma expeditiva en algunas áreas. Participan en su composición gneises, granitos y dioritas antecámbricos, con diferenciaciones pegmatíticas, a la vez que en varios puntos se presentan cubiertas sedimentarias poco espesas, de distintas edades.

Como ya se señaló, las pegmatitas de las Sierras Pampeanas son frecuentemente uraníferas. En el

Tabla 1. Reservas de mineral de uranio segun costos de elaboración de la Torta Amarilla

(en t de U_3O_8)

Fuentes (Distritos)	Mineral (Medido - Indicado - Inferido)			Posibilidades razonables de desarrolo			Posibilidades potenciales		Totales por distrita	Subtotales	
	$ US/lb U_3O_8			$ US/lb U_3O_8			$ US/lb U_3O_8			Por costos	Progresivos
	< 8	8 — 15	15 — 30	< 8	8 — 15	15 — 30	15 — 30	30 — 50			
Zona Norte											
Tonco-Amblayo	2 000	300	—	10 000	1 700	—	—	—	14 000		
Tín Tín-Cachi	20	20	—	50	100	—	500	—	690		
Alemanía	—	1 000	1 000	—	2 000	2 000	10 000	—	16 000		
La Brea (areniscas petrolíferas)	—	—	—	—	—	—	—	2 000	2 000		
Tinogasta	—	50	100	—	250	500	1 000	—	1 900		
Zona Oeste											
Urcal	50	100	—	100	200	—	500	—	950		
Guandacol-Huaco-Jáchal	—	25	—	15	100	—	—	—	140		
Sañogasta	20	30	—	15	100	—	—	—	165		
Barreal-Rodeo-Jáchal	—	—	1 000	—	—	5 000	10 000	20 000	36 000		
Malargüe	300	50	—	200	300	200	—	—	1 050		
San Isidro	10	—	—	10	50	—	—	—	70		
Sierra Pintada-La Escondida	10	25	—	—	50	—	—	—	85		
Esquistos bituminosos Mza.-S. Juan	—	—	—	—	—	1 000	1 000	2 000	4 000		
Zona Centro											
Valle de Punilla	500	2 000	1 000	3 000	2 000	3 000	—	—	11 500		
Comechingones	30	25	—	10	50	—	—	—	115		
Patagonia											
Paso de Indios	250	200	—	—	—	—	1 000	—	1 450		
Sierra Cuadrada	10	25	—	50	200	—	500	—	785		
Río Chico	50	100	—	100	200	—	500	—	950		
Tobas Amarillas-Chubut	—	—	1 000	—	—	3 000	5 000	15 000	24 000		
$\leqslant$ 8 $US/lb U_3O_8	3 250			13 550						16 800	16 800
8-15 $US/lb U_3O_8		3 950			7 300					11 250	28 050
15-30 $US/lb U_3O_8			4 100			14 700	30 000			48 800	76 850
30-50 $US/lb U_3O_8								39 000		39 000	115 850
Subtotales	7 200			20 850			69 000				
	11 300			35 550						115 850	
Totales progresivos	3 250	3 950	4 100	13 550	7 300	14 700	30 000	39 000			
	3 250	7 200	11 300	24 850	32 150	46 850	76 850	115 850			

mismo ambiente están alojados los yacimientos vetiformes « Estela » y « Bella Vista », con minerales de uranio y fluorita, a la vez que ciertas formaciones sedimentarias desarrolladas en su interior o bordes, también son portadoras de depósitos radiactivos de variada importancia, como es el caso del yacimiento « Rodolfo » en el Valle de Punilla.

Ambiente de la Puna y Prepuna

Comprende un área de más de 100 000 km² de las provincias de Salta y Jujuy, en la que participan esquistos, lutitas y granitos antecámbricos; cuarcitas, areniscas y esquistos paleozoicos en sus bordes, y areniscas, calcáreos y margas mesozoicos en distintos puntos, siendo intensa la participación ígnea mesosilícia y ácida terciaria y cuartaria, con la que se relacionan los numeroso yacimientos metalíferos del norte argentino y Bolivia (plata, plomo, cinc, cobre, estaño, etc.).

En este ambiente se conocen pegmatitas uraníferas enclavadas en el granito de Cachi; filones uranotoríferos de la Sierra de Rangel, dentro de ambiente granítico; sedimentos mesozoicos con yacimientos uraníferos en el distrito La Poma-San Carlos y travertinos cuartarios con minerales amarillos de uranio de baja ley en Tolar Grande.

Esta extensa región, con cota media absoluta de cerca de 4 000 m s.n.m., sólo fué revisada en forma muy preliminar en algunos puntos. Su prospección regular ha sido programada para etapas futuras. Si bien el ambiente presenta interés uranífero, nada puede anticiparse sobre su presunto potencial.

CONCLUSIONES

De las áreas con posibilidades uraníferas de la Argentina, se reconocieron hasta el presente menos del 15 % de las mismas, habiéndose descubierto varios distritos y numerosas manifestaciones.

La exploración física, circunscripta a algunos depósitos que ofrecían mayor interés inmediato, permitieron determinar las « reservas de mineral de uranio » que se indican en la tabla 1.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/405 Argentina

Known and estimated uranium reserves in Argentina

By C. T. Friz *et al.*

On the basis of the geological structure of Argentina and of modern concepts of uranium-bearing deposit formation, it is estimated that over 1 million km^2 of the continental territory of the country may contain varying accumulations of uranium minerals. Of this area, about 400 000 km^2 are especially promising, in view of the types and locations of the geological formations present. It is here that both State and private prospecting and exploration have been concentrated.

So far, regular prospecting, especially by air, has covered more than 75 000 km^2 in which over 150 localities have been found with deposits of varying uranium content, in some cases still to be determined.

Exploration and assay work have been carried out on a very small number of deposits, in keeping with budget allocations and national nuclear requirements.

The uranium-bearing areas of the country contain three main types of deposit: (*a*) sedimentary; (*b*) vein-type; and (*c*) pegmatitic. The first of these contains the largest concentrations; the vein-type deposits constitute only a small part of the whole and those contained in pegmatites are, with a few exceptions, of no economic importance.

The paper briefly describes the main features of the principal areas or deposits (Tonco-Amblayo, Tinogasta, Guandacol-Jáchal, Sañogasta, San Roque, Huaco, San Isidro, Malargüe, Comechingones, Valle de Punilla, Chihuidos, Rahueco, Sierra Cuadrada, Paso de Indios, Río Chico and pegmatites in the Sierras Pampeanas) and indicates the volumes of the reserves measured so far and the estimated uranium content in each case, the volumes measured being classified according to the production costs of commercial-grade concentrates (greater or less than US $8/1b).

It also contains a table showing the total uranium reserves in Argentina classified according to the cost of production.

A/405 Argentine

Ressources et possibilités uranifères en Argentine

par C. T. Friz *et al.*

Compte tenu de la structure géologique de l'Argentine et des conceptions modernes sur la genèse des gisements uranifères, on estime possible que plus de 1 000 000 de km^2 de son territoire continental contiennent des gisements de minerai d'uranium d'importance variable. Sur ce total, près de 400 000 km^2 offrent des perspectives plus favorables, par suite, d'une part, des caractéristiques géologiques environnantes et, d'autre part, de leur situation géographique. C'est justement dans ces limites que se sont concentrées les activités de prospection et d'exploration aussi bien officielles que privées.

Jusqu'à présent, on a prospecté d'une manière régulière, spécialement par prospection aérienne, 75 000 m^2 dans lesquels on a découvert plus de 150 emplacements de dépôts uranifères d'intérêt variable ou non encore déterminé.

Les travaux d'exploration et d'évaluation minière ont été effectués sur un nombre très réduit de manifestations, en accord avec le budget et les nécessités nucléaires de l'Argentine.

Les districts uranifères du pays comprennent trois types principaux de gisements : *a*) avec contrôle sédimentaire, *b*) filoniens, et *c*) en pegmatites.

Dans les premières sont compris les plus grands dépôts; les filoniens ont une importance très réduite dans le cadre général et ceux qui sont du type pegmatite, à part quelques exceptions, ne présentent pas d'intérêt économique.

On donne des détails succincts sur les caractéristiques principales des districts ou gisements les plus importants (Tonco-Amblayo, Tinogasta, Guandacol-Jáchal, Sañogasta, San Roque, Huaco, San Isidro, Malargüe, Comechingones, Valle de Punilla, Chihuidos, Rahueco, Sierra Cuadrada, Paso de Indios, Río Chico et pegmatites des Sierras Pampeanas), en indiquant le volume des réserves calculées jusqu'à présent et le potentiel uranifère estimé dans chaque cas.

On donne un tableau des réserves totales d'uranium en Argentine, classées suivant les prix de revient des concentrés de qualité commerciale (supérieur ou inférieur à 8 $/lb).

A/405 Аргентина

Запасы урана в Аргентине

К. Т. Фриц *et al.*

Исходя из геологической структуры Аргентины и современных концепций о происхождении урановых месторождений, полагают, что различные по запасам и содержанию залежи урановых руд располагаются более чем на

1 000 000 *км*² континентальной территории Аргентины. Часть этой территории площадью примерно 400 000 *км*² представляет собой наиболее благоприятный район с точки зрения типов и размещения геологических формаций. Именно в этом районе сосредоточены основные работы государственных и частных организаций по разведке и эксплуатации месторождений.

До настоящего времени систематическими поисками и особенно воздушной разведкой детально изучен район площадью более 75 000 *км*², где обнаружено свыше 150 залежей урановой руды с различным содержанием урана. В некоторых случаях содержание урана в руде еще не определено.

Детальная разведка и количественный анализ руд были проведены лишь на незначительной части открытых месторождений. Это объясняется количеством бюджетных ассигнований и потребностями национальной атомной промышленности.

Ураноносные районы страны содержат три типа месторождений: a) осадочные, b) жильные и c) пегматитовые отложения. Наиболее богатыми являются месторождения первого типа; жильные формации составляют лишь незначительную часть всех месторождений, а скопление урана в пегматитах, за несколькими исключениями, не представляет экономической ценности.

В докладе приводятся краткие сведения об основных особенностях наиболее важных ураноносных районов (Тонко-Амблаяо, Тиногаста, Гуандакол-Жашал, Саногаста, Сан-Рок, Хуако, Сан-Исидро, Маларгюэ, Комечингонес, Валле-де-Пунилла, Чихидос, Рахуэко, Сьерра-Куадрада, Пасо-де-Индиос, Рио-Чико и пегматиты Сьерра-Пампеанас), указываются общий объем установленных запасов и содержание урана в каждом месторождении, а также стоимость концентратов промышленного обогащения.

Наконец, приводится таблица всех запасов урана в Аргентине с классификацией по производительности месторождений.

Uranium deposits in tertiary volcanic rocks of north-eastern Macedonia

By R. Pantić, D. Radusinović, B. Sikošek and M. Obrenović *

Important uranium deposits have recently been discovered in the Kratovo-Zletovo volcanic area, in north-eastern Macedonia, already known for its lead and zinc deposits, which covers an area of about 1 500 km^2.

The extensive, thick volcanic series are responsible for the specific morphology, very broken country with a deeply cut and comparatively well developed river system. The main hydrographic artery, Zletovska Reka (the Zletovo river) and its tributaries, runs along its whole course through gorge-shaped valleys, with steep cliffs, which demonstrate the relatively young erosional state of this area. The mean elevation is about 1 000 metres, with some peaks rising to 2 000 metres. Vegetation is generally scarce, and the climate continental, although this part of Macedonia is under strong Mediterranean influence.

GENERAL GEOLOGY AND STRUCTURAL FEATURES OF ZLETOVO-KRATOVO AND THE SURROUNDING AREA

Geologically, this area displays a distinct contrast between old crystalline formations, mainly Paleozoic, and tertiary volcanic and sedimentary rocks. The young volcanic series mark the line of the primary structural feature, the deep lineament which represents the boundary between two sizeable geotectonic categories, the orogenic trunk of the Dinarides and the crystalline internide mass, which means that this area is located in the axial zone of the Alpine orogenesis in this part of its extension (Fig. 1.).

The lithologic sequence of the metamorphic rocks which compose the rim zone of the internide crystalline complex is represented by the following members: muscovite-chlorite gneisses, mica schists, chlorite schists, mica-bearing schists, phyllite-graphitic schists, with the quartzites as the youngest members.

Structurally, plicative as well as disjunctive structures, connected with the earlier orogenic phases, are prominent in this complex. The rim-zone fracture system abounds in reverse faults along which, during the different compressive phases of the Alpine orogenesis, the horizontal displacements of the rock masses took place; in the more recent phases, characterized by decompression, deep fractures were formed, providing channels through which large masses of magmatic rocks erupted, filling up the newly-formed depressions in which intensive sedimentation also took place. The newly-formed volcanic mantle covered the old, mosaic crystalline basement. Neotectonic stresses, particularly intensive in the axial zone of the orogen, reactivated the old basement structures and reflected their position through the younger volcanic mantle on the surface. In addition to these old, reactivated structures, new dislocations occurred, running in very definite directions.

The fractures in this area run basically NNW-SSE (N-S) and ENE-WSW (E-W), with very steep, almost vertical planes. The first system is the dominant one, and forms part of the younger structures of the Alpine orogen in this part of its extension. On this view, the E-W direction could reflect the influence of the old fractures in the crystalline basement.

The size of the basic network of intersecting dislocations varies from a few hundred metres to two kilometres, and the breadth of the tectonized zones along the primary structures up to and beyond 100 metres.

GEOLOGY OF THE VOLCANIC COMPLEX

The volcanic complex is composed of andesites, dacites and their pyroclastic equivalents the ignimbrites and tuffs. The following types of volcanic rock have been identified; they are listed in order of eruptive succession:

(*a*) Hornblende-biotite andesites and related tuffaceous breccias and tuffs;

(*b*) Ignimbrites and clasto-crystalline tuffs (tuffaceous breccias, stratified tuffs and agglomerated tuffs and breccias);

(*c*) Hornblende-biotite dacites and quartz-latites with dacitoid and andesite (trachyandesite) differentiates; and

(*d*) Labradorite-augite andesites (mostly trachyandesites) and related tuffs.

The hornblende-biotite andesites were formed during the initial phase of volcanic activity. They form tabular masses. These rocks are accompanied

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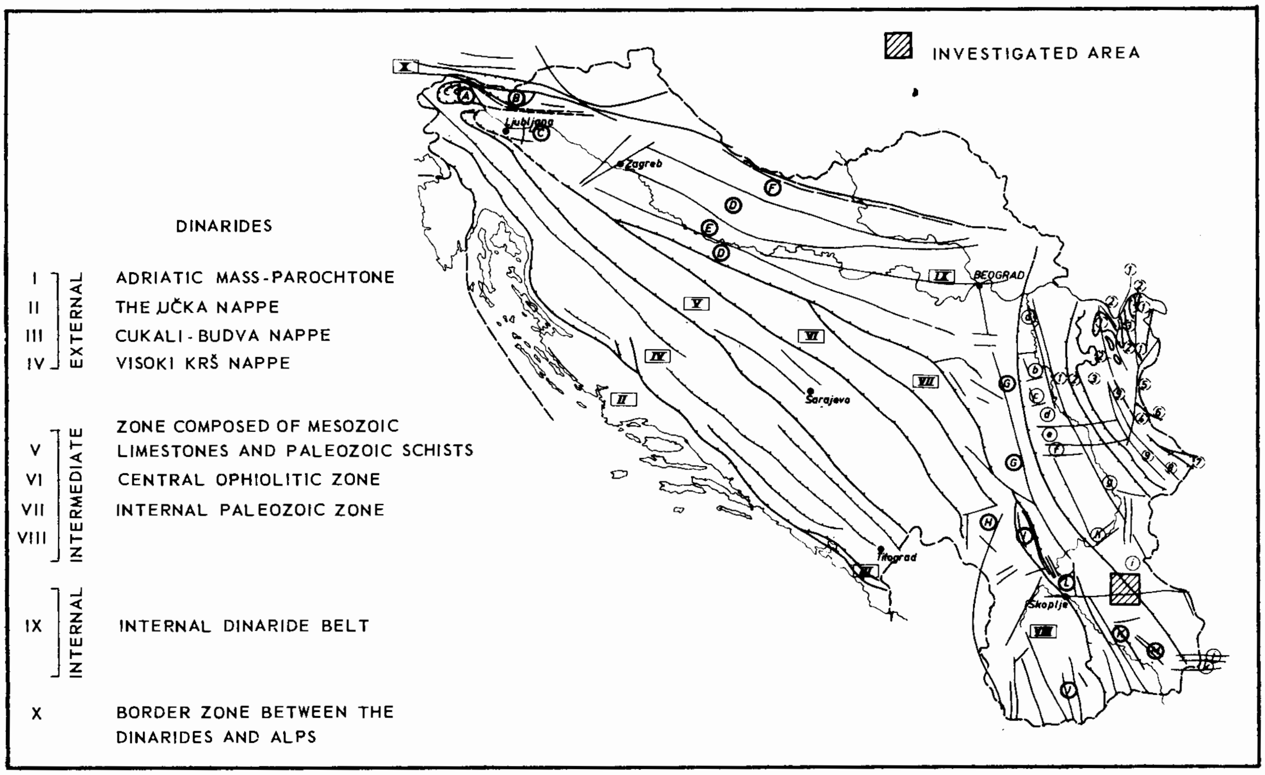

Figure 1. Schematic geotectonic map of Yugoslavia (according to K. Petkovic, B. Sikosek and B. Maksimović)

Dinarides:

(A) Julian Alps; (B) Kamnian Alps; (C) Sava folds; (D) Inner Dinaric horsts; (E) Tectonic trench of Sava River; (F) Tectonic trench of Drava River; (G) Inner ophiolitic zone; (H) Tectonic depression of Metohija; (I) Tectonic depression of Kosovo; (J) Tectonic depression of Pelagonija; (K) Vardar zone; (L) Basin of Skoplje; (M) Kriva Lakavica trench.

Serbo-Macedonian internide mass: (*a*) Trench of Morava; (*b*) Horst of Crni Vrh; (*c*) Horst of Juhor; (*d*) Basin (trench) of Krusevac; (*e*) Horst of Jastrebac; (*f*) Basin (trench) of Prokuplje; (*g*) Basin (trench) of Leskovac; (*h*) Basin (trench) of Vranje; (*i*) Serbo-Macedonian mass; (*j*) Basin (trench) of the Strumica field; (*k*) Horst of Belasica.

Carpatho-Balkanian Range: (1) Nappe of Morava (Geticum); (2) Infrageticum (Parochtone); (3) Danubicum (Autochtone); (4) Anticlinorium of Stara Planina; (5) Vrška Čuka anticline; (6) Minicevo-Kadibogaz syncline; (7) Imbricate structure of Visočka; (8) Imbricate structure of Vidliča; (9) Senonian tectonic trench.

by tuffaceous breccias and tuffs of identical composition.

The most widely distributed rocks in the area are the ignimbrites. These were formed after the extrusion of the andesitic rocks during a very intensive eruptive phase, in which "incandescent clouds" and lava flows, composed of incandescent solid particles, water vapour and other hot gases, were represented. The solid particles were fragments of phenocrysts, mainly plagioclase (An 37-42%),* biotite, hornblende, quartz, sometimes sanidine and augite, accompanied by particles of semi-molten glass and tiny fragments of the volcanic and basement rocks. The ignimbrites sprang mainly from the hornblende-biotite, dacite and quartz-latite. Their composition is generally the same as that of the mother rocks, but the microstructure is basically different; this is particularly apparent in the heterogeneous microstructural features of the groundmass. The particular types of microstructure often vary greatly, but basically clasto-crystalline and vitroclastic structures predominate. The tuffaceous breccias and tuffs overlie the ignimbrites. In some parts of the area stratified tuffs were found, which lithologically could correspond to politic sandstones, partly overlaid by agglomerated tuffs and breccias. The latter are composed mainly of ignimbrites, rarely of crystalline schists. In some parts of the area, the gradual transition of the ignimbrites into tuffs could be observed.

Hornblende-biotite andesites and quartz-latites, with dacitoid and andesite varieties, break through the ignimbrites and form cones and dykes.

The labradorite-augite andesites and their tuffs form a mantle over the ignimbrites. This superpositioning suggests that these rocks represent the latest extrusive phase in this area.

The petrochemical features of the volcanic rocks of the area suggest that they were formed from a granodioritic magma, although there were variations in the magmatic type. Ignimbrites have the petrochemical

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* An = percentage of anorphite in felspars.

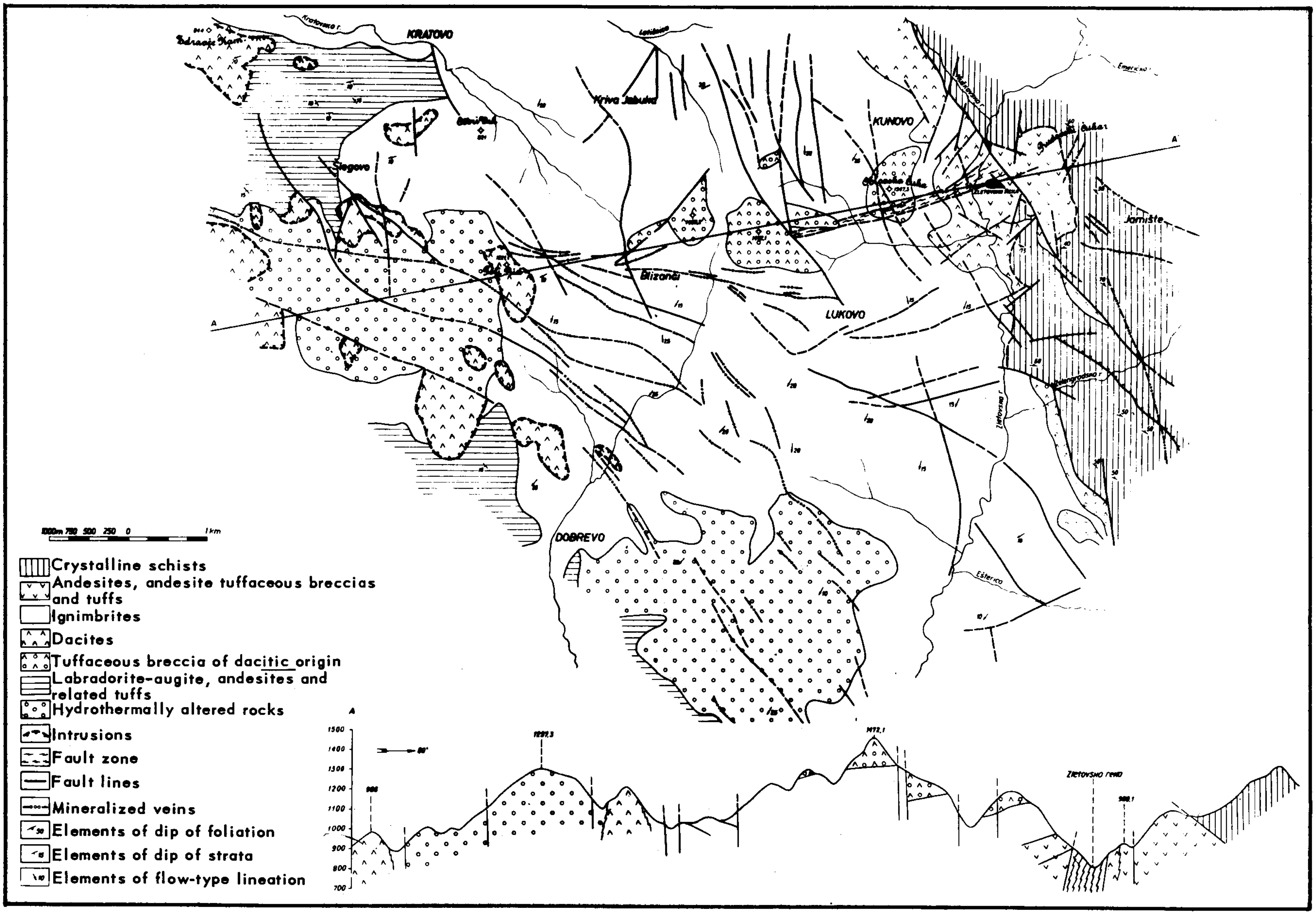

Figure 2. Geologic and petrographic map of south-eastern part of Kratovo-Zletovo area (according to N. Mijazković, B. Stanić, S. Divljan, D. Pešić and G. Roncević)

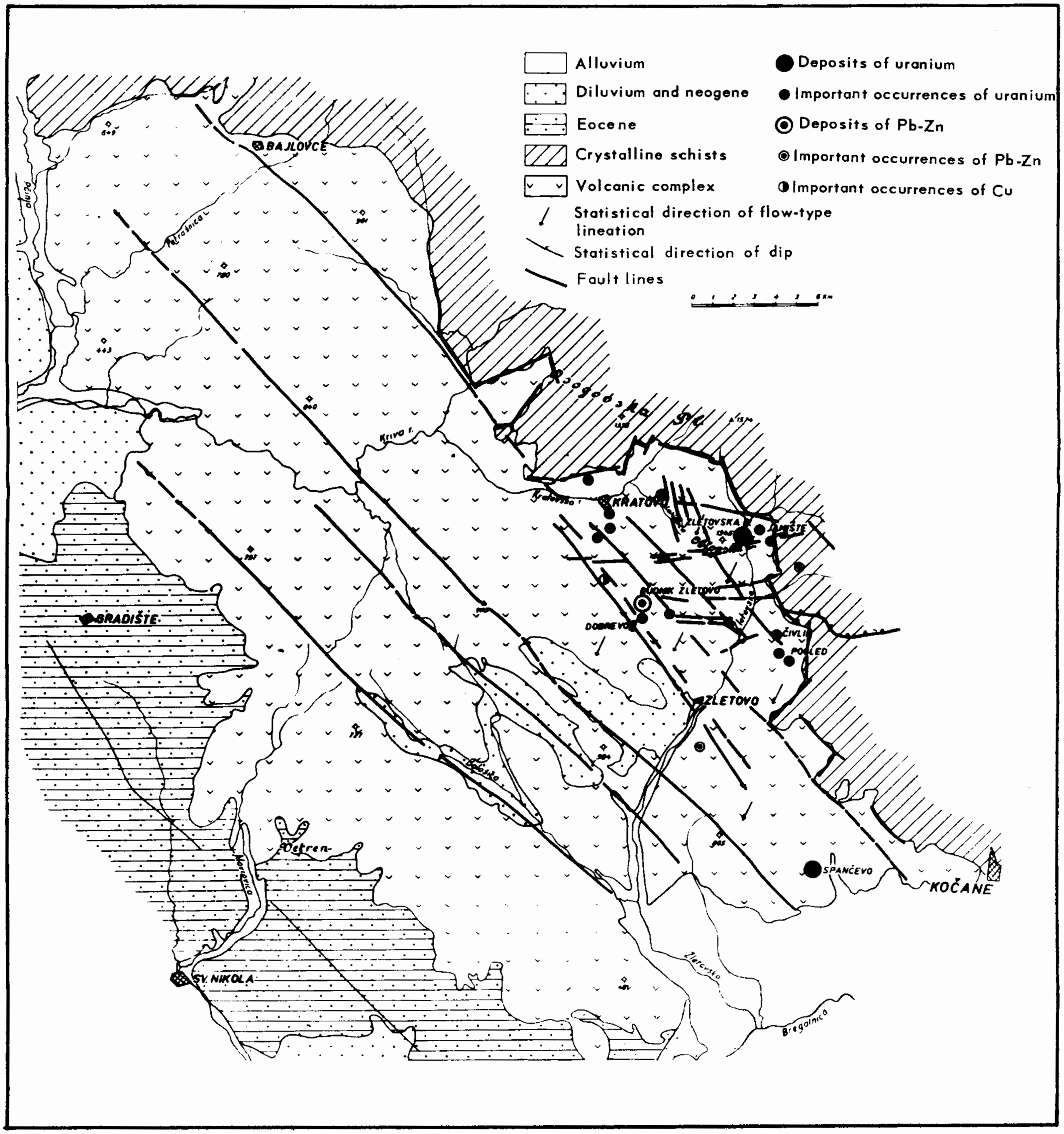

Figure 3. Schematic geologic map showing mineral deposits of Kratovo-Zletovo volcanic area

features of monzonites, i.e., calco-alkali syenites and some granodiorites, the andesites corresponding to the different, but mainly syenitic (monzonitic), types of magma.

The types of rock listed occur in a fairly definite order of succession, at least in the area explored, as shown on the map in Fig. 2.

The thickness of particular members of the sequence varies rather markedly from place to place, but the following values can be considered as average:

Tuffaceous breccias of dacitic origin — about 150 metres;

Ignimbrites of dacitic origin — about 300 metres;

Andesites and related tuffs and breccias, representing the deepest-lying members — at present unknown, but possibly about 200 metres.

Silicification and hydrothermal alteration have affected various members, depending on the location of the structures along which these actions took place; as a consequence, the altered zones could not be treated as definite levels or horizons superpositionally.

The flow-type features in the volcanic series dip generally S-SW. The contacts with the older crystalline complex are distinctly tectonic. The system of dislocations, mentioned above, which intersects the volcanic rocks, has had a different effect on different members of the lithologic series. The tectonization, which followed the faulting, is particularly well marked at the deeper, andesite-breccia level. At the higher levels, strongly tectonized zones are limited to areas close to the dislocation, or are even absent, which makes it very difficult to trace the structures on the surface. This feature also influenced the distribution of mineralization.

The fractures which intersect the volcanic complex can be grouped in two systems, the first striking N 15 E and the second N 80 E; the latter gives rise to a well pronounced zone of intensive tectonization and mineralization, the Zletovska Reka zone, about 250 metres wide (Figs. 2 and 3).

A number of mineral occurrences and deposits of lead, zinc, copper and uranium are located in this area. The majority are to be found in the tertiary extrusives, in the faults and tectonized zones, rarely in the rim zone of the crystalline schists.

The extrusive rocks in which the mineralizations occur have been highly propylitized over a large area by autohydration and have undergone considerable hydrothermal alteration along the mineralized fractures, in a number of tectonized zones and along the contacts with the ore bodies.

Three types of mineral occurrence and deposit were identified in the area namely, lead-zinc deposits and occurrences, occurrences of copper minerals and occurrences and deposits of uranium.

The most numerous, and economically the most important, are the lead and zinc occurrences. In the production of lead and zinc in Yugoslavia this area is second only to the Trepča mine. These occurrences can be classified genetically as of the hydrothermal vein type.

Copper occurrences are very extensive, and copper paragenesis is present in almost all lead and zinc mineralizations, but large concentrations are rare. Some concentrations of copper minerals appear in the western part of the volcanic area, where enargite-pyrite ore bodies, carrying traces of minerals from lead-zinc paragenesis, are located.

Uranium occurrences are met with over the whole area, but the largest number is grouped between Zletovo and Kratovo. They are very often located inside the lead-zinc veins, but also form separate deposits. The main mineral is pitchblende, although there are several occurrences with secondary uranium minerals. Few of the occurrences were explored in detail.

It may be concluded that the large number of mineral occurrences and deposits of important metals found in this area are to some extent interdependent; but their abundance varies greatly from deposit to deposit. Lead, zinc and copper are strongly interrelated, but the uranium appears not only in association with these metals but also on its own.

OCCURRENCES AND DEPOSITS OF URANIUM

A few dozen uranium occurrences were discovered, but most of them are of no economic value. The area aroused particular interest only after systematic aerial prospection in 1962 revealed the uranium deposits of Zletovska Reka and Spančevo.

The known uranium occurrences and deposits in the area can be grouped, by mineral composition and mode of occurrence, in two classes, namely occurrences and deposits of monometallic uranium and occurrences of uranium in lead-zinc veins.

Characteristic representatives of the first type are the deposits of Zletovska Reka, Spančevo and Latisnica; the second type is represented by the occurrences in the Zletovo lead-zinc mine.

Zletovska Reka

The Zletovska Reka uranium deposit is the most important discovered in the area so far. It is located at the eastern rim of the volcanic complex, in the vicinity of the contact with the crystalline schists of the internides.

The immediate vicinity of the deposit is composed of hornblende-biotite andesites, andesitic tuffaceous breccias and tuffs, ignimbrites of hornblende-biotite dacitic origin and hornblende-biotite dacites.

The local tectonics have been influenced by the general structural features of the area. The volcanic rocks close to the deposit were affected by the well-marked, purely disjunctive tectonics of the two systems earlier mentioned, the older one running NNW-SSE and the younger one ENE-WSW.

The predominant structural feature in the neighbourhood of the deposit is a tectonized zone about 250 metres wide running ENE-WSW, which has been traced over a length of 2 500 metres, and inside which a number of staggered secondary fractures have been located. This tectonized zone is characterized by intensive mechanical and hydrothermal alterations. Sizable displacements took place in certain directions within the zone, inducing intensive cataclysing, which permitted the circulation of the hydrothermal solutions and hence the subsequent alteration of the rocks. Hydrothermal activity is manifested by the products of kaolinization, silicification, chloritization, carbonatization, zeolitization and alunitization.

The uranium mineralization is located mainly inside the tectonized zone. A number of occurrences were discovered, but only one has been explored in detail. A direct connection was established between the mineralization and the structural and lithologic factors by which it was controlled. The data collected indicate that the more basic environment, the andesites and andesitic breccias, was more favourable to the formation of larger concentrations of uranium than were the more acid dacitic rocks. However, it is still not clear whether the chemical composition of the environment or depth played the decisive part in the formation of the deposit.

The uranium mineralization appears in two forms, dispersed through the cataclysed and kaolinized material of the tectonized zone and concentrated in veinlets, films and fillings.

The first type is characteristic of those parts of the mineralization that are found in the volcanic breccia, and the second of those found in the rather more compact andesite.

The main mineral is pitchblende. Among the secondary minerals, inside the oxidised zone of the deposit, autunite, torbernite, kasolite and uranophane were identified.

In addition to uranium minerals, sphalerite, pyrite, galena, marcasite, bravoite and tetrahedrite are present, although in very small quantities. Only the sphalerite intergrows with the pitchblende; the others have no direct contact with the pitchblende, so their paragenetic relationship is not yet clear. Even intergrowths of pitchblende and sphalerite are very rare; the pitchblende was deposited at the edges of the sphalerite grains. The gangue minerals are represented by siderite, baryte, chalcedony and fluorite, although they occur in insignificant quantities.

The explorations, which covered only a relatively small part of the mineralized area, showed that the uranium occurs in ore bodies of irregular shape. One of these ore bodies was explored in greater detail (Fig. 4). It is about 300 metres along the strike, about 100 metres along the dip and between 3 and 25 metres thick.

The uranium content of this ore body varies from a few hundredths to a few tenths of one per cent. According to the coefficient of variation ($V = 75\%$), this deposit could be classified as irregular, the maximum frequency occurring with samples containing slightly more than 0.1% U_3O_8.

Local disequilibria between uranium and radium are pronounced in both directions. Samples with less than 0.1% U_3O_8 have an equivalent radium to uranium ratio (eRa/U) of 100-130% whereas for those with more than 0.1% U_3O_8 it is 60-100%.

In that part of the deposit so far explored, the estimated ore reserves amount to about 400 000 tons,

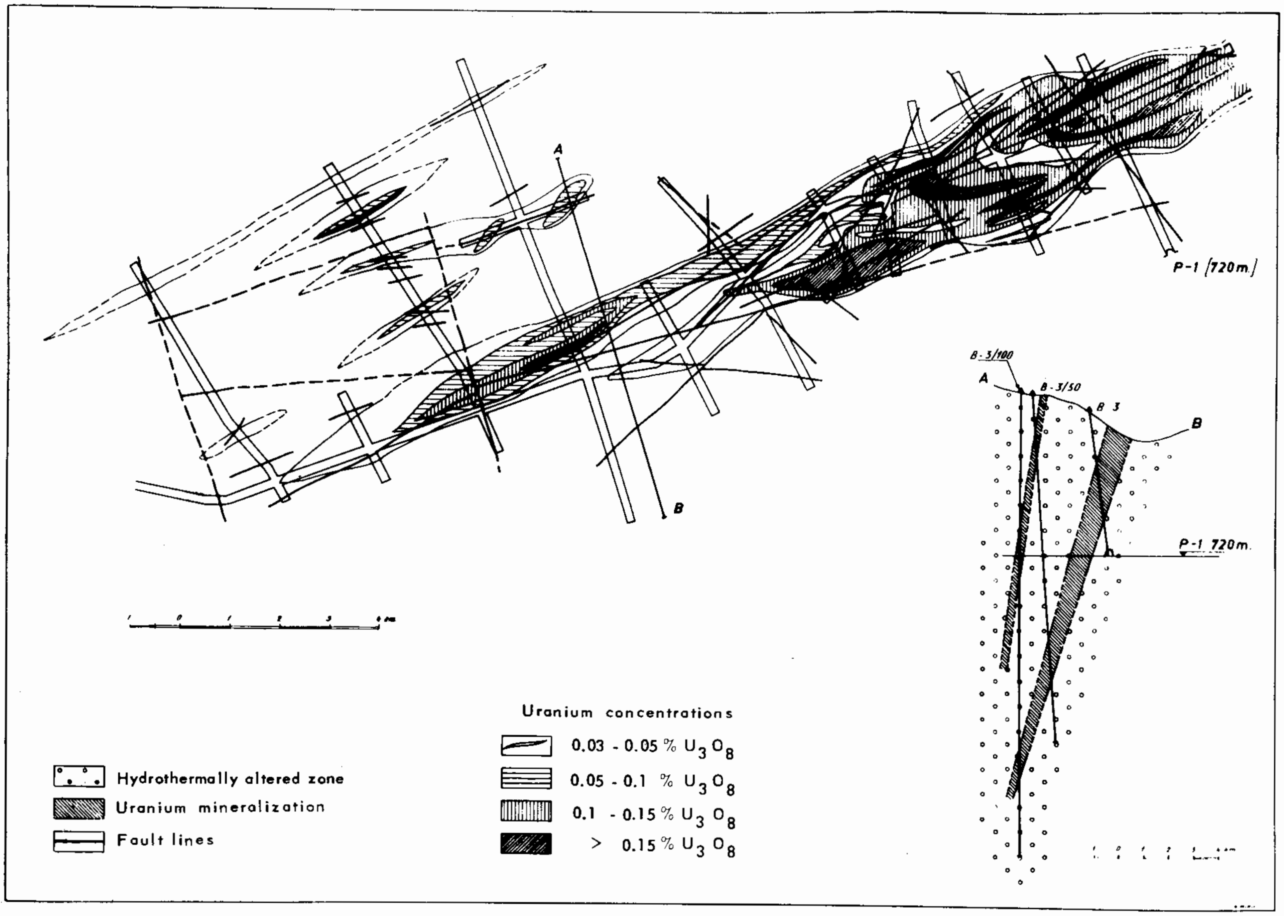

Figure 4. Zletovska Reka deposit. Ore body No. 1

with a mean grade of 0.15% U_3O_8. As only a limited part of the zone of mineralization has been explored, and as similar occurrences of uranium have been discovered in the immediate vicinity, it may confidently be expected that more ore bodies of the same kind will be found.

Spančevo

The Spančevo uranium deposit is situated close to the south-eastern rim of the volcanic complex, about 16 kilometres in a straight line from the Zletovska Reka ore bodies.

The surrounding area is composed mainly of pyroclastic rocks, that is of microbreccias and andesitic agglomerated tuffs, which made it difficult to observe the structure clearly. It could be identified only by the intensive alteration, involving opalization, kaolinization, carbonatization, chloritization and pyritization.

The rich concentrations of secondary uranium minerals are associated with opalized agglomerated tuffs. A mass of mineralized opalized tuff, running N-S, has been discovered over an area of 90 × 7-15 metres. The concentration of uranium in this zone is highly variable, running from a few hundredths of one per cent up to more than 1%. Among the uranium minerals, autunite, torbernite and uranophane have been identified. The uranium mineralization was accompanied by hematization.

So far the deposit has been explored only close to the surface; there is no conclusive information on the uranium mineralization in this area.

Latisnica

Monometallic uranium mineralization has been discovered in a tectonized zone in the ignimbritic rocks. The zone runs NE-SW and is about 16 metres thick. The rocks inside the mineralized zone were subjected to intensive hydrothermal alteration, resulting in intensive kaolinization and chloritization.

So far, exploration has been limited to the uppermost parts of the deposit; autunite and torbernite have been identified, but no accompanying minerals.

Zletovo

The most important uranium occurrences associated with lead-zinc mineralization are located in the lead-zinc mine at Zletovo. There, in some parts of the sulphide-ore veins, pitchblende occurs together with the minerals of normal lead-zinc paragenesis. In this typical hydrothermal Pb-Zn deposit, the paragenetic relationships indicate a number of phases of mineral formation: the high temperature-contact phase, followed by extraction of the lead-zinc minerals in the form of gel, and finally the deposition of the bulk of the lead-zinc ores in the form of mineral aggregates with sizable crystals.

After the bulk of the lead-zinc ores had been formed the fractures were reopened during a decompressive tectonic phase. The voids thus created inside the sulphide ore bodies served as the channels for the uranium-bearing solutions, which deposited the pitchblende, with insignificant quantities of sulphides, in the central zones of the ore bodies. The paragenetic history suggests that the uranium mineralization was deposited in a separate phase, independently of the process by which the lead-zinc ores in the Zletovo mine were formed.

CONCLUSION

The Kratovo-Zletovo volcanic area, like others in Yugoslavia, has only recently been prospected for uranium, since the opinion was firmly held in the past that the young Alpine volcanic rocks did not favour the deposition of this element.

The prospection for uranium in the tertiary volcanic rocks in north-eastern Macedonia gave promising results. The uranium deposits discovered are associated with post-volcanic hydrothermal activity and have been laid down in the younger structures during a separate phase, after lead-zinc deposits had already formed. The uranium mineralization represents the final phase of the mineralogenic activity in this area. According to the modes of occurrence described, two hypotheses are possible as to the origin of the uranium: it was either directly associated with the young magmatic source, or remobilized from the old crystalline basement.

If further exploration confirms the first hypothesis, it will be necessary to revise current opinions about the metallogenic characteristics of the Alpine metallogenic epoch, so far as uranium is concerned. This may prove to be of first importance, due to the substantial potentialities of the discovery of new uranium deposits in the young volcanic series of the Alpine orogen.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/415 Yougoslavie

Les gisements d'uranium dans les roches volcaniques tertiaires du nord-est de la Macédoine

par R. Pantić *et al.*

Dans la région volcanique de Kratovo-Zletovo (nord-est de la Macédoine), qui est bien connue pour ses riches gisements de plomb et de zinc, on a découvert récemment d'importants gisements d'uranium. Cette région se trouve dans la zone limitrophe de l'arc orogénique des Dinarides et des Internides, c'est-à-dire dans la partie axiale de la zone orogénique alpine dans cette partie de la péninsule balkanique.

Le cadre géologique est relativement simple et les principales formations sont des schistes cristallins du Paléozoïque et du Palézoïque inférieur, des roches volcaniques tertiaires et des sédiments tertiaires.

Les roches volcaniques couvrent une surface de plus de 1 500 km^2 et sont liées à une fracture de fond bien exprimée, située près de la zone limite. Vers le nord, cette fracture est marquée de la même façon par des complexes volcaniques similaires.

La composition structurale reflète un système de fractures formées pendant plusieurs phases de l'orogenèse alpine. Les directions principales de ces failles sont NNO-SSE (N-S) et ENE-OSO (E-O) avec des pendages très abrupts, presque verticaux. La première direction est dominante et elle représente la caractéristique tectonique fondamentale de cette partie de la zone orogénique alpine. L'étendue du réseau de base d'intersections de ces dislocations varie de quelques centaines de mètres à deux kilomètres, tandis que la largeur des zones tectoniques qui jalonnent les structures primaires s'élève jusqu'à 100 m et plus.

Les éruptions volcaniques à plusieurs phases ont formé différents types de roches : des andésites amphibolo-biotitiques et leurs tufs agglomérés, des ignimbrites d'origine dacitique et quartz-latitique, des tufs stratifiés d'origine dacitique, des andésites et quartz-latitites amphibolo-biotitiques ainsi que des andésites à labradorite-augite et leurs tufs. Les ignimbrites d'origine dacitique et quartz-latitique ont la plus grande extension.

Les venues de minéraux et minerais sont liées aux failles et aux zones tectoniques. La minéralisation uranifère se manifeste de deux manières : comme formation uranifère propre ou avec une minéralisation de plomb et de zinc.

Un représentant caractéristique du premier type de minéralisation est le gisement de Zletovska Reka, qui a été découvert vers le milieu de 1962. Ce gisement se trouve dans les roches volcaniques, à proximité de leur contact avec les schistes cristallins des Internides. La composition structurale locale est caractérisée par des zones intensivement altérées tectoniquement et par des actions hydrothermales, qui ont la direction est-ouest; la largeur de ces zones est de 20 à 100 m, avec une longueur de plus de 3 km. Ces zones déterminent la minéralisation uranifère.

L'une d'entre elles a été explorée jusqu'à présent sur 300 m dans la direction et sur 150 m dans le pendage. Les masses de minerai d'uranium sont seulement faiblement oxydées; dans les niveaux plus profonds, elles se composent presque exclusivement de pechblende.

Dans la partie explorée de la zone, les réserves de minerai s'élèvent à peu près à 400 000 t avec une teneur moyenne de 0,15 % U_3O_8.

La découverte de gisements d'uranium dans les structures et les formations rocheuses décrites a une importance fondamentale; elle ouvre de grandes perspectives pour la découverte de gisements d'uranium similaires dans les roches volcaniques d'origine plus récente de la zone orogénique alpine.

A/415 Югославия

Урановые месторождения в третичных вулканических горных породах северо-восточной части Македонии

Р. Пантич *et al.*

В вулканическом районе Кратово — Злетово (северо-восточная Македония), который хорошо известен богатыми залежами свинца и цинка, в последнее время были открыты также значительные месторождения урана. Этот район находится в пограничной области динарского орогенного пояса, то есть в осевой части альпийского горообразования этой части Балканского полуострова.

Геологическое строение района относительно простое: палеозойские и нижнепалеозойские древние кристаллические сланцы, третичные вулкинические горные породы и третичные осадочные отложения. Вулканические горные породы покрывают площадь более 1500 *км*^{2} и связаны с обширной и глубокой зоной сбросов, расположенной вблизи пограничного района. К северу эта зона также отмечена аналогичными вулканическими комплексами.

Эта структура образовалась под влиянием дизъюнктивной системы в ряде фаз альпийского горообразования. Зона сбросов простирается в основном по линии север — юг и восток — запад с очень крутым, почти вертикальным падением склонов. Первое направление является доминирующим и представляет собой основную архитектоническую характеристику этой части альпийского горообразования. Протяженность этой сети сбросов и смещений колеблется от нескольких сотен метров до 2 *км*, в то время как ширина тектонических зон вдоль основных структур составляет более 100 *м*.

Многократные вулканические извержения способствовали образованию различных типов пород: амфибол-биототовые андезиты и их агглютинированные туфы, игнимбриты дацитового и кварце-латитового происхождения, дацитовые слоистые туфы, амфибол-биотитовые андезиты и кварце-латиты, а также лабродорит-авгитовые андезиты и сопровождающие их туфы. Наибольшее распространение имеют игнимбриты дацитового кварце-латитового происхождения.

Залегание минералов и руд связано со сбросами и с тектоническими зонами. Минерализация урана происходит двумя путями: независимым процессом минерализации урана и совместно с минерализацией свинца и цинка.

Наиболее характерным для первого типа минерализации является месторождение «Злетовска река», открытое в 1962 году. Месторождение расположено в вулканических горных породах в непосредственном контакте с кристаллическими сланцами. Локальные структуры характеризуются зонами сбросов, интенсивно тектонизированных и измененных в результате гидротермальных воздействий, простирающихся с востока на запад. Ширина этих зон от 20 до 100 *м*, длина более 3 *км*. В них и происходит минерализация урана.

Одна из этих зон разработана до настоящего времени на 300 *м* по простиранию и на 150 *м* по падению. Урановые рудные тела только незначительно окислены, в то время как в более глубоких слоях находится почти исключительно уранинит.

В разработанной части зоны минерализации запасы руды достигают почти 400 000 *т* со средним содержанием U_3O_8 15%.

Обнаружение урана в таких структурах и формациях имеет громадное значение, так как способствует открытию аналогичных урановых отложений в более молодых вулканических горных породах альпийского орогенеза.

A/415 Yugoslavia

Depósitos de uranio en rocas volcánicas terciarias del nordeste de Macedonia

por R. Pantić *et al.*

En la zona volcánica de Kratovo y Zletovo (NE de Macedonia), ya conocida por sus ricos depósitos de plomo-zinc, han sido descubiertos recientemente importantes depósitos de uranio. Esta región está ubicada en la zona limítrofe de la faja orogénica dinárica, o sea en la parte axial del orógeno alpino de esta zona de la Península Balcánica.

La geología general es relativamente simple y las principales formaciones son pizarras cristalinas paleozoicas inferiores, volcanitas terciarias y sedimentos terciarios.

Las volcanitas cubren un área de más de 1 500 km^2 y están en conexión con una grande y profunda zona de falla, situada cerca de la zona fronteriza. Esta zona exhibe también en el norte complejos volcánicos similares.

La estructura está formada bajo la influencia de un sistema disyuntivo, creado en las sucesivas fases de la orogénesis alpina. La zona de fallas se extiende fundamentalmente de NNO a SSE (N-S) y ENE a OSO (E-O), con gran buzamiento, casi verticalmente. El primer sistema es dominante y representa el elemento estructural básico de esta parte del orógeno alpino. La red básica de las intersecciones de estas dislocaciones va desde unos pocos cientos de metros a dos kilómetros y el ancho de la zona tectonizada a lo largo de las principales estructuras alcanza y sobrepasa los 100 m.

Las múltiples fases de erupciones volcánicas han producido varias clases de rocas : andesitas anfibolíticas, biotíticas y aglomerados de tobas volcánicas, las ignibritas de origen dacítico y cuarzo-latítico, tobas estratificadas dacíticas, andesitas anfibolíticas-biotíticas y cuarzos latíticos y andesitas de augita y labradorita y tobas volcánicas asociadas. La mayor parte de la zona está cubierta por ignibritas de origen dacítico y cuarzo-latítico.

El mineral y la mena aparecen en relación con las fallas y zonas tectonizadas. Las mineralizaciones de uranio se pueden dividir en dos clases : como mineralizaciones independientes y en conexión con mineralizaciones de Pb-Zn.

El representante característico del primer grupo es el depósito de Zletovska Reka, descubierto a mediados del año 1962. El depósito está localizado en volcanitas, cerca de su contacto con las pizarras cristalinas de los internidos. Las estructuras locales están representadas por zonas modificadas por una intensiva tectónica e hidrotermalidad, extendiéndose de E-O, de 20 a 100 m de ancho y más de 3 km de largo. Estas zonas presentan las características más determinativas del mineral.

Una de estas zonas ha sido explorada cerca de 300 m en dirección y 150 m según el buzamiento. Las masas mineralizadas de uranio están ligeramente oxidadas y en los niveles más inferiores están compuestas exclusivamente de pechblenda.

Las reservas de la parte explorada de la zona alcanzan cerca de 400 000 t de mineral, con una ley media en uranio del 0,15 % en U_3O_8.

El descubrimiento de uranio en tales estructuras y formaciones es de capital importancia, debido al gran potencial de posibilidades que se abren para poder descubrir depósitos similares en el más joven volcanismo del orógeno alpino.

P/483 Brazil

Nuclear fuel supply: programme and results in Brazil

By E. Távora *

The Nuclear Energy National Commission of Brazil was founded in 1956. Since then the Department of Mineral Exploration has been equipping its field parties and laboratories and carrying out a programme of uranium prospecting, but intensive effort in this direction did not develop until after 1962.

Owing to the vast dimensions of the Brazilian territory, special financial engagements for the technical programmes had to be carefully planned, in order to repay the investment, avoid overlap of methods and lower production cost without affecting the technical standard of the operations.

In short, the Department's main objective is to make an inventory of the Brazilian resources of nuclear fuel in the shortest time possible.

PROGRAMME OF THE DEPARTMENT OF MINERAL EXPLORATION

The size of Brazil (over 8 000 000 km²) and the time limitation for the work imposed the logical solution, at least temporarily, of investigating the existence of uranium deposits only in the parts of the territory close to the supplying centres and easily accessible.

The Department of Mineral Exploration can at present count on 40 Brazilian geologists, 4 French experts (geologists of the Commissariat à l'énergie atomique, working under the terms of the Brazilian-French bilateral co-operation agreement), 30 prospectors specially trained by the Brazilian Nuclear Energy National Commission and 14 auxiliary field workers. Furthermore, the Department is equipped with 48 vehicles of assorted types suitable for field work and 93 radiation detection instruments. It is obvious that these resources would be insufficient if, *ab initio*, the search for uranium extended over the whole territory of Brazil. Therefore the Commission restricted its activities initially to the regions located eastward from a line passing through Cuiabá (State of Mato Grosso) and Belém (State of Pará). Although this ruled out, for the time being, about 50% of the whole national territory, about 4 000 000 km², still remain to be covered, according to the stratigraphic distribution shown in Table 1.

Table 1. Stratigraphic distribution

	%	km²
Pleistocene	1.35	54 000
Tertiary	0.15	6 000
Cretaceous	14.14	565 000
Jurassic	4.42	176 800
Basalts	10.72	428 800
Triassic	5.54	221 600
Permian	2.00	80 000
Upper Carboniferous	8.58	343 200
Lower Carboniferous	0.85	14 000
Upper Devonian	0.67	26 800
Medium Devonian	0.92	36 800
Lower Devonian	4.22	168 800
Silurian	5.95	238 000
Cambro-Ordovician	1.10	44 000
Precambrian	38.12	1 524 800
Total		4 000 000

Since the Commission has decided to seek only for the uranium deposits that are most interesting economically, in other words, those of easy exploitation and low-cost ore dressing and metallurgy, it is evident that there will be no work on thorium minerals, neither will pegmatites nor Precambrian formations be studied. Consequently, the chief effort will be directed towards prospecting the stratiform sedimentary deposits; this is fully justified considering that the great majority of the world deposits are in detritic rocks, which quite often are of continental origin. There are some exceptions, of course, among which are the alkaline rocks (Poços de Caldas, etc.).

SEQUENCES AND PROSPECTING METHODS

Economically, it is essential that the normal sequence of prospection operations is followed in order to avoid, overlap of methods. The normal sequence which prevails at the Department is: bibliography, reconnaissance; car-borne, air-borne or geochemical prospection; detailed work and evaluation (Table 2). The general scheme which follows summarizes the chronological and technical varieties of application; some additional comments are also given:

Bibliography. A critical and accurate bibliography must necessarily constitute the first phase of the operations. A petrographic and radiometric analysis of the available collections is also included. An

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Table 2. Prospecting sequence

GENERAL BIBLIOGRAPHY

Critical study and orientated scrutiny of geological literature. Investigation of the facies and continental sequences presenting multiple cycles under tectonic control.

Constitution of lithologic sequences with notations of the sedimentation environments. Paleogeographical and paleoclimatological reconstitutions. Isopaques. Investigations of the radioactivities of samples. Final decision and justification.

GENERAL RECONNAISSANCE

Constitution of lithological sections with calibrated radiometric determinations. Details on sedimentology and environments. Notes on tectonics. Sampling and analyses. Determination of the favourable layers. Decision on the orientation to follow: abandon, or prospect at regular intervals and justifications.

CAR-BORNE PROSPECTION

If a satisfactory road network exists or if the rough topography rules out air-borne prospection, car-borne prospection can be done quickly and at low operating cost. No automatic recording. The anomalies are lithologically classified. Accurate sampling. Efficiency of 1 500 km/month-vehicle.

STRATEGIC GEOCHEMISTRY

Waters, alluvions and radiometric studies at wide intervals (500 points per square degree). Efficiency, 10 points/day-team.

AIR-BORNE PROSPECTION

Altitude, 75 m; spacing between flight lines, from 1 000 to 3 000 m.

Compilation specific of the first residual. Photogeological and statistical analyses. Efficiency 10 000 km/month plane.

DETAILED AIR-BORNE PROSPECTION

Re-analysis of each anomaly, close flights at different altitudes. New selection. Second residual of the anomalies to check in the field.

EVALUATION

Preliminary radiometric analyses, at about 20 × 20 m metres with the first petrographic and mineralogical samplings. Subsequently, detailed geological and radiometric analyses at close intervals and tactic geochemistry. Light works; decision whether or not to proceed.

Evaluation *sensu strictu:* first stage of trenching, short drillings, wagon-drill. Systematic sampling.

Reconnaissance of the deeper levels. Geometrical definition of the mineralizations. First evaluations.

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analytical and critical bibliographical study carried out under these conditions is in fact a form of prospecting and consequently requires effort of high calibre; it can lead to a negative recommendation which may save a lot of time or, conversely, to the discovery of some discrete but favourable indications that may lead to fruitful prospecting.

Reconnaissance work. This always is a delicate task to carry out because from it a decision is made fairly quickly concerning an extensive region. There is always the danger either of recommending further operations which eventually prove to be unjustified or, on the contrary, ruling out a region that has possibilities. At this stage of prospecting, where a full knowledge of all conditions related to the uranium deposits is required, every decision must be made very carefully.

Car-borne prospection. Since the cost per kilometer of this method of prospecting is low, it is widely used in regions where the road network is sufficiently dense; however, it is a slow method and its results are heterogeneous, which makes any statistical analysis of the results critical.

Geo-chemical reconnaissance. Here waters and alluvions are sampled at wide intervals; it is rapid, economical and efficient if the purpose is to study wide zones or mineralized provinces. It is obvious that if 20 km is the spacing set between two neighbouring sampling points, it is easy for an isolated deposit to remain undetected. A combination of radiometric measurements and geological observations leads to a true general reconnaissance. Such operations provide a good chance of detecting mineralized regions, especially in sedimentary formations.

Air-borne prospection. Air-borne prospecting methods have been a controversial subject. In the Department of Mineral Exploration the following principles are observed:

(*a*) Except for some rare cases, air-borne prospecting is used only for sedimentary formations;

(*b*) In order to heighten the contrasts, the flights are carried out at low altitude (75 m);

(*c*) The compilation achieved is specific and has the advantage of being efficient. The representation of the full field by isorade curves is not attempted; on the contrary, attempts are made to determine the residual field which results from the altimetric corrections and from the elimination of the most obvious local background variations;

(*d*) All residual anomalies are studied further with a light plane (or, better, a helicopter). The corresponding flights are made at different altitudes and at close spacing so that the quality and geometry of the anomaly can be determined. Despite these precautions, the anomaly obtained as a second residual is more significant of the surface radioactivity of the soil than the value of the radioactivity. Analysis of the accumulated data from measurements cannot be taken far because of the limitation imposed by the resolution power of the scintillometers.

Evaluation operations. The discussion of this difficult type of work is not possibile without going into greater detail than is consistent with the character and purpose of this paper. It is evident that with each successive stage of prospecting the financial investment increases and, therefore, a decision taken in a particular case involves costs which progressively increase as the exploitation stage is approached. During development of the final stages of the evaluation great care must be exercised; at this point, one should not hesitate to superimpose and make use of available competitive methods.

OBSERVATIONS ON SOME OBTAINED RESULTS

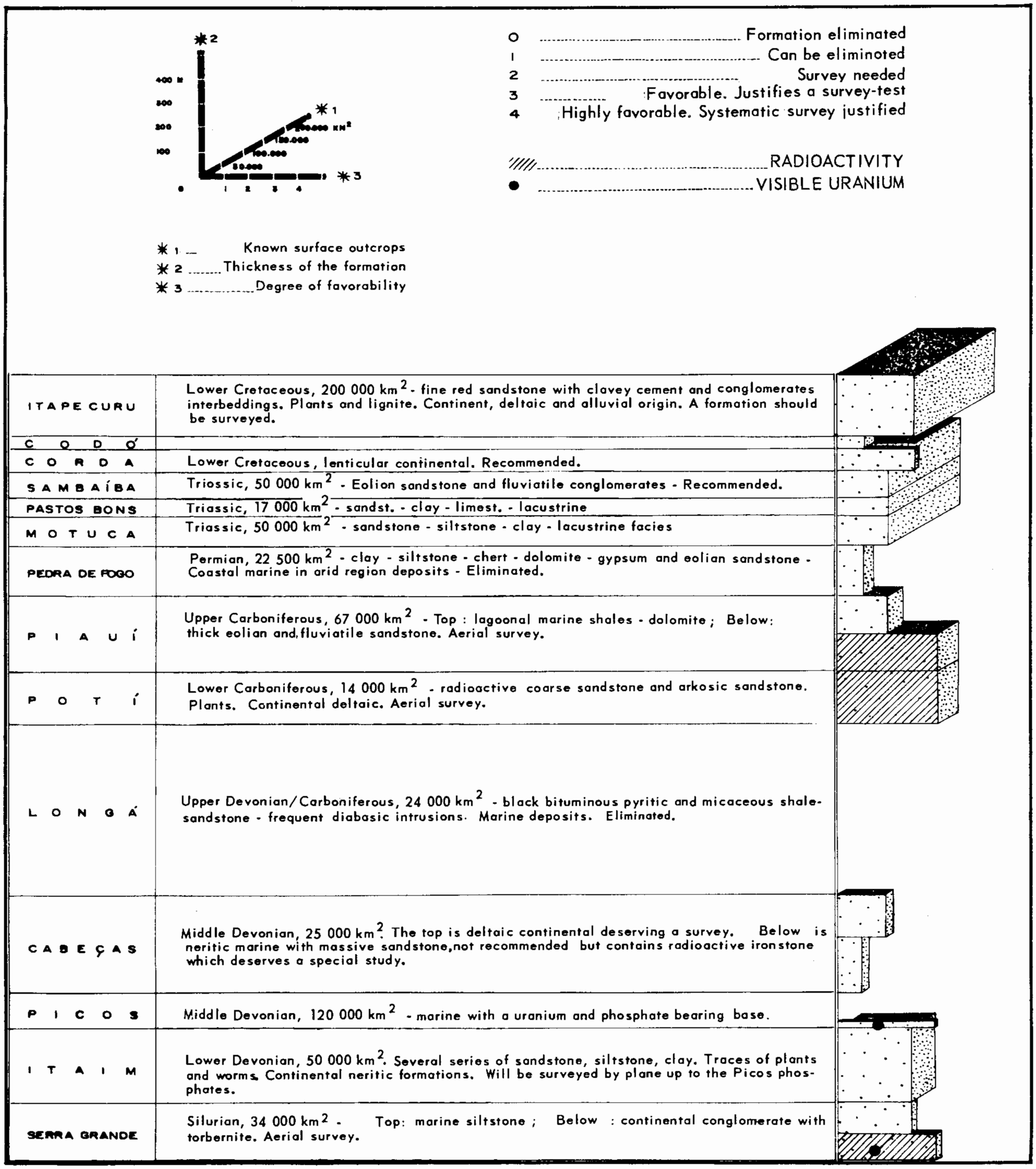
The schematic description of the great structural elements of Brazil are useful in the presentation and discussion of certain of the results obtained. It is incorrect to compare Brazil with the shield of West Africa. Actually, there are, in Brazil, large sedimentary basins. The following were the subject of important studies by the Commission (Fig. 1).

In the south of Brazil there is the *Paraná Basin*, which comprises parts of neighbouring countries. It deals with one of the largest basins of South America. In such a basin everything is gigantic, the glacial formations and the Carboniferous interglacials, the Botucatu desertic eolian sandstones and the huge Jurassic lava flows.

An important arch separates the Paraná Basin from the Minas Basin, which is important to the Nuclear Energy National Commission of Brazil because it embodies the nephelinic rocks of Salitre Serra Negra, Araxá, Tapira and Poços de Caldas.

Minas Gerais Basin. This contains series of relatively small thickness. It may be a platform rather than a basin formed by subsidence, the thick layers of the Bambui limestone excluded. The study of such a platform has just started. As a rule it is abandoned when

Figure 1. Map of Brazil showing position of the most important sedimentary basins and their structural limits



0 .... Formation eliminated
1 .... Can be eliminated
2 .... Survey needed
3 .... Favorable. Justifies a survey-test
4 .... Highly favorable. Systematic survey justified

▨ .... RADIOACTIVITY
● .... VISIBLE URANIUM

✱ 1 — Known surface outcrops
✱ 2 .... Thickness of the formation
✱ 3 .... Degree of favorability

ITAPECURU	Lower Cretaceous, 200 000 km^2 - fine red sandstone with clavey cement and conglomerates interbeddings. Plants and lignite. Continent, deltaic and alluvial origin. A formation should be surveyed.
CODÓ	
CORDA	Lower Cretaceous, lenticular continental. Recommended.
SAMBAÍBA	Triossic, 50 000 km^2 - Eolian sandstone and fluviatile conglomerates - Recommended.
PASTOS BONS	Triassic, 17 000 km^2 - sandst. - clay - limest. - lacustrine
MOTUCA	Triassic, 50 000 km^2 - sandstone - siltstone - clay - lacustrine facies
PEDRA DE FOGO	Permian, 22 500 km^2 - clay - siltstone - chert - dolomite - gypsum and eolian sandstone - Coastal marine in arid region deposits - Eliminated.
PIAUÍ	Upper Carboniferous, 67 000 km^2 - Top : lagoonal marine shales - dolomite ; Below: thick eolian and fluviatile sandstone. Aerial survey.
POTÍ	Lower Carboniferous, 14 000 km^2 - radioactive coarse sandstone and arkosic sandstone. Plants. Continental deltaic. Aerial survey.
LONGÁ	Upper Devonian/Carboniferous, 24 000 km^2 - black bituminous pyritic and micaceous shale-sandstone - frequent diabasic intrusions. Marine deposits. Eliminated.
CABEÇAS	Middle Devonian, 25 000 km^2. The top is deltaic continental deserving a survey. Below is neritic marine with massive sandstone, not recommended but contains radioactive ironstone which deserves a special study.
PICOS	Middle Devonian, 120 000 km^2 - marine with a uranium and phosphate bearing base.
ITAIM	Lower Devonian, 50 000 km^2. Several series of sandstone, siltstone, clay. Traces of plants and worms. Continental neritic formations. Will be surveyed by plane up to the Picos phosphates.
SERRA GRANDE	Silurian, 34 000 km^2 - Top: marine siltstone ; Below : continental conglomerate with torbernite. Aerial survey.

Figure 2. Maranhão Basin

it contains good mineral zoneographies. The auriferous mineralizations of Jacobina are located at the northeastern boundary of this platform.

Atlantic coast. In Brazil, there are four basins—Espírito Santo, Recôncavo, Tucano, Sergipe-Alagôas and Rio Grande do Norte—which can properly be compared with the African coastal basins which are also open to the Atlantic. In one of these basins (Recôncavo-Tucano and its northward extension), numerous indications of the presence of uranium were recorded.

An important arch marks the boundary between the basins of Minas and Maranhão. In the northern direction, this arch also separates the subsidence sedimentations. Beyond that is the particular domain of the Brazilian northeastern shield, where the pellicular sedimentation is restricted to the Cretaceous and Tertiary periods.

To the northwest is first the Maranhão basin and then the three Amazonian basins, which as already said are excluded temporarily from the prospecting programme.

Maranhão Basin. An excellent documentation prepared by the Petrobras SA (the Brazilian oil concern) for the region was a great help to the Nuclear Energy National Commission of Brazil which, otherwise, would have had to handle the whole of this large basin (650 000 km^2). A preliminary reconnaissance by two field parties obtained very interesting results (Fig. 2). The extent of each formation is included in Fig. 2; this represents the degree of interest that a particular formation may arouse in the preliminary stages of prospection; it is obvious that these preliminary indications will become clearer in the future.

Serra Grande, Potí and *Piauí.* These three formations were selected and will be prospected by air-borne scintillometry at 1 500 and 2 000 m intervals during the second half of 1964. The prospects of this planned campaign of 30 000 km are very promising. Extensive reconnaissance work on the formations Cabeças, Sambaíba and Itapecuru will follow in 1965.

Northeastern basins. It was seen elsewhere that two types of sedimentation are recognized. In the northern part of the arch, the stability of the shield is responsible for the small amount of sedimentation. The small basins of Rio Grande do Norte, Rio de Peixe, Iguatu, Araripe and Custodia are evidence of an old Cretaceous deposit, which was relatively thin and has almost completely been destroyed. Some preserved parts form raised *plateaux* (Chapadas) or sunk blocks (Rio do Peixe). No significant result has so far been found in these basins where the reconnaissance operations are being carried out.

South of the arch there is a conspicuous subsidence which was preserved through the geological periods and sometimes even from the Devonian and which provides thick detritic series essentially of continental origin. Prospection on foot and more recently by aerial survey were sucessful, specially on the Sergi and Moxotó formations which belong to the Tucano and Jatobá (Buique-Petrolândia) basins, respectively. Current work is confirming the existence of an uraniferous and vanadium-bearing province in the Tucano basin and a simple uraniferous one based on the presence of phosphate minerals in the north (Jatobá). In both cases, a detailed and intensive prospecting study is in progress consisting of trenching and drilling operations, and from which positive results are expected.

Jacobina region. This region became famous because it contains abundant auriferous mineralization in the pyrite bearing conglomerates of the stratigraphic group of Serra do Corrego. All the work based on the individual activity which was known to extend over 40 km in the north-south direction came to a stop when the maximum capacity of the non-industrial production was attained. At the present time, the only active mine is that of Canavieiras whose modest tonnage of treated ore (about 50 t/d) does not reflect at all the potential production of the region. The uranium is there closely associated with gold, and so far no significant radioactivity has been detected outside that of the auriferous zones. The uranium grade seems to vary around 100 g/t; this value doubtless can be compared with those recorded for the Witwatersrand deposits. The systematic sampling of such a vast region is a hard task which is complicated by an additional difficulty in that a generalized leaching of the superficial zones occurs because of the strong acidity of the water. Again, reconnaissance by drilling is the way suggested to solve the problem. Present knowledge of the distribution of uranium in the Jacobina range leads to the belief that evaluation of the uranium content can be achieved only by the development of an important mining district based on gold exploitation as the main product.

Poços de Caldas-Araxá arch. Close to the boundaries of the Minas and Paraná basins, several chimneys of laccoliths of alkaline rocks are found, namely, those of Salitre, Serra Negra, Araxá Tapira, and Poços de Caldas. Several alkaline thermal springs are located along this axis. Only the case of Poços de Caldas will be considered in this text.

The Poços de Caldas chimney is elliptical in form with a surface area of about 800 km^2. In contrast with other chimneys the nephelinic rocks of Poços de Caldas show good outcrops. Such rocks locally are syenites (foyaites), microsyenites (tinguaites), phonolites and associated tuffs. In the central part of the chimney there is a dense net of thin veins (5 to 25 cm) of the so-called "caldasite", which occurs in interesting eluvial and alluvial concentrations.

Caldasite is not a mineral; it is a mixture of variable proportions of zirconium silicate (zircon) and zirconium oxide (baddeleyite) and other minerals, the first of which seems to bear uranium in its own crystal structure as an accessory constituent. Since zircon is a refractory mineral, the uranium located in its structure (in the tetravalent state), where it replaces zirconium, cannot be extracted easily. A different situation, however, prevails when the uranium is in the highest oxidation state (hexavalent uranium). Then it is an essential constituent of typical uranium minerals such as phosphates which in their turn are associated, as minute inclusions (not structural), with the minerals which form caldasite. The percentage recovery of uranium in the treatment of minerals of the latter type is as high as 90%. Unfortunately, however, the available quantity of minerals which bear uranium in such

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BAURÚ	Cretaceous 305 000 km^2. Pink clayey sandstone. Coarse sandstone and limestone at the basis. Reptiles. Lacustrine facies in hot and wet climate. Many occurrences of radioactive reptile bones.
BASALT	Big lava flows of basalt. Many associated diabase intrusions. Deep lateritic alterations : famous coffee soils. Completely eliminated. Jurassic (rhetian), 410 000 km^2.
BOTUCATU	Jurassic, 46 000 km^2. Eolian crossbedded sandstone. Eliminated.
MORRO PELADO	Upper Permian, 10 000 km^2. Red sandstone and siltstone. Continental.
SERRINHA	Upper Permian, 10 000 km^2. Siltstone and sandstone. Lacustrine.
TERESINA	Lower Permian 25 000 km2. Siltstone, limestone, chert, probably lacustrine. It is the less detrital Permian formation.
SERRA ALTA	Lower Permian, 8 000 km^2. Siltstone and limestone. Lacustrine.
IRATI	Lower Permian, 4 000 km^2. Bituminous shales, radioactive sandstone.
PALERMO	Upper Carboniferous, 5 000 km^2. Siltstone, clay, chert. Lacustrine.
RIO BONITO	Upper Carboniferous. Argillaceous sandstone, continental, coal in the South.
ITARARÉ	Upper Carboniferous, 276 000 km^2. Highly complex glacial and fluvio-glacial series. 5 glacial transgressions, with tillites in the Paraná State. The number and the thickness decrease southwards (Santa Catarina) and north-eastwards (Mato Grosso). Between tillites, intra-glacial siltstone and sandstone. A few marine incursions prove the low altitude of the continent. Favorable elements : coarse sandstones, high isopaques, variable gradient. Unfavorable elements : cold climate, immatured sediments.
PONTA GROSSA	Lower Devonian, 40 000 km^2. Black fossiliferous shales. Deep marine. Eliminated.
FURNAS	Lower Devonian, 32 000 km^2 Neritic sandstone. Eliminated.

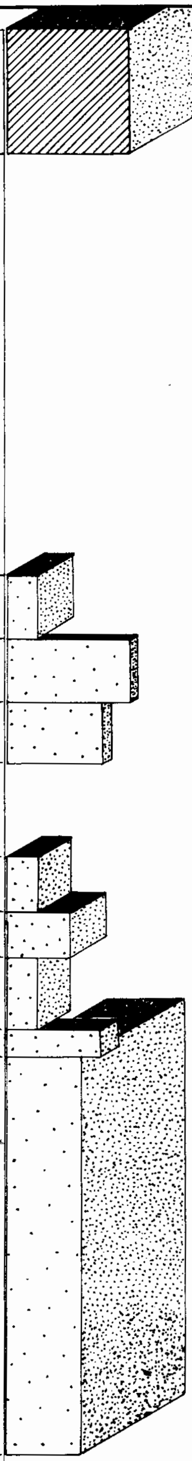

Figure 3. Paraná Basin

favourable form is extremely low as compared with the amount present in the structure of zircon. Consequently, it is quite evident from the industrial viewpoint that references to uranium grades in Poços de Caldas are meaningless unless the type is also given.

A stock of about 22 000 t of zirconium ore is on site at the partially constructed processing plant. This ore contains 62.5% ZrO_2, 21% SiO_2 and 0.37% U_3O_8. The percentage recovery of uranium, however, does not exceed 30%, which in reality means that the actual grade is 0.1%. In short, the whole of this stock contains uranium which is mostly included in the zircon structure for which treatment is costly and of low efficiency. It is therefore quite clear that unless adequate new sources are discovered locally an acceptable solution will come only from the known occurrences. Even by assuming that the so-called caldasite might be used for uranium production, which is very unlikely, another problem would have to be faced, namely, that there are no reliable data on the available tonnage of caldasite nor is the variation of its quality in depth known. In view of these facts and since the Commission wishes to produce uranium at the lowest cost possible, it becomes evident that the decision to stop construction of the processing plant was wise and fully justified. The chief purpose of the geologists of the Commission who work in Poços de Caldas is to find out whether uranium is also present in appreciable quantities, in a favourable form different from that so far considered.

Paraná Basin. This is still larger than that of Maranhão (see Fig. 3). Its Brazilian part, alone, has an area of 1 170 000 km² or 760 000 km² if the 410 000 km² represented by the basaltic lava is eliminated. Some field parties were sent to the basin by the Commission during the last two years: four reconnaissance parties, two car-borne prospecting groups and one air-borne prospecting group (25 000 km). It is planned that two other air-borne prospecting teams should operate in the basin in 1964. So far, results have been negative except for the Bauru formation. It is interesting to analyse the possible reasons of this failure. It may be the fault of certain paleogeographic and paleoclimatic peculiarities of the sedimentary formations. In fact, since interest converges on the sediments deposited in a typically continental environment, it is convenient to take into consideration the processes experienced by the materials before their deposition. The prehistory or pedogenesis of a sediment, the climatic and geographic ambiance of this history have determined the role played by the metallic elements of the deposit. The rough sediments, of incipient maturity, deposited in a cold climate (as in the glacial Itararé formations), have probably received a metallic heritage that is non-transferable. The tropical sediments, on the other hand (as in the Bauru formation), come from much evolved soils, which are sometimes lateritic, where the uranium can be free. Then the metal is free to migrate internally and thus give rise eventually to the ore concentrations that we are seeking. It would, however, be premature to base the programme of uranium prospection upon the hypotheses given above. However, it is interesting that noteworthy levels of radioactivity were detected only in the Bauru formation.

CONCLUSIONS

The Nuclear Energy National Commission concentrates its efforts on finding uranium in the shortest time possible and at the lowest possible cost. In order to achieve this goal all the modern techniques used by France in Africa, in places where the climate is comparable with that of Brazil, have been applied in this country. Without claiming any innovations the Commission nevertheless conscientiously uses all available methods. The Department of Mineral Exploration of the Commission would consider an essential part of its mission to be accomplished if within two or three years it could discover some deposits, however modest, but sufficient to meet its short-term needs, apart from accumulating reliable data on Brazil's ore reserves so that the future can be faced with confidence.

ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/483 Brésil

Approvisionnement en combustibles nucléaires — programme et réalisations au Brésil

par E. Távora

La Commission nationale de l'énergie nucléaire du Brésil, créée en 1956, exécute depuis cette date un programme d'équipement de ses groupes de prospection et laboratoires et de recherches minières générales et détaillées proportionné à ses moyens et ses besoins.

La Commission espère mener à bien avant la fin de 1966 un inventaire de toutes les ressources en combustibles nucléaires facilement accessibles sur le territoire national.

Les bases sur lesquelles reposent les programmes et les réalisations sont :

a) Le besoin de maintenir les frais et les prix du

minerai dans les limites résultant des normes internationales représentatives;

b) La remise à plus tard des travaux de prospection dans les territoires éloignés des principaux centres de production et de consommation;

c) La décision de déterminer la prospection dans les territoires choisis en optant pour :

- i) La recherche des faciès des roches continentales détritiques anciennes ou récentes;
- ii) La prospection des roches des cheminées alcalines;

d) De cette option découle qu'aucune prospection n'est prévue dans les terrains suivants :

- i) Terrains métamorphiques formant pourtant l'essentiel du bouclier brésilien;
- ii) Terrains granitiques, car les granites brésiliens sont pauvres en manifestations hydrothermales;
- iii) Terrains pegmatitiques, desquels l'extraction économique de minéraux contenant de l'uranium, même comme sous-produits, est impossible ou, du moins, très improbable;
- iv) Terrains contenant des minerais de thorium, car la prospection détaillée des sites connus pourrait se faire rapidement, si besoin en était.

On donne ensuite des exemples d'application rigoureuse d'une séquence type de prospection, de la bibliographie critique à la prospection finale détaillée, en utilisant toutes les techniques possibles, telles que la géochimie, la géophysique et la scintillométrie aérienne. Certaines modalités originales d'application de ces méthodes sont énumérées et les résultats obtenus sont discutés pour les régions les plus importantes examinées jusqu'ici.

On s'est proposé d'effectuer cette estimation dans le plus court délai et au meilleur prix. La Commission nationale de l'énergie nucléaire du Brésil aura accompli une partie essentielle de sa tâche lorsqu'elle disposera d'un inventaire approximatif de ses ressources en minerais nucléaires à long terme et si elle peut de plus découvrir au cours des deux ou trois prochaines années quelques gisements d'uranium de dimensions raisonnables permettant au Brésil de pourvoir à ses besoins pendant la prochaine décennie.

A/483 Бразилия

Программа обеспечения ядерного топлива в Бразилии и ее результаты

Э. Тавора

Со времени основания в 1956 году Бразильская национальная комиссия по атомной энергии, учитывая свои возможности и нужды, непрерывно осуществляла программу оборудования своих полевых партий и лабораторий и проведения общей и детальной разведки минералов.

До конца 1966 года Национальная комиссия по атомной энергии рассчитывает закончить оценку всех легкодоступных залежей радиоактивных руд на территории страны.

В основе упомянутой программы и ее выполнения лежит следующее:

a) Необходимость поддерживать стоимость и цены в пределах, установленных международными стандартами.

b) Временный отказ производить поиски и разведку в районах, слишком удаленных от основных центров производства и потребления.

c) Указание производить разведку в определенных районах основывается на следующей альтернативе:

- i) Изучение старых и более поздних континентальных видов обломочных пород;
- ii) Поиски пород щелочных рудных тел.

d) Как следствие вышеизложенного исключаются временно из поисковых работ следующие породы и формации:

- i) Метаморфические формации, составляющие существенную часть Бразильского щита;
- ii) Гранитные формации, поскольку гидротермальные проявления в бразильских гранитах редки;
- iii) Пегматитовые формации, поскольку экономичное извлечение из них радиоактивных минералов даже в качестве побочных продуктов представляется безнадежным или по крайней мере очень маловероятным;
- iv) Как показала детальная разведка известных месторождений торийсодержащих минералов, их можно быстро разрабатывать, если в этом возникает необходимость.

Приведены примеры строгого применения последовательного типа разведки, который начинается от критического анализа литературы и завершается окончательной детальной разведкой с использованием всех методов, включая геохимию, геофизику и сцинтиллометрию воздуха. Описаны также некоторые обычные варианты применения этих методов и приведены данные, полученные до настоящего времени для большой части важных районов.

Задача состояла в том, чтобы провести эту работу в кратчайший срок и при минимальных затратах. Конечная цель, поставленная Национальной комиссией по атомной энергии Бразилии, будет выполнена полностью, если за это время будет дана приблизительная оценка ресурсов радиоактивных руд в стране на отдаленное будущее и в течение двух — трех лет описаны урановые месторождения разумных размеров, которые могли бы удовлетворить нужды страны на ближайшее десятилетие.

A/483 Brasil

Programa de approvisionamiento de combustibles nucleares en el Brasil y resultados obtenidos

por E. Távora

A partir de su creación en 1956, la Comisión Nacional de Energía Nuclear del Brasil ha venido desarrollando, con arreglo a sus medios y necesidades, un programa de dotación de equipo de campaña y laboratorio y de prospección general y detallada de minerales.

La Comisión espera que antes de terminar el año 1966 podrá dar fin a una evaluación de todos los recursos disponibles de minerales nucleares en el territorio nacional.

El programa y su ejecución se basan en los criterios siguientes:

a) Necesidad de mantener costes y precios dentro de los límites impuestos por las normas internacionales;

b) Renuncia, de momento, a toda labor de exploración en territorios alejados de los principales centros de producción y consumo;

c) Exploración de las zonas elegidas con arreglo a las posibilidades siguientes:

- i) Estudio de las facies de rocas detríticas continentales antiguas y recientes;
- ii) Prospección de rocas de chimeneas alcalinas;

d) De acuerdo con esas posibilidades, excluir por ahora de la prospección las siguientes rocas y formaciones:

- i) las metamórficas que constituyen la parte esencial del escudo geológico brasileño;
- ii) las formaciones graníticas, ya que son escasas las manifestaciones hidrotermales en los granitos brasileños;
- iii) las formaciones pegmatíticas de las que es imposible o, por lo menos, muy poco probable, que se extraigan económicamente minerales nucleares, ni aun como subproductos;
- iv) los yacimientos de minerales de torio, dado que, en caso de necesidad, se podrían explorar rápidamente los ya conocidos.

Se presentan ejemplos de aplicación rigurosa de un proceso típico de prospección que se inicia con el análisis crítico de las publicaciones sobre el tema y concluye con una exploración detallada en la que se utilizan todas las técnicas posibles, desde las geoquímicas y geofísicas hasta la centelleometría aérea. Se muestran ciertas variantes originales de aplicación de esos métodos. Se discuten los resultados obtenidos para las regiones más importantes estudiadas hasta ahora.

Se ha hecho lo posible para efectuar la evaluación en un tiempo y a un costo mínimos. Se habrán cumplido los propósitos de la Comisión Nacional de Energía Nuclear del Brasil si se puede dispone de un inventario aproximado de los recursos nucleares a largo plazo y se descubren algunos yacimientos de uranio de magnitud razonable dentro de los próximos 2 ó 3 años para atender a las necesidades del país en el próximo decenio.

El uranio en España : situación actual y perspectivas

por V. Membrillera Membrillera, J. Josa y E. Delgado *

PROSPECCIÓN, INVESTIGACIÓN Y EXPLOTACIÓN DE MINERALES

La prospección de minerales radiactívos en nuestro país se inició en 1948 con el fin de determinar las reservas de los mismos e iniciar los estudios sobre su tratamiento, como primer paso del desarrollo de la energía nuclear en España.

Las primeras zonas prospectadas e investigadas fueron las de Sierra Albarrana (Córdoba) donde se había obtenido mica, berilio y uranio (y de él radio) en disques de pegmatitas, por la empresa privada BRESA; y la de Monesterio (Badajoz) donde se había explotado un yacimiento filoniano por una empresa francesa para la obtención de uranio y radio hacia los años 1914 y 1915. En estas zonas se trabajó hasta fines de 1956, pero los escasos resultados obtenidos y la aparición de otros yacimientos filonianos más prometedores, hizo que cesaran los trabajos, si bien para esta fecha se habían obtenido en Sierra Albarrana algunas toneladas de un mineral con una riqueza media del 26 % en U_3O_8 que alcanzó en ocasiones más del 50 %. Sin embargo, estas toneladas hicieron posible comenzar los estudios sobre tratamiento de minerales en España.

A partir de 1952 se inició la prospección en los macizos cristalinos situados en las provincias de Jaén, Córdoba, Badajoz, Cáceres, Salamanca y Zamora, prospección hoy casi finalizada y, posteriormente, a partir de 1957 se detectaron numeros índices en las pizarras cambrianas de la provincia de Salamanca, algunos convertidos en los yacimientos de mayores reservas de mineral de España.

Posteriormente se prospectó casi todo el contacto granito-pizarra del resto de los macizos graníticos antes citados, sin obtener resultados estimables hasta el pasado año de 1963, en que se contraron índices interesantes y que empiezan a ser muy prometedores, y en las pizarras del sur de la provincia de Cáceres. En el norte de esta provincia se conocían algunos yacimientos de esta clase explorados por el sector privado.

Finalmente, en los últimos años se ha encontrado un yacimiento en el Trías de la provincia de Lérida y ha comenzado la prospección intensiva de todos los terrenos sedimentarios continentales, especialmente las formaciones lacustres. Se han detectado ya numerosos índices que hacen prever un gran aumento de las actuales reservas españolas de uranio.

Estado actual de los trabajos de prospección e investigación minera

Los trabajos realizados para la valoración de los índices aparecidos, han desembocado en el hallazgo de diversos yacimientos, más o menos importantes por su contenido de mineral, por su situación geográfica, etc. En ellos se han llevado a cabo trabajos de prospección geológica, geofísica y en algunos geoquímica (aunque en pequeña escala), sondeos con testigo y con *wagon-drill*, continuándose, cuando se ha considerado necesario con labores de interior, ayudadas con sondeos horizontales a percusión, radiometría de ellos, desmuestres y análisis. Estos trabajos han permitido en muchos casos determinar las reservas de mineral de dichos yacimientos y su riqueza. Algunos de ellos, los yacimientos filonianos existentes en las provincias de Córdoba y Jaén, se han explotado para alimentar la fábrica de uranio « General Hernández Vidal ».

Los yacimientos filonianos encontrados en las provincias de Córdoba y Jaén, presentan características variadas : en unos la mineralización va ligada a la existencia de roca básica, otros son simples fracturas de acompañamiento de filones de cuarzo y en otros, entre los que se encuentra el más importante, denominado « La Virgen », su mineralización va unida al cobre. Hasta el nivel —45 se encuentra en forma de silicatos y carbonatos y a partir de ahí empiezan a aparecer los sulfuros. Su riqueza en cobre, con una ley media del 5 %, permite la recuperación de este metal, además del uranio. Actualmente se reconoce el nivel —185 y todavía nos encontramos en la zona de cementación, si bien la mineralización en uranio ha disminuído mucho en longitud.

La zona de las provincias de Cáceres y Badajoz se ha prospectado casi por completo. En los asomos graníticos son numerosos los índices y pequeños yacimientos encontrados con mineralizaciones secundarias así como con óxidos negros y pezblenda. Sin embargo, sus mineralizaciones no profundizan más de 40 o 50 m. En esta zona quedan por reconocer algunos indicios encontrados al sur de la provincia de Badajoz. El yacimiento más importante de esta

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zona es el denominado « Los Ratones » en Albalá (Cáceres) con mineralización en pezblenda masiva, óxidos negros y gummitas, cuyo nivel —120 se investiga actualmente, con buenos resultados. En esta zona se han prospectado también las pizarras, en su contacto con el granito, y como resultado, en estos últimos meses han aparecido, en la parte sur de Cáceres, indicios que ofrecen muy buenas perspectivas y en los que se ha iniciado la investigación.

En la zona de Salamanca y Zamora ha terminado prácticamente la prospección, con espléndidos resultados, en las pizarras donde se han encontrado los yacimientos de más volumen de mineral, con una ley media del 1,2 por mil en U_3O_8. Los resultados no han sido tan satisfactorios en los granitos donde, aparte de algún pequeño yacimiento con mineralización muy superficial, solo se han encontrado dos de algún volumen, el primero es el de Valdemascaño en Lumbrales (Salamanca) en el que el uranio viene asociado a galena y, sobre todo, a blenda. Está reconocido hasta los 120 m y la mineralización se presenta en una serie de filoncillos irregulares de pezblenda de carácter radicular. El más interesante es el segundo, que corresponde a Villar de Peralonso, en la misma provincia en el que efectuadas todas las labores de investigación previas, se encontró mineralización hasta los 300 m de profundidad. Actualmente se termina un pozo de 200 m para efectuar la labor de investigación minera de interior; las leyes del mineral son, aproximadamente del 1 por mil en U_3O_8 y abundan la pezblenda, muy menuda, con antozonita y jaspe.

En Cenicientos (Madrid) se ha localizado otro yacimiento encajado en granito cuya labor de investigación está prácticamente terminada. El volumen de mineral será reducido puesto que la mineralización alcanza solamente los 50 m de profundidad pero su ley es relativamente elevada. Asociado con el uranio existe también mineral de cobre pero de baja riqueza.

También se han prospectado otras zonas de granito y pizarra pero los índices encontrados o no han tenido mucho valor o no ha sido determinado éste todavía, pudiendo señalarse que el sector privado posee algunos yacimientos en pizarras, análogos a los de la JEN y recientemente ha empezado a investigar otro yacimiento en el Trías del Pirineo de Lérida, con muy buenas perspectivas y en el que el uranio viene acompañado del vanadio y cobre en buenas proporciones.

En los últimos meses se ha iniciado la prospección de todo el sedimentario continental español de origen lacustre y aunque los trabajos están en su comienzo se han detectado ya numerosos índices y se han iniciado las investigaciones. Las perspectivas que se abren con motivo de estos hallazgos en terrenos de diversos tipos (oligoceno, mioceno, trías, cretáceo, carbonífero, etc.) puede decirse que son francamente alentadoras y de acuerdo con los resultados obtenidos hasta la fecha se confía incrementar considerablemente las reservas españolas.

Reservas de uranio

Las actuales reservas de uranio en nuestro país pueden evaluarse en 10 000 toneladas de U_3O_8 contenido en los minerales con leyes variables de unos yacimientos a otros. De estas reservas 6 000 toneladas de U_3O_8 corresponden a los yacimientos investigados por la JEN en los diversos sectores y 4 000 toneladas de U_3O_8 a las estimaciones de yacimientos que no han sido todavía investigados con detalle pero donde los trabajos se encuentran avanzados. Estas reservas se refieren a minerales que pueden producir concentrados a precios del orden de 8 $/libra de U_3O_8.

No se han tenido en cuenta en estas reservas las perspectivas muy prometedoras que hemos dicho se han encontrado en los últimos meses en los terrenos sedimentarios y que podrán elevar considerablemente estas reservas. Tampoco se han considerado otras zonas como la de Despeñaperros, en el norte de la provincia de Jaén y sur de la de Ciudad Real, donde se han detectado numerosos indicios radiactivos en una extensa zona de areniscas. La cubicación de los minerales de esta zona alcanza millones de toneladas pero la riqueza en uranio es pequeña, del orden del 0,5 por mil y además gran parte del uranio se encuentra dentro de las redes cristalinas del circón que acompaña a los minerales. Esto hace que el coste de recuperación del uranio sea bastante superior a 8 $/libra de U_3O_8 y no se considere por ahora su explotación.

La zona de mayor importancia, en cuanto a reservas, la constituyen los yacimientos de pizarras de la provincia de Salamanca que presentan una ley media del 1,2 por mil en U_3O_8, aun cuando haya zonas mucho más ricas. En los yacimientos filonianos de esta misma zona la ley media es también del 1,2 por mil en U_3O_8 excepto el de Villar de Peralonso en que esta riqueza media es del 1 por mil, a pesar de ser su mineralización en pezblenda.

El segundo lugar lo ocupa la zona de Cáceres en la que la ley media es muy variable. Dentro de esta zona destaca por sus reservas el mejor yacimiento filoniano encontrado en España hasta la fecha, el yacimiento denominado « Los Ratones », cuyas leyes varían desde algunas unidades por ciento hasta el 1 por mil en U_3O_8.

La zona de Andújar ha sido explotada en su mayor parte y las reservas actuales están constituídas fundamentalmente por las contenidas en la mina « La Virgen » en la que, como hemos dicho anteriormente, el uranio se presenta en unión del cobre. La ley media del cobre de esta mina es del 5,13 % mientras que la del uranio alcanza una riqueza media un poco superior al 1 por mil.

El conjunto de los yacimientos mejor estudiados de las zonas consideradas, que son los yacimientos a los que corresponde las 6 000 toneladas de contenido de U_3O_8, presentan una cubicación total de 4 615 000 toneladas de mineral con una ley media del 1,3 por mil de U_3O_8.

Coste de las investigaciones

El coste de las investigaciones realizadas para la fijación de las reservas señaladas anteriormente (4 615 000 toneladas de mineral con 6 000 toneladas de U_3O_8 contenido) ha sido de 353 millones de pesetas (5,88 millones de $), lo que corresponde a 58,85 ptas (0,98 $) por kg de U_3O_8 contenido en las reservas de mineral.

En esta cifra se han tenido en cuenta los gastos efectuados en prospección geológica, geofísica, sondeos con testigo, sondeos de *wagon-drill*, trabajos, de investigación minera y sondeos a percusión. No se han considerado los gastos realizados en zonas todavía sin valorar con exactitud.

El reparto de estos gastos en las distintas fases se da en la tabla 1.

La pequeña proporción en que intervienen los gastos de prospección geofísica hace ver la influencia que en el conjunto de las reservas tienen las existentes en pizarras, para la determinación de las cuales no ha intervenido prácticamente, por sus especiales características, dicha prospección. El porcentaje de gastos de sondeos de *wagon-drill* se incrementará en el futuro, pues se va a intensificar el empleo de esta clase de trabajo no solo para determinación más exacta de las reservas existentes en las pizarras, sino también como preparatorio de su explotación al conocer de antemano su situación exacta.

La tabla 2 nos da los costos medios unitarios de algunas de estas labores. Estos costos son directos, sobre los cuales hay que gravar en el caso de las labores mineras un 30 % de costos indirectos mina y, en todos, los gastos generales de la Sección o Servicio, que suponen otro 30 %, por término medio entre unos y otros Servicios y los gastos generales de División que son el 5 % exceptuándose de esto los de sondeos cuyos gastos generales Servicio, sólo son un 15 %.

Claro es que estos datos son muy variables entre los distintos terrenos a trabajar y de los yacimientos filonianos a los de pizarras, pero aquí solo se ha querido dejar constancia de la media resultante de la agrupación de todos ellos.

Coste de las explotaciones

Teniendo en cuenta que para llegar a explotar una mina hay que hacer aparte de las labores de investigación ya señaladas, otras de preparación, mantenimiento de las labores hechas hasta su abandono (conservación, ventilación y desagüe), construcciones y varios, los gastos hechos hasta la fecha en las zonas a que antes hemos hecho mención, suponen 106 millones de pesetas (1,76 millones de $) cuyo reparto aproximado se da en la tabla 3.

Tabla 1. Distribución del coste de la investigación

	%
Prospección geológica	16,57
Prospección geofísica	1,13
Sondeos con testigo	20,97
Sondeos con *wagon-drill*	3,54
Investigaciones mineras y sondeos a percusión	57,79
Total	100,00

Tabla 2. Costes medios unitarios de algunas labores[a]

Prospección geofísica	1 284 pts/Ha
Sondeos con testigo	927 pts/m
Sondeos con *wagon-drill*	127 pts/m
Pozo de 3,20 × 2,20	28 000 pts/m
Pozo de 2,40 × 1,40	10 000 pts/m
Chimeneas 2,— × 1,—	7 000 pts/m
Cruceros 3,20 × 2,20	12 000 pts/m
Galerías 1,80 × 2,30	4 500 pts/m

[a] 60 pts = 1 dólar.

Tabla 3. Distribución del coste de explotación

	%
Preparatorios	26,89
Mantenimiento	41,98
Construcciones	29,24
Varios	1,89
Total	100,00

En cuanto al costo directo medio, en las explotaciones llevadas a cabo en los yacimientos filonianos es de 150 pts (2,5 $) el kg de U_3O_8, lo que habría de ser gravado en los tantos por ciento citados con anterioridad, o sea, un 65 %, para llegar al precio total medio de 247 pts (4,1 $ el kg de U_3O_8.)

Por lo que respecta al costo directo medio en las explotaciones llevadas a efecto en los yacimientos de pizarras es de 45 pts (0,75 $) el kg de U_3O_8 y el total con los tantos por ciento correspondientes resulta a 75 pts (1.25 $).

TRATAMIENTO DE MINERALES DE URANIO

El tratamiento de los minerales de uranio en España siguió un desarrollo paralelo al de la prospección y minería. Los primeros estudios empezaron a finales de los años cuarenta, cuando había muy poca información disponible sobre este tema. En aquella época se trataron concentrados ricos de brannerita, con leyes hasta de 50 % de U_3O_8. También se trabajó mucho sobre purificación de concentrados con éter etílico llegando hasta la escala de planta piloto. Hacia los años 54-55 se realizaron los primeros trabajos con minerales secundarios de uranio con leyes de 0,2-0,3 % U_3O_8 y sustituyendo la purificación con TBP al empleo del éter etílico. A partir de la primera Conferencia de Ginebra sobre usos pacíficos de la

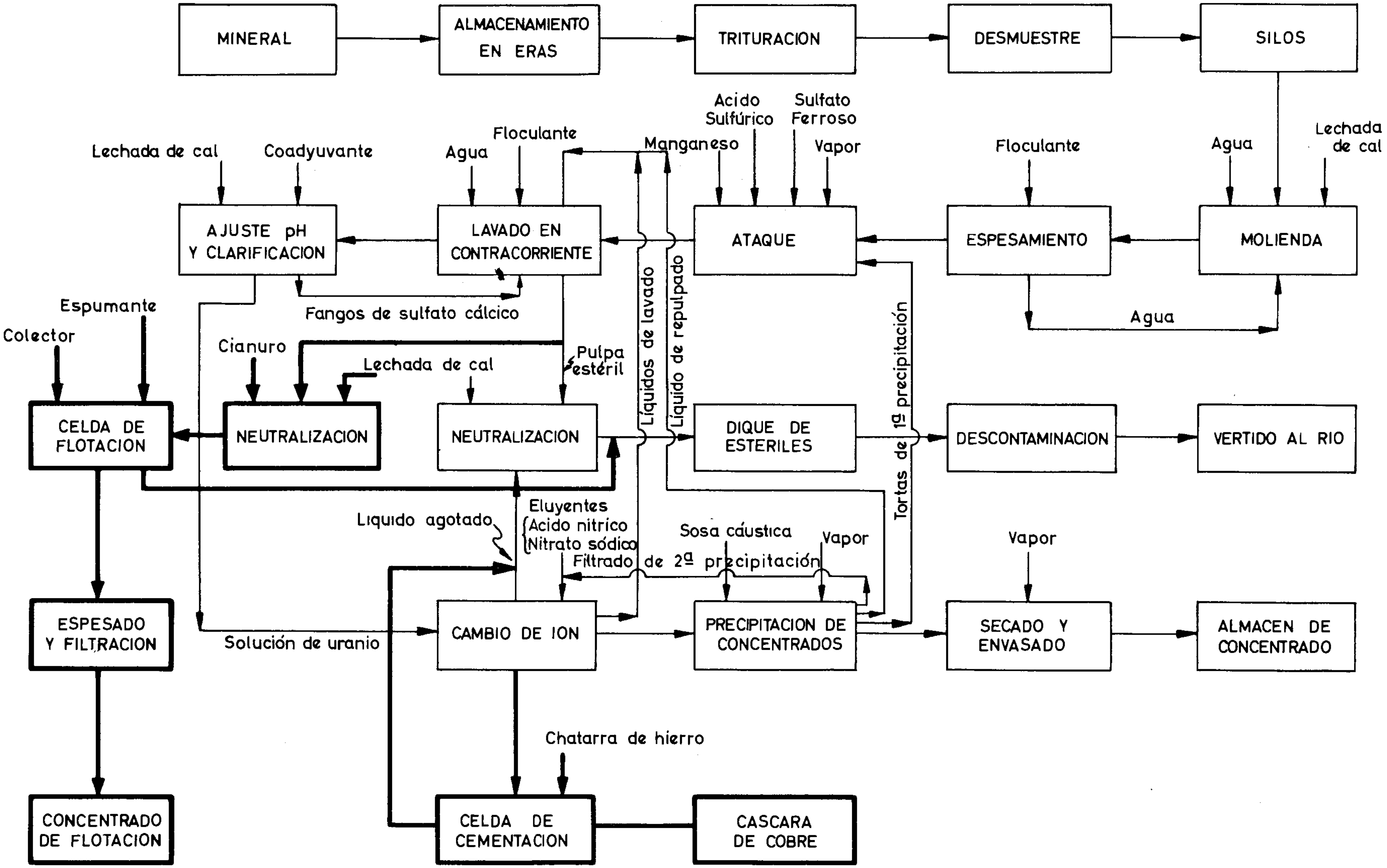

Figura 1. Esquema de fabricación para minerales de uranio y de uranio-cobre (▬) de la fábrica de uranio « General Hernández Vidal »

Tabla 4. Minerales tratados en la fábrica de uranio « General Hernández Vidal » de Andújar

Procedencia	Propiedad	Tipo	Cantidad tratada		Leyes, %	
			t	%	U_3O_8	Cu
Cardeña	JEN	Granitos	108 011	54,0	0,08-0,15	0,20-0,60
Santuario	JEN	Granito-sulfuros	38 809	19,4	0,06-0,13	2,0 -7,5
Albalá	JEN	Granitos	26 564	13,3	0,15-0,25	—
Salamanca	JEN	Pizarras	23 180	11,6	0,15-0,25	—
Varios . .	Privados	Pizarras	3 484	1,7	0,15-0,25	—
		Total	200 048	100,0		

Energía Atómica, España, con otras naciones del mundo, se benefició de la información presentada, haciendo un esfuerzo para el estudio de tres o cuatro de sus yacimientos, y elaborando el proyecto de una planta industrial, que empezó a funcionar a finales de 1959. La existencia de la fábrica supuso un estímulo considerable, aumentando paulatinamente las reservas de mineral. Hubo que realizar el estudio de nuevos tipos de menas [1] y se puso en marcha un grupo de trabajo para considerar las posibilidades de beneficio de los nuevos yacimientos que la prospección geológica y minera puso de manifiesto.

Fábrica de uranio « General Hernández Vidal »

La única planta comercial de tratamiento de minerales de uranio en España está situada en Andújar (Jaén) y próxima a los yacimientos de Andalucía. Su capacidad de trabajo es de 200 t/d para minerales de leyes del orden de 1,5 por mil en U_3O_8. Su diagrama de flujo es el indicado en la figura 1 y corresponde a un proceso clásico de lixiviación ácida, lavado por doble línea de ciclones y espesadores y recuperación del uranio por cambio de ion-precipitación. Una característica adicional es que está acondicionada para el tratamiento de minerales de uranio-cobre, con recuperación de este último como subproducto, en forma de cemento de cobre y de concentrado de flotación.

La fábrica [2] ha trabajado satisfactoriamente desde su puesta en marcha (rendimientos 85-95 %), mostrando una gran flexibilidad para adaptarse a los más diversos tipos de minerales. Ha tratado minerales de las minas que la JEN tiene en la zona, lotes de minerales privados, y muestras de tonelaje apreciable procedentes de trabajos de investigación minera en yacimientos que la JEN tiene en otras regiones de España. En total ha manejado unos veinte tipos distintos de minerales, solos o en forma de mezclas, y comprendiendo fundamentalmente minerales secundarios de uranio aunque también a veces ha tratado minerales de pezblenda; las gangas fundamentales han sido graníticas y pizarras. En la tabla 4 se resumen los minerales tratados hasta finales de 1963, y sobre ella conviene indicar que el último año la fábrica funcionó a capacidad limitada, de acuerdo con el programa establecido, aunque actualmente trabaja a su ritmo normal.

El trabajo a escala comercial ha permitido confirmar y completar los resultados obtenidos a escala de laboratorio y piloto proporcionando un sólido fundamento de extrapolación y sirviendo de base para la creación de una industria española de tratamiento de minerales de uranio. Los concentrados obtenidos son de una calidad que cumplen las especificaciones internacionales para los mismos (U_3O_8 80-84 %; P_2O_5 0,1-0,4 %; SO_4 1,0-4,0 %; Fe 0,2-0,8 %). Junto a estos concentrados se han recuperado unas 1 300 t de cobre metal entre concentrados de flotación (18-28 % Cu) y de cementación (70-80 % Cu).

Otra consecuencia del funcionamiento de la fábrica ha sido la obtención de una experiencia directa sobre costes de instalación y de tratamiento, así como de su distribución, que será de gran valor para las futuras fábricas. En la tabla 5 se dan los costes de instalación mientras que en la tabla 6 se indica una distribución media de los de transformación para los tres primeros años de funcionamiento.

Tabla 5. Costes de instalación de la fábrica

Concepto	Distribución, %	
	Relativo	Total
Terrenos	—	1,41
Edificios y obras	—	41,66
Instalaciones fabricación	—	42,19
Instalaciones auxiliares	—	10,24
Gastos diversos	—	4,50
Total	—	100,00
Descomposición por secciones de fabricación		
Parque de minerales	12,40	7,09
Trituración y desmuestre	12,35	7,06
Silos y molienda	9,15	5,21
Espesamiento neutro, ataque.	11,60	6,60
Lavado CCD	23,20	13,24
Ajuste de pH, cambio de ión	18,30	10,48
Precipitación de concentrados	6,60	3,77
Lechada de cal.	2,50	1,46
Neutralización de residuos.	3,90	2,22
Total	100,00	57,13

Tabla 6. Descomposición por secciones (%) del coste del tratamiento de minerales de uranio

Sección	Mano de obra	Reactivos material aux.	Fuerza motriz	Combustibles	Varios	Mantenimiento	Amortización	Total
Parque de minerales	23,59	—	—	0,34	19,74	9,43	47,18	3,63
Trituración y desmuestre	27,40	0,76	3,71	7,16	13,09	16,10	31,75	6,93
Silos y molienda	20,81	30,35	18,70	0,56	—	9,40	20,16	7,50
Ataque	4,16	39,37	12,84	0,12	1,54	7,30	14,63	15,72
Lavado CCD	15,24	28,67	7,48	0,15	—	17,11	31,33	8,70
Ajuste de pH	18,82	31,35	5,12	0,008	3,63	13,83	27,22	4,45
Cambio de ión	13,23	41,95	3,29	0,06	1,92	14,03	25,50	8,42
Precipitación de concentrados	17,24	34,81	2,12	0,05	4,15	13,89	27,71	5,84
Neutralización residuos	22,51	34,82	7,92	0,08	2,89	10,31	21,44	5,58
Costo neto fabricación	15,74	34,53	8,09	0,87	3,88	11,95	24,90	66,81
Gastos generales	36,90	—	—	—	36,0	4,99	22,10	18,31
Servicios auxiliares	32,39	8,32	4,10	8,67	3,63	8,59	34,00	13,76
Gastos especiales	—	—	—	—	—	—	—	1,10
Coste total tratamiento	21,74	24,23	5,99	1,80	10,79	10,08	25,37	100,00

Los costes de tratamiento fueron variables de unos minerales a otros, ya que dependían de las características de la ganga y de la ley del mineral. Para la mayoría de los minerales, que requieren consumos de ácido sulfúrico del orden de 45 kg/t o inferior se puede tomar como cifra tope unas 462 pts/kg de U_3O_8 (3,5 $/libra de U_3O_8). No obstante con los minerales de cobre, el consumo de ácido sube a veces hasta 130-140 kg/t, pero en este caso el ácido adicional se compensa con creces por el cobre subproducto.

Otros estudios de tratamiento

Además de los minerales de la zona de Andújar, la JEN cuenta, como hemos dicho, con otras dos zonas en que la investigación minera está muy avanzada; son la de Salamanca con pizarras y granitos y la de Cáceres con granitos, fundamentalmente. Sobre el tratamiento de los minerales de estas zonas se tiene mucho trabajo realizado y todavía se continúa. Para el tratamiento de las pizarras de Salamanca se ha realizado el anteproyecto de una fábrica de 1 000 t/d de capacidad; estos minerales parece que en principio necesitarán un consumo de reactivos ligeramente mayor que los de granito, pero el coste total se podrá reducir a la vista de la experiencia de Andújar y con la mayor capacidad de la fábrica.

Al lado de las fábricas convencionales, se han considerado otras posibilidades para el beneficio de minas pequeñas o de fracciones marginales que no interese transportar a las fábricas convencionales. Se trata de procesos con un paso de lixiviación estática del mineral triturado, seguido de la recuperación por extracción con aminas o por cambio de ión con resinas. Se ha trabajado en escala de laboratorio y piloto y se ha visto que en lixiviación es factible la realización de una contracorriente consiguiéndose ahorros de ácido entre 25 % y 50 % del que se requiere en lixiviación con agitación, especialmente con minerales que necesitan un ataque de gran acidez final. En la fábrica de uranio de Andújar está actualmente en prueba una instalación piloto de extracción con aminas para 50 m^3/d, concebida con vistas a un traslado fácil, y que después de un período de estudio inicial se desmontará para instalarla en una mina pequeña, trabajando a un ritmo aproximado de 50 t/d. Otro proyecto que se tiene casi terminado es uno de lixiviación estática-cambio de ión, en el que el 75 % de esta última parte estará montado en un camión con el fin de que una misma instalación pueda servir simultáneamente a dos minas pequeñas y próximas, empleando un régimen de trabajo alternativo por semanas, con períodos de almacenamiento y tratamiento de líquidos sucesivamente; su capacidad corresponde a unas 20-30 t/d de mineral.

Por otra parte, dentro de la misma filosofía de instalaciones sencillas se está realizando un proyecto para el tratamiento de un mineral privado de uranio-vanadio-cobre a razón de 30-50 t/d, con un diagrama de flujo que comprende lixiviación estática, extracción con disolventes para uranio y vanadio, y cementación y flotación para el cobre.

Un caso que conviene señalar en relación con los estudios de tratamiento es el de las cuarcitas de Despeñaperros, de las que ya hemos hablado, yacimiento marginal de uranio (130-500 ppm) con titanio (14,3 % TiO_2), circonio (5 % ZrO_2) y torio (600 ppm) del que existen reservas grandes, cuyo estudio se ha iniciado [3], y cuya valoración sería factible en el caso de que simultáneamente se recuperasen titanio y circonio.

CONCLUSIONES

Los trabajos de prospección e investigación de yacimientos de minerales de uranio en España han llevado al establecimiento de unas reservas de 10 000 t de U_3O_8 contenido, teniendo en cuenta únicamente los trabajos de la JEN en sus tres zonas mineras principales. Se espera que en un futuro próximo esta cifra se incrementará considerablemente como consecuencia de los índices detectados en los últimos meses y de los trabajos en curso.

Nuestro país cuenta con una fábrica de tratamiento de minerales de uranio con una capacidad de 200 t/d y está realizando el anteproyecto de una nueva fábrica para 1 000 t/d, lo que elevaría nuestra capacidad hasta una producción de unas 400 t de U_3O_8 al año. Una instalación, ya existente, permitiría transformar estos concentrados en sales puras de uranio [4].

De acuerdo con el programa establecido en otro trabajo presentado a esta conferencia [5], en el año 1975 España contará con una potencia nuclear instalada de 2 280 MW y, como consecuencia, las necesidades de uranio hasta dicha fecha serán del orden de 6 500 t de U_3O_8, cifra inferior a las reservas en 31 de diciembre de 1963. Por tanto, nuestro país cuenta con reservas probadas para iniciar un programa de centrales nucleares y con perspectivas prometedoras para el futuro.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/494 Spain

Uranium in Spain: present situation and prospects

By V. Membrillera Membrillera *et al.*

Spain initiated the prospecting for uranium and thorium about 1948 and, since that time, a large portion of the surface of the country has been prospected and studied. This work has been accomplished largely by the Junta de Energía Nuclear with some assistance, in some cases, from private groups or companies.

The results obtained to date have established known uranium reserves of more than 6 000 metric tons of contained U_3O_8, recoverable at present market prices. These reserves increase considerably at higher costs of recovery. Results for thorium have not been very satisfactory, as only small quantities have been found.

In this paper is presented a description of the work completed to date and the results obtained in the various regions studied. The methods of prospecting and investigation followed are presented in detail and some economic data related to the area explored and the reserves discovered are given.

The exploitation of several mines has been initiated to provide feed material for an ore concentration plant. Comparative technical and economic data related to various exploitations and to the treatment of various types of ore are also given.

The future prospects for the mining of uranium in Spain are examined in view of the results obtained to date.

Finally, the present uranium reserves in Spain are compared with future needs in accordance with the programme described in another paper presented at this Conference.

A/494 Espagne

L'uranium en Espagne : situation actuelle et perspectives

par V. Membrillera Membrillera *et al.*

L'Espagne s'est mise vers 1948 à la prospection de l'uranium et du thorium et, depuis lors, une grande partie du territoire national a fait l'objet d'études et de recherches. Les travaux ont été effectués surtout par la Commission de l'énergie nucléaire, avec dans certains cas une modeste participation de sociétés ou de groupes privés.

Les résultats obtenus jusqu'à présent ont permis de fixer à plus de 6 000 tonnes de U_3O_8 contenu les réserves d'uranium d'où il serait rentable, aux prix actuels, d'extraire U_3O_8. Ces réserves augmentent considérablement avec le coût de l'extraction. En ce qui concerne le thorium, les résultats ont été peu satisfaisants jusqu'à présent, cette matière n'ayant été localisée qu'en petites quantités.

Les auteurs exposent les travaux effectués jusqu'à ce jour ainsi que les résultats obtenus dans les diverses régions étudiées. Ils présentent en détail les méthodes de prospection et de recherche suivies et quelques données sur les prix de revient en fonction de la superficie explorée et des réserves localisées.

L'exploitation de plusieurs mines ayant été entre-

prise en vue d'alimenter une fabrique de minerais enrichis, les auteurs fournissent également des données techniques et économiques comparées relatives à plusieurs exploitations et à des usines de traitement de divers types de minéraux.

Ils examinent les perspectives de l'extraction de l'uranium en Espagne, compte tenu des résultats obtenus jusqu'à présent.

Ils comparent enfin les réserves actuelles d'uranium du pays avec ses besoins au cours des prochaines années, en fonction du programme décrit dans un autre mémoire présenté à la Conférence.

A/494 Испания

Уран в Испании. Состояние вопроса и перспективы

В. Мембриллера В. Мембриллера *et al.*

Геологическая разведка залежей урана и тория началась в Испании примерно в 1948 году. С этого времени большая часть поверхности страны была разведана и изучена. Исследования проводились главным образом Хунтой по ядерной энергии при некоторой помощи частных групп или компаний.

В результате этой работы удалось определить запасы урана, которые к настоящему времени составляют более 6000 *т* U_3O_8, разрабатываемых по существующим рыночным ценам. Эти запасы значительно возрастут при более высоких ценах на уран. В отношении тория результаты в настоящее время далеко не удовлетворительны, запасы тория исчисляются в небольших количествах.

В докладе описываются состояние работ и результаты проведенных исследований. Детально рассматриваются методы разведки и последующего изучения месторождений, а также некоторые экономические данные, касающиеся изучаемых районов и открытых залежей.

В связи с вводом в эксплуатацию нескольких рудников и пуска обогатительной фабрики в докладе приводятся сравнительные технические и экономические данные, касающиеся условий эксплуатации и переработки различных видов руд. Рассматриваются перспективы разведки и эксплуатации месторождений урана и тория в Испании. Наконец, существующие в Испании запасы урана сравниваются с потребностями страны в последующие годы в соответствии с программой, изложенной в другом докладе, представленном на данной конференции.

Portuguese requirements and supply capabilities regarding nuclear fuels

By J. Rocha Cabral * and F. Marques Videira **

The main purpose of this paper is to make a rough evaluation of the requirements of nuclear fuel in Metropolitan Portugal for the production of electrical energy up to the end of the century, and to examine some aspects of the possible expansion of the uranium industry.

Such long range estimates have necessarily a speculative character due to the large number of hypotheses which have to be taken into account. Hence a short description of the development of uranium prospecting and mining and of electrical energy production is briefly presented as a basis for the extrapolations made, it being understood that the latter represent mere orders of magnitude.

URANIUM RESERVES

The mining of uranium-bearing ores was initiated in Portugal in 1909 for recovering radium. The conversion of the industry to the production of uranium concentrates was made in 1950-51, and approximately 1 100 t U have been mined and exported since then. Systematic prospecting was initiated in 1955 by the Junta de Energia Nuclear (JEN), the uranium reserves in the metropolitan territory of Portugal having been provisionally estimated at 5 100 t U, contained in 3.26×10^6 t of certain and probable ore.

The cut-off value generally accepted for estimating these reserves is around 0.1 % U_3O_8. It is likely that very important quantities of uranium may be contained in some other occurrences of low grade ores which have been found but not yet studied. Furthermore, because of the vein type of some deposits, their exploitation will probably add new reserves to those presently evaluated. Thus we will also consider as an alternative, 10 000 t U for the uranium reserves.

The whole of the uranium mining industry is at present under the direct management of JEN. The latter also runs the chemical treatment plant at Urgeiriça which has a capacity of 120 t ore/day as well as a mobile plant for 35 t ore/day, thus having available a total capacity of about 75 t U/year in the form of concentrates. A pilot plant for the production of nuclear pure uranium, with a capacity of 15-50 t U/year is installed at the Sacavém Research Centre.

ELECTRICAL ENERGY PRODUCTION

The development of the Portuguese electrical energy production system can be more easily analysed with reference to periods of 25 years, because it has shown, and will probably continue to show, well defined and different patterns in different quarters of the century.

The first quarter of this century was characterized by the constitution of the first public utilities at the main consumption centres. The system was almost exclusively thermal and the contribution of the autoproducers rather important.

In the second quarter of the century the production developed at an annual mean rate of 7 %, the production by public utilities becoming predominant. Hydro power stations reached almost 50 % of the

Table 1. Development of the electrical energy production system [5]

Year	1927	1950	1963
Installed capacity MW(e)			
Thermal	101	192	291
Hydro	33	153	1 204
Total	134	345	1 495
Production GWh			
Thermal	132	505	300
Hydro	55	437	4 002
Total	187	942	4 302
Installed capacity MW(e)			
Public utilities	95	272	1 371
Auto producers	39	73	124
Consumption GWh			
Public supply	107	704	3 432
Auto producers	52	76	208
Total	159	780	3 640
Average specific consumption kWh per inhabitant	26	99	439

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total installed capacity but no interconnection existed between the production centres. The main figures for 1927 (first year for which we have reliable statistics) and for 1950 are shown in Table 1.

The intensive development of hydroelectric resources and the interconnection of the system took place from 1950 onwards, resulting in consumption growing at an annual mean rate of about 13 %, as can be deduced from the figures presented in Table 1. The small increase in thermal capacity was necessary as a stand-by for the dry season.

Further development of hydroelectric resources and an increase in thermal capacity is expected to continue until 1975. The load factor of the thermal capacity will gradually increase. The consumption growth rate should decline slightly, a tendency already noticeable in more recent years.

The lack of important fuel resources and the expansion of thermal capacity favour the construction of nuclear power stations. It is hoped that the first nuclear plant may be installed before 1975.

The fourth quarter of the century will be characterized by the complete development of hydroelectric resources and the predominance of thermal energy, a reasonable assumption being that after 1985-90 the increase in capacity will have to be met exclusively by thermal stations.

Estimates for the period 1965-2000 are based on studies involving the integration of nuclear energy within the Portuguese system [1], [2], [3], and take into account consumption growth rates generally derived from the work of J. A. Jukes [4]. Production capacity under construction and short term consumption estimates lead to the values for 1965 presented in Table 2. Public utilities only were considered.

Table 2. Estimated development of the electrical production system

Year	1965	1975	2000	
Installed capacity MW(e)				
Hydro	1 500	2 500	4 400	
Thermal.	150	615	6 000	2 400
Nuclear	—	235	6 000	9 600
Total	1 650	3 350	16 400	
Production TWh				
Hydro.	4.8	9.3	14.2	
Thermal.	0.2	2.3	18.0	7.2
Nuclear	—	1.4	34.8	45.6
Total	5.0	13.0	67.0	

As previously mentioned, consumption growth rate will probably continue to decline after 1965, although, bearing in mind the general economic development of Portugal, this tendency is not expected to be too strongly marked.

Assuming that annual mean rates of growth of production in successive quinquennia are 10.5, 9.5, 8.5, 7.5, 6.5, 6.0 and 5.5 %, respectively, a value of 67 TWh for the energy production in the year 2000 has been found. Taking into consideration the expected characteristics of the load diagram, a capacity of 16 400 MW(e) (net) is predicted for that year.

NUCLEAR PROGRAMMES

It follows from these assumptions that an additional capacity of about 15 000 MW(e) would have to be installed between 1965 and the year 2000, and that a grand total of about 1 000 TWh would have to be produced during that period.

The assignment of such additional capacity and total power produced as amongst hydroelectric, conventional thermal and nuclear stations, will ultimately depend on the respective generating costs, under the conditions inherent to the system.

The fallibility of such long range economic forecasts and the impossibility of a more precise treatment led to the assignment of the additional capacity and total power production amongst the different types of stations in accordance with a few assumptions that are deemed reasonable.

Assuming that the full development of economic hydroelectric resources will be achieved by 1985-90, reaching a total installed hydro capacity of 4 400 MW(e) and a production of 14.2 TWh in a normal year, a total of 410 TWh of hydroelectric power will be produced from 1965 to the year 2000. Under these circumstances a total of 590 TWh will have to be produced during that same period by thermal plants, the latter reaching a total capacity of 12 000 MW(e) (net) by the year 2000.

The figures for capacity and production in 1975, which is estimated as the first year for effective nuclear production, are shown in Table 2. The estimated figures for the year 2000 are also given and two possible alternatives are then considered for the assignment of capacity and power between conventional and nuclear plants.

It was assumed firstly that nuclear power stations would have relatively high and constant load factors. In such a case about 40 % of the capacity installed from 1965 to the year 2000 would be nuclear and nuclear production would amount to 410 TWh in the same period.

If nuclear power stations should become competitive at lower load factors, as contemplated in the second alternative, capacity and production would be about 65 % and 475 TWh, respectively.

FUEL REQUIREMENTS

If the introduction of nuclear power be postulated exclusively on economic grounds, the choice of reactors will be limited to those types which will have been fully tested and for which there is a considerable amount of operational experience.

For the purpose of this paper both natural uranium and enriched uranium reactors will be characterized according to the quantities of natural uranium per installed MW(e) net and per TWh produced. The following values of these parameters seem to be compatible with the expected development technology:

Natural uranium reactors:	0.2 or 0.8 t/MW(e) net 15 or 35 t/TWh
Enriched uranium reactors:	0.8 t/MW(e) net 30 t/TWh

Capacity and power has been assigned amongst different types of reactors bearing in mind typical running costs. The various possible programmes which have been examined lead to an average of about 1/3 natural uranium reactors and 2/3 enriched uranium reactors.

Obviously breeders should not be forgotten in the evaluation of nuclear fuel requirements. Nevertheless, considering that the more advanced countries are assuming that breeders will not be competitive before the last decade of the century and considering also the economic and technological problems yet to be solved, one should not take the impact of breeders into account on a quantitative basis. In any case, however, it would appear most unlikely that the introduction of breeders could significantly reduce fuel requirements in Portugal before the year 2000.

As a result of all these assumptions, fuel requirements for the period 1965-2000 are of the order of 15 500 and 20 000 t of natural uranium for each of the nuclear programmes considered: 6 000 MW(e) and 410 TWh; 9,600 MW(e) and 475 TWh.

Since such quantities would have to be mined and processed before being utilised in the reactors, it is expected that 17 000 to 22 000 t of natural uranium would have to be mined before the year 2000.

SUPPLY CAPABILITIES

National uranium requirements and supplies will thus depend on the following factors:

(*a*) The first nuclear power station will probably be integrated within the production system by 1975; uranium mined and processed in Portugal will have to be available well in advance if national resources are to be used;

(*b*) It is not yet possible to define the planning for installing further nuclear capacity;

(*c*) Natural uranium requirements will be relatively modest in the beginning, and will grow quickly thereafter;

(*d*) The existence of a uranium mining industry and the need to study further the development of national resources and to train personnel, must be taken into account.

These considerations and the social and technical problems that would arise as a result of a temporary closing down of the mining industry, seem to justify that the exploitation of the existing installations be continued, although at a minimum rate of production.

Moreover experience will be gained in this way on processing other ores and it will be possible to build up a reasonable stock of concentrate, allowing the production to fit the demand in the most convenient way, once the nuclear programme is established.

Later the development of the mining industry will be dependent among other factors on the resources available (quantities and location) on the nuclear programme that is established and on the economics of the exploitation of various mines and of the processing units to be installed.

A preliminary analysis of this problem seems to indicate a maximum annual mining capacity of about 7 % of the resources available. This figure is only slightly dependent on the nuclear programme, which, obviously will dictate the rate of expansion of the industry up to the attainment of that maximum capacity and will determine therefore the time when the reserves will have been exhausted.

The anticipated annual fuel requirements and national supply capabilities are presented in Fig. 1.

It can be seen that Portugal would have to import uranium from 1982-85 onwards, and that national

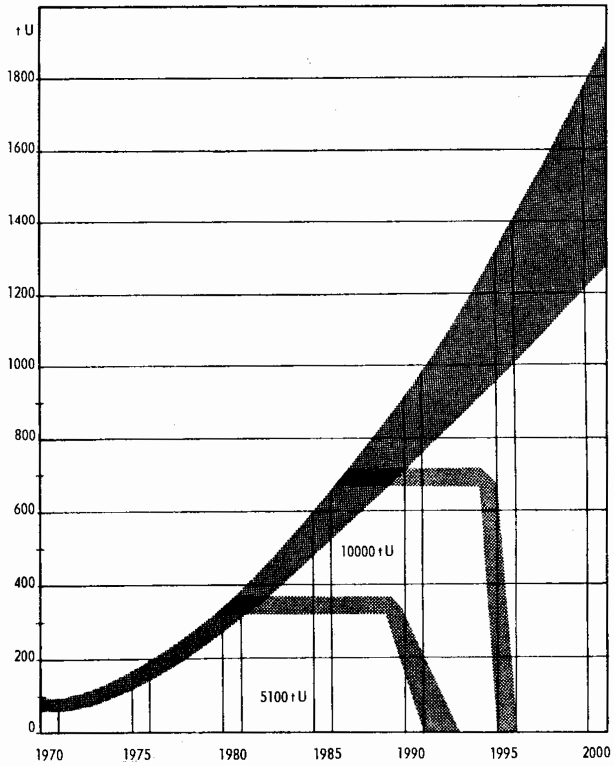

Figure 1. Annual fuel requirements and supply capabilities

resources would have been exhausted by 1991-95, if the latter were to be used regardless of fuel cycles adopted.

The fuel quantities to be imported during this century, expressed in terms of natural uranium, are presented in Table 3 for the various alternatives considered.

Table 3. Fuel quantities to be imported up to the year 2000 (t natural uranium)

	Requirements	
	17 000	22 000
National resources		
5 100	11 900	16 900
10 000	7 000	12 000

The resources represented by the irradiated fuel and the possibilities offered by plutonium recycling and breeding will certainly allow Portugal not to depend so heavily on external supplies.

Should national resources be used only in natural uranium reactors, their exhaustion is not likely to take place during this century. It will then be necessary to import enriched fuel from the beginning of the nuclear programme.

The steadily growing demand for nuclear fuel will most certainly justify the installation in Portugal of some of the other fuel cycle industries, namely those which do not require high investments, e.g. fuel element fabrication.

The possibility of making optimum use of national uranium resources will depend in any case on continued co-operation from other countries.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/504 Portugal

Besoins de combustibles nucléaires au Portugal et possibilités d'approvisionnement

par J. Rocha Cabral et F. Marques Videira

L'existence au Portugal de réserves considérables d'uranium et d'une industrie d'exploitation de ce métal ainsi que l'évolution prévisible de la consommation d'énergie électrique jusqu'à l'année 2000 et la participation de l'énergie nucléaire à l'augmentation correspondante de la production sont présentées par les auteurs en tant qu'éléments de base pour cette étude.

En prenant en considération la consommation qualitative et quantitative de combustible des différentes filières de réacteurs, les auteurs définissent les quantités d'uranium nécessaires pour chaque type de réacteur et pour chaque programme nucléaire envisagé.

Tenant compte des besoins ainsi précisés et de l'importance des réserves, on examine le problème de la dimension de l'industrie minière, ainsi que certains des facteurs qui la déterminent. L'intérêt que l'on manifeste pour les industries de fabrication d'éléments de combustibles, la possibilité de leur installation et les problèmes de politique générale que soulève cette question sont aussi discutés.

On analyse finalement les différentes possibilités de mise en valeur des ressources d'uranium, ainsi que les conséquences dans le domaine de la coopération internationale qui résulteraient de l'application de certaines solutions.

A/504 Португалия

Потребности в ядерном топливе и возможности обеспечения им в Португалии

Х. Р. Кабрал, Ф. М. Видейра

Наличие в Португалии значительных урановых запасов и урановой горнодобывающей промышленности, а также предполагаемое увеличение потребления электроэнергии до 2000 г. и роль ядерной энергии в соответствующем увеличении производства электроэнергии представлены в качестве основных положений настоящего исследования.

Принимая во внимание количественное и качественное потребление топлива различными реакторами, авторы определяют количество урана, необходимого в каждом случае.

На основании данных о потребностях в уране и данных о запасах урана рассматривается вопрос о масштабе работ уранодобывающей промышленности, а также некоторые факторы, от которых зависит ее рост. Обсуждаются также значение и возможности промышленных установок по производству тепловыделяющих элементов и другие связанные с этим вопросы.

Наконец, анализируются различные возможности разработки использования запасов урана, а также вопросы международного сотрудничества.

A/504 Portugal

Demanda portuguesa y capacidad de suministro en relación con los combustibles nucleares

por J. Rocha Cabral y F. Marques Videira

Los autores de la memoria, al presentar los datos básicos, se refieren a la existencia en Portugal de grandes reservas de uranio y de una industria minera del uranio, así como al aumento previsible del consumo de energía eléctrica hasta el año 2000 y a la posible participación de la energía nuclear para satisfacer la creciente demanda de energía.

Un examen del consumo de combustible en diversos tipos de reactores, tanto en términos cualitativos como cuantitativos, conduce a la determinación de las necesidades de uranio para cada uno de dichos tipos y para varios programas de energía nuclear supuestos por los autores.

Después se estudian el volumen de la industria minera del uranio y algunos de los factores de que depende, comparándolos con las reservas de uranio y las necesidades de éste, determinadas como se indica anteriormente. También se discuten la conveniencia y las posibilidades de montar instalaciones de fabricación de elementos combustibles, así como problemas anejos de política general.

Finalmente se analizan las posibilidades de desarrollar la utilización de los recursos de uranio y las consiguientes repercusiones en el campo de la cooperación internacional.

A review of uranium and thorium deposits in India

By K. L. Bhola, K. K. Dar, Y. N. Rama Rao, C. Suri Sastry and N. R. Mehta *

Since the establishment of the Indian Atomic Energy Commission in 1949, the Atomic Minerals Division has been engaged in a country-wide systematic search for uranium and other atomic energy minerals. Ground surveys, car-borne and air-borne surveys, borehole drilling and underground development, etc., constituting a phased programme of intensive prospecting and exploration for uranium, have yielded useful results in widely scattered areas of India, the most favourable being the Singhbhum Thrust Belt in Bihar, where recent investigations have brought to light significant uranium ore deposits. Some of the less important uranium deposits are located in parts of Rajasthan and, of late, favourable indications were found in the Himalayas in the Kulu district of Punjab and Chamoli district of Uttar Pradesh, which are currently being investigated. Most of these deposits are in pre-Cambrian metasedimentary rocks.

Investigations have also brought to light some radioactivity in pre-Cambrian granites, syenites and rhyolites in Peninsular India, some of which may form a potential source of uranium when rich deposits are depleted.

Monazite, the chief thorium mineral, together with useful quantities of ilmenite, rutile, zircon, etc., occurs in beach placers, coastal dune sands and in the sea bed along the west and east coasts of India. There are some rich inland placer deposits of monazite in Eastern India as well. The monazite deposits of India are perhaps the largest in the world.

For India's nuclear power programme, it is expected that thorium will be used in breeder reactors and therefore, it is likely to play an important place amongst India's nuclear fuels.

A brief review of India's uranium and thorium deposits is given in the following paragraphs.

URANIUM DEPOSITS

Bihar

Singhbhum Thrust Belt

Singhbhum district. Located in South Bihar, this east-west trending belt, 160 km long, is well known for copper, apatite-magnetite and kyanite deposits. The constituent rocks of the belt are the pre-Cambrian meta-sediments, comprising in order of superposition (*a*) the closely folded mica schists with subordinate hornblende schists and intermittent thin quartzite bands of the Chaibasa stage; (*b*) the chlorite schists, chlorite-sericite schists and banded quartzites with occasional magnetite of the Iron Ore stage, succeeded by (*c*) thick beds of quartzites, conglomerates and metamorphosed basic lavas of the Dhanjori stage (Figs. 1, 2).

These rocks were subjected to orogenic forces, directed from the north, during which they were strongly over-folded and sometimes over-thrust. Such over-thrusting is discernible for a distance of more than 150 km, along the arcuate trend of the thrust, from around Duarapuram in the west to Bahargora in the southeast, in which the older Chaibasa and Iron Ore stages have been thrust over by the younger Dhanjori rocks, with Singhbhum granite massif on its southern edge acting as a buttress. The resultant structure is an anticlinorium of isoclinally folded rocks dipping consistently towards the north, with the major thrust development at its southern limb, accompanied by severe crushing and

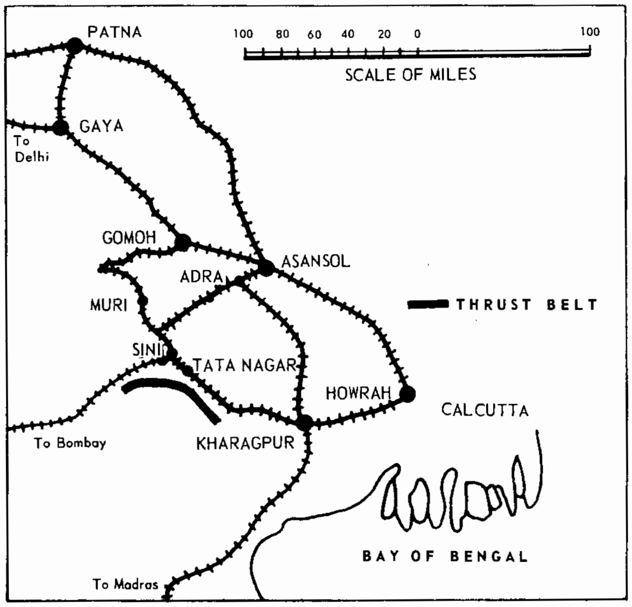

Figure 1. Location map of Singhbhum Thrust Belt

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* Department of Atomic Energy, Government of India, New Delhi.

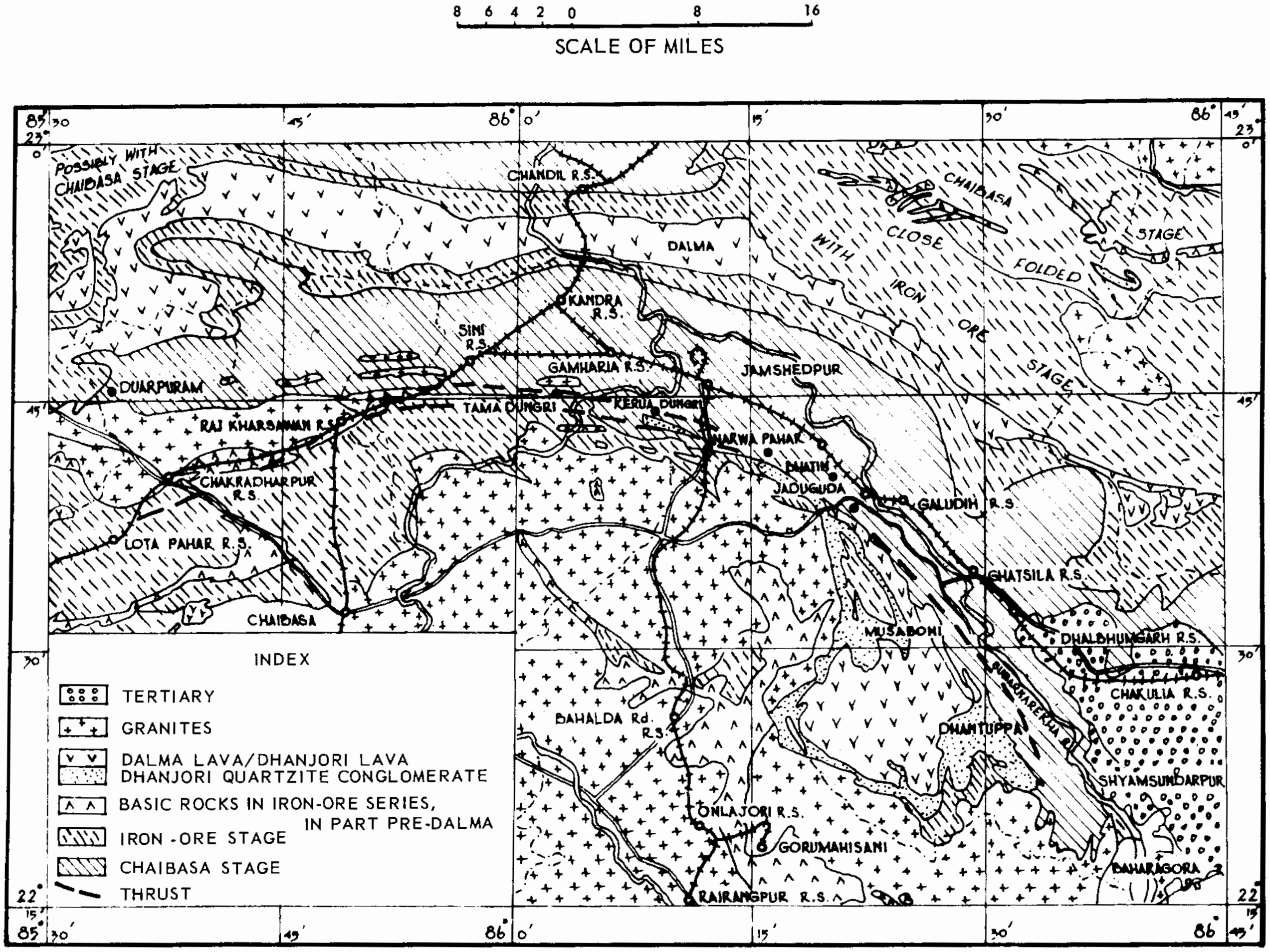

Figure 2. Geological map of Singhbhum Thrust Belt

mylonisation of the rocks in a zone which, in the central part of the belt between the Garanala and Mosabani mines, is only about 100 metres wide while it widens out both to the east and west and also branches into two or more shear zones.

Uranium mineralization is ascribed to the intrusive soda granite, providing the source of hydrothermal solutions, which found an easy passage through the shear planes. Uranium ore occurs as lenses in *en échelon* pattern both along the strike as well as at depth. Along the east-west strike length, these lenses have been observed to shift more towards the hanging wall side. The shear zones appear to form the main control for uranium as well as copper, although the lithological characters of the host rocks have also partly influenced the pattern and grade of mineralization. Workable concentrations of uranium are however observed only where cross-folding and later fractures are dominant.

Studies of mineral paragenesis indicate that mineralization along the thrust belt took place over a long period, the minerals being deposited in two stages, the first to form being apatite; magnetite, closely followed by uranium mineralization and the sulphides including chalcopyrite, were the last to be deposited.

Preliminary reconnaissance in this area in 1950 brought to light good indications of the existence of uranium minerals most of the way along the Thrust Belt and subsequent detailed exploration, especially along shear zone a some 300 m wide has led to the discovery of significant uranium deposits.

During prospecting operations in the sector west of Garanala, uranium mineralization was recognized in a distinct rock type composed of chlorite and sericite in which the foliation was somewhat obliterated and silicification conspicuously absent. On the hanging wall side of this rock are hard, darkish sericite-chlorite schists with tourmaline, magnetite, apatite and patches of quartzite, while the foot wall is formed of chlorite schists with apatite and magnetite, with conspicuous lenticles of quartz. This mineralized host has been traced almost continuously through Narwa Pahar, Garadih, Bayanbil, Keruadungri, Dudra, Basurda and Tama Dungri, a distance of 24 kilometres.

In the central sector, which extends from Garanala to the Mosabani mines, covering Bhatin, Jaduguda, Roam, Surda, etc., the shear zone passes along the foot hills north of Dhanjori Pahar; the host rocks are quartzite breccias and granular biotite-quartz rock sandwiched between mylonites.

In the eastern sector, two mineralized host rocks have been recognised, namely (*a*) the garnetiferous biotite schists of the Chaibasa stage along the eastern shear and (*b*) the apatite-magnetite lenses in the biotite schists which occur along the western shear.

In an area having a heavy rainfall like Singhbhum, leaching of uranium from the outcrops and consequent low order of radioactivity is a common feature in most of the areas chosen for exploration. Particular attention was paid to this fact during detailed prospecting operations, so that, despite lower order radioactivity values on the surface, detailed exploration has at times yielded workable lodes at depth.

Since the ore bodies occur as *en échelon* lenses of varying dimensions generally about 100 to 200 m long, borehole drilling was carried out at rather close intervals. Boreholes were normally spaced at about 60 m centres, in a grid pattern, so that generally 3 lines of holes, progressively exploring deeper levels, have given a fairly good idea of the shape, size and extent of the ore bodies. Thus, by the end of 1963 this Division has carried out nearly 70 000 metres of exploratory drilling at 32 different localities, in the course of which many localities have yielded promising indications of substantial ore reserves. Some—which on the preliminary estimates indicated ore reserves of at least a million tonnes—were considered for development by underground exploration, in order to obtain a clearer picture of the behaviour of the uranium lodes. In the central sector, uranium lodes are generally exposed in hills some 100-200 metres high, and ore bodies are reached by adits which serve also as the main outlets for excavated rock, men and materials as in Jaduguda and Bhatin. In the western sector, the ore bodies occur on low hills or flat terrain, as at Narva Pahar and Keruadungri, and they are reached by shallow exploratory shafts and inclines; levels have been driven from them.

Important deposits

A number of uranium deposits are located in the Singhbhum Thrust Belt among which are the important deposits, from east to west, at Dhantuppa (Khadandungri), Bhalki-Kanyaluka, Surda, Jaduguda, Narva Pahar, Garadih, Keruadungri, Tamadungri and Bijay (Fig. 3). These are briefly described below.

Dhantuppa. Located some 29 km SE of Jaduguda, uranium mineralization was found in biotite schists containing quartz-apatite-magnetite lenses, each varying in length from a few metres to a maximum of 80 m, uranium having a preferential association with the latter. Their uranium content increases with increased magnetite content, but this is not so with apatite. By means of closely spaced trench sampling and borehole drilling aggregating some 2 800 m, ore lenses have been struck over a strike length of about 800 m and it is estimated that approximately 0.63 million tonnes of ore of grade 0.05% equivalent U_3O_8 may be available from this locality.

Occurrences of similar uranium-bearing apatite-magnetite lenses have also been found at Khejurdhari and Purandungri.

Bhalki-Kanyaluka. About 26 to 27 km SE of Jaduguda in the Bhalki-Kanyaluka area, uranium mineralization appears to be confined to two shear zones, the eastern and the western. In the eastern shear, comprising garnetiferous biotite schists the distribution of uranium is more continuous than in the western shear zone and is traceable over a strike distance of 2 000 m.

From drilling data an ore body of 1.5-2 m width with a grade of 0.05% equivalent U_3O_8 was indicated in which the ore mineral is uraninite associated with autunite and torbernite. The indications are that this deposit may reveal sizeable ore reserves on further investigation.

Surda. This deposit situated about 14 km SE of Jaduguda contains two uranium lodes in a quartzite breccia, one of which is exposed on a small hillock for a strike length of 116 m, while the other, on the eastern flank of the Surda hill, extends for 266 m. Exploratory drilling aggregating 4 200 m indicated the presence of a fan-shaped ore body in the small hillock, up to a depth of 166 m from the surface, having an ore potential of approximately 0.26 million tonnes of ore of an average grade of 0.05% equivalent U_3O_8.

Jaduguda. This is by far the best-explored deposit in the Thrust Belt. Extensive investigations by core-drilling (totalling approximately 9 200 m) and underground development have been carried out down to the fourth level through 5 adits and several winzes and drives. Arrangements are in hand to go into full-scale production and a 660 m deep vertical shaft is being sunk.

Here the rocks of the Chaibasa stage are thrust against those of the Dhanjori stage and the intermediate Iron Ore stage has been cut out. The thrust zone is composed mainly of quartzite and quartz schists both of which have undergone various degrees of crushing, fracturing and brecciation with the resultant formation of mylonite, granular rock or breccia depending upon the intensity of shearing.

Uranium mineralization is present as disseminations in a 120 m wide zone but the economic concentrations are restricted to the quartzite breccia surrounded by granular rock. There are two lodes: the main foot-wall lode extends for 700 m, while the subsidiary lode which occurs 50 m on the hanging-wall side of the main lode has been traced for about 200 m. The ore body was found to be more or less continuous with a

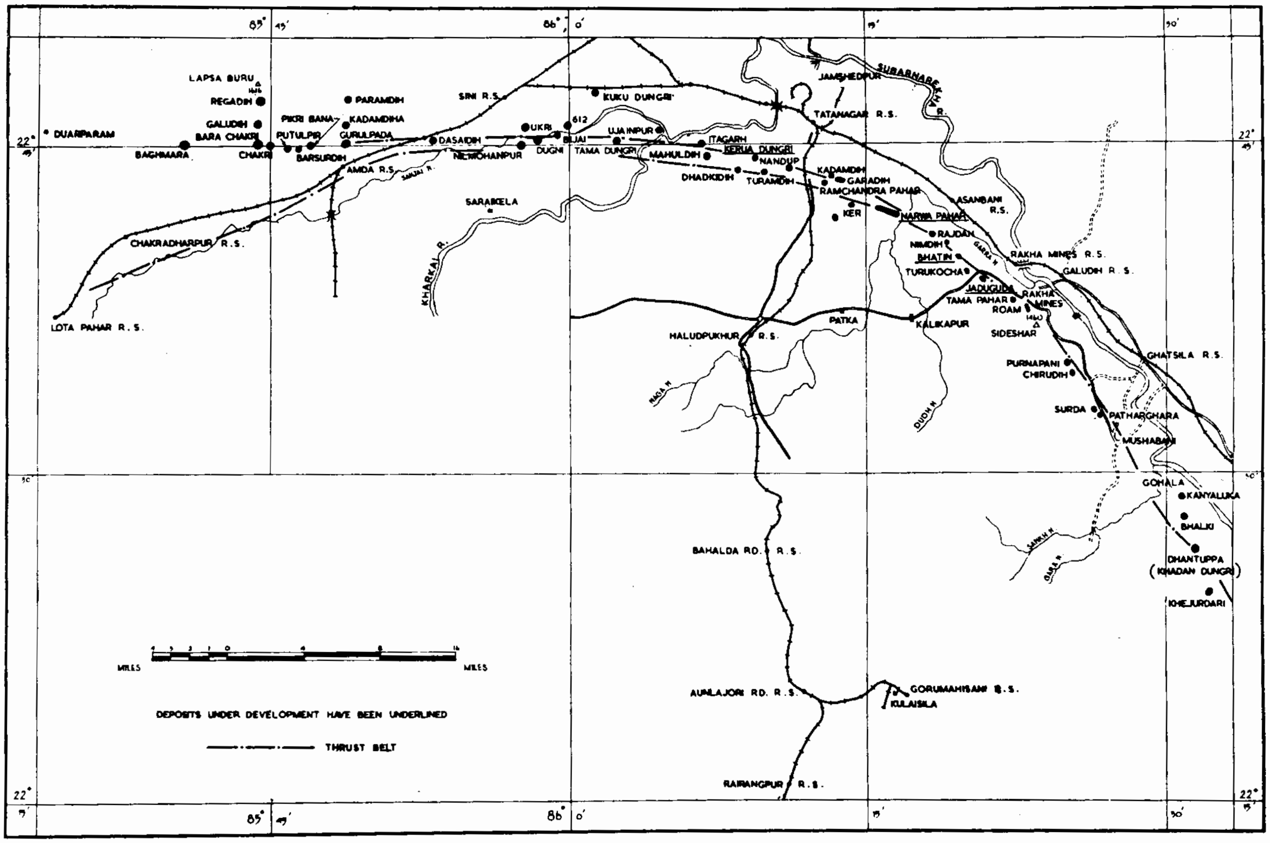

Figure 3. Uranium deposits in Singhbhum Thrust Belt, Bihar

tendency to shift to the hanging-wall as it is followed from west to east. The result is that the richer ore lenses are separated by lean zones. The ore body was seen to persist in depth down to an inclined depth of 660 m up to which exploration has been undertaken.

Uranium mineralization appears to have been controlled by minor cross-folds, the thicker and richer lodes having developed in their synclinal portions while the lean and very poor ones occur in the anticlinal warps. The ore body which at the outcrop is about 3 m thick widens out to 15 m at about 330 m below the ground level.

The chief ore mineral is uraninite occuring as discrete grains along with autunite and torbernite which are noticed frequently in the superficial zone

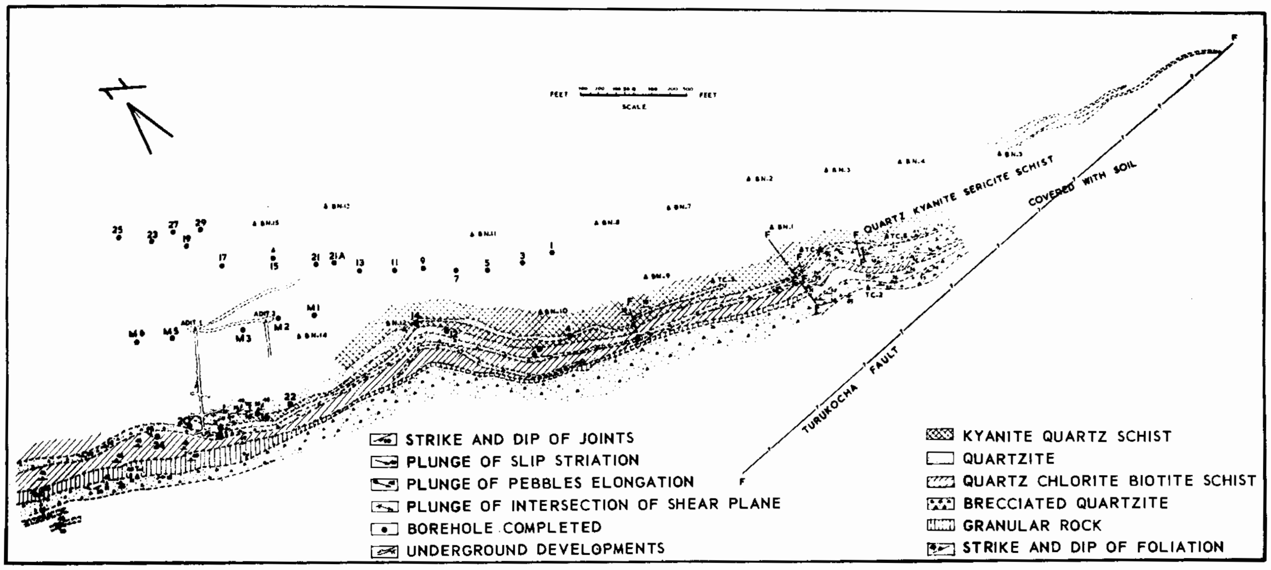

Figure 4. Geological map of Bhatin showing position of boreholes

of weathering. Amenability tests have shown a high percentage recovery of uranium values from the ores by direct leaching.

The indicated reserves calculated from drilling data are of the order of 4 million tonnes at an ore grade of 0.067% equivalent U_3O_8. Some of the deeper boreholes have shown values as high as 0.2% equivalent U_3O_8 and the reserves are thus likely to increase as the deposit is explored to greater depths.

Bhatin. This deposit is about 3.2 km NW of Jaduguda and, like Jaduguda, the host rock is a quartzite-breccia. About 6 000 m of exploratory drilling and some 1 000 m of under-ground development work have indicated two uranium lodes, each 500 m long (Fig. 4).

Down to 300 m depth, the indicated and inferred ore reserves are estimated at about 1 million tonnes of 0.045% equivalent U_3O_8 grade.

Narwapahar. This is by far the largest deposit known in the Singhbhum Thrust Belt and is located 8 km NW of Jaduguda, where uranium mineralization is confined to a 5.5-12 m wide band of a mylonitised chlorite-sericite schist, along a strike length of over 2 000 m in the EW direction. Some of the richer uranium ore lenses are 200 m long and occur in an *en échelon* manner, with a tendency to shift towards the hanging-wall side (Fig. 5).

Up to the end of 1963, about 7 300 m of drilling in 47 boreholes sunk to depths of 50-300 m in a grid pattern, over a portion of the area, has indicated a 3.5 m thick lode and ore reserves of over 1 million tonnes at a grade of 0.077% equivalent U_3O_8. The inferred ore reserves down to a depth of 700 m over the entire mineralized length are estimated at 14 million tonnes and are expected to yield some 10-12 thousand tonnes of uranium oxide.

Garadih. About 13 km NW of Jaduguda near Garadih, uranium mineralization was found along a narrow band, for a distance of about 730 m, in a highly weathered and intensely crushed chlorite-sericite schist. Although the assay values of samples from the surface were low, a few exploratory drill holes have indicated the presence of a 2-2.5 m wide uranium lode, and improvement of assay values up to 0.052% equivalent U_3O_8 at 66 m depth.

The ore reserves are expected to be of the order of 1 million tonnes with an ore grade of 0.05% equivalent U_3O_8.

Keruadungri. This deposit is situated 8 km SW of Jamshedpur town. The host rock for uranium is the chlorite-sericite schist with intensely crushed quartz lenticles. Owing to the effects of weathering and consequent leaching, the ore grade is rather low towards the surface, but at a depth of 30-50 m it improves up to 0.04-0.05% equivalent U_3O_8. Borehole drilling aggregating 7 300 m has proved the existence of two large ore lenses each about 180-200 m long, up to a depth of 100 m, indicating reserves of some 1.25 million tonnes of ore, of grade 0.05% equivalent U_3O_8 (Fig. 6).

Tamadungri. This deposit located some 34 km WNW of Jaduguda is one of the more recent finds in the western part of the Thrust Belt where mineralization has been observed in a 2-3.5 metre-wide band in the chlorite-sericite schists. Boreholes have indicated assay values up to 0.07% equivalent U_3O_8 and further exploratory work is in progress to prove its ore potential.

Bijai. At this locality, situated S of Sanjaynala and about 37 km WNW of Jaduguda, moderately high radioactivity was observed in a 10-15 m wide and 400 m long siliceous chlorite-sericite schist. Assay values of the representative samples from the surface indicated that thorium was present but that uranium had been leached away whereas the drill hole samples have assayed both for uranium and thorium at depth. Further investigations are in progress.

Ore reserves

On the basis of the borehole data and the available geological evidence, it is estimated that down to 700 m depth the four uranium deposits namely, Jaduguda, Bhatin, Narwapahar and Keruadungri and their extensions which are presently under development are capable of yielding uranium ore of the order of 20 million tonnes, which is equivalent to a uranium oxide supply of about 15 000 tonnes. Full scale development of other prospects is likely to increase substantially the present ore reserve estimates, and these may even be doubled as the result of future discoveries. The possibility of recovery of uranium economically as a by-product from copper tailings of the Mosabani, Roam-Sidheshwar and Rakha mines cannot be ruled out, in which case this may also become an additional source of uranium. Thus at this stage, the Singhbhum Thrust Belt appears to be the main source for the uranium required for India's nuclear power programme.

Rajasthan

Udaipur District. Hydrothermal epigenetic uranium-copper mineralization related to the Udaisagar granite boss (post-Algonkian) occurs at two localities on its western flank in Aravalli (Huronian) metasediments. That at Umra, about 4.8 km SW of the southern end of the boss, is confined to the lower limbs of remnant limestone synclines along four main, 1-1.5 m wide, shear zones at the contact of the limestone and the underlying carbonaceous phyllites. Uranium ore occurs as lenses of variable size on the footwall side of the copper zone. The deposit is not economically minable owing to the capricious occurrence of ore lenses and low reserves and grade (0.03%

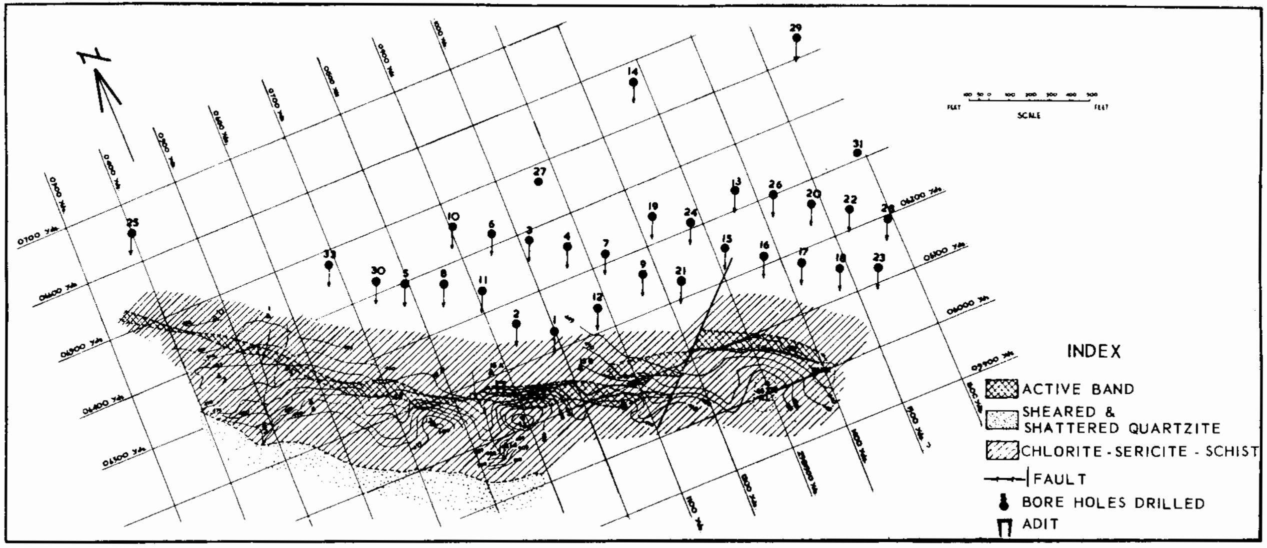

Figure 5. Geological map of Narwa Pahar showing position of boreholes

equivalent U_3O_8). A variety of colourful secondary minerals namely, uranophane, torbernite, metatorbernite, fourmarierite, johannite, zippeite, kasolite, clarkeite, eleisite and gummite with occasional uraninite, however, make the deposit geologically interesting.

The other deposit consisting of streaks, stringers and specks of uraninite and chalcopyrite besides some secondary uranyl minerals, was located by borehole drilling in a brecciated shale zone 213 m long by 6 m wide with abundant clay gouge, between depths of 27 and 46 m from the surface, west of the northern end of the granite boss. This occurrence also is not minable because of the low reserves and grade (0.04% equivalent U_3O_8).

Alwar District. In the old copper workings at Kho-Daribo, torbernite, autunite and infrequent specks of pitchblende occur on the hanging-wall side of the copper zone, in the north-westerly high-angle faults in the strongly folded phyllites, biotite-schists and arkosic quartzites of Delhi (Algonkian) age, intruded

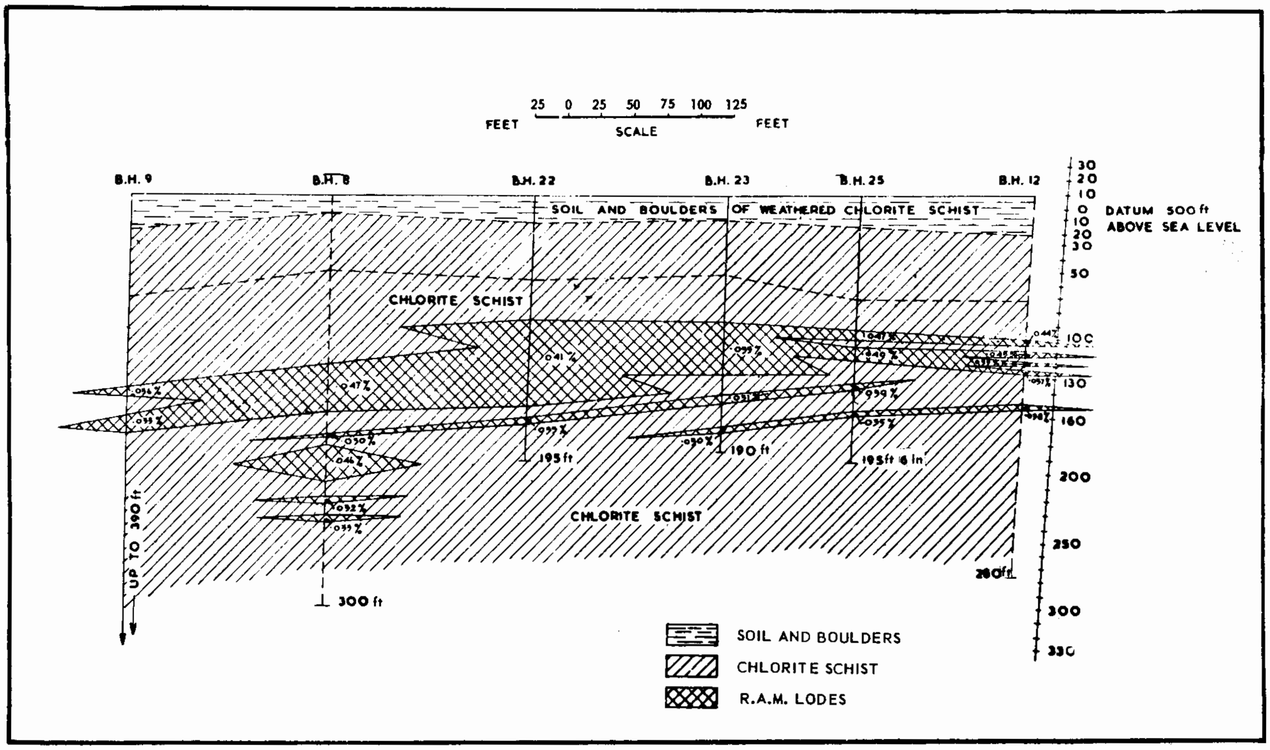

Figure 6. Section along strike through boreholes K/R/D/9, 8, 22, 23, 25 and 12, Keruadungri Hill

by amphibolites, meta-dolerite, and post-Delhi (post-Algonkian) granite, the last named apparently being the source of mineralizing solutions. The fortuitous occurrence and grade of uranium ore (0.01 to 1.99% equivalent U_3O_8) provide little scope for its exploitation except, probably, as a by-product in copper mining.

Jhunjhunu District. Uranium, represented by torbernite and autunite, occurs at Khetri in the 29 km long Babai-Singhana copper belt in Delhi (Algonkian) meta-sediments intruded by dolerite, epidiorite and granite. Samples have analysed up to 0.07% equivalent U_3O_8. Sulphidic copper and iron minerals occur in shears in the underlying garnetiferous schist. Mineralization may be due to the Khetri granite or, alternatively, the source of copper may be epidiorite, and that of uranium the aplite veins. The poverty of ore precludes its extraction.

Punjab

Kulu District. Uraninite associated with brownish quartz veins occurs at Chhinjra in the Parbati River Valley in fold fractures in a quartzite, over-folded to the west with a northerly pitch. This quartzite forms part of the pre-Cambrian (Salkhala) meta-sediments consisting of chloritic phyllites and schists carrying basic sills and some carbonaceous bands and a number of quartzite beds resting on the southwestern flank of the Central Himalaya Gneiss which is of intrusive origin and has invaded rocks of different ages at different periods.

Mineralization is due to post-Salkhala intrusions in the area which are manifested at the surface only by quartz veins traversing the rocks. Test pit samples analysed up to 0.22% U_3O_8. Uraninite or sooty pitchblende occurs as small lenticles, veinlets, dispersed grains, but more commonly as fracture fillings, coatings on the quartz grains or as marginal replacement of quartz grains, and is associated with secondary uranium minerals, tourmaline, occasional specks of chalcopyrite, pyrite, etc., and diagenetic ilmenite and magnetite. Another occurrence of uranium in quartzite was found recently on the western slopes of the Shakiran Dhar, about 45 km south of Chhinjra. These deposits are currently under detailed investigation.

Uttar Pradesh

Chamoli District. Old copper workings occur between Pokhri and Tunji, a distance of about 8 km, at elevations of 1 830-2 135 m in folded north-west trending phyllites and chlorite schists associated with several granite sills, quartzite and limestone bands, basic extrusions, etc., which are regarded by Auden to be a more arenaceous type of the Jaunsars to which Wadia assigns the age as probably Lower or Middle Palaeozoic. The general structure of the area appears to be that of a major anticline overturned to the south-west with possible thrusting and attenuation of the south-westerly limb.

Pitchblende with occasional torbernite occurs in the chlorite-schist as hair-like stringers and minute disseminations along 'S' planes, replacing chlorite at places. Representative test-pit samples analyse up to 0.26% U_3O_8. The sulphide minerals observed are chalcopyrite, pyrite and occasionally stibnite.

Mineralizing solutions appear to have emanated from post-Jaunsar granite intrusives forming part of the Central Himalaya Gneiss, which occurs abundantly about 65-80 km north of this area. The area is being explored for workable uranium deposits.

Other occurrences

Granite plutons and pegmatites

Almost all pre-Cambrian granites and a few syenite occurrences in Peninsular India record some radioactivity, which is due to uranium and/or to thorium in minerals such as monazite, allanite, zircon, xenotime, columbite-tantalite, hematite, magnetite and occasionally, disseminated uraninite, or as an inclusions in accessory minerals, as amorphous material along grain boundaries or in fractures in minerals. Potassium may also contribute substantially to the radioactivity of granites in some cases. Some of the granite occurrences with higher than average radioactivity are noted below.

Salem District, Madras. The radioactivity in some parts of the Suryamalai granite batholith and its pegmatitic facies is due to thorium. In other parts, it is due to uraninite disseminations, secondary uranyl minerals, allanite, minute uraninite inclusions in ilmenite and magnetite and extends down to a depth of about 7.6 m. Bulk samples have assayed 0.03-0.112% equivalent U_3O_8.

Radioactivity in parts of some syenite occurrences at Samalpatti is due to thorite, monazite, an unidentified colourless isotropic vermicular mineral and iron oxide stains.

Mehboobnagar District, Andhra. Low to high radioactivity in patches of granite around Gadwal emanates from sporadic uraninite grains, autunite and possibly zircon.

Udaipur District, Rajasthan. Secondary uranyl minerals, associated with specks of chalcopyrite, pyrite and galena, occuring in intrusive granite up to a depth of 3 m from the surface, are responsible for its radioactivity. Samples analysing 0.015-0.08% U_3O_8 generally show disequilibrium in favour of chemical analysis.

Pegmatites occurring in the mica belts of Bihar, Rajasthan, Andhra and in some localities in Madras, Mysore and Madhya Pradesh, etc., apart from their being a source of beryl and occasionally lepidolite and other minerals contain small pockets and nests of uraninite, e.g., in Bisundini mine (Rajasthan), Abraki Pahar (Bihar) and in Kadawal (Maharashtra). Veins and stringers of uraninite occur in cryolite in a mica pegmatite at Bhunas (Rajasthan). Samarskite, fergusonite, columbite-tantalite, allanite, brannerite, tscheffkinite, triplite, monazite, etc., are also recovered from a few pegmatites during mica mining. Cheralite occurs in small quantities in some pegmatites at Kalkulam (Kerala) and carries 4-6% U_3O_8 and 19-33% ThO_2.

Disseminations of uraninite/pitchblende and smears of secondary uranyl minerals occur in parts of Madhya Pradesh and Maharashtra in three sheared and crushed rhyolite outcrops, sometimes associated with felsite intrusions.

Although generally low-grade, some of the uraniferous granitic outcrops are likely to form future sources of uranium when the richer deposits are depleted, as about 40% of their radioactivity is acid leachable.

Sedimentary rocks

The sedimentary formations of Peninsular India from the Cambrian upwards are essentially thoriferous and only rarely contain sporadic and insignificant amounts of uranium. One such occurrence is in the Motur arkosic sandstone (Middle Permian), a sample of which analysed 0.056% U_3O_8 and traces of ThO_2. Ash samples from a 1.8 m thick coal seam near Nangwal Bibra (Assam), analyse 0.016 to 0.08% U_3O_8 and up to 0.13% V_2O_5. The carbonaceous clay bed overlying the lignite in the Neyveli lignite mine contains 0.004 to 0.086% U_3O_8 accompanied by 3-180 ppm selenium and 90-910 ppm vanadium.

THORIUM DEPOSITS

Monazite, the principal source of thorium, together with ilmenite, sillimanite, zircon, rutile, kyanite and garnet, etc., occurs in beach placers, coastal dune sands and in the sea bed close to the shoreline in Kerala, Madras, Andhra, Orissa, Goa and Gujarat. Inland placers in Madras are locally known as *teri* deposits. River sands found in gneissic and granitic terrains contain variable amounts of these minerals. The inland placers of Purulia (West Bengal) and the adjoining Ranchi Plateau (Bihar), derived form the Archaean granites and gneisses, cover some 608 km^2 in area and contain rich concentrations of monazite. The current-bedded Upper Jurassic sandstones in Kutch and Kathiawar (Gujarat), some Gondwana sandstones and pre-Cambrian conglomerate beds in Rajasthan and Andhra also contain monazite and contribute to its reserves.

Indian monazite analyses 8-10% ThO_2 and contains up to 0.3% U_3O_8.

The monazite deposits of India, perhaps the largest concentrations in the world, are estimated at around 5 million tonnes with a thoria content of 0.45 million tonnes and uranium content of about 15 000 tonnes. The use of thorium in breeder reactors opens up great possibilities of utilizing monazite in the future nuclear power programme of India.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/752 Inde

Aperçus sur les dépôts d'uranium et de thorium en Inde

par K. L. Bhola *et al.*

La Division des minéraux atomiques de la Commission de l'énergie atomique de l'Inde a entrepris à l'échelon national la recherche systématique des minéraux radioactifs. Quelques dépôts d'uranium ont été découverts dans les roches précambriennes en divers points du pays.

Les dépôts les plus importants se trouvent dans les méta-sédiments archéens des charriages de la zone de Singhbhum qui s'étendent sur 140 kilomètres, généralement de l'est vers l'ouest, dans le Bihar du Sud (Inde orientale), où des étages plus anciens de Chaibasa et de minerais d'or sont superposés aux roches Dhanjori plus jeunes.

Les dépôts de valeur commerciale ne se rencontrent que dans certains sites et semblent dépendre en partie de la structure et du caractère physico-chimique des roches, les chloritoschistes siliceux, les schistes biotites et les brèches quartzites étant les plus favorisées.

Des carottages exploratoires faits dans cette zone et représentant au total 65 000 m environ ont permis d'entreprendre des travaux souterrains à Keruadungri, Marwapahar et Bhatin, cependant qu'à Jaduguda une exploitation minière proprement dite a été entamée afin d'alimenter l'usine d'uranium. Les réserves en minerai de la zone sont évaluées à 20 millions de tonnes environ avec une teneur de 0,05 à 0,07 % d'équivalent de U_3O_8. Des recherches plus poussées actuellement en cours pourraient augmenter les réserves de minerais, faisant ainsi de cette zone la source principale d'uranium en Inde.

Des roches précambriennes au Rajasthan contiennent également quelques dépôts sporadiques et moins importants. Des indices très encourageants quant à la présence d'uranium ont été découverts récemment dans le Précambrien de Kulu et dans les roches du début du Paléozoïque du Garwhal dans l'Himalaya central. Dans tous ces cas, les dépôts sont associés au cuivre plutôt qu'au plomb, au zinc ou à l'or. La minéralisation est épigénétique et causée par l'action hydrothermale des fluides provenant des magmas alcalins.

La plupart des granites et des gneiss indiens sont radioactifs en raison de la présence, sous une forme disséminée, d'uranium ou de thorium, ou de ces deux éléments, principalement du dernier. Des minerais secondaires d'uranyle, autunite, uranophane, bayleyite, etc., se rencontrent dans les granites. La plupart des pegmatites contiennent des poches sporadiques de minerais d'uranium et de thorium. Des rhyolites bréchiformes avec des intrusions felsitiques présentent parfois une minéralisation d'uranium.

Les dépôts de thorium sont très dispersés. La monazite, minerai principal de thorium, qui provient des granites et des gneiss du bouclier péninsulaire, se trouve concentrée le long des côtes occidentales et orientales de l'Inde. Il y a quelques riches placers intérieurs et les grès jurassiques de la région du Kutch et du Kathiawar qui contiennent de la monazite.

Les réserves indiennes d'uranium (U_3O_8) et de thorium (ThO_2) sont évaluées respectivement à 30 000 tonnes et 0,5 million de tonnes environ, ces dernières étant parmi les plus importantes du monde.

А/752 Индия

Обзор запасов урана и тория в Индии

К. Л. Бхола *et al.*

Управление атомных минералов Комиссии по атомной энергии Индии занимается систематическими поисками радиоактивных минералов на территории страны. Ряд залежей урана расположен в породах докембрийского периода в различных районах страны.

Наиболее важные залежи приурочены к архейским метаосадочным породам в простирающемся с востока на запад поясе обращенного сброса Сингхбхум длиной 140 *км* в Южном Бихаре (Восточная Индия), где старые стадии Чайбаса и железорудные являются обращенными сбросами над более молодыми породами Дханджори.

Коммерческие залежи ограничены определенными месторождениями и, по-видимому, частично связаны со структурой и физико-химическими особенностями пород, причем наиболее благоприятными являются кремниево-хлоритные сланцы, биотитные сланцы и кварцитная брекчия.

Бурение разведочных скважин составило в общей сложности 65 000 *м* в поясе и позволило провести подземную разведку в районах Керуадунгри, Нарвапахар и Бхатин, тогда как в Джадугуда начата промышленная эксплуатация на обеспечение обогатительной урановой фабрики. Потенциальные запасы руды в этом поясе оцениваются в 20 млн. *т* при содержании закиси-окиси 0,05—0,07%. Проводятся дальнейшие исследования, которые, по-видимому, приведут к увеличению разведанных запасов в этом рудном поле и позволят ему стать главным источником урана в Индии.

В докембрийских породах Раджастана содержатся также небольшие спорадические и малые залежи. Недавно были получены перспективные указания на наличие урана в докембрийских породах Кулу и раннем палеозое района Гарвая в центральных Гималаях. Во всех этих случаях в залежах больше меди, чем свинца, цинка или золота. Минерализация носит эпигенетический характер и образовалась под гидротермическим воздействием жидкостей из сильно щелочной магмы.

Бóльшая часть гранитов и гнейсов в Индии радиоактивна из-за присутствия в них урана и(или) тория, чаще тория. В гранитах встречаются вторичные минералы уранила: отунит, уранофан, бейлиит и др. Большинство пегматитов содержит спорадические карманы урановых и ториевых минералов. Урановые минерализации встречаются иногда в риолитах брекчий с фельзитными интрузиями.

Широко распространены в Индии залежи тория. Залежи основного ториевого минерала монацита, образовавшегося из гранитов и гнейсов полуостровного типа, сосредоточены вдоль западного и восточного побережий Индии. Имеются несколько залежей внутри страны, а также в юрских песчаниках районов Катч и Катиавар.

Индийские запасы урана (U_3O_8) и тория (ThO_2) составляют ориентировочно 30 000 *т* и 0,5 млн. *т* соответственно, причем запасы тория являются одними из крупнейших в мире.

A/752 India

Los yacimientos de uranio y de torio de la India

por K. L. Bhola *et al.*

La Atomic Minerals Division de la Indian Atomic Energy Commission se dedica a la prospección sistemática de minerales radiactivos en toda la nación. Se han hallado varios yacimientos de uranio en formaciones precámbricas de diferentes partes del país.

Los yacimientos más importantes se han encontrado en sedimentos arqueanos, en la zona de fallas de Singhbhum que se extiende en dirección este-oeste a lo largo de 140 km en Bihar meridional (India oriental), en las que los estratos más antiguos de Chaibasa e Iron Ore se han corrido sobre las formaciones más jóvenes de Dhanjori.

Los yacimientos explotables a escala industrial se hallan localizados en ciertas zonas donde parece que se han fijado debido en parte a la estructura y a las características fisicoquímicas de las rocas, entre las que se encuentran los esquistos clorosilíceos, esquistos de biotitas y las brechas de cuarcita como las más ricas en mineral.

En dicha zona se han efectuado sondeos por un total de unos 65 000 metros, que han permitido emprender los trabajos suberráneos en Keruadungri, Marwapahar y Bhatin, mientras que en Jaduguda se ha iniciado la explotación minera a plena escala para alimentar la fábrica de uranio. Se estima que las reservas de la zona se elevan a unos 20 millones de toneladas, con un contenido de U_3O_8 que varía entre el 0,05 y el 0,07 %. Se hallan en curso otras investigaciones que probablemente permitirán cifrar esas reservas en una cantidad superior, con lo que la zona se convertirá en la principal fuente de suministro de uranio en la India.

Las rocas precámbricas de Rajasthan también contienen algunos yacimientos esporádicos y más reducidos. Recientemente se han descubierto indicios favorables de uranio en las formaciones precámbricas de Kulu y en las del comienzo del paleozoico de Garwhal (Himalaya central). En todos estos casos los yacimientos se encuentran asociados más al cobre que al plomo, cinc u oro. La mineralización es epigenética, producida por la acción hidrotérmica de flúidos procedentes de magmas fuertemente alcalinos.

La mayor parte de los granitos y gneis de la India son radiactivos, pues contienen pequeñas cantidades diseminadas de uranio y torio, principalmente este último. También se presentan en los granitos minerales secundarios que contienen uranilos como la autonita, la uranofana, la bayleyita, etc. La major parte de las pegmatitas contienen bolsas esporádicas de minerales de uranio y de torio, así como las brechas de riolitas con intrusiones de felsita presentán también a veces mineralizaciones de uranio.

Los yacimientos de torio se hallan ampliamente difundidos. La monacita, el principal mineral de torio que proviene de los granitos y gneis del escudo peninsular, se concentra a lo largo de la costa occidental y oriental de la India. En el interior se encuentra en algunos ricos placeres y en las areniscas jurásicas de Cutch y Kathiawar.

Las reservas de la India en uranio (U_3O_8) y torio (ThO_2) se calculan en unas 30 000 y 500 000 toneladas respectivamente, figurando las del último entre las más importantes del mundo.

Le gisement gabonais de Mounana

Direction des mines *

HISTORIQUE

Découvert au cours d'un levé radiométrique-auto au scintillomètre le 21 décembre 1956 par une mission du CEA, le gisement de Mounana a été reconnu et mis en exploitation à une allure record. La décision d'exploiter fut prise en effet fin 1958, en même temps qu'était mis à l'étude le traitement du minerai; les travaux d'implantation sur le terrain débutèrent en février 1960. Bien que tout le matériel ait dû être amené par route dans des conditions très difficiles, les usines de traitement mécanique et de concentration chimique du minerai, cette dernière confiée aux Établissements Kuhlmann, étaient terminées au début de 1961 et la production pouvait démarrer en marche industrielle dès le mois de mars de la même année, après un mois seulement d'essais et de mises au point. L'exploitation s'est continuée depuis sans le moindre incident sérieux.

CADRE GÉOLOGIQUE

Le bassin dit Francevillien, dans lequel se trouve le gisement de Mounana, recouvre en discordance totale à l'ouest le massif granitique du Chaillu; il est bordé à l'est, en discordance également, par les sables et grès Batékés, continentaux, d'âge tertiaire.

Le massif du Chaillu, qui représente l'ossature centrale du pays, est constitué par un vaste batholite de granite hétérogène contenant des enclaves de roches métamorphiques et des intrusions de roches basiques, auxquelles sont liés divers indices minéraux (or et bancs de quartzites à oligiste en relation avec les enclaves de roches métamorphiques; colombo-tantalite, étain, dans les filons de pegmatites mis en place dans les roches métamorphiques encaissantes au moment de la formation du granite; nickel et chrome dans les intrusions de roches basiques).

Le bassin de Francevillien lui-même est constitué par une épaisse formation sub horizontale de sédiments détritiques, surtout grèseux, attribuée au Précambrien Moyen. Il se présente comme une cuvette lacustre ou lagunaire remplie par des matériaux arrachés aux chaînes cristallines ou cristallo-phylliennes voisines. Sa stratigraphie apparaît difficile; elle est caractérisée par des alternances successives de sédimentation dans lesquelles on peut reconnaître, en gros:

i) Au sommet, des grès fins avec jaspe et dolomie;

ii) Au centre, des schistes et argilites avec à la base un niveau dolomitique;

iii) A la base des grès grossiers avec feldspath et calcite, avec un niveau inférieur conglomératique.

GISEMENT

Le gisement se présente comme un amas de minerai situé dans les grès grossiers inférieurs remontés à la verticale, et limité d'une part par deux bancs de grès, d'autre part par deux failles qui les recoupent. Les failles mettent en contact les grès grossiers inférieurs, d'une part avec un horst probable du socle, d'autre part avec les séries pélitiques sus-jacentes.

La minéralisation de surface est constituée par une espèce minérale nouvelle, de couleur jaune, dénommée Francevillite. C'est un vanadate d'uranium et de plomb $[(Ba,Pb)O.2UO_3.V_2O_5.5H_2O]$. A partir d'une quarantaine de mètres de profondeur, le minerai consiste en divers oxydes noirs d'uranium mélangés à des quantités plus ou moins grandes d'oxyde de vanadium et de produits d'altération sulfurés; mais la Francevillite peut être présente dans les cassures.

Il semble que l'on puisse estimer les réserves connues à un million de tonnes d'un minerai à une teneur de 0,4 %.

EXPLOITATION

Le gisement est exploité par la C^{ie} des mines d'uranium de Franceville, société gabonaise dont le siège est à Libreville, et dont les principaux actionnaires sont la C^{ie} de Mokta et le Commissariat français à l'énergie atomique. L'exploitation se fait pour l'instant à ciel ouvert et se poursuivra ainsi jusqu'à la profondeur de 78 m (cote 340); mais parallèlement un puits est en creusement pour préparer l'exploitation souterraine, qui viendra sous peu relayer l'exploitation à ciel ouvert actuelle.

Préparation mécanique et traitement chimique

Après concassage et broyage, le minerai est attaqué à froid par l'acide sulfurique dilué, et transformé en sulfate d'uranyle soluble. L'uranium est précipité par la magnésie; l'uranate ainsi obtenu est enfin filtré, séché et mis en fûts. Afin d'éviter le transport de l'acide sulfurique liquide, celui-ci est directement

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* Ministère de l'économie nationale, du plan et des mines.

fabriqué dans une usine annexe, en utilisant du soufre en provenance de Lacq; quant à la magnésie, elle est importée de Grèce.

Production

La production de l'ordre de 120 t de concentrés par mois, est évacuée par route jusqu'à M'Binda, qui est situé à 120 km de Mounana, et où se trouve la tête du chemin de fer Comilog; elle emprunte ce chemin de fer sur 285 km jusqu'à Dolisie (Congo), puis le chemin de fer Congo-Océan sur 200 km jusqu'au port de Pointe-Noire.

Personnel

L'ensemble des chantiers, ateliers et bureaux occupe actuellement 310 personnes; un effort a été fait pour le logement: les maisons, construites non loin des installations entre 500 et 600 m d'altitude, sont relativement très confortables et bénéficient d'un site et d'un climat agréables.

CONCLUSION

En dépit de difficultés d'accès considérables au début, l'installation industrielle de Mounana constitue l'exemple type de la mise en valeur d'un nouveau gisement par des moyens modernes, dans des conditions exceptionnelles de rapidité et de sûreté. Il va sans dire que la collaboration a été à tout moment complète entre l'État et la société exploitante.

ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/883 Gabon

The Gabonese mineral deposits in Mounana

Direction des mines

The Francevillian basin, attributed to middle Precambrian, which covers the Chaillu massif (the central spine of Gabon) includes the uraniferous deposits of Mounana.

These last contain, on the surface, a yellow type of mineral, called Francevillite, which is a vanadate of uranium and lead, $[(Ba,Pb)O.2UO_3.V_2O_5.5H_2O]$. At greater depths black oxides of uranium mixed with varying quantities of vanadium oxides and contaminated with sulphur products are found, but Francevillite may be present in fractures. The known reserves are estimated at one million tonnes of mineral of a 0.4 % content.

The Mounana deposit has been worked since 1961. So far, the actual extraction has been by surface mining but underground mining will be used in the near future. The mineral is mechanically dressed and chemically concentrated in plants at the mine. The chemical treatment consists of a cold leaching with dilute sulphuric acid followed by precipitation of uranate from the resulting uranyl sulphate solution using magnesia. The precipitate is then filtered and dried.

The production is of the order of 120 tonnes of concentrate a month.

A/883 Габон

Габонское месторождение Мунана

Управление рудника

Урановое месторождение Мунана находится в Франсвильском бассейне, относящемся к средней докембрийской эпохе и расположенном в массиве Шеллю (центральная часть Габона).

На поверхности этого месторождения встречается молодая порода, получившая название франсвиллит, которая представляет собой ванадат урана и свинца $(Ba, Pb)O \cdot 2UO_3 \cdot V_2O_5 \cdot 5H_2O$); в глубине залегают различные черные окислы урана, смешанные с различными количествами окиси ванадия и сернистыми продуктами, но франсвиллит может также встречаться и в складках. Известные запасы франсвиллита оцениваются в 1 млн. *т* с содержанием 0,4%.

Месторождение Мунана разрабатывается с 1961 г .В настоящее время добыча ведется открытым способом, однако в ближайшем будущем намечается также использовать подземные выработки. Минерал перерабатывается в концентрат механическим и химическим методами на установках, расположенных в районе рудника. Химическая переработка включает в себя обработку минерала холодной разбавленной серной кислотой; затем полученный растворимый в воде уранилсульфат обрабатывают окисью магния для получения уранита, который выпадает в осадок, отфильтровывается и высушивается.

Производительность — порядка 120 *т* концентрата в месяц.

A/883 Gabón

El yacimiento gabonés de Mounana

Direction des mines

La cuenca denominada Francevillana, atribuida al precámbrico medio, que recubre el macizo de Chaillu (armadura central del Gabón) contiene el yacimiento uranífero de Mounana.

En dicho yacimiento se halla en superficie una especie mineral amarilla, denominada Francevillita, que es un vanadato de uranio y plomo $[(Ba,Pb)O.2UO_3.V_2O_5.5H_2O]$; en profundidad se encuentran diversos óxidos negros de uranio mezclados a cantidades variables de óxido de vanadio y de productos de alteración sulfurados, pero la Francevillita puede existir en las fisuras. Las reservas conocidas se calculan en un millón de toneladas de mineral de riqueza del 0,4 %.

El yacimiento de Mounana está en explotación desde 1961. La extracción se efectúa a cielo abierto, pero en un futuro próximo se proyecta la explotación subterránea. El mineral se somete a tratamiento sobre el terreno en las fábricas de preparación mecánica y de concentración química. El tratamiento químico comprende un ataque en frío con ácido sulfúrico diluido; se trata después el sulfato de uranilo soluble así formado con magnesio para obtener un precipitado de uranato, que se filtra y seca.

La producción es del orden de las 120 toneladas de concentrados al mes.

Record of session 2.11

Uranium and thorium resources and requirements

Chairman: O. A. Quihillalt (Argentina)

Paper P/72 (presented by J. Mabile)

DISCUSSION

R. L. FAULKNER (United States of America): In the paper you presented it is noted that exploration and development are needed to find new deposits to meet future requirements. Do you think it probable that sufficient low-cost uranium will be found to meet requirements during a period of several decades?

J. MABILE (France): It would be unreasonable to assume that the world reserves of low-cost uranium-bearing ores are found only in areas where traces or deposits were discovered long before the atomic age. I believe that economically exploitable deposits could also be found in other areas, but prospecting would have to be carried out in less familiar terrain than that in which the present deposits are mined. In this connection, France's experience in Africa prompts a certain degree of prudence. Expenditure on prospecting, as part of the cost-price, would certainly increase as a result of the difficulties involved and thus it would be difficult to maintain present prices. It should also be borne in mind that it has only been possible to exploit the rich deposits known at present by agreeing to pay higher prices for large quantities, \$10-11/1b U_3O_8, than those obtaining at present.

Paper P/883 (presented by F. N'Guema N'Dong)

DISCUSSION

J. GABELMAN (United States of America): Has prospecting indicated the possibility of finding other uranium deposits in Gabon similar to the one you described?

I should also like to ask if the Mounana deposit bears any relation to the Congo uranium deposits or the Northern Rhodesian copper belt.

F. N'GUEMA N'DONG (Gabon): Apart from the deposit worked at Mounana, there have been many indications that similar ores exist in various parts of Gabon and surveys are continuing, but it is still impossible to say whether such surveys will show that new deposits exist.

As to your second question, the only thing that can be said at present is that the Mounana deposit lies in the same Precambrian formations as surround the Congo basin. It is still impossible to correlate the Rhodesian Precambrian formations with those in the Francevillien basin in Gabon.

Paper P/636 (presented by J. J. Went)

DISCUSSION

E. SVENKE (Sweden): Several papers allocated to this session have stressed the importance of continuing uranium prospecting and also expressed the fear that there would be a shortage of uranium within a few decades which would result in an increase in price. In the paper presented by Dr. Went, conclusions are drawn with regard to the course to be followed in the development of nuclear power and the choice of reactor types. It is stated in the paper that the present known reserves of uranium available at \$10/1b U_3O_8 are 450 000 metric tons and that the amount available at up to \$30/1b U_3O_8 might be 1 650 000 metric tons. The last figure includes uranium available in the Swedish uranium-bearing shales. I can now give more details of this situation in Sweden. The shale resources are calculated to contain at least 1 million metric tons of uranium. They are located mainly in one homogeneous deposit, easily accessible in the central-southern part of the country. A mine and a milling plant, which will be in operation from the middle of 1965, will be able to produce 120 metric tons of uranium per year and the plant will provide accurate information regarding the appropriate technique and the cost of recovery. However, I can already state that, when the operation is on a still larger scale, it will be possible to recover concentrates from this enormous potential body of ore at a cost well below half the maximum figure of \$30 and perhaps even at a cost of about \$10.

The authors of paper P/636 also do not take account of the fact that there are already heavy water power systems which make very efficient use of uranium.

Having regard to these factors, I do not agree with the conclusion in the paper that the fast development of breeder reactors is urgent, and I disagree, in particular, with the conclusion that the large-scale application of present-day power reactors is undesirable. The increase in the known world reserves resulting from further exploration, together with the large, proven Swedish reserve of uranium, which will be available with an extraction cost only slightly higher than that for existing rich raw material, will stabilize prices for a long time at a level not very much higher than at present and thus ensure that the existing power reactor systems can be utilized.

J. J. WENT (Netherlands): While an extra 1 million tons of uranium in the $10-30/1b range would be very desirable, it would not fundamentally alter the conclusions in the paper I presented since millions of tons of cheap uranium will be required to carry out future large-scale nuclear energy programmes. An additional million tons at a price two to three times the present price would merely extend by a few years the period in which breeder reactors could be developed. Thus the development of such reactors is urgently required to enable us to start the production programme in 1970, on the lines indicated in Table 4.

I should also like to point out that the GCR and BWR reactors, not the heavy water reactor, are the proven types. Only small prototypes of heavy water reactors are available and, as stated in the conclusions to the paper, they could be useful during an intermediate period.

Paper P/494 (presented by V. Membrillera Membrillera)

DISCUSSION

J. LECOQ (France): Are the figures given in the paper for the deposits discovered in shales in Spain regarded as definitive, or is any increase hoped for, particularly by extending the depth of workings?

I should also like to ask if there is any reason to expect that the mobile or semi-mobile ore processing plants now planned or being tested will operate at cost-prices equal or similar to those obtained at conventional plants.

V. MEMBRILLERA MEMBRILLERA (Spain): We estimate that the uranium reserves already discovered in the Cambrian shales in Salamanca amount to more than 3 500 000 tons, or 3 500 tons of U_3O_8; our surveys, however, lead us to believe that they will not exceed 4 000 or 5 000 tons of U_3O_8. Although core drilling has shown that there are mineral deposits at a depth of 60 metres, these are only sporadic, and we continue to believe that the average depth at which such deposits will be found is 25 to 30 metres.

I should like to ask my colleague, Dr. Josa García, to answer your second question.

J. M. JOSA GARCÍA (Spain): I do not think the question can be answered in general terms. With certain minerals, however, and in certain cases of small tonnage, etc., conversion costs can be obtained which are similar to those in a conventional lay-out, mainly because of a better use of reagents, a smaller volume of liquids and less depreciation.

J. GABELMAN (United States of America): In view of the discovery of new uranium deposits, does Dr. Membrillera think that Spain will become an exporter of uranium?

V. MEMBRILLERA MEMBRILLERA (Spain): My colleagues and I cannot give a definite answer, since the decision will obviously have to be taken at a higher level. It is reasonable to assume, however, that the answer to your question will depend on the Spanish nuclear energy programme and the market conditions with regard to uranium in the future.

Paper P/752 (presented by K. K. Dar)

DISCUSSION

V. ZIEGLER (France): Has the Atomic Minerals Division done any surveys on formations in the Gondwana series? If so, what were the results?

K. K. DAR (India): We have carried out radiometric surveys of almost all horizons of the Gondwana formations, but no significant concentrations of uranium have been found so far. On the other hand, local concentrations of thorium in narrow bands have been located. The remaining parts of the Gondwana formations are being surveyed and the results to date show that these formations are essentially thorium-bearing.

Papers P/256 (presented by R. L. Faulkner) and P/24 (presented by J. W. Griffith)

(It was agreed that these papers should be discussed together.)

DISCUSSION

J. L. GILLAMS (United Kingdom): Could Dr. Faulkner please explain the grounds on which paper P/256 predicts a level of world U_3O_8 production in 1970 as high as 14 000 tons per annum? Is it not possible, and even likely, that stocks of uranium already in hand in the United States and in other countries will lead to a demand on new production in 1970 substantially less than this?

R. L. FAULKNER (United States of America): The figure of 14 000 tons per annum in 1970 includes about 8 000 tons to be purchased in 1970 by the United States Atomic Energy Commission from United States mines. This leaves about 6 000 tons, the production of which is now planned by other countries such as South Africa, Canada, France, Australia, etc. It is expected that requirements will increase so rapidly after 1970 that the world stocks in hand would have no more than a temporary effect on the demand. The United States does not intend to sell any uranium it may have on hand in a manner which would be deleterious to the domestic mining industry.

R. BLOCH (Israel): I gather from paper P/256 that after 1970 considerable quantities of lower-grade uranium ores will have to be processed. Will this necessitate important changes and new processing techniques?

R. L. Faulkner (United States of America): I do not envisage any immediate change in the grade of material mined and processed. Provided that the exploration programmes are successful, the present grades may continue to be used for a long time. However, improved mining and milling techniques have made it possible to mine and process successively lower grades of material.

J. Mabile (France): It would appear from these papers that the reserves reported in the \$10-30/lb U_3O_8 price range are relatively small, for they represent, including the potential resources, 700 000 tons of U_3O_8 in the United States and 300 000 tons in Canada, making a total of 1 million tons. This seems to be a small addition to the reserves in the \$5-10 range (a total of 350 000 plus 450 000 tons, i.e. 800 000 tons) and it may therefore be assumed that the exhaustion of reserves at current prices (\$8-10) will be followed closely by that of reserves at \$30. Accordingly, it is to be feared that prices will quite soon rise to \$30 and more, taking into account the estimated requirements for the next twenty years or so. Is such pessimism concerning the future development of nuclear energy in fact well-founded?

R. L. Faulkner (United States of America): I am optimistic regarding the probability of finding larger supplies of uranium in the \$8-10 range, but I agree that such optimism should be tempered with caution. I believe that we shall discover many more deposits of the kind now supplying uranium.

J. W. Griffith (Canada): Our future reserves, including the present reserves, should amount to about 1 million tons of U_3O_8. In our view, this is a significant figure.

R. L. Faulkner (United States of America): The paper presented by Dr. Griffith states that Canada should be able to find as much uranium in the future as it has in the past. Does Dr. Griffith expect that the Canadian mining industry will take note of the rising demand and undertake the necessary exploration and development?

J. W. Griffith (Canada): Yes, I expect that the Canadian mining industry will take note of a rising demand for uranium when there is some firm indication that orders and long-term contracts will be obtained. In other words, the industry is not likely to undertake exploration and development until it can be assured of a market for its product.

A. Gangloff (France): You say that the Canadian reserves in January 1964 amounted to 188 000 metric tons of U_3O_8. The EURATOM publication* referred to gave a figure of 170 000 tons of U_3O_8 for January 1962 or, taking into account the operations in 1962 and 1963, 150 000 tons for January 1964. There is therefore apparently a considerable increase. The EURATOM publication drew attention to the possible existence of 70 000 supplementary tons at Elliot Lake but did not include them in the reserves. Do you think that the difference between your figures and those given in the EURATOM publication results from a re-assessment of the mine or is it due to the addition of the potential reserves which the EURATOM publication did not take into consideration?

J. W. Griffith (Canada): Partly one and partly the other. In fact about one half of the 70 000 tons reported by EURATOM as a supplementary amount, was included in our reserve figure for January 1964. The reason for not including the entire 70 000 tons is that we felt the remainder should now be reported as potential ore, as explained in our paper.

J. Mabile (France): With regard to the French reserves, you indicated in your oral presentation that the earlier estimate of 50 000 tons had been reduced to 28 000 tons. The estimate has not, in fact, been reduced: the figure of 50 000 tons, given in 1958, represented the total potential that could be hoped for in France and the figure of 28 000 tons of uranium metal represents the proven reserves today. The potential is still estimated at 50 000 tons, which represents a slight increase, taking into account the tonnage mined since 1958.

Paper P/405 (presented by P. N. Stipanicic)

DISCUSSION

A. Gangloff (France): The paper mentions a certain number of lodes which, after a fairly small amount of work had been carried out, yielded ores of very high grade. Is the importance of these lodes fairly limited or do you think that additional investigations should be carried out to determine their extent, both lateral and in depth, or that their satellite structures should be scanned?

P. N. Stipanicic (Argentina): So far the two lodes in question, which are in the Estela and San Sebastian deposits, have yielded, after some years of work, small quantities of high-grade ore, amounting in all to 5 000 tons. In the first case the U_3O_8 content was 0.5% and in the second 0.85%. Exploration of the San Sebastian deposits showed that the grade decreases with depth. Preliminary geochemical surveys in the San Sebastian area and the existence of various deposits not yet explored, because they are owned by private firms, indicate that the district may be of some interest. Near the Estela deposits only some small amounts of ore have been found (which are of current interest since the price is \$8/lb U_3O_8) but the development

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* P/24, Ref. 1.

of these deposits to date does not suggest that there are great possibilities of further development. For those reasons, even if further exploration shows that these lode deposits are larger, taking into account the parameters of those already known, it is preferable at present not to attach greater importance to them than to sedimentary deposits.

J. LECOQ (France): In addition to the deposits and indications described in the paper, do you think uranium may be found in Argentina under the recent geological horizon in the pampas and is it intended to investigate this possibility?

P. N. STIPANICIC (Argentina): Almost throughout the entire area selected in Argentina as potentially uranium-bearing, totalling approximately 1 200 000 square kilometres, there is no recent geological horizon. In the remaining area, which amounts to over 1 800 000 square kilometres, there is a tertiary and quaternary sedimentary horizon, the depth of which ranges from hundreds to thousands of metres. The outcrops of these Cenozoic formations near the edges of the oldest cores have not yet shown any interesting indications of uranium-bearing accumulations. For that reason, these areas are not likely to be of major importance in the immediate future and thus there are no current plans for investigating their possibilities.

Under the terrain there are Triassic formations (sediments and vulcanites), Anthracolithic formations (sediments) and Devonian formations (sediments) which might be uranium-bearing, but on account of the depth at which they lie they have not been included in the present or future programmes as there are much more favourable zones available.

L. GUTIÉRREZ JODRA (Spain): In the heap-leaching process the pre-concentrates are obtained by precipitation with lime; if I understand correctly, they contain approximately 5% of U_3O_8. I should like to know, first, what subsequent treatment is used to recover uranium and, secondly, the total cost of the nuclear-pure uranium obtained by this method or how it compares with that of uranium obtained by conventional leaching.

P. N. STIPANICIC (Argentina): The pre-concentrates are sent to the Córdoba plant for final refining. At present they are treated with sulphuric acid solution and the charged liquids go through the amine-solvent plant, which yields concentrates with 82-85% U_3O_8 content. In October the process will be varied in order to obtain ammonium uranyl tricarbonate of high purity (sub-nuclear).

As to your second question, it has been found preferable to establish a comparison between the costs of yellow cake produced from the pre-concentrates and those of yellow cake produced by conventional plants. The Don Otto deposit contains an ore very suitable for heap leaching and the yellow cake obtained is lower in price, by about $1-1.50 per lb, than that from conventional plants.

T. BATUECAS RODRIGUEZ (Spain): What is the price of the uranium pre-concentrate when the Don Otto leaching process is used? I should also like to ask if you intend to use another method of recovery, apart from the direct precipitation of the leaching liquids.

P. N. STIPANICIC (Argentina): The price is between $6 and $6.50 per lb of U_3O_8 to which must be added the cost of transport to the Córdoba plant and its final refining. It should be stressed that the price of sulphuric acid has a very considerable effect on the cost, since it must be transported a distance of 1 400 kilometres over difficult roads. At present attention is being given to the possibility of reducing costs, by using other leaching agents, at least up to specified levels of extraction. These agents would be ferric and ferrous sulphates, the cost of which is low in Argentina.

With regard to your second question, I should like to point out that the heap-leaching method is suitable for the extraction of uranium from ore. On the other hand, although the results obtained in the calcium precipitation of the loaded liquids are being improved, plans are being made for the establishment of an amine-solvent plant in Don Otto for the production of yellow cake with a U_3O_8 content of over 80%.

GENERAL DISCUSSION

R. SPENCE (United Kingdom): We have for some years been studying the extraction of uranium from sea water. This now appears to be technically feasible, but considerable development will be required before an industrial plant can be specified. Our estimates of cost are necessarily extremely tentative but we think production of U_3O_8 in the medium price range, i.e. about $20 per lb, will be possible Our findings will be published in the next issue of *Nature*.*

J. J. WENT (Netherlands): If uranium can be extracted from sea water on an industrial scale at a cost of about $20 per lb, breeder reactors will merely be interesting from the economic point of view. For this purpose, however, the proven types of existing power reactors may be very uneconomic.

O. A. QUIHILLALT (Chairman): Extraction of uranium from sea water at reasonable cost would of course have an important bearing on the whole situation. The present position can, I think, be summed up as follows. The uranium reserves of the Western world can be estimated at 500 000 tons which can be recovered at a cost of $8 per lb. It is hoped that reserves will be doubled in the next 20 years. Some 3 million tons will be required by the year 2 000. If the use of heavy-

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* Davies, R.V., Kennedy, J., McIlroy, R.W., Spence, R. and Hill, K.M., *Extraction of Uranium from Sea Water*, Nature, 203, 1110 (1964).

water reactors or breeders is intensified, the figure may be reduced to 1-2 million tons. All the estimated resources must be checked in the near future, and for this purpose it is essential to recommence prospecting and exploration immediately. Finally, there are large thorium resources, but is it still rather premature to introduce them into present-day nuclear energy programmes.

Compte rendu de la séance 2.11

Ressources et besoins en uranium et thorium

Président : O. A. Quihillalt (Argentine)

Mémoire P/72 (présenté par J. Mabile)

DISCUSSION

R. L. Faulkner (États-Unis d'Amérique) : Le mémoire que vous avez présenté souligne qu'il est nécessaire de continuer la prospection et les études des gisements pour trouver de nouveaux dépôts en vue de faire face aux besoins futurs. Estimez-vous qu'il est probable que l'on trouvera suffisamment d'uranium à bas prix pour satisfaire les besoins au cours d'une période de plusieurs décennies?

J. Mabile (France) : Je pense qu'il serait paradoxal d'affirmer que les seules réserves mondiales de minerais d'uranium à bas prix n'existent que dans les régions dans lesquelles des indices ou des gisements ont été découverts bien avant ce que l'on peut appeler l'ère atomique. Je pense que l'on pourra trouver aussi dans d'autres régions des gisements exploitables économiquement, mais il faudra prospecter dans des zones moins familières que celles dans lesquelles les gisements actuels sont exploités. A ce sujet, l'expérience française en Afrique incite à une certaine prudence. La part des prospections dans le prix de revient ira en croissant en raison des difficultés rencontrées, et il sera difficile de maintenir les prix actuels. Il faut également se rappeler qu'il n'a été possible d'exploiter les riches gisements actuellement connus qu'en acceptant de payer pour des tonnages importants des prix plus élevés, 10 à 11 dollars par livre de U_3O_8, que ceux pratiqués à l'heure actuelle.

Mémoire P/883 (présenté par F. N'Guema N'Dong)

DISCUSSION

J. Gabelman (États-Unis d'Amérique) : Les prospections permettent-elles d'envisager la possibilité de trouver d'autres gisements d'uranium au Gabon, analogues à celui que vous avez décrit?

Je voudrais aussi demander si le gisement de Mounana a une relation quelconque avec les dépôts d'uranium du Congo et avec la ceinture du cuivre de la Rhodésie du Nord.

F. N'Guema N'Dong (Gabon) : En dehors du gisement exploité à Mounana, il y a de nombreux indices de l'existence de minerais semblables dans diverses parties du Gabon, et les levés continuent, mais il est encore impossible de dire si ces levés révéleront l'existence de nouveaux gisements.

En ce qui concerne votre seconde question, la seule chose que l'on puisse dire pour le moment c'est que le gisement de Mounana se trouve dans les mêmes formations précambriennes que celles qui entourent le bassin du Congo. Il est encore impossible de lier les formations précambriennes de Rhodésie à celles du bassin de Franceville au Gabon.

Mémoire P/636 (présenté par J. J. Went)

DISCUSSION

E. Svenke (Suède) : Plusieurs mémoires présentés à cette séance ont souligné l'importance que présente la prospection de l'uranium à l'avenir, et aussi exprimé la crainte de voir apparaître dans quelques décennies une pénurie d'uranium, qui entraînerait une augmentation des prix. Le mémoire présenté par le D^r Went formule des conclusions concernant la façon de développer l'énergie nucléaire et le choix des types de réacteurs. Il est indiqué dans le mémoire que les réserves actuellement connues d'uranium disponible à 10 dollars par livre de U_3O_8 s'élèvent à 450 000 t et que les quantités disponibles à des prix allant jusqu'à 30 dollars par livre de U_3O_8 pourraient être de 1 650 000 t. Ce dernier chiffre comprend l'uranium disponible dans les schistes uranifères suédois. Je peux donner maintenant plus de détails sur la situation en Suède dans ce domaine. Les ressources en schistes contiennent, d'après les calculs, au moins 1 million de tonnes d'uranium. Elles sont essentiellement situées dans un seul gisement homogène, facilement accessible dans la partie centre-sud du pays. Une mine et une usine de traitement, qui entreront en service au milieu de 1965, permettront de produire 120 t d'uranium par an, et l'usine fournira des renseignements précis sur la technique appropriée et le coût du traitement. Cependant, je peux déjà dire qu'en opérant à plus grande échelle il sera possible de produire des concentrés à partir de cette énorme masse potentielle de minerai à un prix qui sera nettement inférieur à la moitié du chiffre maximal de 30 dollars, et peut-être même à un prix voisin de 10 dollars.

Les auteurs du mémoire P/636 ne tiennent pas compte non plus du fait qu'il y a déjà des réacteurs de puissance à eau lourde qui utilisent très efficacement l'uranium.

Compte tenu de ces facteurs, je ne suis pas d'accord avec les conclusions du mémoire, selon lesquelles le développement rapide des réacteurs surgénérateurs est un problème urgent, et je ne suis pas d'accord, en particulier, avec la conclusion selon laquelle l'utilisation à grande échelle des réacteurs de puissance actuels n'est pas souhaitable. L'augmentation des réserves mondiales reconnues grâce à la continuation de la prospection, ainsi que les réserves d'uranium suédois, importantes et prouvées, qui seront disponibles à un coût d'extraction légèrement supérieur seulement au prix correspondant pour les minerais riches existants, stabiliseront les prix pour longtemps à un niveau à peine supérieur au niveau actuel, et assurent donc la possibilité d'utilisation des systèmes existants de réacteurs de puissance.

J. J. Went (Pays-Bas) : Bien qu'un million de tonnes supplémentaires d'uranium dans l'intervalle de prix de 10 à 30 dollars la livre soit très souhaitable, ceci ne change pas fondamentalement les conclusions du mémoire que j'ai présenté, car il faudra des millions de tonnes d'uranium à bon marché pour entreprendre les programmes futurs d'énergie nucléaire à grande échelle. Un supplément d'un million de tonnes à un prix égal à deux à trois fois le prix actuel ne ferait que prolonger de quelques années la période au cours de laquelle les réacteurs surgénérateurs pourraient être mis au point. Ainsi, le développement de ces réacteurs est nécessaire et urgent pour nous permettre de commencer la mise en œuvre du programme de production en 1970, selon le plan indiqué dans le tableau 4.

Je voudrais aussi souligner que les réacteurs à gaz et les réacteurs à eau bouillante, et non pas les réacteurs à eau lourde, représentent les types éprouvés. Il n'existe que de petits prototypes de réacteurs à eau lourde et, comme l'indiquent les conclusions du mémoire, ils pourraient être utiles pendant une période intermédiaire.

Mémoire P/494 (présenté par V. Membrillera Membrillera)

DISCUSSION

J. Lecoq (France) : Les chiffres de réserves donnés dans ce mémoire pour les gisements découverts dans les schistes en Espagne sont-ils considérés comme définitifs, ou bien espère-t-on les augmenter, en particulier par une extension en profondeur de l'extraction?

Je voudrais aussi demander s'il y a des raisons d'espérer obtenir dans les installations de traitement de minerai mobiles ou semi-mobiles, actuellement à l'essai ou en projet, un prix de revient égal ou voisin de celui qu'on obtient dans une usine de type classique.

V. Membrillera Membrillera (Espagne) : Nous estimons que les réserves d'uranium déjà découvertes dans les schistes cambriens de Salamanque s'élèvent à plus de 3 500 000 t, soit 3 500 t de U_3O_8; nos levés, cependant, nous conduisent à penser qu'elles ne dépasseront pas 4 000 ou 5 000 t de U_3O_8. Bien que des sondages aient montré qu'il y avait des dépôts à une profondeur de 60 m, ces dépôts sont seulement sporadiques, et nous continuons à penser que la profondeur moyenne à laquelle on trouvera de tels dépôts est de 25 à 30 m.

Je voudrais demander à mon collègue, le D^r Josa García, de répondre à votre seconde question.

J. M. Josa García (Espagne) : Je ne pense pas qu'il soit possible de répondre à cette question de façon générale. Pour certains minerais, cependant, et dans certains cas correspondant à des tonnages faibles, etc., on peut obtenir des coûts de conversion analogues à ceux que donnerait une installation de conception classique, principalement grâce à une meilleure utilisation des réactifs, à un plus faible volume de solutions, et à une dépréciation plus faible.

J. Gabelman (États-Unis d'Amérique) : A la suite de la découverte de nouveaux gisements d'uranium, le D^r Membrillera pense-t-il que l'Espagne va devenir un exportateur d'uranium?

V. Membrillera Membrillera (Espagne) : Mes collègues et moi-même ne pouvons pas donner de réponse définitive, car la décision sera évidemment prise à un échelon plus élevé. Il est raisonnable de supposer, cependant, que la réponse à votre question dépendra du programme nucléaire de l'Espagne, et des conditions du marché de l'uranium dans les années à venir.

Mémoire P/752 (présenté par K. K. Dar)

DISCUSSION

V. Ziegler (France) : L'Atomic Minerals Division a-t-elle eu l'occasion d'effectuer des prospections sur des formations appartenant à la série des Gondwana? Dans l'affirmative, quels ont été les résultats?

K. K. Dar (Inde) : Nous avons fait des prospections radiométriques de presque tous les horizons des formations de Gondwana, mais nous n'avons trouvé jusqu'à présent aucune concentration notable d'uranium. D'autre part, nous avons repéré des concentrations locales de thorium en bandes étroites. Le reste des formations de Gondwana est en cours de prospection et les résultats obtenus à ce jour montrent que ces formations sont essentiellement thorifères.

Mémoires P/256 (présenté par R. L. Faulkner) et P/24 (présenté par J. W. Griffith)

(*Il a été convenu que ces mémoires seraient discutés ensemble.*)

DISCUSSION

J. L. Gillams (Royaume-Uni) : Le Dr Faulkner pourrait-il expliquer d'après quelles hypothèses le mémoire P/256 prédit un niveau de production mondiale de U_3O_8 en 1970 atteignant 14 000 t par an. N'est-il pas possible, et même probable, que les stocks d'uranium existant aux États-Unis et dans d'autres pays conduisent à une demande portant sur les nouvelles productions en 1970 très inférieure à ce chiffre?

R. L. Faulkner (États-Unis d'Amérique) : Le chiffre de 14 000 t/a en 1970 comprend environ 8 000 t qui seront achetées par l'Atomic Energy Commission des États-Unis à des mines des États-Unis. Ce qui laisse environ 6 000 t, dont la production est actuellement envisagée par d'autres pays tels que l'Afrique du Sud, le Canada, la France, l'Australie, etc. On prévoit que les besoins croîtront si rapidement après 1970 que les stocks mondiaux disponibles n'auront qu'un effet temporaire sur la demande. Les États-Unis veulent éviter que la vente de l'uranium dont ils pourraient disposer porte préjudice à leur industrie minière.

R. Bloch (Israël) : Le mémoire P/256 indique qu'il faudra traiter après 1970 des quantités considérables de minerais d'uranium à plus faible teneur. Ceci entraînera-t-il des changements importants et de nouvelles techniques de traitement?

R. L. Faulkner (États-Unis d'Amérique) : Je ne prévois pas de changement immédiat de la teneur des minerais extraits et traités. A condition que les programmes de prospection réussissent, on pourra continuer pendant longtemps à utiliser les qualités actuelles. Cependant, l'amélioration des techniques d'extraction et de traitement a rendu possible l'extraction et le traitement de minerais de teneurs de plus en plus faibles.

J. Mabile (France) : Il apparaît d'après ces mémoires que les réserves correspondant au domaine de prix de 10 à 30 dollars la livre de U_3O_8 sont assez modestes, car elles représentent, y compris les ressources possibles, 700 000 t de U_3O_8 aux États-Unis et 300 000 t au Canada, soit un total de 1 million de tonnes. Ceci semble constituer un faible apport aux réserves pour les prix de 5 à 10 dollars (un total de 350 000 plus 450 000 t, soit 800 000 t), et on peut donc supposer que l'épuisement des réserves au cours actuel (8 à 10 dollars) sera rapidement suivi par celui des réserves à 30 dollars. On peut donc craindre que les prix s'élèvent très rapidement à 30 dollars et plus, compte tenu des besoins admis d'ici une vingtaine d'années. Un tel pessimisme concernant le développement de l'énergie nucléaire est-il fondé?

R. L. Faulkner (États-Unis d'Amérique) : Je suis optimiste en ce qui concerne la probabilité de trouver de grandes quantités d'uranium dans les limites 8-10 dollars, mais je reconnais qu'un tel optimisme doit être tempéré de prudence. Je crois que nous trouverons beaucoup d'autres gisements du type de ceux qui nous donnent actuellement l'uranium.

J. W. Griffith (Canada) : Nos réserves futures, y compris les réserves actuelles, doivent s'élever à environ 1 million de tonnes de U_3O_8. A notre avis, c'est un chiffre significatif.

R. L. Faulkner (États-Unis d'Amérique) : Le mémoire présenté par le Dr Griffith indique que le Canada devrait pouvoir trouver à l'avenir autant d'uranium qu'il en a trouvé dans le passé. Le Dr Griffith pense-t-il que l'industrie minière canadienne va tenir compte de la demande croissante et entreprendre la prospection et le développement nécessaires?

J. W. Griffith (Canada) : Oui, je pense que l'industrie minière canadienne tiendra compte de la demande croissante d'uranium dès qu'il y aura quelque indication sérieuse sur la possibilité de commandes et de contrats à long terme. En d'autres termes, il est peu probable que l'industrie entreprenne des prospections et des développements tant qu'elle ne sera pas assurée qu'il y a un marché pour son produit.

A. Gangloff (France) : Vous dites que les réserves canadiennes en janvier 1964 s'élevaient à 188 000 t de U_3O_8. La publication de l'EURATOM citée * donnait un chiffre de 170 000 t de U_3O_8 en janvier 1962, soit, en tenant compte de l'exploitation en 1962 et 1963, 150 000 t pour janvier 1964. Il y a donc apparemment une notable augmentation. Le rapport d'EURATOM signalait l'existence possible de 70 000 t supplémentaires à Elliot Lake, mais sans les incorporer dans les réserves. Pensez-vous que la différence entre vos chiffres et ceux du rapport de l'EURATOM résulte d'une réévaluation des mines ou de l'addition de ces réserves possibles que le rapport de l'EURATOM n'aurait pas prises en considération?

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* P/24, ref. 1.

J. W. GRIFFITH (Canada) : Les deux explications doivent intervenir. En fait, la moitié environ des 70 000 t signalées par l'EURATOM comme quantité supplémentaire figurait dans nos chiffres de réserves pour janvier 1964. Nous n'avons pas inclus la totalité des 70 000 t parce que nous pensons que le reste devrait maintenant faire partie des minerais potentiels, comme l'explique notre mémoire.

J. MABILE (France) : En ce qui concerne les réserves françaises, vous avez indiqué dans votre présentation orale que l'estimation initiale de 50 000 t avait été ramenée à 28 000 t. En fait, l'estimation n'a pas été réduite : le chiffre de 50 000 t, donné en 1958, représentait le total du potentiel que l'on pouvait espérer en France et le chiffre de 28 000 t d'uranium métallique représente les réserves prouvées à l'heure actuelle. Le potentiel reste toujours évalué à 50 000 t, ce qui représente une légère augmentation, compte tenu du tonnage extrait depuis 1958.

Mémoire P/405 (présenté par P. N. Stipanicic)

DISCUSSION

A. GANGLOFF (France) : Le mémoire mentionne un certain nombre de gisements filoniens qui, après des travaux assez limités, ont livré des minerais à très bonne teneur. L'importance de ces gisements filoniens est-elle assez limitée, ou bien pensez-vous qu'il faudrait faire des études additionnelles pour déterminer leur extension, tant latéralement qu'en profondeur, ou que les structures satellites devraient être explorées?

P. N. STIPANICIC (Argentine) : Jusqu'à présent les deux gisements filoniens en question, qui sont dans les dépôts Estela et San Sebastian, ont livré, après quelques années de travail, de petites quantités de minerai à haute teneur, représentant au total 5 000 t. Dans le premier cas la teneur en U_3O_8 était de 0,5 % et dans le second de 0,85 %. Les prospections dans les dépôts San Sebastian ont montré que la teneur diminue avec la profondeur. Les études géochimiques préliminaires entreprises dans la région de San Sebastian et l'existence de divers dépôts non encore prospectés, parce qu'ils appartiennent à des sociétés privées, indiquent que le district peut présenter un certain intérêt. Au voisinage des dépôts Estela on n'a trouvé que de petites quantités de minerai (qui sont cependant intéressantes parce que le prix correspondant est de 8 dollars la livre de U_3O_8), mais l'exploitation de ces dépôts à ce jour ne laisse pas espérer de grandes possibilités de développement ultérieur. Pour ces raisons, même si les prospections futures montrent que ces dépôts filoniens sont plus importants, compte tenu des paramètres des gisements déjà connus, il est préférable pour le moment, de ne pas leur accorder plus d'importance qu'aux dépôts sédimentaires.

J. LECOQ (France) : A part les gisements et les indices décrits dans le mémoire, pensez-vous qu'on peut trouver de l'uranium en Argentine sous la couverture géologique récente des pampas et envisagez-vous d'explorer ces possibilités?

P. N. STIPANICIC (Argentine) : Dans presque toute la région reconnue en Argentine comme potentiellement uranifère, au total environ 1 200 000 km^2, il n'y a pas de couverture géologique récente. Dans le reste de la superficie, qui dépasse 1 800 000 km^2, il y a une couverture sédimentaire tertiaire et quaternaire, dont la profondeur va de quelques centaines à quelques milliers de mètres. Les affleurements de ces formations cénozoïques, aux bords des anciens noyaux, n'ont encore donné aucune indication d'accumulations uranifères. C'est pourquoi ces régions n'ont probablement pas une grande importance pour l'avenir immédiat, et nous n'envisageons pas actuellement d'en explorer les possibilités.

Sous le terrain, il y a des formations triasiques (sédiments et vulcanites), des formations anthracolithiques (sédiments), et des formations dévoniennes (sédiments) qui pourraient être uranifères, mais en raison de leur profondeur on ne les a pas incluses dans les programmes présents et futurs car il existe des zones beaucoup plus favorables.

L. GUTIÉRREZ JODRA (Espagne) : Dans le procédé de lixiviation en tas les préconcentrés sont obtenus par précipitation à la chaux; si j'ai bien compris, ils contiennent environ 5 % de U_3O_8. Je voudrais savoir, d'abord, quel est le traitement ultérieur en vue de récupérer l'uranium et, ensuite, quel est le prix total de l'uranium de pureté nucléaire obtenu par cette méthode, ou comment ce prix se compare aux prix de l'uranium obtenu par attaque classique.

P. N. STIPANICIC (Argentine) : Les préconcentrés sont envoyés à l'usine de Córdoba pour le raffinage final. Pour le moment, ils sont traités par une solution d'acide sulfurique, et les solutions mères passent dans l'usine de solvant aminé, qui donne des concentrés ayant une teneur en U_3O_8 de 82-85 %. En octobre, le procédé sera modifié en vue d'obtenir du tricarbonate d'uranyle et d'ammonium de pureté élevée (sous-nucléaire).

En ce qui concerne votre seconde question, nous avons jugé préférable de comparer les prix du gâteau jaune (*yellow cake*) produit à partir des préconcentrés et de celui fourni par les usines de type classique. Le gisement Don Otto contient un minerai convenant très bien à la lixiviation en tas et le coût du gâteau obtenu est inférieur, d'environ 1-1,50 dollar la livre, à celui de l'oxyde des usines classiques.

T. BATUECAS RODRIGUEZ (Espagne) : Quel est le prix des préconcentrés d'uranium avec le procédé d'attaque Don Otto? Je voudrais aussi demander si vous avez l'intention d'utiliser une autre méthode de récupération, en dehors de la précipitation directe à partir des liquides d'attaque.

P. N. STIPANICIC (Argentine) : Le prix est compris entre 6 et 6,50 dollars par livre de U_3O_8, auquel il faut ajouter le coût du transport à l'usine de Córdoba et le raffinage final. Il faut souligner que le prix de l'acide sulfurique a une influence considérable sur le coût, car il doit être transporté sur une distance de 1 400 km par des routes difficiles. Nous étudions actuellement la possibilité de réduire les coûts, en utilisant d'autres agents d'extraction, au moins jusqu'à un certain niveau d'extraction. Ces agents pourraient être des sulfates ferriques et ferreux, dont le coût est faible en Argentine.

En réponse à votre seconde question, je voudrais souligner que la méthode de lixiviation d'attaque en tas convient à l'extraction de l'uranium des minerais. D'autre part, bien que les résultats obtenus dans la précipitation calcique des solutions mères aient été améliorés, nous préparons un projet d'usine d'extraction par solvant aminé à Don Otto, en vue de produire un gâteau jaune ayant une teneur en U_3O_8 supérieure à 80 %.

DISCUSSION GÉNÉRALE

R. SPENCE (Royaume-Uni) : Nous étudions depuis quelques années l'extraction de l'uranium à partir de l'eau de mer. Ceci semble maintenant techniquement réalisable, mais il faudra des études de mise au point considérables avant de pouvoir faire le projet d'une installation industrielle. Nos évaluations de coût sont par nécessité très incertaines mais nous pensons que la production de U_3O_8 dans un domaine de prix moyen, c'est-à-dire environ 20 dollars la livre, sera possible. Nos résultats seront publiés dans le prochain numéro de *Nature* *.

J. J. WENT (Pays-Bas) : Si on peut extraire l'uranium de l'eau de mer à l'échelle industrielle à un prix voisin de 20 dollars la livre, les réacteurs surgénérateurs ne seront intéressants qu'au point de vue économique. A ce point de vue, cependant, les réacteurs existants de type éprouvé seront peut-être très coûteux.

O. A. QUIHILLALT (Président) : L'extraction à un prix raisonnable de l'uranium à partir de l'eau de mer aurait évidemment une influence importante sur l'ensemble de la situation. Je pense qu'on peut résumer ainsi les conditions actuelles. Les réserves d'uranium du monde occidental peuvent être estimées à 500 000 t récupérables à un prix de 8 dollars la livre. On espère que les réserves seront doublées au cours des vingt prochaines années. Il faudra quelque 3 millions de tonnes d'ici à l'an 2000. Si l'utilisation des réacteurs à eau lourde ou des surgénérateurs s'accroît, ce chiffre pourrait être ramené à 1-2 millions de tonnes. Toutes les ressources estimées doivent être vérifiées dans le proche avenir, et il est essentiel de recommencer immédiatement l'exploration et la prospection. Enfin, il y a de grandes réserves de thorium, mais il est encore assez prématuré de les faire figurer dans les programmes actuels d'énergie nucléaire.

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* Davies, R. V., Kennedy, J., McIlroy, R. W., Spence, R., et Hill, K. M., *Extraction of Uranium from Sea Water*, Nature, *203*, 1110 (1964).

Протокол заседания 2.11

Запасы урана и тория и потребности

Председатель: О. А. Киллальт (Аргентина)

Доклад P/72 (представил Ж. Мабиль)

ДИСКУССИЯ

Р. Л. ФОЛКНЕР (США): В докладе, который Вы представили, отмечается, что для обеспечения будущих потребностей необходимо провести разведку и разработку новых месторождений. Считаете ли Вы возможным нахождение достаточного количества дешевого урана для обеспечения потребностей на несколько десятилетий?

Ж. МАБИЛЬ (Франция): Было бы неправильным считать, что мировые запасы дешевых урановых руд встречаются только в районах, где рудопроявления или месторождения урана были открыты задолго до «атомного» века. Я думаю, что рентабельные для разработки месторождения могут быть также найдены в других районах, но разведочные работы придется вести в отложениях менее изученных, чем те, в которых в настоящее время разрабатываются месторождения. В связи с этим опыт Франции в африканских разведках показывает определенную целесообразность таких работ. Расходы на разведочные работы, слагающие часть себестоимости урана, определенно повысятся в результате возникших трудностей, и поэтому будет трудно поддерживать цены на заранее установленном уровне. Следует также иметь в виду, что оказалось возможным разрабатывать лишь наиболее богатые месторождения из известных в настоящее время при согласии платить более высокие цены — 26—28,5 долларов за 1 *кг* урана — и при большем объеме производства, чем в настоящее время.

Доклад P/883 (представил Ф. Н'Уэма Н'Донг)

ДИСКУССИЯ

Дж. У. СЕЙБЛХЭН (США): Показали ли разведочные работы возможность открытия в Габоне других месторождений урана, аналогичных месторождению, которое Вы описали?

Мне также бы хотелось спросить, имеет ли месторождение Мунана какое-либо отношение к урановым месторождениям Конго или к медному поясу Северной Родезии.

Ф. Н'УЭМА Н'ДОНГ (Габон): Помимо месторождений, разрабатываемых в Мунана, было много признаков, что такие же руды имеются в различных частях Габона и поиски продолжаются; однако пока невозможно сказать, приведут ли они к открытию новых месторождений.

Что касается Вашего второго вопроса, сейчас можно отметить единственно: месторождения Мунана лежат в тех же докембрийских формациях, которые окружают бассейн Конго. Все еще невозможно подвергнуть корреляции докембрийские формации Родезии с формациями в Франсвилльском бассейне Габона.

Доклад P/636 (представил Дж. Дж. Уэнт)

ДИСКУССИЯ

Э. СВЕНКЕ (Швеция): В нескольких докладах, представленных на это заседание, подчеркивалось важное значение продолжения разведочных работ по урану и также выражались опасения, что через несколько десятилетий будет ощущаться нехватка урана, которая приведет в результате к повышению цены на него. В докладе, представленном д-ром Уэнтом, сделаны заключения относительно курса, которого следует придерживаться при развитии ядерной энергетики и при выборе типов реактора. В докладе указывается, что известные в настоящее время запасы урана, рентабельные при цене 26 долларов за 1 *кг* металла в закиси-окиси, составляют 450 тыс. *т*, а запасы урана, рентабельные при ценах до 30 долларов за 1 *кг*, могут составить 1650 тыс. *т*. В последнюю цифру включен уран, содержащийся в шведских урановых сланцах. Я могу сейчас сообщить более подробные данные о положении в этом отношении в Швеции. По расчетам, запасы сланца содержат по крайней мере 1 млн. *т* урана. Они находятся главным образом в одном гомогенном легкодоступном месторождении в центре южной части страны. Рудник и обогатительная фабрика, которые начнут работать с середины 1965 года, будут производить 120 *т* урана в год; обогатительная фабрика позволит получить точные данные относительно приемлемой технологии и стоимости извлечения урана. Однако уже сейчас я могу сказать, что при еще большем масштабе этих работ можно будет получать концентраты из руд данного огромного потенциального источника по стоимости, значительно меньшей максимальной величины в 70 долларов и, возможно, даже по стоимости около 26 долларов.

Авторы доклада P/636 также не принимают во внимание то, что уже существуют тяжеловодные энергетические системы, которые очень эффективно используют уран.

Учитывая упомянутые мной факторы, я не согласен с заключением, изложенным в докладе, о том, что быстрое развитие реакторов-размножителей является крайне необходимым, и особенно не согласен с тем, что использование в крупном масштабе существующих в настоящее время энергетических реакторов является нежелательным. Увеличение известных мировых запасов в результате дальнейших поисков вместе с большими запасами урана, разведанными в Швеции, стоимость извлечения урана из которых будет лишь не намного превышать стоимость извлечения его из существующего богатого сырья, будут стабилизировать цены в течение длительного периода на уровне, который мало превысит современный, и, таким образом, обеспечат возможность использования существующих систем энергетических реакторов.

Дж. Дж. УЭНТ (Нидерланды): Хотя дополнительные запасы в 1 млн. *т* урана, рентабельные при ценах в пределах от 26 до 78 долл. за 1 *кг*, будут весьма желательны, они принципиально не изменят заключений доклада, который я представил, поскольку для осуществления будущей крупной программы по атомной энергетике потребуются миллионы тонн дешевого урана. Дополнительный миллион тонн со стоимостью, в два-три раза превышающей современную стоимость, просто продлит на несколько лет период, в течение которого будут разрабатываться реакторы-размножители. Таким образом, разработка таких реакторов крайне необходима, чтобы мы получили возможность начать производственную программу в 1970 году в направлении, указанном в табл. 4.

Я также хотел бы отметить, что апробированными типами реакторов являются реактор с газовым охлаждением и кипящий реактор, но не тяжеловодный реактор. Имеются только небольшие прототипы тяжеловодных реакторов и, как говорится в выводах доклада, они могут быть полезны только в промежуточный период.

Доклад Р/494 (представил В. Мембриллера)

ДИСКУССИЯ

Ж. ЛЕКОК (Франция): Можно ли рассматривать приведенные в докладе цифровые данные по открытым месторождениям в сланцах в Испании как окончательные или существует надежда увеличить их, особенно с увеличением глубины работ?

Мне хотелось бы также спросить, есть какие-либо основания надеяться, что стоимость переработки руды на передвижных или полупередвижных установках, которые в настоящее время проектируются или испытываются, будет такой же, как и на обычных заводах?

В. МЕМБРИЛЛЕРА (Испания): По нашей оценке уже открытые запасы в кембрийских сланцах в Саламанке составляют более 500 тыс. *т*, или 3000 *т* урана; однако проведенные нами изыскания показывают, что эти запасы не превысят 3500—4000 *т* урана. Хотя колонковое бурение показало, что руда встречается на глубине 60 *м*, она представлена здесь только отдельными линзами, и мы продолжаем считать, что средней глубиной, на которой могут быть найдены такие месторождения, будет 25—30 *м*.

Я хотел бы попросить моего коллегу д-ра Хоза Гарсия ответить на Ваш второй вопрос.

Х. М. ХОСА ГАРСИЯ (Испания): Я не думаю, что на этот вопрос можно ответить общими показателями. Однако для некоторых руд и в определенных условиях: при небольшом объеме переработки и т. д., можно получить стоимость, аналогичную величинам стоимости для обычных заводов, главным образом вследствие лучшего использования реагентов, меньшего объема растворов и пониженной амортизации.

Дж. ГЭЙБЛМЕН (США): С учетом открытия новых урановых месторождений считает ли д-р Мембриллера, что Испания станет экспортером урана?

В. МЕМБРИЛЛЕРА (Испания): Мои коллеги и я не можем дать определенного ответа, поскольку такое решение, очевидно, должно приниматься на более высоком уровне. Однако есть основания полагать, что ответ на Ваш вопрос будет зависеть от испанской программы по атомной энергии и от положения на рынке урана в будущем.

Доклад Р/752 (представил К. К. Дар)

ДИСКУССИЯ

В. ЦИГЛЕР (Франция): Проводило ли Отделение атомных минералов какое-либо обследование формаций в системе Гондвана? Если да, то какие были результаты?

К. К. ДАР (Индия): Мы провели радиометрическое обследование почти всех горизонтов в формациях Гондвана, но до сих пор не было обнаружено значительных концентраций урана. С другой стороны, местные концентрации тория были обнаружены в узких перегибах. В настоящее время обследуется остальная часть формаций Гондвана и полученные к настоящему времени результаты показывают, что эти формации в основном несут в себе торий.

Доклад Р/256 (представил Р. Л. Фолкнер) и доклад Р/24 (представил Гриффитс)

(Было принято решение о совместном обсуждении этих докладов.)

ДИСКУССИЯ

Дж. Д. ДЖИЛЛЕМС (Соединенное Королевство): Не мог бы д-р Фолкнер объяснить, на какой основе в докладе Р/236 дается прогноз мирового производства урана в 1970 году на уровне 12 000 *т* в год? Не окажется ли так, что уже имеющиеся в Соединенных Штатах и других странах запасы добытого урана приведут к производству урана в 1970 году значительно ниже этого уровня?

Р. Л. ФОЛКНЕР (США): В цифру 12 000 *т* в год входят около 7000 *т*, которые будут закуплены Комиссией по атомной энергии США в 1970 году у рудников в Соединенных Штатах. В результате остается около 5000 *т*, производство которых в настоящее время планируется другими странами, например Южно-Африканской Республикой, Канадой, Францией, Австралией и т. д. Ожидается, что после 1970 года потребности будут возрастать настолько быстро, что имеющиеся мировые запасы добытого урана окажут лишь временное влияние на спрос. Соединенные Штаты не намереваются продавать имеющийся уран, что может нанести вред американской уранодобывающей промышленности.

Р. БЛОХ (Израиль): Из доклада Р/256 я заключил, что после 1970 года придется перерабатывать значительные количества бедных урановых руд. Потребует ли это введения значительных усовершенствований и новых методов переработки?

Р. Л. ФОЛКНЕР (США): Я не думаю, что в ближайшем будущем предвидятся какие-либо изменения в содержании добываемой или перерабатываемой руды. При условии, что программы поисков окажутся успешными, в течение длительного времени смогут использоваться такие же по качеству руды, как и теперь. Однако усовершенствованные методы добычи и переработки позволили бы успешно получать уран из бедных руд.

Ж. МАБИЛЬ (Франция): На основе этих докладов может показаться, что запасы руды, рентабельные для разработки при цене за 1 *кг* урана в закиси-окиси в пределах от 26 до 78 долларов, являются относительно небольшими, поскольку они составляют, включая забалансовые запасы, 600 тыс. *т* урана в Соединенных Штатах и 250 тыс. *т* в Канаде, что дает вместе менее 1 млн. *т*. Это, по-видимому, является небольшим дополнением к запасам, рентабельным при цене в пределах от 13 до 26 долларов (всего 300 тыс. *т* плюс 380 тыс. *т*, т. е. 680 тыс. *т*), поэтому можно полагать, что за отработкой запасов, рентабельных при теперешних ценах (21—26 долларов), вскоре будут отработаны и запасы, рентабельные при цене 78 долларов. Поэтому следует опасаться, что цены весьма быстро поднимутся до 78 и более долларов, принимая во внимание рассчитанные потребности примерно на следующие двадцать лет. Имеет ли такой пессимизм относительно будущего развития атомной энергии какие-либо фактические основания?

Р. Л. ФОЛКНЕР (США): Я оптимистически смотрю на возможность того, что мы сможем разведать еще большие дополнительные запасы урана, рентабельные для отработки при ценах в пределах от 21 до 26 долларов, но я согласен с тем, что такой оптимизм должен сочетаться с осторожностью. Полагаю, что мы откроем еще много урановых месторождений такого же типа, как и разрабатываемые в настоящее время.

Дж. У. ГРИФФИТС (Канада): Наши будущие запасы, включая уже разведанные, должны достичь порядка 850 тыс. *т* урана. По нашему мнению, это довольно значительная цифра.

Р. Л. ФОЛКНЕР (США): В докладе, представленном д-ром Гриффитсом, говорится, что Канада сможет найти месторождения с такими же запасами урана в будущем, какие были разведаны в прошлом. Считает ли д-р Гриффитс, что канадская уранодобывающая промышленность учтет ожидаемое увеличение спроса и предпримет необходимые меры для расширения поисков и разработки месторождений?

Дж. У. ГРИФФИТС (Канада): Да, я думаю, что канадская уранодобывающая промышленность учтет увеличение спроса на уран, после подтверждения возможности получения заказов и заключения долгосрочных контрактов. Другими словами, промышленность вряд ли начнет разведку и подготовку месторождений до того, как убедится, что имеется рынок для ее продукции.

А. ГАНГЛОВ (Франция): Вы говорите, что канадские запасы составили в январе 1964 года 160 тыс. *т* урана. В одной публикации * Евратома дается цифра 145 тыс. *т* урана на январь 1962 года или с учетом добычи в 1962 и в 1963 годах 127 тыс. *т* к январю 1964 года. Поэтому, видимо, имеется значительный прирост запасов. В публикации Евратома обращается внимание на возможное наличие дополнительных 70 тыс. *т* у озера Эллиот, но это количество не включено в балансовые запасы. Как Вы считаете, чем вызвано отличие приведенных Вами цифр от цифр, которые даются в публикации Евратома, переоценкой запасов рудников или добавлением забалансовых запасов, которые публикация Евратома не приняла во внимание?

Дж. У. ГРИФФИТС (Канада): Как тем, так и другим. Фактически около половины от 60 тыс. *т* урана, которые Евратом отнес к дополнительному количеству, было включено в нашу цифру запасов на январь 1964 года. Причина, по которой мы не включаем все 60 тыс. *т*, состоит в том, что, по нашему мнению, остальная часть в настоящее время должна быть отнесена к забалансовым запасам руды, как объясняется в нашем докладе.

Ж. МАБИЛЬ (Франция): Что касается французских запасов, то Вы указали в Вашем устном выступлении, что прежняя оценка в 50 тыс. *т* уменьшена до 28 тыс. *т*. Фактически оценка не была уменьшена: цифра 50 тыс. *т*, данная в 1958 году, представляла общие прогнозы запасов, которые могли иметься во Франции, а цифра 28 тыс. *т* металлического урана означает разведанные в настоящее время запасы. Прогнозные запасы оцениваются по-прежнему в 50 тыс. *т*, что свидетельствует даже о небольшом увеличении, если учесть количество урана, добытого начиная с 1958 года.

Доклад Р/405 (представил П. Н. Стипаничич)

ДИСКУССИЯ

А. ГАНГЛОВ (Франция): В докладе упоминается некоторое количество жил, в которых после относительно небольшого объема проведенных работ выявлены руды с очень высоким содержанием урана. Являются ли эти жилы довольно ограниченными или Вы считаете, что следует провести дополнительную разведку для определения их размеров по простиранию и на глубину, а также изучения их ответвлений?

П. Н. СТИПАНИЧИЧ (Аргентина): До сих пор две рассматриваемые жилы, которые находятся на месторождениях Эстела и Сан-Себастьян, дали после нескольких лет разработок небольшие количества высококачественной руды, составившие в общей сложности до 5000 *т*. В первом случае содержание урана было 0,42% и во втором 0,72%. Разведка, проведенная на месторождении Сан-Себастьян, показала, что с

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* Ссылка [1] в докладе Р/24.

увеличением глубины содержание урана в руде снижается. Предварительные геохимические исследования, проведенные в районе месторождения Сан-Себастьян, и наличие еще неразведанных месторождений, принадлежащих частным фирмам, показывают, что данная провинция может представлять некоторый интерес. Поблизости от месторождения Эстела были найдены лишь небольшие запасы руды (которая представляет интерес в настоящее время при цене 21 доллар за 1*кг* урана в закиси-окиси), но вскрытие их в настоящее время представляется нецелесообразным, поскольку в дальнейшем оно может быть сделано более рационально. По этим причинам, даже если последующая разведка покажет, что данные жилы крупнее, чем предполагалось, принимая во внимание параметры уже известных месторождений, предпочитают не придавать им большого значения в течение некоторого времени по сравнению с осадочными месторождениями.

Ж. ЛЕКОК (Франция): Кроме месторождений и рудопроявлений, описанных в докладе, как Вы думаете, можно ли найти уран в Аргентине под молодыми геологическими отложениями в пампе и есть ли намерения исследовать такую возможность?

П. Н. СТИПАНИЧИЧ (Аргентина): Почти во всех районах, выбранных в Аргентине в качестве потенциальных носителей урана и имеющих площадь примерно 1 200 000 *км*^{2}, нет молодого геологического горизонта. В остальной области, которая имеет площадь более 1 800 000 *км*^{2}, имеется третичный и четвертичный осадочный горизонт, глубина которого изменяется от сотен до тысяч метров. Обнажения этих кайнозойских формаций поблизости от границ самых древних ядер не показали еще каких-либо интересных признаков урановых накоплений. По этой причине данные районы не рассматривались как имеющие крупное значение в ближайшем будущем, как следствие в настоящее время нет планов для их опоискования.

Под земной поверхностью расположены триасовые формации (осадочные и вулканические породы), антраколитовые формации (осадочные отложения) и девонские формации (осадочные породы), которые могут содержать уран, но, учитывая глубину их залегания, они не были включены ни в текущую, ни в будущую программу поисков, поскольку имеются значительно более перспективные зоны.

Л. ГУТИЕРРЕС ХОДРА (Испания): В процессе «кучного выщелачивания» грубые концентраты получают путем осаждения урана известью; если я понимаю правильно, в них содержится приблизительно 4—5% урана. Мне хотелось бы знать, во-первых, какая последующая обработка используется для извлечения урана и, во-вторых, какая общая себестоимость полученного этим методом ядерночистого урана и как она выглядит по сравнению с себестоимостью урана, полученного обычным выщелачиванием.

П. Н. СТИПАНИЧИЧ (Аргентина): Грубые концентраты посылаются для окончательной очистки на завод в Кордове. В настоящее время они обрабатываются серной кислотой и урановые растворы проходят через экстракционную установку с аминорастворителем, в результате чего получают концентраты с содержанием урана порядка 70—73%. В октябре этот процесс будет изменен для того, чтобы получать трикарбонат уранила аммония высокой чистоты (субъядерной).

Что касается Вашего второго вопроса, считается предпочтительным провести сравнение между стоимостью желтого кека, полученного из грубых концентратов и полученного на обычном заводе. В случае месторождения Дон Отто, руда которого весьма подходит для кучного выщелачивания, желтый кек, полученный по этому процессу, имеет себестоимость примерно на 2,2—3,3 доллара ниже (за 1 *кг*), чем для кека, полученного на обычных заводах.

Т. БАТЮКАС РОДРИГЕС (Испания): Какова стоимость грубого уранового концентрата, полученного путем процесса выщелачивания, используемого на месторождении Дон Отто? Я хотел бы также спросить, предполагаете ли Вы использовать другой метод извлечения, помимо непосредственного осаждения из растворов выщелачивания?

П. Н. СТИПАНИЧИЧ (Аргентина): Стоимость находится в пределах 15,5—17 долларов за 1 *кг* урана, к которой необходимо добавить стоимость транспортировки в Кордову и стоимость окончательной очистки. Следует подчеркнуть, что цена серной кислоты оказывает весьма существенное влияние на общую стоимость, поскольку кислоту приходится перевозить на расстояние 1400 *км* по плохим дорогам. В настоящее время обращается внимание на возможность снижения расходов путем использования других выщелачивающих агентов, по крайней мере до заданных уровней извлечения. Этими агентами будут сернокислое железо и сернистое железо, стоимость которых в Аргентине невысока.

В отношении Вашего второго вопроса я хотел бы указать, что метод кучного выщелачивания пригоден для извлечения урана из руды. С другой стороны, хотя полученные результаты по осаждению урана из растворов выщелачивания кальцием улучшаются, составляются планы постройки установки с аминовым растворителем в Дон Отто для производства желтого кека с содержанием урана около 70%.

ОБЩАЯ ДИСКУССИЯ

Р. СПЕНС (Соединенное Королевство): В течение нескольких лет мы изучали извлечение урана из морской воды. В настоящее время это, по-видимому, технически осуществимый процесс, но потребуется провести значительное количество экспериментов, прежде чем мы сможем составить спецификации на промышленную установку. Наша оценка расходов безусловно носит весьма предварительный характер, однако мы считаем, что имеется возможность получать уран в закиси-окиси по стоимости, лежащей в средних пределах, то есть порядка 52 долларов за 1 *кг*. Полученные нами результаты будут опубликованы в следующем номере журнала Nature *.

Дж. Дж. УЭНТ (Нидерланды): Если уран можно извлекать из морской воды в промышленном масштабе со стоимостью порядка 52 долларов за 1 *кг*, то реакторы-размножители будут представлять интерес просто с экономической точки зрения. Однако с этой целью зарекомендовавшие себя типы существующих энергетических реакторов могут оказаться весьма неэкономичными.

С. А. КИЛЛАЛЬТ (председатель): Извлечение урана из морской воды по приемлемой цене, конечно, оказало бы важное влияние на всю ситуацию. Положение, существующее в настоящее время, может быть, по моему мнению, охарактеризовано следующим образом. Запасы урана в странах западного мира, рентабельные при цене 21 доллар за 1 *кг*, можно оценить в 500 тыс. *т*. Как надеются, в ближайшие 20 лет эти запасы будут удвоены. К 2000 году потребуется около 3 млн. *т*. Если использование тяжеловодных реакторов или реакторов-размножителей будет расширено, то эта цифра может быть уменьшена до 1—2 млн. *т*. Все оцененные таким образом запасы должны быть разведаны в ближайшем будущем и с этой целью необходимо немедленно возобновить поиски и разведку. И последнее, имеются большие запасы тория, но все же пока довольно преждевременно учитывать их в современных программах по развитию атомной энергии.

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* R. V. Davis, Y. Kennedy, R. W. Mc.Irloy, R. Spence and K. M. Hill. Extraction of Uranium from sea water. Nature, *203,* 1110—1115 (1964).

Acta de la sesión 2.11

Recursos y necesidades en uranio y torio

Presidente : O. A. Quihillalt (Argentina)

Documento P/72 (presentado por J. Mabile)

DISCUSIÓN

R. L. Faulkner (Estados Unidos de América): En la memoria presentada por Vd. se hace notar que son necesarias exploraciones y desarrollos para encontrar nuevos yacimientos para hacer frente a las necesidades futuras. ¿Piensa Vd. que será probable el hallazgo de uranio a bajo coste que cubra las necesidades durante un período de varios decenios?

J. Mabile (Francia): No sería razonable suponer que las reservas mundiales de minerales que contienen uranio de bajo coste se encuentran únicamente en las zonas donde se descubrieron indicios o yacimientos mucho antes de la era atómica. Creo que podrían encontrarse yacimientos económicamente explotables en otras zonas, pero la prospección tendría que realizarse en terrenos menos familiares que los correspondientes a las explotaciones mineras actuales. En este sentido la experiencia francesa en Africa señala cierto grado de prudencia. Los gastos en prospección, como parte del precio de coste, aumentarán sin duda como resultado de las dificultades surgidas y, en consecuencia, será difícil mantener los precios actuales. Debe recordarse también que la explotación de los ricos yacimientos conocidos actualmente ha sido posible únicamente mediante el convenio de pagar para grandes cantidades precios más elevados — de 10 a 11 dólares/libra de U_3O_8 — que los que se consiguen en la actualidad.

Documento P/883 (presentado por F. N'Guema N'Dong)

DISCUSIÓN

J. Gabelman (Estados Unidos de América): ¿Ha indicado la prospección la posibilidad de encontrar en el Gabón otros yacimientos semejantes al descrito por Vd.?

Desearía también preguntar si el yacimiento de Mounana tiene alguna relación con los yacimientos uraníferos del Congo o el cinturón cuprífero de Rhodesia del Norte.

F. N'Guema N'Dong (Gabón): Además del yacimiento explotado en Mounana hay muchas indicaciones sobre la existencia de minerales semejantes en diferentes partes del Gabón y continúan las exploraciones, pero por ahora es imposible decir si tales exploraciones indicarán la existencia de nuevos yacimientos.

En cuanto a su segunda pregunta, lo único que puede decirse en la actualidad es que el yacimiento de Mounana se encuentra en las mismas formaciones precámbricas que rodean la cuenca del Congo. Por ahora es imposible relacionar las formaciones precámbricas rhodesianas con las de la cuenca de Francesville en el Gabón.

Documento P/636 (presentado por J. J. Went)

DISCUSIÓN

E. Svenke (Suecia): Varias memorias correspondientes a esta sesión han resaltado la importancia de continuar la prospección de uranio y han expresado también el temor de una escasez de uranio en el transcurso de unos pocos decenios que originaría una subida de precio. En la memoria presentada por el Dr. Went se han sacado conclusiones en relación con el camino a seguir en el desarrollo de la energía nuclear y la elección de tipos de reactores. En la memoria se afirma que las reservas conocidas en la actualidad de uranio explotable a 10 dólares/libra de U_3O_8, son 450 000 toneladas métricas y hasta 30 dólares/libra de U_3O_8 1 650 000 toneladas métricas. Esta última cifra incluye el uranio disponible en las pizarras uraníferas suecas. Ahora puedo dar más detalles sobre el particular relativos a Suecia. Se calcula que los recursos de pizarras contendrán del orden de 1 millón de toneladas métricas de uranio como mínimo. Estos recursos están situados principalmente en un yacimiento homogéneo, fácilmente accesible en la parte centro-sur del país. Una mina y una fábrica de concentrados que estará en funcionamiento a mediados de 1965, podrán producir 120 toneladas métricas de uranio por año y la fábrica aportará información exacta sobre la técnica apropiada y el costo de la recuperación. Sin embargo, me encuentro ya en condiciones de afirmar que cuando la explotación se efectúe a una escala aún mayor, será posible recuperar concentrados de esta inmensa masa potencial de mineral a un costo bastante inferior a la mitad del valor máximo de 30 dólares y quizá incluso a un coste de unos 10 dólares.

Los autores del documento P/636 tampoco tienen en cuenta el hecho de que existen ya sistemas de agua pesada productores de energía que hacen un uso muy eficaz del uranio.

Teniendo en cuenta esos factores, no estoy de acuerdo con la conclusión a que se llega en la memoria sobre la urgencia de un desarrollo acelerado de los reactores reproductores y disiento especialmente con la conclusión de que no es de desear la utilización en gran escala de las centrales nucleares actuales. El aumento de las reservas mundiales conocidas como consecuencia de más amplias exploraciones, junto con las grandes y comprobadas reservas suecas de uranio, que podrián explotarse a un costo sólo ligeramente superior al de las materias primas ricas existentes, establizarán los precios durante largo tiempo en un valor no muy superior al actual, asegurando de este modo la posibilidad de utilización de los tipos actuales de centrales nucleares.

J. J. Went (Paises Bajos): Aunque sea muy bien recibido otro millón más de toneladas de uranio en el intervalo de 10-30 dólares/libra este aumento no alteraría fundamentalmente las conclusiones que presenté en mi memoria, puesto que se necesitarían millones de toneladas de uranio barato para llevar a cabo los futuros programas energéticos nucleares a gran escala. Un millón adicional de toneladas a un precio doble o triple que el actual no haría más que ampliar en unos pocos años el período de desarrollo de los reactores reproductores. En consecuencia, el desarrollo de tales reactores se necesita de modo urgente para permitirnos iniciar el programa de producción en 1970 con las líneas de conducta indicadas en la Tabla 4.

Desearía también resaltar que los reactores refrigerados por gas y los reactores de agua en ebullición (no los reactores de agua pesada) son los tipos comprobados. No se dispone más que de pequeños prototipos de reactores de agua pesada y, como se dice en las conclusiones de la memoria, podrían ser útiles durante un período intermedio.

Documento P/494 (presentado por V. Membrillera Membrillera)

DISCUSIÓN

J. Lecoq (Francia): ¿Se consideran definitivas las cifras dadas en la memoria para los yacimientos descubiertos en pizarras españolas o se espera un aumento en ellas, especialmente al aumentar la profundidad de los trabajos?

Desearía también preguntar si hay alguna razón para esperar que las plantas móvil y semimóvil de tratamiento de mineral que se proyectan o ensayan en la actualidad funcionen a costes iguales o semejantes a los obtenidos en plantas convencionales.

V. Membrillera Membrillera (España): Estimamos que las reservas ya descubiertas en las pizarras cámbricas de Salamanca ascienden a más de 3 500 000 toneladas, es decir, 3 500 toneladas de U_3O_8; sin embargo, las exploraciones realizadas nos inducen a creer que no se sobrepasarán las 4 000 ó 5 000 toneladas de U_3O_8. Aunque los sondeos con testigo han indicado la presencia de mineralizaciones de uranio a una profundidad de 60 metros, la localización a tal profundidad ha sido esporádica y seguimos creyendo que la profundidad media de mineralización es de 25 a 30 metros.

Ruego a mi compañero Dr. Josa García que conteste a su segunda pregunta.

J. M. Josa García (España): No creo que la pregunta pueda contestarse de forma general. Con ciertos minerales y en casos de pequeño tonelaje, etc., pueden conseguirse costes de transformación análogos a los de un diagrama convencional, a causa fundamentalmente del mejor aprovechamiento de los reactivos, el menor volumen de líquido y la menor influencia de las partidas de amortización.

J. Gabelman (Estados Unidos de América): En vista del descubrimiento de nuevos yacimientos de uranio, ¿piensa el Dr. Membrillera que España se convertirá en un país exportador de uranio?

V. Membrillera Membrillera (España): La respuesta a su pregunta no corresponde exactamente a la competencia de mis compañeros ni a la mía, puesto que la decisión ha de tomarse por las autoridades de mi país. Sin embargo, parece razonable suponer que la respuesta dependerá principalmente del programa nuclear español, así como de las condiciones futuras del mercado del uranio.

Documento P/752 (presentado por K. K. Dar)

DISCUSIÓN

V. Ziegler (Francia): ¿Ha hecho la División de Minerales Atómicos alguna exploración de las formaciones de la serie de Gondwana? En caso afirmativo ¿cuáles fueron los resultados?

K. K. Dar (India): Hemos realizado exploraciones radiométricas de casi todos los horizontes de las formaciones de Gondwana, pero no se han encontrado hasta la fecha concentraciones importantes de uranio. Por otra parte, se han localizado concentraciones locales de torio en bandas estrechas. Las partes restantes de las formaciones de Gondwana se están explorando y los resultados obtenidos hasta la fecha indican que estas formaciones contienen principalmente torio.

Documento P/256 (presentado por R. L. Faulkner) y P/24 (presentado por J. W. Griffith)

(Se convino en que estos documentos se discutieran conjuntamente.)

DISCUSIÓN

J. L. Gillams (Reino Unido): ¿Sería tan amable el Dr. Faulkner de explicar los motivos por los que el documento P/256 predice un valor tan elevado como 14 000 toneladas anuales para la producción mundial de U_3O_8 en 1970? ¿No es posible, e incluso probable, que las existencias de uranio de que se dispone ya en los Estados Unidos y en otros países originen una demanda sobre la nueva producción en 1970 considerablemente menor que la indicada?

R. L. Faulkner (Estados Unidos de América): La cifra de 14 000 toneladas anuales en 1970 incluye unas 8 000 toneladas procedentes de minas del país que la Comisión de Energía Atómica de los Estados Unidos comprará en ese año. Con esto quedan unas 6 000 toneladas para la producción prevista por otros países como Sudáfrica, Canadá, Francia, Australia, etc. Se espera que las necesidades aumenten tan rápidamente después de 1970 que las existencias mundiales disponibles no tendrán más que un efecto transitorio sobre la demanda. Los Estados Unidos no tienen intención de vender uranio en condiciones que perjudiquen a la industria minera nacional.

R. Bloch (Israel): Deduzco del documento P/256 que después de 1970 habrá que tratar cantidades considerables de minerales de uranio de pequeña riqueza: ¿Supondrá esto cambios importantes y nuevas técnicas de tratamiento?

R. L. Faulkner (Estados Unidos de América): No preveo ningún cambio inmediato en la riqueza del mineral extraído y tratado. Si tienen éxito los programas de prospección podrán continuar utilizándose durante largo tiempo las riquezas actuales. Sin embargo, las mejoras realizadas en las técnicas de minería y tratamiento han hecho posible la extracción y tratamiento de materiales de riquezas cada vez inferiores.

J. Mabile (Francia): Podría parecer a la vista de estas memorias que las reservas citadas en el margen de precios de 10-30 dólares/libra de U_3O_8 son relativamente pequeñas, puesto que representan, incluyendo las reservas potenciales, 700 000 toneladas de U_3O_8 en los Estados Unidos y 300 000 toneladas en Canadá, haciendo un total de 1 millón de toneladas. Al parecer esto representa una adición pequeña a las reservas en el intervalo de 5 a 10 dólares (un total de 350 000 más 450 000 toneladas, es decir, 800 000 toneladas) y podría, por tanto, suponerse que el agotamiento de las reservas a precios actuales (8-10 dólares) estaría seguido muy de cerca por el de las reservas a 30 dólares.

En estas condiciones hay que temer muy próximamente una subida de los precios a 30 dólares o más, teniendo en cuenta las necesidades estimadas para los próximos 20 años. ¿Está realmente bien fundado tal pesimismo respecto al futuro desarrollo de la energía nuclear?

R. L. Faulkner (Estados Unidos de América): Soy optimista respecto a la posibilidad de encontrar mayores reservas de uranio en el intervalo de 8 a 10 dólares, aunque estoy de acuerdo con que tal optimismo deberá estar moderado por la prudencia. Creo que se descubrirán muchos más depósitos del tipo de los que actualmente proporcionan uranio.

J. W. Griffith (Canadá): Nuestras reservas futuras, incluyendo las actuales, representarán aproximadamente 1 millón de toneladas de U_3O_8. En nuestra opinión, ésta es una cifra importante.

R. L. Faulkner (Estados Unidos de América): La memoria presentada por el Dr. Griffith afirma que el Canadá podrá encontrar tanto uranio en el futuro como el ya encontrado. ¿Espera el Dr. Griffith que la industria minera canadiense tome nota de la demanda creciente y emprenda los trabajos necesarios de exploración y desarrollo?

J. W. Griffith (Canadá): Sí; espero que la industria minera canadiense tome nota de esa demanda de uranio creciente cuando haya alguna indicación firme de obtención de pedidos y contratos a largo plazo. En otras palabras, no es probable que la industria emprenda los trabajos de exploración y desarrollo hasta que pueda asegurarse de que existe un mercado para sus productos.

A. Gangloff (Francia): Vd. dice que las reservas canadienses en enero de 1964 ascendían a 188 000 toneladas métricas de U_3O_8. La publicación de EURATOM a que hace referencia daba una cifra de 170 000 toneladas de U_3O_8 para enero de 1962 ó, teniendo en cuenta las operaciones de 1962 y 1963, 150 000 toneladas para enero de 1964. Por tanto hay, al parecer, un aumento considerable. La publicación de EURATOM * llamaba la atención sobre la posible existencia de 70 000 toneladas suplementarias en el lago Elliot, pero no las incluía en las reservas. ¿Piensa Vd. que la diferencia entre sus cifras y las dadas por la publicación de EURATOM procede de una reestimación de la mina o se debe a la inclusión de las reservas potenciales que la publicación de EURATOM no tenía en cuenta?

J. W. Griffith (Canadá): La diferencia se debe en parte al primero y en parte al segundo de los motivos. En realidad aproximadamente la mitad de las 70 000 toneladas citadas por EURATOM como suplementarias se incluyeron en nuestra cifra de reservas para enero de 1964. La razón de no incluir la totalidad de las 70 000 toneladas fue que, en nuestra opinión, el resto debería considerarse, por ahora, mineral potencial, como se explica en nuestra memoria.

J. Mabile (Francia): En relación con las reservas francesas indicó Vd. en su presentación verbal que la primitiva estimación de 50 000 toneladas se había reducido a 28 000 toneladas. En realidad, la estimación no ha sufrido reducción; la cifra de 50 000 toneladas dada en 1958, representaba el potencial total que podría esperarse en Francia y la cifra de 28 000 toneladas de uranio metal representa las reservas comprobadas hoy día. El potencial sigue estimándose en 50 000 toneladas, lo cual representa un ligero incremento teniendo en cuenta las toneladas extraídas desde 1958.

Documento P/405 (presentado por P. N. Stipanicic)

DISCUSIÓN

A. Gangloff (Francia): La memoria menciona ciertos tipos de lodos que, sometidos a algunos procesos poco laboriosos, proporcionan minerales de concentración muy elevada. ¿Es la importancia de estos lodos más bien limitada o piensa Vd. que deberían realizarse más investigaciones para determinar su extensión, tanto lateralmente como en profundidad, o bien que deberían investigarse las estructuras acompañantes?

P. N. Stipanicic (Argentina): Respecto a los dos lodos en cuestión, que se encuentran en los yacimientos Estela y San Sebastián, han producido, después de varios años de trabajo, pequeñas cantidades de mineral de elevada riqueza, ascendiendo a un total de 5 000 toneladas. En el primer caso el contenido en U_3O_8 fue 0,5 % y en el segundo 0,85 %. La exploración de los yacimientos San Sebastián indicó que el contenido disminuía con la profundidad. Estudios geoquímicos preliminares realizados en la zona San Sebastián y la existencia de varios depósitos aún sin explorar (por pertenecer a compañías privadas) indican que el distrito puede tener cierto interés. Junto a los depósitos Estela se han encontrado únicamente pequeñas cantidades de mineral (que son de un interés actual puesto que su precio es de 8 dólares/libra U_3O_8), pero la evolución de estos depósitos hasta la fecha no sugiere la existencia de grandes posibilidades de desarrollo futuro. Por estos motivos, aunque exploraciones posteriores indicaran que estos depósitos de lodos son mayores, teniendo en cuenta sus características ya conocidas, se piensa que, por ahora, es preferible no atribuirles mayor importancia que a depósitos sedimentarios.

J. Lecoq (Francia): Además de los yacimientos e indicios descritos en la memoria, ¿piensa Vd. que podría encontrarse uranio en Argentina bajo el horizonte geológico reciente de las pampas y se piensa investigar tal posibilidad?

P. N. Stipanicic (Argentina): En casi toda la zona seleccionada en Argentina como potencialmente uranífera, que abarca aproximadamente 1 200 000 km², no hay horizonte geológico reciente. En el área restante, que sobrepasa 1 800 000 km², hay un horizonte sedimentario terciario y cuaternario, cuya profundidad varía de cientos a miles de metros. Los afloramientos de estas formaciones cenozoicas junto a los bordes de los núcleos más antiguos no han presentado hasta ahora indicios interesantes de acumulaciones uraníferas. Por este motivo no es probable

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* P/24, Ref. [1].

que estas zonas puedan ser de gran importancia en un futuro inmediato y, en consecuencia, no hay en la actualidad planes para investigar sus posibilidades.

Bajo el terreno hay formaciones triásicas (sedimentos y vulcanitas), formaciones antracolíticas (sedimentos) y formaciones devonianas (sedimentos) que podrían ser uraníferos, pero que, teniendo en cuenta la profundidad a que se presentan, no se han incluído en los programas presentes o futuros puesto que hay disponibles zonas mucho más favorables.

L. GUTIÉRREZ JODRA (España): En el proceso de lixiviación en pila los preconcentrados se obtienen por precipitación con cal y el Sr. Stipanicic ha indicado que contienen el 5 % de U_3O_8. Desearía un comentario del Sr. Stipanicic sobre los siguientes puntos: En primer lugar sobre el tipo de tratamiento posterior para recuperar el uranio, y en segundo lugar sobre el costo total del uranio nuclearmente puro obtenido por este método comparado con el obtenido por lixiviación convencional.

P. N. STIPANICIC (Argentina): Los preconcentrados se envían a la planta de Córdoba para su purificación final. Actualmente se tratan con solución de ácido sulfúrico y los líquidos de tratamiento pasan por la planta de disolventes aminados que produce concentrados con un contenido de 82-85 % de U_3O_8. En octubre el proceso se modificará para obtener uranil tricarbonato amónico de gran pureza (sub-nuclear).

En cuanto a su segunda pregunta, parece preferible establecer una comparación entre el coste del concentrado de uranio producido a partir de los preconcentrados y el correspondiente a la producción del mismo por plantas convencionales. El yacimiento Don Otto contiene un mineral muy adecuado para lixiviación en pila y el concentrado obtenido por este proceso es de precio inferior en 1-1,50 dólares/libra al correspondiente a plantas convencionales.

T. BATUECAS RODRIGUEZ (España): ¿Cuál es el precio del preconcentrado de uranio cuando se utiliza el proceso de lixiviación Don Otto? Me gustaría también saber si se piensa utilizar algún otro método de recuperación además del de precipitación directa de los líquidos de lixiviación.

P. N. STIPANICIC (Argentina): El precio está entre 6 y 6,5 dólares/libra de U_3O_8, al que hay que añadir el coste de transporte a la planta de Córdoba y su purificación final. Debe hacerse resaltar que el precio del ácido sulfúrico tiene un efecto muy importante en el coste, puesto que hay que transportarlo a distancias de 1 400 km por carreteras difíciles. En la actualidad se está prestando atención a la posibilidad de reducir los costes utilizando otros agentes de lixiviación, al menos hasta ciertos valores específicos de extracción. Estos agentes serían sulfatos ferroso y férrico cuyo coste es bajo en Argentina.

En relación con su segunda pregunta, me gustaría hacer notar que el método de lixiviación en pila es adecuado para la extracción de uranio del mineral. Por otra parte, aunque se están mejorando los resultados de la precipitación cálcica, existen planes para la instalación en Don Otto de una planta de disolventes aminados que produciría concentrados con un contenido en U_3O_8 superior al 80 %.

DISCUSIÓN GENERAL

R. SPENCE (Reino Unido): Hemos estado estudiando durante algunos años la extracción del uranio del agua del mar. Actualmente parece que puede realizarse técnicamente este proceso, aunque se necesitará un desarrollo considerable antes de poder hacer las especificaciones de una planta industrial. Nuestras estimaciones de costos son por necesidad muy provisionales, pero pensamos que será posible la producción de U_3O_8 en el intervalo de precios medios, es decir, a unos 20 dólares por libra. Nuestros resultados se publicarán en el próximo número de *Nature* *.

J. J. WENT (Países Bajos): Si puede extraerse uranio del agua del mar a escala industrial y a un precio de unos 20 dólares por libra, los reactores reproductores serán interesantes únicamente desde el punto de vista económico. Sin embargo, para este objetivo los tipos comprobados de reactores de potencia que existen pueden ser muy poco económicos.

O. A. QUIHILLALT (Presidente): La extracción del uranio del agua del mar a un coste razonable tendría, naturalmente, un influjo importante en toda la situación. Las circunstancias actuales creo que podrían resumirse de la siguiente forma. Las reservas de uranio del mundo occidental pueden estimarse en unas 500 000 toneladas que podrían extraerse a un coste de 8 dólares por libra. Se espera que las reservas se dupliquen en los próximos 20 años. En el año 2 000 se necesitarán unos 3 millones de toneladas. Si se intensifica la utilización de reactores de agua pesada o reproductores la cifra puede reducirse a 1-2 millones. Todas las reservas estimadas deberán comprobarse en un futuro próximo y con este fin es indispensable reanudar inmediatamente los trabajos de prospección y exploración. Por último, hay grandes reservas de torio pero es aún algo prematuro incluirlas en los programas actuales de energía nuclear.

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* Davies, R. V., Kennedy, J., McIlroy, R. W., Spence, R., y Hill, K. M., *Extraction of Uranium from Sea Water*, Nature, *203*, 1110 (1964).

Session 2.12

PROSPECTING TECHNIQUES AND RECOVERY FROM ORES

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Évolution de l'industrie de l'uranium en France

par P. Maget *, P. Vertès * et F. Bazile **

Depuis 1958, le développement de l'industrie française de l'uranium a été caractérisé par le maintien d'une importante activité de recherches tant en France qu'en Afrique et à Madagascar, par l'achèvement du programme d'équipement des ensembles miniers, des usines de concentration et des usines de raffinage qui était déjà amorcé lors de la précédente Conférence, et par la mise en régime des exploitations au fur et à mesure de leur équipement, à un rythme qui est cependant resté inférieur au rythme primitivement prévu.

Quelques chiffres caractérisent ce développement:

La production des mines françaises est passée de 700 t de métal contenu en 1958 à 1 075 t en 1963;

La production de concentrés marchands, uranates de magnésie et nitrate d'uranyle, de 500 t en 1958 à 1 470 t en 1963;

La production d'uranium raffiné de 400 t en 1958 à 1 200 t en 1963.

En raison de la conjoncture des récentes années, ces productions ont été stabilisées dès 1961 sensiblement au niveau actuel, tandis que les capacités annuelles des installations sont de l'ordre de 2 000 t de métal pour les usines de concentration et de 1 800 t pour les usines de raffinage.

LES PROSPECTIONS ET LES RECHERCHES

Les prospections et recherches en France se sont poursuivies dans les principaux districts uranifères déjà connus en 1958. Parallèlement, elles se développaient dans d'autres régions et en mettaient de nouveaux en évidence, tant dans des régions cristallines à formations filoniennes que dans des régions sédimentaires. De plus, le Commissariat a poursuivi ses recherches au Gabon et à Madagascar, et en a entrepris de nouvelles dans différents États africains, tels que le Niger et la République Centre-Africaine.

Les gisements filoniens

Nous rappelons brièvement que les districts uranifères déjà décrits sont ceux du Limousin, du Forez et de la Vendée. Ils ont pour caractère commun d'appartenir à ce qu'il est convenu d'appeler les massifs hercyniens, essentiellement granitiques et métamorphiques. Tous les gisements connus y sont d'origine hydrothermale et se présentent sous forme de filons ou d'amas dont la mise en place est étroitement déterminée par des facteurs tectoniques.

Depuis 1958, les travaux du CEA dans ces trois districts ont surtout porté sur la mise en valeur, l'exploitation et le développement des gîtes connus. D'une façon générale, on observe un accroissement des réserves, compensant largement le minerai exploité durant le même temps. Il est à noter cependant que les niveaux profonds, au-delà de 200 m, n'ont pas été étudiés de façon systématique; les espoirs de développement existent donc encore de ce côté.

De nouveaux districts uranifères se sont dessinés, qui sont, comme les précédents, en relation avec les massifs cristallins hercyniens:

1) *Le district de la Margeride*, immédiatement à l'ouest de la haute vallée de l'Allier et de la ville de Langogne, a été découvert et mis en valeur par la Compagnie française des minerais d'uranium (CFMU). Actuellement, deux gisements importants situés dans le massif granitique de Grandrieu sont en cours de reconnaissance : Le Cellier et Les Pierres Plantées.

Le gisement du Cellier a été reconnu par travaux miniers jusqu'à 100 m de profondeur et par sondages jusqu'à 150 m. Il est en liaison avec une zone tectonique de direction NNW-SSE suivie sur plusieurs kilomètres. La minéralisation principale est constituée d'oxydes noirs d'uranium en enduits dans un granite finement diaclasé et broyé. Le gisement des Pierres Plantées, situé à 3,5 km au nord-ouest du précédent, est d'un type très différent. Il s'agit d'une épisyénite minéralisée en pechblende et produits secondaires. Cette épisyénite, contenue dans un granite à deux micas, a la forme d'une colonne de section irrégulière convexe dont le plus petit diamètre est de 20 m et le plus grand de 50 m. Elle est à peu près verticale sur les 100 premiers mètres; elle a ensuite une extension horizontale de 80 m, après quoi, à partir de 140 m de profondeur, elle se digite en plusieurs rameaux plus ou moins verticaux reconnus jusqu'à 200 m.

2) *Le district de Bretagne*, dont l'intérêt est actuellement beaucoup moindre que les précédents, est localisé dans un massif de granite à deux micas situé à l'ouest de Pontivy. Un certain nombre de petits gisements y ont été trouvés. Le principal est celui de Bonote, appartenant à la Société industrielle et

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* Commissariat à l'énergie atomique.

** Société industrielle des minerais de l'Ouest.

minière de l'uranium (SIMURA). Il s'agit d'un riche filon de pechblende qui n'a malheureusement qu'une extension limitée à 180 m de longueur et 150 m de hauteur.

L'effort de prospection et de valorisation d'indices consenti depuis la fin de 1958 dans le domaine des massifs cristallins hercyniens a donc permis un développement substantiel des ressources uranifères françaises. Depuis cette date, les gisements intragranitiques ont vu leurs réserves croître de 15 000 à 21 000 t tout en assurant une production de 4 000 tonnes d'uranium.

Les gisements sédimentaires

Parallèlement, les recherches se sont développées dans les terrains sédimentaires. Dans ce domaine, nous assistons à une croissance rapide des réserves qui, pendant la même période, se sont élevées de 2 000 à 7 000 t d'uranium, auxquelles s'ajoute une production de 500 t. La part du sédimentaire dans les ressources est donc passée de 8,5 à 25 %. Ceci souligne toute l'importance que peut avoir également en France ce type de minéralisation. Il est à noter que toutes les recherches poursuivies actuellement par le Commissariat en Afrique portent sur des régions de ce genre, et que le gisement de Mounana, actuellement exploité au Gabon, se situe également dans des terrains sédimentaires.

Parmi les plus importants gîtes sédimentaires français, en dehors de celui des Vosges qui a déjà été décrit par le CEA [1] et n'a pratiquement pas fait l'objet de travaux depuis 1958, citons:

1) *Les gisements du Permien de l'Hérault*, mis en évidence par le CEA dans la région de Lodève. Le principal est celui de Mas-d'Alary. La minéralisation est localisée dans les pelites de l'Autunien plus ou moins carbonatées et chargées de matières organiques; elle peut être stratiforme (sans minéraux exprimés) ou en remplissage de filonnets (pechblende).

2) *Les gisements du Tertiaire continental*, qui ont fourni de nombreux indices dans le Massif Central. Deux d'entre eux sont plus importants:

a) Saint-Pierre-de-Cantal, travaillé par la Société centrale de l'uranium et des minerais et métaux radioactifs (SCUMRA), au sud de Bort-les-Orgues; la minéralisation est y constituée par des phosphates et vanadates d'uranium dans des sables fluviotorrentiels oligocènes.

b) Grézieux-le-Fromental, situé dans des argiles sableuses lacustres de la région de Montbrison; la minéralisation y est rarement exprimée et le minerai a une très faible teneur.

LES EXPLOITATIONS MINIÈRES

Les mines du CEA

La production française est essentiellement assurée par le Commissariat dans ses trois divisions minières de La Crouzille (Limousin), de Vendée et du Forez.

La mise en exploitation des mines de ces divisions a été conditionnée, d'une part, par l'équipement des sièges miniers eux-mêmes, d'autre part, par l'implantation d'usines de traitement au cœur de chaque district.

Caractéristiques générales des exploitations du Commissariat

A l'exception de la Division du Forez dont l'usine est alimentée par une seule mine d'une capacité de 1 000 t/j de minerai, les autres divisions comprennent plusieurs sièges miniers ou exploitations à ciel ouvert, dont les productions sont transportées sur au plus 50 km à une station centrale de stockage et de préparation des minerais, située elle-même à proximité de l'un des gisements et de l'usine de traitement. Les capacités journalières de ces sièges miniers, équipés en fonction de leurs réserves connues, sont de l'ordre de 300 à 1 000 t/j.

Les équipements des mines sont normalisés, l'extraction en particulier est assurée par des tours, des poulies Kœpe et des skips à marche automatique permettant la desserte de plusieurs étages.

On a généralement adopté, pour les relevés d'étage, une hauteur de 40 m, qui paraît le maximum compatible avec la reconnaissance de gisements le plus souvent complexes et irréguliers; un étage sur deux est normalement équipé pour l'extraction.

Les profondeurs d'exploitation actuelles ne dépassent pas 200 m, mais les sièges principaux sont équipés pour permettre d'abord des travaux de reconnaissance et ensuite l'exploitation jusqu'à 400 m.

Les gisements exploités par le Commissariat sont tous filoniens. Les teneurs en uranium varient de 0,8 kg à plusieurs kilogrammes par tonne et se situent, en général, entre 1 et 1,6 ‰.

Les formations sont le plus souvent linéaires et subverticales, avec des puissances de l'ordre du mètre; cependant, certaines colonnes minéralisées, en particulier dans la mine des Bois-Noirs au Forez, atteignent et dépassent 10 m de puissance. Dans d'autres cas, comme à la mine de l'Ecarpière, en Vendée, et à la mine du Brugeaud, dans le Limousin, des réseaux filoniens très denses, avec des encaissants minéralisés, forment de véritables amas de grandes dimensions.

Les méthodes d'exploitation

Ces diverses formes de gisements, ainsi que la nature des encaissants, ont conduit à mettre en œuvre des méthodes d'exploitation assez variées, telles que:

a) Les sous-niveaux et chambres vides, dans les formations linéaires et les amas dont les épontes sont suffisamment solides. Cette méthode se montre particulièrement efficace en Vendée, où, dans une roche relativement saine, le réseau filonien est très irrégulier et très dense, les sous-niveaux constituant non seulement une phase de l'exploitation, mais un moyen de reconnaissance que l'on complète par de très nombreux sondages percutants dans les parements;

b) Les chambres charpentées, dans les lentilles particulièrement riches à épontes ébouleuses dans certains gisements du Limousin;

c) Les tranches montantes avec remblayage hydraulique, dans les formations puissantes et de tenue médiocre du Forez;

d) Les exploitations à ciel ouvert, utilisées soit pour l'exploitation d'amas particulièrement importants comme celui du Brugeaud, en Limousin, soit pour l'exploitation des têtes de filon. Ce type d'exploitation a fourni 15 % des minerais produits en 1963.

L'expérience de huit années d'exploitation industrielle des mines filoniennes a permis de dégager certaines conclusions:

a) L'irrégularité très générale des minéralisations justifie dans tous les cas un contrôle géologique extrêmement minutieux, avec relevé géologique et radiométrique des fronts, radiocarottages de nombreux sondages percutants faits à partir des galeries et des chantiers, radiocarottages dans les carrières de tous les trous de foration pour l'identification des minerais avant l'abattage;

b) Dans les formations minces et riches, les méthodes les plus coûteuses sont souvent préférables aux autres parce qu'elles permettent de réduire le salissage;

c) La reconnaissance des encaissants par sondages percutants en cours d'exploitation conduit dans la plupart des cas à augmenter très sensiblement les réserves prévues;

d) La diffusion de la minéralisation dans les parties superficielles des gisements justifie fréquemment leur exploitation par découverte même dans le cas de formations linéaires apparemment étroites et simples;

e) Le stérile des usines, convenablement cycloné ($+ 44\,\mu$), constitue un excellent remblai hydraulique utilisable tant dans les méthodes montantes remblayées que dans les méthodes de chambres vides pour le remplissage des cavités laissées par l'exploitation.

Économie des exploitations du Commissariat

Les prix de revient obtenus dans les exploitations du Commissariat sont de l'ordre de 40 à 50 F/t rendue sur le carreau des usines, ces prix s'entendant sans amortissement, frais généraux et taxes. Ceci conduit, suivant les gisements exploités, à des coûts variant de 2,5 à 4 dollars par livre de U_3O_8 contenu.

La conduite des exploitations est basée sur l'établissement de bilans prévisionnels qui permettent la récupération des minerais marginaux et une stricte économie des réserves. Sont considérés comme exploitables tous les minerais, à quelque stade qu'ils se trouvent, pour lesquels les dépenses restant à engager pour récupérer sous forme de concentrés le métal contenu sont inférieures à la valeur de ce métal.

Les bilans prévisionnels sont établis grâce à une estimation aussi précise que possible des teneurs des minerais en place, à une bonne connaissance des coûts des différentes opérations élémentaires de l'exploitation, et à une comptabilité précise des productions permettant, dans chaque cas particulier, une bonne estimation des résultats d'exploitation et, notamment des salissages et des pertes.

Cette comptabilité est basée sur des mesures faites à la sortie du puits dans un dispositif automatique original de triage et de comptage radiométrique.

Les produits sortant du skip sont déversés dans un cylindre, garni extérieurement de compteurs Geiger-Müller et monté sur ressorts dynamométriques, où ils séjournent 40 secondes. La radioactivité et les poids mesurés sont inscrits sur bande par un téléscripteur ainsi qu'un numéro indiquant l'origine du produit, transmis directement au téléscripteur depuis la recette du fond; après comptage, une commande automatique oriente la goulotte de déversement du cylindre sur la position « stérile » ou la position « minerai » suivant que la radioactivité est inférieure ou supérieure au seuil pour lequel l'appareil a été réglé.

Ce cylindre de comptage, outre qu'il assure une première élimination du stérile, permet au géologue de faire des bilans journaliers des productions pour l'ensemble de la mine comme pour chaque chantier élémentaire dont l'origine a été distinguée. Les corrélations radioactivité/teneur sont vérifiées par des échantillonnages journaliers de *skips test*. Ces corrélations sont généralement suffisamment bonnes pour que le géologue renonce au procédé coûteux d'échantillonnage par rainurage et utilise les résultats du cylindre pour évaluer les teneurs des chantiers de reconnaissance et établir ses calculs de réserves.

Pour les mines du Commissariat, les teneurs de coupure auxquelles on arrive varient suivant les exploitations:

Pour un produit en place dans un panneau vierge reconnu par voie de base et voie de tête: de 0,5 à 0,7 ‰ U;

Pour un minerai abattu en place: de 0,3 à 0,4 ‰ U;

Pour un minerai sorti du puits: de 0,2 à 0,35 ‰ U.

Les exploitations privées

Outre les chantiers de recherches, dont les productions globales restent peu importantes, situés surtout en Bretagne et dans le Massif Central, des sociétés privées exploitent régulièrement et à petite cadence quatre gisements :

Celui du Bonote en Bretagne;

Ceux du Cellier et de Pierres-Plantées dans le district de Margeride, en découverte;

Celui de Saint-Pierre-du-Cantal également en découverte. Il est à noter que ce gisement est le seul du type sédimentaire actuellement en exploitation en France.

Ces minerais sont à teneurs élevées (de 2 à 5 ‰ U) et sont transportés sur des distances de plusieurs centaines de kilomètres jusqu'aux stations d'achats du Commissariat situées sur la Division de la Crouzille et celle de Vendée.

LA CONCENTRATION

Les minerais français, tant du Commissariat que des exploitants privés, après une préparation plus ou moins sommaire dans les ateliers de préparation du Commissariat, sont concentrés dans les trois usines de Bessines sur la Division de la Crouzille, du Forez sur la Division du Forez, et de l'Ecarpière sur la Division de Vendée.

A ces usines de concentration des minerais métropolitains, il faut ajouter l'usine de Gueugnon, où le Commissariat retraite les préconcentrés produits à la mine de Mounana par la Compagnie des mines d'uranium de Franceville (COMUF) et importés du Gabon.

De plus, des concentrés physiques d'uranothorianite sont importés de Madagascar et traités directement dans l'usine de raffinage du Bouchet.

Les procédés de concentration physique

Ces procédés, assez largement utilisés il y a une dizaine d'années (flottation, séparation par liqueur dense), ont été peu à peu abandonnés.

Actuellement, ils ne sont plus employés que dans les cas suivants:

1) *Triage radiométrique en continu* dans l'atelier de préparation de Bessines.

Le minerai concassé à 120 mm est débourbé puis criblé. Les deux fractions granulométriques (40-70 mm et 70-120 mm) sont envoyées sur deux convoyeurs de triage et l'on effectue en continu la mesure du poids et de la radioactivité. La séparation entre minerai et stérile, basée sur cette double donnée, est faite par un volet mobile, lors de la chute des cailloux à l'extrémité de chaque convoyeur. Chaque convoyeur de triage peut traiter entre 20 et 25 t par heure; les rejets ont une teneur en uranium de 0,10 à 0,12 ‰ et représentent environ 15 % en poids du minerai entré dans l'atelier.

Cette installation fonctionne depuis l'été 1963.

2) *Traitement par appareils gravimétriques*

Dans le sud de Madagascar le CEA exploite en carrière des minerais d'uranothorianite tenant environ 0,6 ‰ U et 2 ‰ Th.

Le principe du traitement est le suivant: après concassage et broyage à environ 2 mm par broyeur à barres, un premier traitement par jigs permet de récupérer de 30 à 40 % de la thorianite. Les rejets des jigs sont criblés à 1,5 mm et traités par spirales; le préconcentré obtenu par spirales est enrichi sur tables à secousses.

Ces opérations de concentrations gravimétriques ont d'abord été effectuées dans de petites laveries situées à proximité des chantiers à partir de 1954. Depuis 1959, le CEA a regroupé ses installations et, actuellement, seule fonctionne une laverie à Betioky, d'une capacité de 500 t de minerai par 24 h.

On obtient ainsi des concentrés qui titrent de 15 à 22 ‰ en U et de 50 à 60 % en Th. Le rendement de récupération est compris entre 80 et 85 % et le taux d'enrichissement est voisin de 300.

Les procédés de concentration chimique

Les usines exploitées par la société industrielle des minerais de l'Ouest (SIMO)

Au cours des dernières années, la SIMO a exploité régulièrement les trois usines de traitement de minerais français: Bessines et l'Ecarpière, qui sont ses propriétés et le Forez, qui lui est donné en gérance par le CEA.

Dans les deux premières usines, qui mettent en œuvre une lixiviation sulfurique et des résines, les résultats obtenus ont été en constante amélioration, tant en ce qui concerne les capacités de production que les rendements d'extraction et les prix de revient.

A titre d'exemple, l'usine de l'Ecarpière a traité un peu plus de 300 000 t de minerais en 1963, avec un rendement global d'extraction de l'uranium voisin de 96 %, pour des minerais ayant des teneurs en uranium voisines de 1 ‰. Le prix de revient moyen de l'usine a été de 26 F/t, ce qui équivaut approximativement à 2 dollars par livre de U_3O_8 produite.

Dans les mêmes conditions, l'usine de Bessines, avec des minerais d'une teneur moyenne voisine de 1,5 ‰, a obtenu un prix de revient de 31 F/t, soit 1,6 dollar par livre d'U_3O_8 produite, bien qu'elle ne soit pas alimentée à pleine capacité.

Ces prix s'entendent sans amortissement et frais financiers, et hors taxes.

La SIMO a parallèlement continué son effort dans le domaine des procédés nouveaux.

Ainsi, à l'usine de Bessines, l'atelier d'extraction par solvant, prévu en parallèle avec les résines échangeuses d'ions, pour une part de la production de l'usine, a été essayé avec plein succès. Il a été possible, en particulier, de mettre au point des dispositifs évitant toutes difficultés dues aux émulsions, qui se présentent souvent avec ce procédé.

Un effort particulier doit être mentionné, qui concerne le procédé dit « calcique », breveté par la SIMO en 1958 et qui avait fait l'objet d'une communication à la seconde Conférence de Genève [2].

Ce procédé permet, après une précipitation en deux temps, par la chaux, des solutions d'attaque sulfurique des minerais et la lixiviation nitrique de l'uranate de chaux obtenu, de produire du nitrate d'uranyle très pur par purification au tributylphosphate.

Il constitue donc un raccourcissement important du cycle habituel de fabrication des produits nucléaires, puisqu'il exclut les résines et les difficultés (risques d'empoisonnements) toujours attachées à ce procédé, et la fabrication des produits très impurs et peu utiles, quant au but cherché, que sont les uranates.

L'usine du Forez, mise en route dans le courant de l'année 1960, utilise ce procédé (sa capacité de traitement est de 180 000 t de minerais et elle peut produire 330 t d'uranium).

Elle produit actuellement du nitrate d'uranyle liquide, tout à fait conforme à ce qui était prévu, dont la pureté déjà très grande (quelques centaines de parties par million seulement d'impuretés) pourrait très aisément être rendue de qualité dite « nucléaire » si on le souhaitait. Des difficultés normales de mise au point ont dû être surmontées, mais il est important de noter qu'elles ont eu pour seules causes l'appareillage utilisé, sans que jamais le processus chimique soit mis en défaut.

Il demeure donc très probable que ce procédé, qui ne s'adapte pas sans précautions à toutes les qualités de minerais, permettra de faire progresser l'économie d'ensemble du cycle de matières premières à base d'uranium. On peut ajouter qu'en utilisant seulement la première partie de ce procédé (les deux précipitations aboutissant à un uranate très impur) on dispose d'un procédé de traitement sommaire, qui peut s'appliquer dans certains cas particuliers, comme celui d'une usine très isolée située loin de toute industrie.

C'est cette position qui a été adoptée pour l'usine d'uranium qui a été construite en République gabonaise pour la COMUF.

L'usine de Gueugnon

L'usine de Gueugnon a été la première usine construite par le Commissariat en France pour traiter des minerais pauvres. Elle a démarré en 1955. D'une capacité d'environ 35 000 t de minerais par an, elle a subi différentes modifications de procédés et est devenue de plus en plus, entre 1959 et 1961, une usine expérimentale à mesure que le démarrage d'unités plus importantes (Ecarpière, Bessines) la libérait des tâches de production.

En 1961, elle a été reconvertie pour assurer la purification des préconcentrés produits par la COMUF à Mounana et achetés par le CEA.

Ces préconcentrés sont obtenus après lixiviation sulfurique d'un minerai complexe d'uranium et de vanadium, lavage par décanteurs à contre-courant, et précipitation directe par la magnésie.

Ils titrent de 25 à 35 % en U et de 5 à 10 % en V. Ils sont séchés à 3-4 % d'humidité pour le transport, chargés en sacs papier placés à l'intérieur de fûts en bois et transportés en France par bateau.

Le procédé de traitement utilisé à Gueugnon est le suivant: l'uranium est malaxé pendant au moins une demi-heure avec de l'acide sulfurique. On ajoute ensuite du nitrate de chaux et, après environ une heure de mélange, on filtre le résidu de sulfate de chaux. Le nitrate d'uranyle obtenu est purifié par solvant TBP. Après réextraction à l'eau, on obtient un nitrate d'uranyle qui est concentré par évaporation jusqu'à 400 g U/l.

Le raffinat de l'extraction par TBP est neutralisé en deux temps par un lait de chaux; dans le premier temps à pH 2,5, on récupère du vanadate de chaux à 15-20 % de V sur sec; dans un deuxième temps à pH 10, on précipite les hydroxydes de fer et d'alumine qui sont éliminés et on récupère un jus de nitrate de chaux qui est concentré par évaporation puis recyclé à la lixiviation.

Le rendement est compris entre 99 et 99,5 %. L'usine est capable de produire, sous forme de nitrate d'uranyle, environ 430 t d'uranium par an.

Elle emploie un total de 50 personnes. Le prix du traitement est voisin de 5,80 F par kg de U produit, soit environ 0,5 dollar par livre d'oxyde U_3O_8.

Autres procédés de lixiviation

Après des études en laboratoire [3], on a expérimenté à l'échelle semi-industrielle divers procédés pour tirer parti de certains minerais, ou trop pauvres pour justifier leur traitement dans une usine classique, ou possédant des caractères qui gênent ce traitement [4]

1) Les *schistes houillers des Vosges* contiennent une minéralisation extrêmement diffuse rendant la récupération de l'uranium difficile. On a essayé la lixiviation alcaline par capillarité d'une part, et par immersion d'autre part. Cette dernière méthode a donné de meilleurs résultats mais les essais se poursuivent;

2) *Le minerai granitique de Bauzot*, qui consommait beaucoup d'acide en usine, contient des éléments provoquant l'empoisonnement des résines. Un tas de 5 000 t a été soumis, près de l'usine de Gueugnon, à un arrosage par acide dilué. Une récupération voisine de 85 % a été obtenue avec une consommation d'acide plus faible et les jus n'ont pas créé les mêmes ennuis aux résines. Une souche de bactéries ferro-oxydantes a été ensemencée sur le tas et y a subsisté;

3) *L'arrosage acide d'un minerai très pauvre*, et normalement irrécupérable, abattu dans la mine de Brugeaud et laissé *in situ*, a donné des jus à teneur extrêmement élevée pendant un mois.

Sur ces premiers résultats encourageants, la méthode va être étendue à d'autres minerais qui seront traités dans des installations à l'échelle industrielle.

Des réunions périodiques entre ingénieurs des

JEN espagnole et portugaise et du CEA ont permis de mettre en commun leurs expériences respectives et de perfectionner les applications du procédé.

PRODUCTION DES PRODUITS NUCLÉAIREMENT PURS À PARTIR DES CONCENTRÉS

Deux usines appartenant au CEA assurent la transformation des concentrés d'uranium en produits nucléairement purs:

a) L'usine de Malvesi (dans le Midi de la France, près de Narbonne), gérée par la Société de raffinage de l'uranium (SRU), où le CEA est associé avec les sociétés Saint-Gobain et Potasse et engrais chimiques.

b) L'usine du Bouchet, exploitée directement par le CEA. Sa capacité de production est environ la moitié de celle de Malvesi en uranium métallique, mais elle est en plus équipée pour le traitement des minerais d'uranothorianite de Madagascar et dotée d'ateliers pilotes pour le développement des procédés. Ce développement est poussé au Bouchet jusqu'au stade industriel, ce qui fait que ce Centre, beaucoup plus ancien en date, possède certaines installations des plus modernes.

Le Bouchet est également spécialisé dans la production de l'oxyde d'uranium (UO_2) frittable, destiné à la préparation d'éléments combustibles céramiques.

A l'exemple des pays anglo-saxons, la production française s'oriente vers l'emploi du magnésium comme métal réducteur dans l'élaboration de l'uranium. Toutefois, fidèle à la technique des fours verticaux (*moving bed*) pour la préparation du tétrafluorure, elle a porté le maximum d'effort au perfectionnement de ces procédés qui lui permettent actuellement d'obtenir une qualité de fluorure particulière à un prix de revient très bas.

La réactivité de ce fluorure a conduit à la simplification de la technique d'élaboration du métal, qui se fait de plus avec un excellent rendement, quelle que soit la taille des lingots. Cette élaboration se fait encore principalement en calciothermie, mais une unité pilote de magnésiothermie (300 t/an) fonctionne régulièrement en donnant toute satisfaction, grâce notamment à la réactivité du tétrafluorure. L'extension de ce procédé à toute l'élaboration est en cours. Les lingots produits par ce procédé sont de 100 à 1 000 kg, mais la taille la plus couramment fabriquée est de 200 kg environ en raison des exigences des équipements déjà existants pour les traitements ultérieurs.

La refusion des lingots bruts produits par magnésiothermie a été également expérimentée au Bouchet dans un four prototype muni d'un dispositif de condensation des produits volatils.

Ce four permet en même temps l'affinage du métal et la division des lingots de gros modèle en fonction de la demande.

L'équipement le plus récent mettant en œuvre la technique des fours verticaux consiste en un four combiné effectuant la transformation directe de l'oxyde UO_3 en UF_4.

Dans ce four (modèle LC), qui est une variante perfectionnée du four en « L » signalé déjà à la conférence de Genève en 1958 [5], la descente du produit est réalisée dans un tube unique, par une vis d'extraction unique, cette dernière agissant en même temps comme finisseur de fluoruration.

Les réactifs gazeux sont introduits dans le four à différents niveaux, mais la sortie des gaz résiduels est unique.

Les réactifs employés sont l'ammoniac et l'acide fluorhydrique. L'absorption de ce dernier par l'oxyde d'uranium est totale, ce qui, en dehors de l'économie en réactif, permet une simplification de l'appareillage qui ne comprend pas de dispositifs de recyclage ou de récupération.

Le courant gazeux n'entraînant pratiquement pas de poussières, le problème de dépoussiérage est également supprimé.

Le four, qui ne comprend qu'un minimum de partie mécanique est d'une robustesse remarquable et d'un entretien facile. La régularité de son fonctionnement a permis de réduire le personnel de surveillance au strict minimum.

La capacité unitaire des fours LC est de 100 à 400 t d'uranium par an.

L'oxyde UO_3 à employer dans le four LC se présente sous forme de granulés obtenus à partir du diuranate par calcination modérée, sans dispositif particulier de granulation.

Le désir de pouvoir adapter le procédé à l'oxyde obtenu par dénitration thermique a conduit le CEA à étudier la possibilité d'obtention directe de granulés d'UO_3 dans un appareillage original dont la première version industrielle est en construction à l'usine du Bouchet.

La production d'oxyde d'uranium de qualité frittable a fait l'objet de nombreuses études et d'essais pratiques au stade demi-industriel.

Le Bouchet est actuellement équipé pour cette production en fours de différents modèles permettant l'obtention de plusieurs qualités d'oxydes.

C'est ainsi qu'une installation conçue pour la fabrication d'oxyde légèrement enrichi effectue la réduction en four tournant.

D'autres fours, comportant des installations de préparation et de finissage, procèdent à la réduction en système vertical par l'hydrogène ou par l'ammoniac.

La capacité et la souplesse de ces installations permettent au Bouchet de faire face largement à la demande en oxyde naturel ou légèrement enrichi.

Une partie des matières premières employées au Bouchet arrive sous forme de concentré physique de minerais d'uranothorianite. Bien que la teneur en uranium (10 à 20 %) soit trois à cinq fois plus faible que celle en thorium, ce concentré n'en constitue pas moins une source d'uranium très intéressante.

La séparation des deux éléments, suivant le mode primitivement employé au Bouchet, a eu lieu par précipitation oxalique. Ce procédé est actuellement abandonné en faveur de la séparation par extraction sélective au phosphate tributylique. Ce perfectionnement, très intéressant sur le plan économique, permet en même temps une pureté plus poussée des deux produits finaux, qui sont les nitrates nucléairement purs de ces deux éléments.

L'usine de Malvesi, construite en 1958, utilise encore des techniques antérieures à cette date. En particulier, l'élaboration du métal y est encore effectuée par calciothermie.

La modernisation de cette usine est en cours (introduction des fours LC de fluoruration et de la magnésiothermie), en collaboration avec les sociétés qui en assurent la gestion. Les transformations s'effectuent par étapes pour ne pas arrêter la production indispensable. On prévoit en même temps une augmentation notable de la capacité du Centre, qui doit assurer le gros de la production française d'uranium métal par magnésiothermie dès 1966.

Il paraît superflu de rappeler que l'intérêt de la magnésiothermie est surtout d'ordre économique, le calcium étant actuellement un réactif encore très coûteux.

Il convient de remarquer toutefois que les techniques procédant par calciothermie ont été notablement améliorées ces dernières années et qu'en particulier, en effectuant des élaborations par le calcium dans des creusets du type magnésiothermie, on est parvenu à abaisser de façon appréciable la consommation de ce réactif.

CONCLUSIONS

Les six années qui se sont écoulées depuis la précédente Conférence de Genève, ont vu les réserves françaises connues se consolider et s'accroître de telle façon qu'elles garantissent à la France une trentaine d'années de production à la cadence actuelle.

Le développement de l'industrie de l'uranium, s'il a été freiné par les circonstances, n'en a pas moins permis de mettre en service un outil suffisant pour assurer les besoins de la France dans les prochaines années au moins et de mettre au point, surtout dans les domaines de la concentration et du raffinage, des méthodes industrielles en vue de développements nouveaux.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/56 France

Evolution of the uranium industry in France

by P. Maget *et al.*

The main feature in the development of the French uranium industry during the last few years is the completion of the programme, started in 1958, for the equipping of mining units and treatment plants.

It was thus possible by 1961 to reach a production capacity of about 2 000 t of metal contained in concentrates, and about 1 800 t of metal of nuclear purity.

The prospecting and research carried on in France by the Commissariat and by private industry have brought about not only a satisfactory renewal of the reserves under exploitation, but also the development of two new uranium-producing regions. One is of the usual type in France, in the crystalline formations to the south-east of the Massif Central, the other in the Permian sedimentary formations in the department of Hérault.

Ore extraction is essentially taken care of by the Commissariat à l'énergie atomique in the three mining districts Vendée, Limousin and Forez, private industry having been unable to form any large production unit under the conditions prevailing in recent years.

Physical methods of concentration have been gradually abandoned, with the exception of a continuous radiometric sorting at the Bessines plant and

the gravimetric concentration of uranothorianite ores in Madagascar.

Uraniferous concentrates are produced in two forms. On the one hand, two chemical plants run by a combined Commissariat-private industry firm, the Société industrielle des minerais de l'Ouest, produce magnesium uranates by a conventional process in the Vendée and at La Crouzille. On the other hand, two Commissariat plants, one managed by the same Society in the Forez, the other run directly by the Commissariat at Gueugnon in the Grury mining district, at present inactive, produce uranyl nitrate. The former from ore extracted in the Forez region, the latter from magnesium uranate preconcentrates imported from Gabon.

Two Commissariat plants convert the concentrates into a product of nuclear purity. One at Le Bouchet, run by the CEA also deals with development studies. The other at Malvesi, managed by a Commissariat-private industry combine, the Société de raffinage de l'uranium has a production capacity about double that of Le Bouchet and uses the same manufacturing processes.

The bulk of the uranium metal is still produced by calcium reduction, but the Le Bouchet plant is already equipped for magnesium reduction and is using this process.

Uranium fluoride is obtained, by a technique peculiar to the French process, in combined vertical furnaces giving a direct transformation of trioxide (UO_3) to fluoride with a very low oxygen content; particularly adventageous production yields can thus be obtained. The equipment of the Malvesi plant will be modernised in the near future to make use of this process.

The plant at Le Bouchet also contains equipment for the treatment of uranothorianite concentrates imported from Madagascar. The original process, based on solvent purification and oxalic separation, has been replaced by a more modern method using selective dissolution, which enables pure nitrates to be produced under excellent conditions.

A/56 Франция

Развитие урановой промышленности во Франции

П. Маже *et al.*

За последние годы развитие французской урановой промышленности характеризуется в основном завершением программы технического оснащения рудников и заводов по переработке урана, которая была принята к исполнению в 1958 году.

В соответствии с этой программой уже в 1961 году Франция получила 2000 *т* концентратов и около 1800 *т* металлического урана, пригодного для использования в реакторах.

Благодаря геологическим исследованиям и разработкам, ведущимся Комиссариатом по атомной энергии и частной промышленностью, во Франции не только возобновлены разработки заброшенных рудников, но и начата разработка двух новых месторождений урановых руд: одно на юго-востоке центрального массива Франции, где руды залегают в кристаллических формациях, другое — в департаменте Эро, в пермских отложениях.

Ввиду того что частная промышленность за последние годы не смогла создать ни одного крупного промышленного производства, разработка руд ведется главным образом Комиссариатом по атомной энергии в трех горных районах департамента Вандея, в провинциях Лимузен и Форез.

От метода концентрирования руд физическим путем пришлось постепенно отказаться; только на заводе в Бессине применяют метод непрерывной радиометрической сортировки руд, а на Мадагаскаре — метод гравитационной концентрации урано-торианитовых руд.

Производство концентрированных урановых руд ведется двумя методами:

— два химических завода смешанной компании «Сосьете эндюстриель де Минере де л'Уест», созданной Комиссариатом по атомной энергии и частным капиталом, получают уранат магния в Вандее и в Крузейе классическим методом;

— два завода Комиссариата по атомной энергии (один в Форезе находится в ведении смешанного общества, другой в Гёньоне в районе бездействующего рудника находится в ведении КАЭ Франции) производят уранилнитрат: первый — из руд, добываемых в Форезе, другой — из обогащенных руд ураната магния, импортируемых из Габона.

Два завода, принадлежащих Комиссариату по атомной энергии, перерабатывают концентрированные руды в металлический уран:

— завод в Буше, который, кроме того, ведет исследования и изыскания в области производства урана;

— завод в Мальвези, управляемый смешанной компанией «Сосьете де рафинаж де л'ураниум», созданным Комиссариатом по атомной энергии и частным капиталом.

Производительность завода в Мальвези почти вдвое выше производительности завода в Буше, хотя на них применяется один и тот же технологический процесс.

Наибольшая часть металлического урана производится методом кальцийтермического восстановления, хотя завод в Буше уже переоборудован на производство чистого металлического урана магнийтермическим восстановлением, который уже применяется в производстве.

Для получения фторида урана применяют французский метод, который заключается в следующем: в двух комбинированных, вертикально расположенных печах производится прямое превращение трехокиси урана (UO_3) во фторид с очень низким содержанием кислорода, что обеспечивает высокую экономичность производства. В ближайшее время завод в Мальвези будет переоборудован для работы по этому методу.

Кроме того, на заводе в Буше имеется установка для переработки уран-торианитовых концентратов, импортируемых из Мадагаскара. Применяемый первое время метод, основанный на очистке руд путем растворения и последующего разделения с помощью щавелевой кислоты, заменен более современным методом очистки путем селективного растворения, который позволяет получать чистые нитраты по низким ценам.

A/56 Francia

Evolución de la industria del uranio en Francia

por P. Maget *et al.*

El desarrollo de la industria francesa del uranio en los últimos años, se ha caracterizado, sobre todo, por la terminación del programa para equipar los conjuntos mineros y las fábricas de tratamiento, que ya se había iniciado en 1958.

Como resultado se ha alcanzado desde 1961 una capacidad de producción de unas 2 000 t de uranio en forma de concentrados y de unas 1 800 t de metal nuclearmente puro.

Las prospecciones y las investigaciones realizadas en Francia por el Commissariat y la industria privada han tenido como resultado, además de una renovación satisfactoria de las reservas explotadas, el desarrollo de dos nuevos distritos uraníferos : uno, de tipo clásico en Francia, en las formaciones cristalinas del sudeste del Macizo Central, y el otro en las formaciones sedimentarias permianas del departamento del Hérault.

La extracción de los minerales está esencialmente a cargo del Commissariat à l'énergie atomique en los tres distritos mineros de Vendée, Limousin y Forez, ya que la industria privada no ha podido crear ningún centro de producción importante en la coyuntura de los últimos años.

Los procedimientos de concentración por vía física han sido abandonados paulatinamente, con excepción de una preparación radiómetrica continua que se utiliza en la fábrica de Bessines y la concentración gravimétrica de los minerales de uranotorianita en Madagascar.

La producción de concentrados de uranio se realiza de dos formas : Por una parte, dos fábricas químicas pertenecientes a una sociedad mixta (Commissariat-industria privada) la Société industrielle des minerais de l'Ouest que, siguiendo un procedimiento clásico, producen uranatos de magnesio, en Vendée y en La Crouzille. Por otra parte, dos fábricas del Commissariat : una en Forez, administrada por la misma sociedad y la otra en Gueugnon, en el distrito minero de Grury, inactivo en la actualidad, explotada directamente por el Commissariat, que producen nitrato de uranilo; la primera partiendo del mineral extraido en Forez, la segunda partiendo de concentrados de uranato de magnesio importados del Gabón.

Dos fábricas pertenecientes al Commissariat realizan la transformación de los concentrados en un producto nuclearmente puro. La de Bouchet, explotada por el CEA, que se encarga también de los estudios de desarrollo; la de Malvesi, administrada por una sociedad mixta (Commissariat-industria privada) la Société de raffinage de l'uranium.

Esta última tiene una capacidad de producción de, aproximadamente, el doble que la de Bouchet y utiliza los mismos procedimientos de fabricación.

La partida más importante de la producción total de uranio metálico se obtiene todavía por calciotermia, pero la fábrica de Bouchet está ya equipada para realizar la magnesiotermia y trabaja según este último procedimiento.

El fluoruro de uranio se obtiene por una técnica apropiada para el procedimiento francés en hornos verticales combinados en los que se transforma el trióxido (UO_3) directamente en fluoruro, con muy bajo contenido de oxígeno, lo que permite unos rendimientos muy interesantes. El equipo de la fábrica de Malvesi va a ser modernizado en un futuro próximo, para utilizar este procedimiento.

En la fábrica de Bouchet está también la instalación de tratamiento de concentrados de uranotorianita importados de Madagascar El procedimiento que se empleaba inicialmente, basado en la purificación con disolvente y en la separación oxálica, ha sido reemplazado por un procedimiento más moderno basado en la disolución selectiva, que permite obtener los nitratos puros en condiciones excelentes.

P/408 Argentina

Concentración física de menas de uranio arcilloso-calcáreas de baja ley

por M. Mochulsky *

Las menas utilizadas como materia prima para la obtención del uranio y de sus compuestos se caracterizan por tener leyes superiores al 0,1 % U_3O_8. El progreso de las técnicas de beneficio por métodos físicos o físico-químicos (procedimientos gravitacionales, flotación, etc., ha posibilitado el aprovechamiento de menas de leyes inferiores al 0,1 % U_3O_8, asimismo como el de otras en que los minerales de uranio se hallan asociados con calcita, materias bituminosas o arcillas. Estos componentes interfieren en el tratamiento químico eficiente de las menas y afectan a la economía del proceso, por lo que se recurre a su separación por algunos de los procedimientos indicados [1-7].

Las menas de uranio de baja ley, motivo del presente estudio, procedían de varios puntos del sector sur del yacimiento « Don Rodolfo » (Cosquín, Dpto. Punilla, provincia de Córdoba, República Argentina) y fueron extraídas en el curso de los trabajos de exploración efectuados por la Delegación Centro de la Comisión Nacional de Energía Atómica (CNEA).

La mineralización uranífera se presenta en parte como impregnaciones de carnotita y tyuyamunita y bajo la forma de cristales de 0,1-0,5 mm de longitud, en globados en conglomerados arcilloso-calcáreos que también contienen cuarzo, feldespato y regular a pequeña proporción de yeso [8, 9].

La ley media del yacimiento en el sector explorado es del 0,03 % U_3O_8 y su reserva geológica ha sido estimada en 3 millones de toneladas. La consideración de los sectores de ley media del 0,053 % U_3O_8 ha indicado una reserva de 765 000 t de mena, y la de ley media 0,04 % U_3O_8 ascendería a 2 millones de toneladas.

A continuación se expone el análisis químico del lote común (CQ-300), obtenido por la mezcla de cuatro lotes representativos (CQ-1000, CQ-2000, CQ-3000 y CQ-4000), y de leyes comprendidas entre 0,014 % y 0,056 % (tabla 1): U_3O_8: 0.035 %; V_2O_5: 0,03 %; SiO_2: 43,30 %; Al_2O_3: 11,60 %; Fe_2O_3: 3,90 % CaO: 13,80 %; MgO: 2,30 %; MnO: 0,60 %; ($Na_2O + K_2O$): 2,60 %; CO_2 : 7,10 %; P_2O_5 : 0,20 %; Humedad: 7,8 %.

De la observación de estos valores resalta el contenido de V_2O_5, que no exhibe la relación con el U_3O_8 que debiera existir en la carnotita y tyuyamunita. Se ha comprobado que el excedente de V_2O_5 se halla en la fracción arcillosa, probablemente combinado con algunos de sus constituyentes y su recuperación no es posible por métodos físicos ni económica por procedimientos químicos. La investigación de otros elementos cuya presencia en tenor suficiente favorecería el tratamiento económico de estas menas, tales como el Mo, W y Se, acusó solamente vestigios.

En la tabla 2, se dan los datos correspondientes al análisis granulométrico y distribución del U_3O_8 en el lote citado, y el de los lotes componentes; también se incluye el relativo al lote CQ-7000 y CQ-X-1.

El propósito de este trabajo ha sido:

1. La determinación de las posibilidades de concentración por métodos sencillos, de una muestra del común de cuatro menas de distintas leyes representativas del yacimiento;
2. El ensayo, con técnica similar, del tratamiento de los cuatro lotes individuales, con el fin de decidir sobre la conveniencia de incluir los en el común;
3. La experimentación del ciclonado de dos muestras de menas en aparatos de 1, 2 y 3 etapas.

APARATOS Y DISPOSITIVOS UTILIZADOS

Para la realización de los ensayos se han utilizado los siguientes aparatos (figura 1):

Un ciclón hidráulico tipo Dutch State Mines de 75 mm ∅ interior, de chapa de hierro [10, 11] capacidad de tratamiento 1800-3000 l pulpa/h.

Un ciclón hidráulico tipo Krebs compuesto de un ante-ciclón (70 mm ∅) y de un ciclón cónico de 50 mm, de chapa de fundición. Ambas cámaras están provistas de sus respectivos capta-vórtices.

Tabla 1. Composición del lote común CQ-300

	Peso %	Ley U_3O_8 %	Distrib. del U_3O_8 %	Leyes límites de los componentes U_3O_8 %
Lote CQ-1000 .	18,6	0,014	8,0	0,001-0,019
Lote CQ-2000 .	35,0	0,024	25,1	0,020-0,029
Lote CQ-3000 .	15,6	0,036	17,5	0,034-0,040
Lote CQ-4000 .	30,8	0,056	49,4	0,042-0,068
CQ-300 .	100,0	0,033	100,0	

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* Comisión Nacional de Energía Atómica.

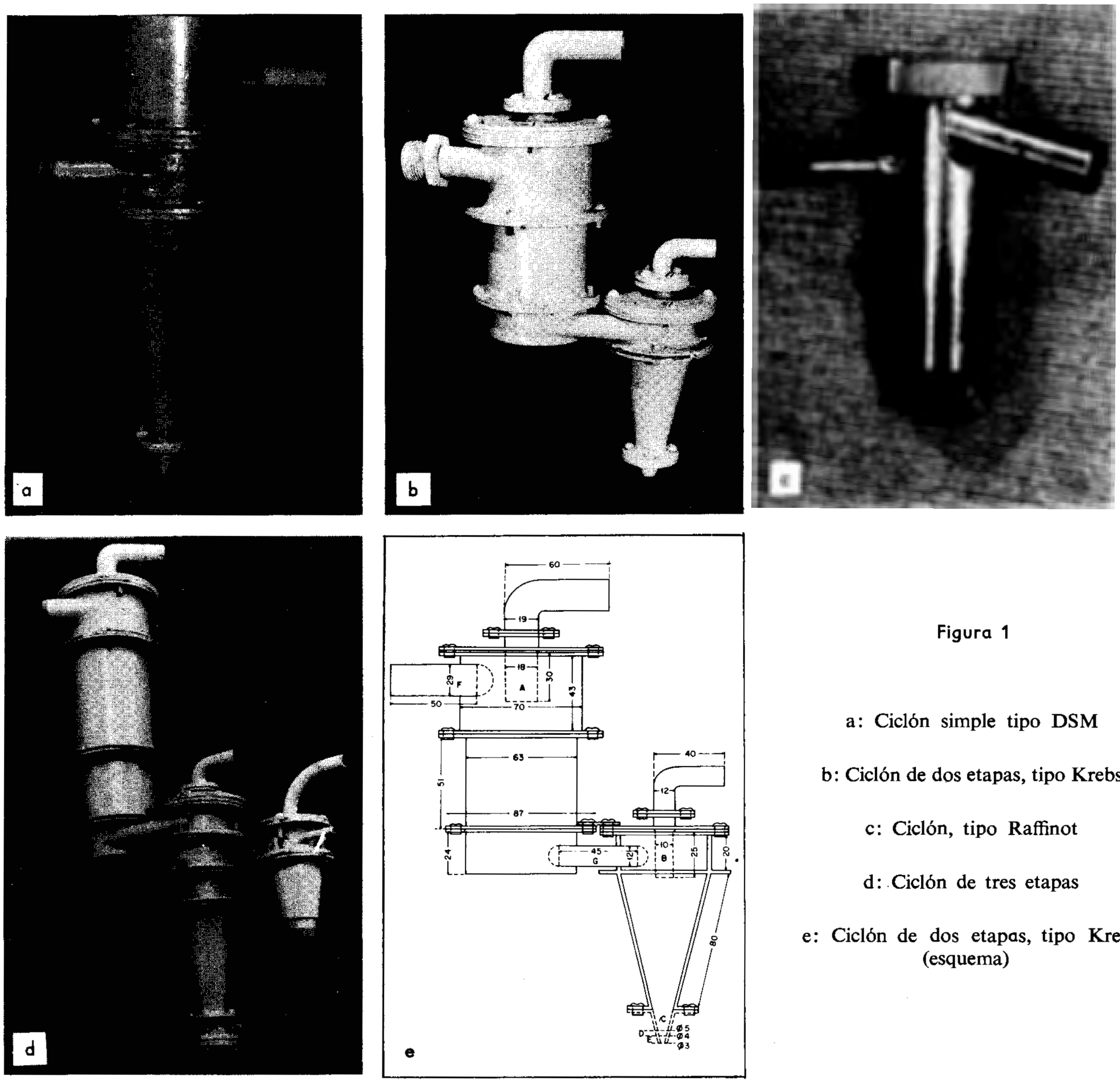

Figura 1

a: Ciclón simple tipo DSM

b: Ciclón de dos etapas, tipo Krebs

c: Ciclón, tipo Raffinot

d: Ciclón de tres etapas

e: Ciclón de dos etapas, tipo Krebs (esquema)

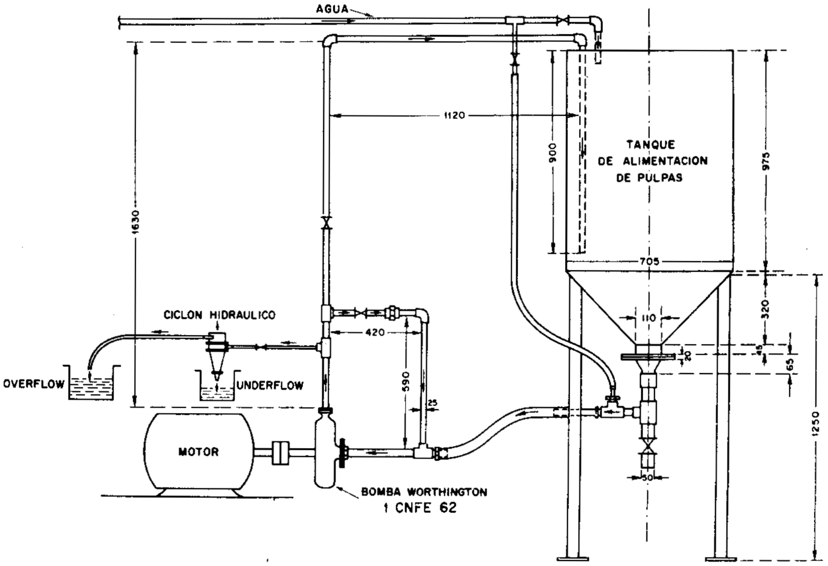

Figura 2. Instalación de alimentación y circulación de pulpas para ciclones hidráulicos (esquema)

Tabla 2

	Malla n.º	Peso %	U_3O_8 %	Distribución %
Lote CQ-300 (común)	35	9,2	0,068	19,4
	65	5,8	0,134	23,9
	100	2,4	0,137	10,1
	— 100	82,6	0,018	46,6
		100,0	0,032	100,0
Lote CQ-1000	35	6,3	0,034	15,2
	65	3,7	0,063	23,3
	100	1,7	0,110	6,5
	— 100	88,3	0,008	55,0
		100,0	0,014	100,0
Lote CQ-2000	35	14,7	0,032	20,2
	65	5,2	0,062	13,8
	100	2,1	0,086	8,2
	— 100	78,0	0,017	57,8
		100,0	0,023	100,0
Lote CQ-3000	35	8,4	0,100	20,8
	65	10,4	0,100	25,8
	100	3,9	0,125	12,0
	— 100	77,3	0,022	41,4
		100,0	0,040	100,0
Lote CQ-4000	35	5,0	0,190	17,4
	65	5,5	0,270	27,4
	100	2,3	0,213	9,0
	— 100	87,2	0,029	46,2
		100,0	0,054	100,0
Lote CQ-7000	35	18,9	0,226	36,2
	65	19,1	0,153	24,8
	100	13,4	0,116	13,2
	— 100	48,6	0,062	25,8
		100,0	0,117	100,0
Lote CQ-X1	35	16,0	0,033	13,5
	65	16,3	0,074	31,5
	100	5,3	0,100	13,6
	— 100	62,4	0,026	41,4
		100,0	0,039	100,0

El rebose del ciclón cónico puede ser retornado al tanque de alimentación. Capacidad: 1 800-3 200 l/h. Un ciclón de tres etapas, basado en la adaptación al aparato precedente de un ciclón cónico suplementario (35 mm ∅), con lo que se intentó reunir en un solo aparato las ventajas de los dispositivos Krebs y Denver-Morton. Capacidad: 2 600-3 200 l/h. Un cliclón tipo Raffinot de 30 mm ∅ interior, realizado en acero inoxidable. Capacidad: 300-500 l/h [14].

Los dispositivos de alimentación empleados han consistido en un tanque alimentador cónico (en la primera serie de ensayos) y de otro cilíndrico y de fondo cónico; sus capacidades eran de 80 y 430 l, respectivamente. La alimentación de las pulpas a los ciclones se efectuó por gravedad (diferencia de nivel: 4,70 m) en primer término y, posteriormente, mediante una bomba centrífuga vertical de arenas Denver de 25 mm ∅.

La pulpa procedente del tanque cilíndrico-cónico se inyectó en los ciclones mediante una bomba centrífuga de barros Worthington (38 × 25,4 mm ∅), conectada con una derivación lateral y un tubo de retorno al recipiente (figura 2).

Los ensayos de tratamiento en mesa vibratoria se realizaron utilizando un equipo Deister-Overstrom de laboratorio (con cubiertas para gruesos y para finos, de 920 × 490 mm). El empaste de las menas con agua se hizo, en la segunda serie de experiencias, mediante el empleo de una hormigonera de tambor basculante (capacidad 240 l). Los ciclones hidráulicos y los dispositivos de alimentación de pulpas se construyeron en los talleres de la CNEA.

PROCEDIMIENTO

La técnica aplicada fué similar para el lote CQ-300 y para los componentes del mismo (lotes CQ-1000, CQ-2000, CQ-3000, CQ-4000), y constó de las siguientes etapas:

a) Empaste de la mena con agua hasta 30 % de sólidos, con remoción continua;

b) Tamizado de la pulpa por la malla n.º 20 (escala Tyler), trituración de la fracción de + 20 mallas a — 20 mallas y su incorporación al resto de la pulpa;

c) Remoción y sifonado doble de la suspensión sobrenadante. El residuo obtenido se reunió con el primero. Se obtuvieron dos fracciones: lamas y residuo de deslamado;

d) Las lamas se diluyeron a 20-25 % sólidos y desde el tanque cónico (desnivel 4,70 m), se alimentó por gravedad, mediante un tubo de goma de 19 mm ∅ al ciclón hidráulico de 30 mm ∅ (capta-vórtice de 5 mm ∅ y boquilla de descarga: 2 mm ∅). Resultaron dos productos: descarga inferior (*Underflow*) y rebose (*Overflow*);

e) El *underflow* se trató en la mesa vibratoria (provista de la cubierta para finos), obteniéndose un concentrado y una cola finales;

f) Al margen del procedimiento anterior, se experimentó el fraccionamiento del residuo de deslamado por tamizado a través de las mallas n.os 35, 65 y 100 y las fracciones obtenidas se alimentaron a la mesa vibratoria (cubierta para gruesos). En todos los ensayos se lograron concentrados de alta ley, apreciable reducción de peso, pero a la vez la recuperación disminuyó sensiblemente; por lo tanto, se considera que sus perspectivas económicas son poco alentadoras.

RESULTADOS EXPERIMENTALES

A continuación se resumen los datos correspondientes a los ensayos típicos efectuados sobre los lotes men-

Tabla 3

	N.°	Producto	Peso (%)	Ley U_3O_8 (%)	Distribución (%)	Razón de concentración	
Lote CQ-300 (común). .	CQ-536	Residuo de deslamado	22,0	0,100	66,7		*Ciclonado:* Pulpa: 21 % sólidos. Velocidad de alimentación: 230 kg (pulpa/hora (48 kg sólidos/hora). Pulpa *underflow:* 45,8 % sólidos. Pulpa *overflow:* 16 % sólidos.
	CQ-537	Lamas	78,0	0,015	33,7		
	CQ-300	(Alimentación)	100,0	0,033	100,0		
	CQ-538	*Underflow* ciclonado	40,8	0,021	60,4		
	CQ-539	*Overflow*	59,2	0,012	39,6		
	CQ-537	. . . .	100,0	0,015	100,0		
	CQ-550	Reunión de CQ-536 + 0,25 CQ-538	30,0	0,080	71,7	3,3	
	CQ-551	Reunión de CQ-539 + 0,75 CQ-538	70,0	0,014	28,3		
	CQ-300	. . . .	100,0	0,034	100,0		
Lote CQ-1000.	CQ-1002	Residuo de deslamado	21,2	0,036	54,7		*Ciclonado:* Pulpa: 23 % sólidos. Velocidad de alimentación: 450 kg pulpa/hora (103 kg sólidos/hora). Pulpa *underflow:* 51 % sólidos. Pulpa *overflow:* 16,5 % sólidos.
	CQ-1001	Lamas	78,8	0,008	45,3		
	CQ-1000	(Alimentación)	100,0	0,014	100,0		
	CQ-1004	*Underflow* ciclonado	28,4	0,015	46,6		
	CQ-1005	*Overflow* ciclonado.	71,6	0,006	53,4		
	CQ-1001	. . . .	100,0	0,009	100,0		
	CQ-1037	Concentrado mesa.	3,7	0,092	21,0		
	CQ-1038	Cola mesa	96,3	0,013	79,0		
	CQ-1004	. . . .	100,0	0,015	100,0		
	CQ-1100	Reunión CQ-1002 + CQ-1037 . .	22,0	0,038	59,7	4,3	
	CQ-1101	Reunión CQ-1005 + CQ-1038 . .	78,0	0,008	40,3		
	CQ-1000	. . . .	100,0	0,015	100,0		
Lote CQ-2000.	CQ-2003	Residuo de deslamado	36,7	0,036	57,0		*Ciclonado:* Pulpa: 22,8 % sólidos. Velocidad de alimentación: 455 kg pulpa/hora (104 kg sólidos/hora). Pulpa *underflow:* 54,6 % sólidos. Pulpa *overflow:* 15,1 % sólidos.
	CQ-2002	Lamas	63,3	0,016	43,0		
	CQ-2000	(Alimentación)	100,0	0,023	100,0		
	CQ-2004	*Underflow* ciclonado	34,2	0,025	52,0		
	CQ-2005	*Overflow* ciclonado	65,8	0,012	48,0		
	CQ-2002	. . . .	100,0	0,016	100,0		
	CQ-2070	Concentrado de mesa	4,0	0,180	28,6		
	CQ-2071	Cola de mesa	96,0	0,019	71,4		
	CQ-2004	. . . .	100,0	0,025	100,0		
	CQ-2100	Reunión de CQ-2003 + CQ-2070	37,6	0,040	61,6	2,6	
	CQ-2101	Reunión de CQ-2005 + CQ-2071	62,4	0,014	38,4		
	CQ-2000	. . . .	100,0	0,024	100,0		
Lote CQ-3000.	CQ-3002	Residuo de deslamado	37,2	0,078	72,0		*Ciclonado:* Pulpa: 20,8 % sólidos. Velocidad de alimentación: 387 kg pulpa/hora (80,5 kg sólidos/hora). Pulpa *underflow:* 51,6 % sólidos. Pulpa *overflow:* 12,5 % sólidos.
	CQ-3001	Lamas	62,8	0,018	28,0		
	CQ-3000	(Alimentación)	100,0	0,040	100,0		
	CQ-3004	*Underflow* ciclonado	32,7	0,028	50,5		
	CQ-3005	*Overflow* ciclonado	67,3	0,014	49,5		
	CQ-3001	. . . .	100,0	0,018	100,0		
	CQ-3076	Concentrado de mesa	1,2	0,242	10,2		
	CQ-3080	Cola de mesa	98,8	0,026	89,8		
	CQ-3004	. . . .	100,0	0,028	100,0		
	CQ-3100	Reunión de CQ-3002 + CQ-3076	37,4	0,080	72,5	2,7	
	CQ-3101	Reunión de CQ-3005 + CQ-3080	62,6	0,018	27,5		
	CQ-3000	. . . .	100,0	0,041	100,0		

Tabla 3 (*continuación*)

	N.°	Producto	Peso (%)	Ley U_3O_8 (%)	Distribución (%)	Razón de concentración	
Lote CQ-4000.	CQ-4002	Residuo de deslamado	19,1	0,175	60,4		*Ciclonado:* Pulpa: 20,6 % sólidos. Velocidad de alimentación: 400 kg pulpa/hora (82 kg sólidos/hora). Pulpa *underflow:* 53,6 % sólidos. Pulpa *overflow:* 12,5 % sólidos.
	CQ-4001	Lamas	80,9	0,026	39,6		
	CQ-4000	(Alimentación)	100,0	0,055	100,0		
	CQ-4003	*Underflow* ciclonado	38,1	0,043	62,5		
	CQ-4004	*Overflow* ciclonado	61,9	0,016	37,5		
	CQ-4001		100,0	0,026	100,0		
	CQ-4070	Concentrado de mesa	27,4	0,089	55,4		
	CQ-4071	Cola de mesa	72,6	0,027	44,6		
	CQ-4003		100,0	0,044	100,0		
	CQ-4100	Reunión de CQ-4002 + CQ-4070	27,5	0,150	74,5	3,6	
	CQ-4101	Reunión de CQ-4004 + CQ-4071	72,5	0,019	25,5		
	CQ-4000		100,0	0,055	100,0		

cionados. En la tabla 3 se exponen los valores obtenidos por las fracciones intermedias y las condiciones experimentales:

El lote CQ-300 (común) (ley 0,034 % U_3O_8) rindió un concentrado con una ley de 0,080 % U_3O_8 y una recuperación en U y peso de 71,7 % y 30,0 % respectivamente.

El lote CQ-1000 (ley 0,015 % U_3O_8), permitió obtener un concentrado de ley 0,038 % U_3O_8 y recuperaciones en U y peso de 59,7 % y 22 %.

El lote CQ-2000 (ley 0,024 % U_3O_8) rindió un concentrado de ley 0,040 % U_3O_8, recuperación de 61,6 % del U y de 37,6 % en peso.

El lote CQ-3000 (ley 0,041 % U_3O_8) dió por resultado un concentrado de ley 0,080 % U_3O_8 y recuperaciones de 72,5 % y 37,4 % del U y peso, respectivamente.

El lote CQ-4000 (ley 0,055 % U_3O_8) produjo un concentrado de ley 0,150 % U_3O_8 y recuperaciones de 74,5 % y 27,5 % en peso.

El examen de los datos que preceden permite observar lo siguiente:

1) Con el incremento de las leyes de los lotes se lograron concentrados de leyes más elevadas.

2) Las recuperaciones del U aumentaron a la vez con la ley del lote:

Lotes	Ley U_3O_8 %	Ley del concentrado U_3O_8 %	Recuperación %
CQ-1000 . . .	0,015	0,038	59,7
CQ-2000 . . .	0,024	0,040	61,6
CQ-3000 . . .	0,041	0,080	72,5
CQ-4000 . . .	0,055	0,150	74,5
CQ-300 . . .	0,034	0,080	71,7

Esto permite predecir que la exclusión de los lotes CQ-1000 y CQ-2000 del común CQ-300, hará posible la obtención de concentrados de leyes y recuperaciones más elevadas (ver tabla 1).

Ensayo de concentración del lote CQ-7000

La mena correspondiente al lote CQ-7000 procedía del mismo yacimiento que las anteriores y de mineralización análoga, si bien su ley era de 0,115 % U_3O_8 y sus reservas de volumen mucho menor.

El procedimiento de ensayo se efectuó con las siguientes variantes : la pulpa se alimentó mediante la bomba de arenas vertical, al ciclón simple de 75 mm ∅ ; el *underflow* primario obtenido se recicló (previa dilución) por el mismo aparato y el *overflow* resultante se reunió con el similar primario. Esta suspensión se inyectó en el ciclón de 30 mm ∅.

Se obtuvo un concentrado de ley 0,173 % U_3O_8 y recuperaciones de uranio y en peso de 91,0 % y 60,5 %, respectivamente (tabla 4). Los valores obtenidos demuestran que esta mena exhibe condiciones de concentrabilidad muy favorables, que confirman la deducción relativa a los lotes de leyes crecientes.

Ensayo de concentración del lote CQ-I-1

Este lote era de constitución similar al del CQ-4000: U_3O_8; 0,052 %; V_2O_5 : 0,035 %; CaO: 17,0 %.

El empaste y agitación de la mena con agua se llevó a cabo en la hormigonera (con alimentación continua de agua y rebalse de las lamas). Estas últimas y el residuo se tamizaron por la malla n.° 20 y el rechazo se trituró a —20 mallas. El ciclonado se efectuó con el dispositivo integrado por el tanque cilíndrico-cónico, bomba centrífuga Worthington, circuito corto (*by-pass*), ciclón compuesto tipo Krebs, ciclón cónico de 75 mm ∅ y ciclón de 30 mm ∅. El segundo *overflow* del ciclón compuesto se retornó al tanque alimentador; el similar procedente del anteciclón se alimentó al ciclón de 75 mm ∅ y el *underflow* producido por éste se inyectó en el ciclón de 30 mm ∅.

Tabla 4. Lote CQ-7000

N.°	Producto	Peso (%)	Ley U_3O_8 (%)	Distribución (%)
CQ-7101	*Underflow* ciclonado . .	48,3	0,198	84,5
CQ-7102	*Overflow* ciclonado. . .	51,7	0,034	15,5
CQ-7000	(Alimentación).	100,0	0,114	100,0
CQ-7103	*Underflow* ciclonado . .	66,3	0,276	92,4
CQ-7104	*Overflow* ciclonado . . .	33,7	0,045	7,6
CQ-7101	. . . .	100,0	0,198	100,0
CQ-7106	*Underflow* ciclonado . .	41,6	0,052	58,4
CQ-7107	*Overflow* ciclonado . . .	58,4	0,026	41,6
CQ-7105	(Reunión de CQ-7102 + CQ-7104)	100,0	0,037	100,0
CQ-7130	Reunión de CQ-7103 + CQ-7106[a]	60,5	0,173	91,0
CQ-7131	Colas *(overflow)*	39,5	0,026	9,0
CQ-7000	. . . .	100,0	0,115	100,0

[a] Razon de concentración: 7,60.

Ciclonado:	Ciclonado primario	Ciclonado secundario	Ciclonado de lamas
Ciclon (mm ⌀)	75	75	30
Pulpa (% sól.)	20	16,9	14,6
Velocidad de alimentación pulpa (kg/h).	2 140	1 890	357
Velocidad de alimentación sólidos (kg/h).	428	320	52
Pulpa underflow (% sól.) . . .	43,7	50,5	40
Pulpa overflow (% sól.)	9,7	7,3	10,1

Rindió un concentrado de ley 0,103 % U_3O_8 y recuperaciones de uranio y en peso de 81,1 % y 43,1 % respectivamente (tabla 5). La determinación de CaO en el concentrado acusó 26,6 %, equivalente a 61,1 % del CaO presente en la mena. Este enriquecimiento gravitacional de la calcita, se registró en todos los ensayos de las menas de Cosquín.

Ensayo de concentración del lote CQ-X-1

La composición de esta muestra era semejante a la del lote CQ-3000: U_3O_8: 0,041 %; V_2O_5: 0,027 %; CaO: 9,7 %.

Se operó de igual manera que en el ensayo precedente, hasta el ciclonado, en el que se utilizó el ciclón de tres etapas (figura 4). Se obtuvieron 3 *overflows* y 2 *underflows*. Los *overflows* se alimentaron al ciclón de 30 mm ⌀. Resultó un concentrado de ley 0,080 % U_3O_8 y recuperaciones de U y en peso de 78,1 % y 39,9 % (tabla 6).

Este ensayo rindió una recuperación superior a la del ensayo sobre el lote CQ-3000. La ley en CaO del concentrado fué de 16,8 % CaO y distribución de 71,9 % del CaO total.

ENSAYOS DE FLOTACIÓN

Se realizaron numerosos ensayos de flotación selectiva sobre el lote CQ-300 (común), en los que se utilizaron combinaciones de reactivos específicos ya sea para la carnotita o para los minerales de ganga, con resultados negativos. Se estima que la presencia de partículas de arcilla y calcita, de tamaños del orden de los micrones y en muy abundante proporción, interfieren con la acción de los reactivos de flotación.

La friabilidad de los cristales de carnotita y tyuyamunita también puede ser causa de la reducción rápida de los mismos a partículas de tamaño submicrónico, por acción de la atrición que en mayor o menor grado se registra durante la molienda y agitación previas a la flotación.

CONCLUSIONES

Las menas del yacimiento « Don Rodolfo » (Cosquín, provincia de Córdoba, República Argentina), caracterizadas por su baja ley media (0,03 % U_3O_8) y la importancia de sus reservas, ofrecen posibilidades de ser beneficiadas por métodos gravitacionales sencillos.

Los ensayos efectuados hasta el presente permiten concluir que las técnicas de tratamiento de mejores perspectivas, se basan en la dispersión en medio acuoso de la fracción arcilloso-calcárea, deslamado, clasificación del residuo por la malla n.° 20, molienda del rechazo a — 20 mallas y ciclonado de la pulpa resultante total, en una o más etapas. La recuperación puede aumentar por el pasaje de las medianías de ciclonado por mesa vibratoria.

Los resultados obtenidos han demostrado que es posible llegar a concentrados de uranio cuyas leyes se hallan entre el doble y el cuádruple de la

Tabla 5. Lote CQ-I-1

N.°	Producto	Peso (%)	Ley U_3O_8 (%)	Distribución (%)
CQ-I-43	*Underflow* 1.° ciclonado	34,4	0,120	75,1
CQ-I-46	*Overflow* 2.° ciclonado .	51,1	0,018	16,8
CQ-I-47	*Underflow* 3.° ciclonado	8,7	0,038	6,0
CQ-I-48	*Overflow* 3.° ciclonado .	5,8	0,021	2,1
CQ-I-1	(Alimentación).	100,0	0,055	100,0
CQ-I-49	Reunión de CQ-I-43 + CQ-I-47[a]	43,1	0,103	81,1
CQ-I-50	Reunión de CQ-I-46 + CQ-I-48 .	56,9	0,018	18,9
CQ-I-1	. . . .	100,0	0,055	100,0

[a] Razon de concentración: 2,3.

Ciclonado:	Ciclonado primario	Ciclonado secundario	Ciclonado de lamas
Ciclón	Comp. (Krebs)	Simple, 75 mm	Simple, 30 mm
1.° capta-vórtice (mm ⌀)	16	16	6
2.° capta vórtice (mm ⌀)	10	—	—
Boquillas de descarga (mm ⌀)	5	5	3
Pulpa (alimentación) (% sol.) . .	1,91	11,6	16,3
Veloc. de alim. pulpa (kg/h) . . .	1 980	2 795	545
Veloc. de alim. sólidos (kg/h) . .	378	324	89
Pulpa *underflow* (% sól.)	61	24,5	51,1
Pulpa *overflow* (% sól.)	11,6	9,8	7,9

Tabla 6. Lote CQ-X-1

N.°	Producto	Peso (%)	Ley U_3O_8 (%)	Distribución (%)	CaO (%)	Distribución (%)
CQ-X-53	1.° *underflow*	18,0	0,115	50,3	17,8	30,0
CQ-X-57	2.° *underflow*	11,5	0,072	20,2	16,2	17,5
CQ-X-59	*Underflow* ciclonado lamas	10,4	0,030	7,6	25,1	24,4
CQ-X-60	*Overflow* ciclonado lamas	60,1	0,015	21,9	5,0	28,1
CQ-X-1	Alimentación	100,0	0,041	100,0	10,7	100,0
CQ-X-150	Reunión 3 *underflows*[a]	39,9	0,080	78,1	16,8	71,9
CQ-X-151	*Overflow*	60,1	0,015	21,9	5,0	28,1
CQ-X-1		100,0	0,041	100,0	10,7	100,0

[a] Razón de concentración: 2,5.

Ciclonado:

	Ciclonado primario	Ciclonado de lamas
Ciclon	Compuesto (3 etapas)	Simple, 30 mm ⌀
Pulpa (alimentación) (% sólidos)	14,7	12,0
Velocidad de alim. pulpa (kg/h)	2 650	450
Velocidad de alim. sólidos (kg/h)	390	50
Pulpa 1.° *underflow* (% sól.)	31,4	58,7
Pulpa 2.° *underflow* (% sól.)	24,2	
Pulpa comun 3.° *overflow* (% sól.)	12	
Pulpa *overflow* (% sól.)		10,0

alimentación, con recuperaciones de uranio y en peso del orden de 80-70 % y 40-20 %, respectivamente.

Se observó que con el incremento de las leyes de las menas aumentaron las recuperaciones y las leyes de los concentrados obtenidos, siendo esos valores más favorables a partir del lote de ley 0,041 % U_3O_8.

Las menas de leyes inferiores a 0,040 % pueden ser beneficiadas por técnicas similares pero que incluyen cierto número de etapas de reciclado de medianías.

Simultáneamente con el enriquecimiento del uranio, se produce el del $CaCO_3$ en los concentrados, lo que hace previsible la aplicación de procedimientos de lixiviación alcalinos.

El empleo del ciclón de tres etapas permitió obtener una recuperación de uranio más elevada.

Se deberá estudiar intensivamente la recuperación de las partículas muy finas de los minerales de uranio que se pierden en las lamas y colas de tratamiento (equivalente a 20-30 % del uranio total).

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/408 Argentina

The physical concentration of low-grade argillocalcareous uranium ores

By M. Mochulsky

The Don Rodolfo (Cosquín, Province of Córdoba) uranium ore deposit is characterized by large reserves of low content, thus necessitating preliminary concentration by physical methods to achieve economic recovery of the uranium they contain.

In this deposit the metal is present as carnotite and tyuyamunite, contained in argillocalcareous gangue, with contents ranging between 0.014% and 0.10% U_3O_8.

Assays of concentration were carried out as described below:

Malaxation of the ore in water,

Sifting through a Tyler 20-mesh screen,

Milling the oversize from + 20 mesh to — 20 mesh,

Desliming the pulp by siphoning,

Treatment of the suspension by hydraulic cyclone separator in one or more stages to obtain concentrate and middlings, followed in some cases by processing of the fraction on shaking tables, in accordance with various operational techniques.

The results obtained show that concentrates with a uranium content 3-4 times higher than that of the unsorted ore can be achieved, as well as recoveries of close on 70%.

A supplementary operation consisting in processing with a shaking table leads to higher recovery of the uranium contained in the middlings.

From a study of the results of upgrading the ore by these gravitational processes which are based on using hydraulic cyclone separators in conjunction with shaking tables, it is concluded that the higher the uranium content of the ore processed, the higher will be the content and recovery of the concentrate obtained. Since calcium carbonate enrichment of the concentrates occurs simultaneously with that of uranium, acid leaching is excluded as a method for the subsequent processing of the products obtained.

A/408 Argentine

Concentration physique des minerais argileux-calcaires d'uranium à basse teneur en Argentine

par M. Mochulsky

Le gisement de minerais d'uranium « Don Rodolfo » (Cosquín, province de Córdoba), est caractérisé par ses grandes réserves et sa basse teneur, ce qui impose une préconcentration par des moyens physiques pour permettre une extraction économique de l'uranium.

Dans ce gisement, le métal est sous la forme de carnotite et tyuyamunite, ces minéraux étant englobés dans des conglomérats argileux-calcaires, avec des teneurs comprises entre 0,014 % et 0,10 % de U_3O_8.

Les essais de concentration ont été réalisés comme décrit ci-dessous :

a) Malaxage du minerai dans l'eau;

b) Tamisage par un crible à 20 mesh (Tyler);

c) Broyage du refus de + 20 mesh à — 20 mesh;

d) Déschlammage de la pulpe par siphonnage;

e) Traitement de la suspension par des hydrocyclones en une ou plusieurs étapes avec obtention d'un concentré et de mixte suivi, dans certains essais, d'un triage sur tables à secousses, selon le schéma de traitement.

Les résultats obtenus ont démontré qu'il est possible d'obtenir des concentrés avec des teneurs en uranium trois à quatre fois supérieures à celles du minerai initial et des extractions proches de 70 %.

Le traitement par table à secousses, en tant qu'opération complémentaire, se traduit par une augmentation de l'extraction de l'uranium contenu dans les mixtes.

De l'étude des résultats de l'enrichissement des minerais à l'aide de tels procédés par gravité fondés sur l'utilisation d'hydro-cyclones complétés par des tables à secousses, on peut conclure que plus est haute la teneur en uranium du minerai traité, plus seront élevées l'extraction du métal et sa teneur dans le concentré obtenu. L'enrichissement des concentrés en carbonate de calcium est parallèle à celui en uranium de sorte que l'attaque acide est à exclure en tant que traitement ultérieur des produits obtenus.

A/408 Аргентина

Обогащение бедных глинисто-известковых урановых руд в Аргентине

М. Мошульский

Урановое месторождение «Дон Родольфо» (Коскин, провинция Кордова) характеризуется большими запасами руд с низким содержанием урана, что заставляет прибегать к их обогащению физическими методами для достижения экономически выгодного извлечения урана из этих руд.

В этом месторождении уран содержится в карнотитах и тюямунитах, эти минералы встречаются в глинисто-известковых бедных рудных жилах. Количество урана в виде U_3O_8 в них составляет 0,014%—0,10%. Обогащение проводится следующим образом:

Смачивание руды в воде.

Просеивание через сито крупностью 20 меш.

Дробление отсева (от +20 до —20 меш).

Дешламация пульпы сифонированием.

Обработка суспензии в двух или более ступенчатых гидроциклонах для получения концентрата и последующая подача в некоторых случаях этой фракции на концентрационные столы согласно различным схемам обогащения.

В результате получаются концентраты с содержанием урана в 3—4 раза больше первоначального количества урана в неотсортированной руде, извлечение урана приближается к 70%.

Дополнительная обработка на концентрационных столах приводит к повышению количества урана в концентратах.

На основании изучения результатов обогащения рассматриваемых руд гравитационными методами, основанными на применении гидроциклонов и концентрационных столов, установлено, что чем выше содержание урана в обрабатываемой руде, тем выше выход полученных концентратов. Обогащение концентратов карбонатом кальция исключает процесс кислотного выщелачивания как метод последующей переработки продукта.

Recent results in the processing of Hungarian uranium ores

By E. Szabó, L. Bakos, B. Czeglédi, M. Fodor and P. Müller *

Some problems arising in the processing of Hungarian uranium ores were discussed in a paper presented at the Second Geneva Conference [1]. Further investigations in this field are reported below.

WEIGHTING OF RADIOMETER READINGS AND DETERMINATION OF OPTIMUM SIZE DISTRIBUTION IN RADIOMETRIC ORE CONCENTRATION

In concentrating uranium ore with the help of gamma counters, the pieces of ore are sorted by the activity detected, irrespective of particle size. Efficient concentration, however, calls for classification by relative concentration of uranium. This can be achieved by automatic weighting of the particles and corresponding weighting of the activities measured.

This can be done by one of three methods: the photo-effect, the inductive feeler, or the dielectric. The choice between them depends primarily on the contrast properties of the ore and on the design of the sorting machinery. Chutes are used for concentrating ores with high contrast and in this case the photo-effect provides a good estimate of the weighting factor to be applied. For classifying ores with low contrast, particularly in small pieces, the sensitivity must be higher (threshold < 70 mg U) and the time of measurement longer. Conveyer belts are therefore used, but it was found that the conventional weightometer type of scale was inadequate for our automatic weighting procedure because of the irregular spacing of the pieces of ore and their light weights.

An apparatus based on the photo-effect was accordingly constructed in 1958. It consisted of photocell screens mounted on either side of the belt ahead of the radiation detector. The maximum weight pulse was first stored and subsequently combined with the radiation signal, the combined signal being used for controlling the sorting machinery. The photocells were later replaced by photo-resistances. The systematic errors in this procedure result from the fact that the signals are proportionate to the particle length along the axis of the belt, and therefore not fully linear with the actual particle weight, and from the accumulation of dust from the ore on the photo-resistances, which affects their reliability.

In the case of larger lumps, inductive electric feelers work satisfactorily and have been found efficient even for the preliminary screening of ore conveyed in bulk by belt. This method is particularly convenient where radiometric devices cannot be installed (e.g., underground). In this apparatus, illustrated in Fig. 1, the electric feelers are angularly displaced by the particles moving along the belt. The angular displacements are converted to voltage pulses by the inductive device located at the point of suspension of the feelers. The converter comprises emitting and receiving coils. The transmitted pulses can be shaped by the movement of an aluminium plate attached to the feeling arms. By choosing a plate of suitable shape the weighting factor can be varied at will. The emitter is fed from a power supply at 40 kHz. Each of the receiving coils has a peak rectifier, which is charged to amplitudes corresponding to the magnitude of the angular displacement. The output voltage of the integrating capacitor senses the number of feelers, the amplitudes and the time involved. In this way, the three dimensions of the particle that are of interest can be covered. The radiation pulse superimposes on the weight pulse. The threshold values for both are shown in Fig. 2. The apparatus is simple, reliable and easily

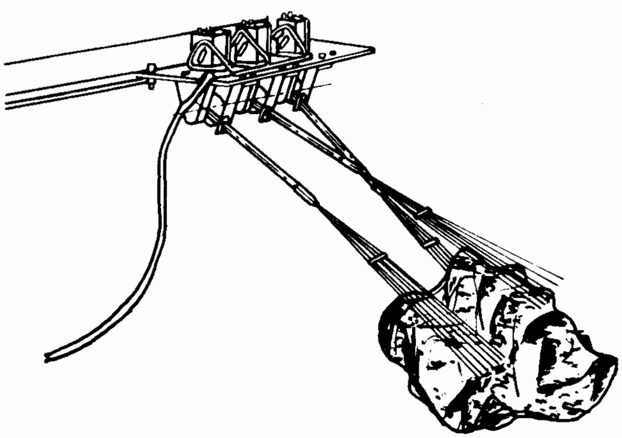

Figure 1. Mechanical sorter for pieces of uranium ore with inductive feelers for weighting

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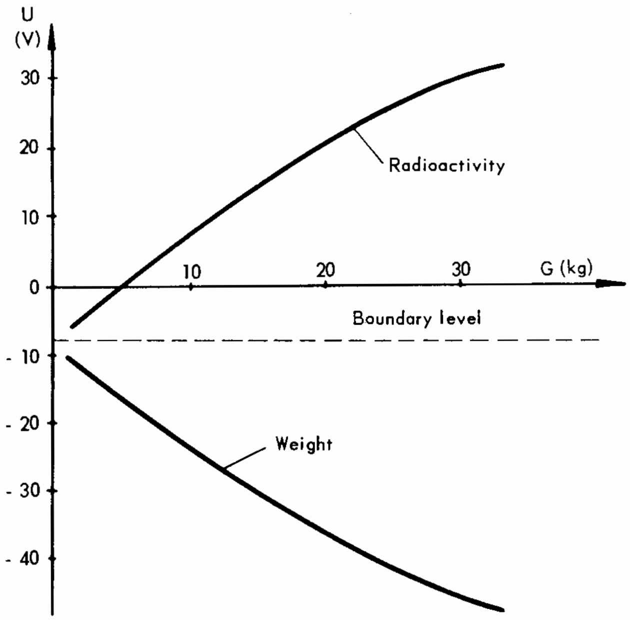

Figure 2. Characteristic threshold curves of radioactivity and weight signals

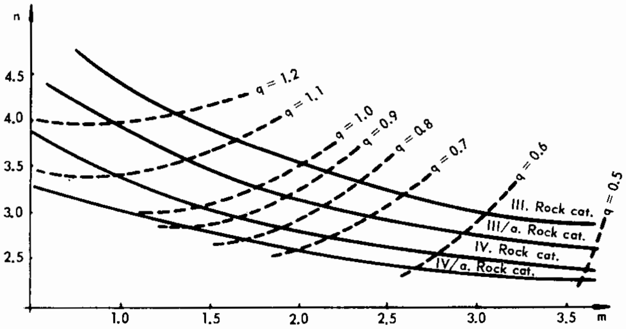

Figure 4. Nomogram of optimum indices for two free-surface explosions

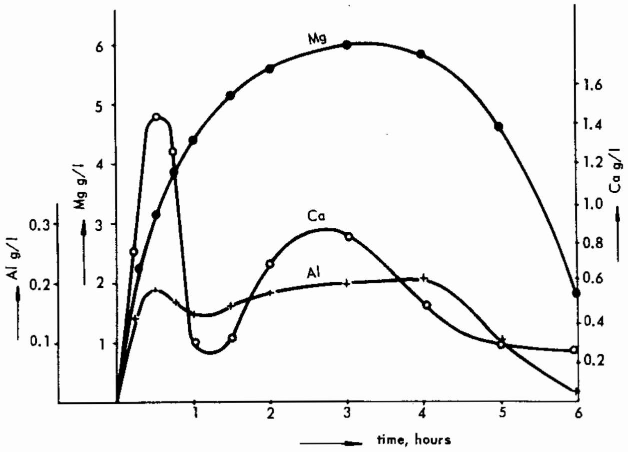

Figure 6. Variation in Ca, Mg, Al concentrations of leaching liquor with leaching time

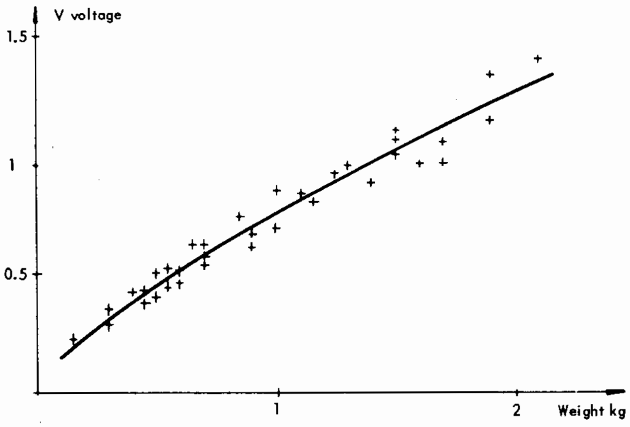

Figure 3. Weight vs. voltage curve of the dielectric device

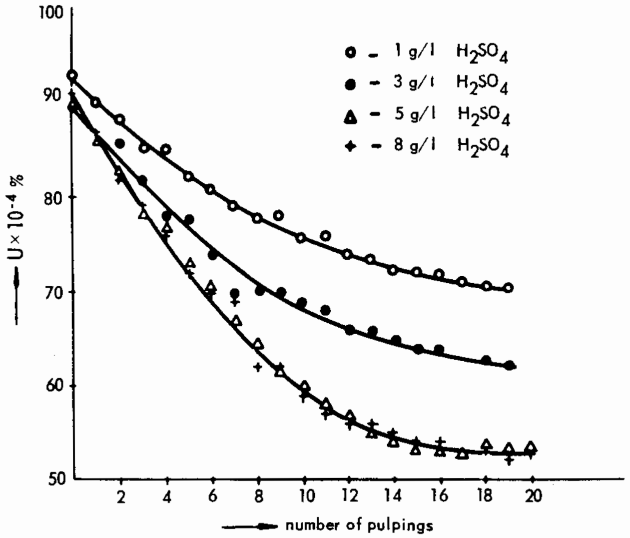

Figure 5. Uranium content of residue as a function of the number of pulpings for various concentrations of sulphuric acid

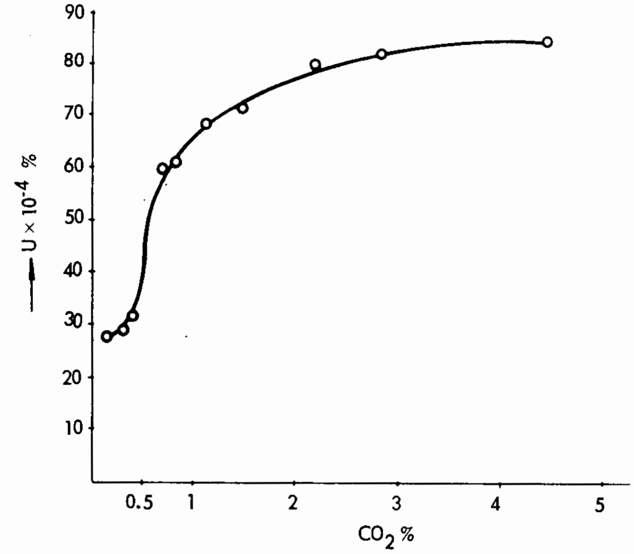

Figure 7. Uranium content of residue for ores with different carbonate concentrations

installed. Its particular advantage is that the weighting factor can be applied to the integrating circuit of the radiometer without amplification. The introduction of this method raised efficiency by 6 per cent.

For the radiometric concentration of small particles, the dielectric weighting method was found to be the most suitable. Ore particles travelling on a belt induce variations in the capacities of capacitors placed above and below the belt which are measured by a bridge. The dielectric weighting curve is illustrated in Fig. 3. The weight signal is used to correct the radiation pulse in the same way as with the electric feelers.

Weighting makes radiometric concentration simpler and more efficient even for ores with poor contrast.

The economics of radiometric concentration are strongly influenced by the size of the ore particles to be treated. This in turn depends on the physical properties of the ore, but can be controlled to some extent by appropriate mining techniques. This is why the breaking parameters were thoroughly studied with a view to obtaining the optimum size distribution of ore from sandstone deposits. The effect of depth of drilling, packing density, specific consumption of explosive, type of explosive and shot timing were investigated. The drill-hole diameter and pattern were those established for maximum output, and were not varied during the experiments.

Drilling depth seems to have no appreciable bearing on particle size, which was found to be affected mainly by the quantity and type of explosive, by the packing density and by the breaking technique used. In the experiments, rather weak explosives causing no excessive shattering werre used.

The experimental results are shown in a nomogram (Fig. 4) with drilling depth per cubic metre as ordinate and thickness of deposit as abscissa. The solid lines represent the parameters for rock of varying hardness on the Protodyakonov scale. The dotted lines are the isotherms for optimum specific consumption of explosive. The nomograms can be used to determine the packing density and specific consumption of explosive to give the best size distribution for a given deposit.

Similar nomograms have been plotted for breaking technique and shot timing. It has been found that the use of these nomograms results in a 5 to 10 per cent improvement in particle size distribution.

MINIMIZING LEACHING LOSSES FROM URANIUM ORES CONTAINING CARBONATES

In the sulphuric acid leaching of sandy ores containing 6 to 12% carbonate (dolomite), the amount of uranium in the residue cannot as a rule be reduced below about 0.008-0.009%. Experiments were therefore carried out to determine the chemical form of the uranium present in the residue.

The sulphuric acid residue was pulped repeatedly, using different concentrations of sulphuric acid, at a solid to liquid ratio of 1 : 1.5 and filtered after vigorous agitation for 20 minutes before the uranium content of the solid phase was determined. The results (Fig. 5) show that at best, with 5 g/l H_2SO_4 and 15-16 pulpings, the residual uranium can be reduced from 0.009 to about 0.005%. This implies that uranium has entered the solid phase during the leaching process by becoming bound to a component that has low solubility in weak sulphuric acid. Co-precipitation with gypsum was suspected. Further reduction in the uranium content on washing the residue with sulphuric acid-Complexon III confirmed this assumption.

Considering, on the other hand, the variations in the calcium, magnesium and aluminium contents of the leach with time (Fig. 6), it is apparent that since the sulphuric acid-dolomite reaction highly supersaturates the solution at the beginning with calcium, which is precipitated shortly afterwards, co-crystallization of uranium and gypsum could also be responsible for the loss of uranium. Some supersaturation is apparent even later in the process. Similar behaviour could be observed, though with less variation, for the concentration of aluminium and magnesium. Thus, considerable co-precipitation with gypsum is to be expected, and this was accordingly studied during the peak leaching period (1.5 to 2 hours). Since gypsum has a known tendency to recrystallize with magnesium and other metallic sulphates, the concentration of each leaching component in the precipitates was studied. Analysing the components co-precipitated in 48 hours with gypsum from the filtrate from the sulphuric acid leach after leaching the ore for 30 minutes containing 9% dolomite, the concentrations in mg/l were found to be: Ca, 840; Mg, 405; Fe, 80; Al, 40; U, 30 and sulphate, 4 710.

Thus the precipitate is seen to contain an appreciable amount of uranium as well. This agrees well with the earlier results. But, though effective, repeated pulping and washing of the residue is impractical for economic reasons.

Experiments on ores with various contents of carbonate show, as is apparent from the uranium residue vs. carbonate concentration curves in Fig. 7, that the precipitation of uranium falls off in the range 0.5 to 0.7% CO_2 and ceases below 0.4% CO_2. It has thus been established that about half the loss in uranium experienced with sulphuric acid leaching can be attributed to co-precipitation with gypsum from the liquid phase. For ores with medium carbonate content (7 to 10%), the los can be reduced by flotation before leaching. The flowsheet in Fig. 8 is used with 2-3 kg reagent per run, and 150μ particles of ore and silicates containing less than 0.4% CO_2 are obtained which can be efficiently leached with sulphuric acid.

The uranium content of the residue is about 0.0030 to 0.0035% for 5-10 g/l of free H_2SO_4 at 460 mV redox potential at room temperature with 1.5 h agitation.

The flotation agent (90% sulfo-soap and 10% Turkey red oil) is added only to the primary flotation cells. The concentrate obtained from secondary (cleaning) flotation, containing 15% carbonate by weight of ore, can be alkaline leached at 2 to 2.5 atmospheres overpressure at 100-105 °C in 7 to 9 hour runs.

Flotation followed by leaching reduces the uranium losses, as compared with simple sulphuric acid leaching, by a factor of 2. Moreover, the cost of leaching agents is lower for the combined method, and for ores containing 6 to 7% dolomite the savings are sufficient to cover the cost of installing and operating the flotation plant.

RECOVERY OF HIGH PURITY URANIUM COMPOUNDS BY EXTRACTION METHODS

The direct recovery of uranium from eluates of ion exchange resins was studied. It is known that from anion exchange resins the adsorbed uranium is most simply and cheaply eluted by chloride in dilute hydrochloric acid. The concentrations in the eluate vary with the nature of both ore and resin, and lie in the g/l range, i.e., uranium: 4 to 18; chloride: 15 to 40; sulphate: 15 to 40; iron: 0.5 to 4; hydrochloric acid: 10 to 25.

For extracting the uranium from this eluate, dialkyl phosphoric acid, suggested in the literature, was chosen because of its efficiency. With the extraction methods described [2-6], the raffinate contains appreciable quantities of uranium in addition to sulphate or nitrate anions partly in their acid form. This is why the solution still rich in uranium has to be recycled.

In the present experiments, uranium is eluted from the anion exchange resin by a chloride-rich eluent, which means that the raffinate cannot be recycled. An extraction procedure has accordingly to be developed in which the uranium concentration in the raffinate would not exceed the permissible maximum of 0.003 g/l for spent solutions.

Considering the various properties of extractants (including possible synergism), the use of dialkyl phosphoric acid, trialkyl phosphates, their mixtures and tri-n-octylamine was tried. Kerosene was used as diluent. The extraction isotherms were determined for multi-stage counter-current extraction and re-extraction (Table 1). The experimental data determined the choice from among 18 extractants of those to be studied further.

Good results were obtained with di-octyl phosphate (DOP) and tri-octyl phosphate (TOP) in 1:1 mixture. The uranium distribution isotherms are shown in Figs. 9 and 10. It is apparent that the concentration of uranium in the eluate fell to 0.003 g U/l if the acidity of the liquid phase was not higher than 0.25 and the uranium concentration in the recycled organic

Table 1. Characteristics and composition of extractants
(aqueous phase : 10 g/l uranium; stripped with ammonium carbonate)

Symbol of solution	Reagent concentration M/l kerosene diluent	Distribution coefficient $D_{o/a}$	$D_{a/o}$	Remarks
TBP	0.1 TBP	1.10^{-4}	—	
TnOA	0.1 TnOA	4.10^{-2}	—	
D2EHPA	Mixture of mono- and di-2-(ethylhexyl) phosphate, assay 60% (di- 59%, mono- 41%) concentration of di-ester 0.06	95	166	High losses in extraction
D1MHPA	Mixture of mono- and di-1-(methylhexyl) phosphate, assay 46% (di- 49%, mono- 51%) concentration of di-ester 0.046	34	—	Emulsion, high separation time
D2EHPA	0.1, titratable 98.4% (di-97.9%)	5	95	
R I	0.061 D2EHPA; 0.06 M2EHPA; 0.1 TBP	139	31	High losses in stripping
R II	0.061 D2EHPA; 0.06 M2EHPA; 0.1 TnOA	541	—	High separation time
R III	The same as D1MHPA + 0.1 TnOA	97	—	High separation time
R IV	The same as D1MHPA + 0.1 TBP	193	—	High separation time
R_2I	0.1 D2EHPA; 0.1 M2EHPA; 0.1 TBP	228	11	Good
R_2III	0.064 D1MHPA; 0.052 M1MHPA; 0.1 TnOA	44	—	High separation time
R_2IV	0.064 D1MHPA; 0.052 M1MHPA; 0.1 TBP	203	—	High separation time
T I	0.1 D2EHPA (97.8%); 0.1 TBP	3	92	Good
T II	0.1 D2EHPA (97.8%); 0.1 TBP	8	2	
T III	0.1 D1MHPA; 0.1 TnOA	—	—	High separation time
T IV	0.1 D1MHPA; 0.1 TBP	10	—	Emulsion
T V	DOPA + TOP[a]	+	+	Good
T_2I	0.1 D2EHPA (99.18%); 0.1 TBP	1	6 000	Good

[a] Prepared from synthetic C_8 alcohols.

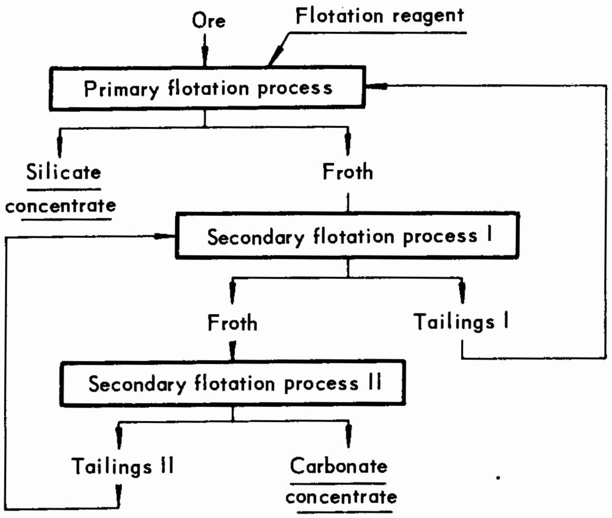

Figure 8. Separation by flotation of uranium ore with medium carbonate content into carbonate and silicate concentrates

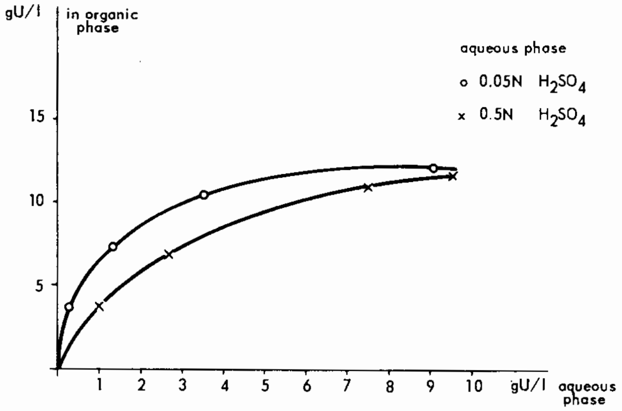

Figure 9. Effect of acid concentration in the aqueous phase on uranium distribution coefficient

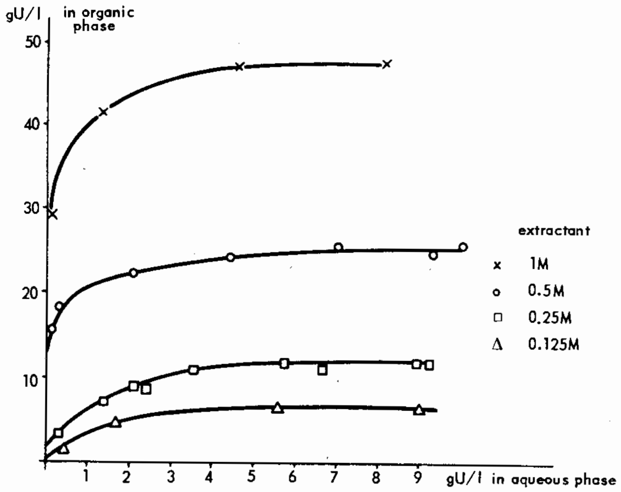

Figure 10. Distribution of uranium for 0.05*M* sulphuric acid and Dop-Top/kerosene

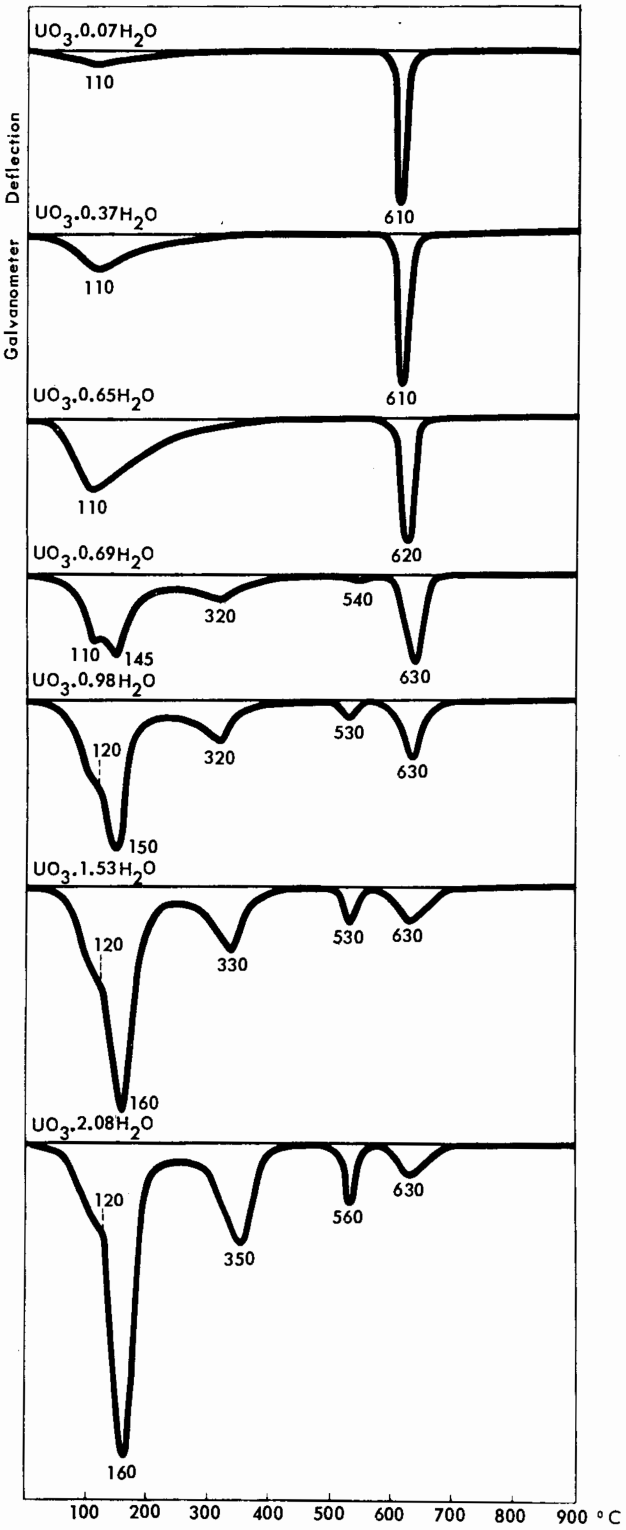

Figure 11. Differential thermogravimetric curve of hydrated $UO_3.2H_2O$ samples

phase less than 0.5 g/l before extraction. Uranium concentrations of this order can be obtained by stripping with ammonium carbonate if the concentrations of both extractant and ammonium carbonate, as well as the solid to liquid phase ratio, are kept at suitable values. Some difficulties may arise from the presence of mono-octylphosphoric acid (MOP) in the extractant. In the stripping process, ammonium salts may precipitate, causing appreciable loss in extractant and uranium. In a solution containing kerosene, ammonium salts of DOP are not precipitated in the presence of alcohols with long carbon chains and trialkyl phosphates. As established in earlier studies, the solubility of ammonium salts in kerosene is increased by the formation of associates.

The TI, T_2I and D2EHPA solutions (see Table 1) proved to be suitable extractants. Owing to its high mono-ester content, R_2I cannot be used in a continuous countercurrent process. The T_2I solutions are preferable to the TI solution.

Pure D2EHPA has better extracting and T_2I better stripping properties. Mixtures of 0.2 to 0.4M D2EHPA and 0.05 to 0.1M tributylphosphate (TBP) were found to be the most suitable extractants in the present case. For re-extracting uranium,

$$NH_4HCO_3\ (0.4M) + (NH_4)_2CO_3\ (0.2M)$$

proved the most successful. Products of reactor grade purity were obtained.

Study of the methods of purifying uranium concentrates [7] has shown that using TBP diluted with xylene better values can be achieved than with a 40% TBP/kerosene system reported in the literature [8].

In order to reduce the separation time when re-extracting with water, and also to increase the variety of starting materials for the production of UO_2, other potential re-extraction methods were studied. Uranium was recovered from 38% TBP/xylene solvent using a solution of urea. The time required for the separation of the phases could then be reduced by a factor of 10 to 20 as compared with water re-extraction. A further advantage is the distinct separation of the phases. In two stage re-extraction using 8M and 4M solutions of urea, 97.2% and 95.1% respectively of the uranium could be brought into the aqueous phase, from which it could most conveniently be recovered by homogeneous precipitation. 1M ammonium carbonate solution works equally well; in addition, in this case the end product is precipitated in crystalline form so that the re-extractant can be recycled. The product proved to be of the highest purity (e.g., Cd $<$ 1 ppm) achieved in the current series of experiments.

For purifying uranium concentrates, a laboratory, counter-current, gravitation type mixer-settler with a total throughput of 13 l/h was used. The usual stages of the operation can be carried out continuously. Using conventional technology, UO_2 pellets with more than 95% theoretical density could be obtained [9].

STUDIES ON THE THERMAL DECOMPOSITION OF URANIUM TRIOXIDE HYDRATES AND AMMONIUM URANATES

In developing ceramic UO_2 fuel elements, the thermal decomposition of ammonium uranates precipitated at different pH was found to differ, but to a progressively varying extent; a close analogy with the thermal decomposition of uranium trioxide hydrates is also observable. It seemed of interest, therefore, to study the formation and thermal decomposition of these compounds.

Thermogravimetric measurements were carried out by derivatograph [10]. The differential thermogravimetric (DTG) and thermo-analytic (DTA) curves plotted simultaneously allowed accurate evaluation of the thermogravimetric (TG) curve even in cases where some of the thermal decomposition processes seemed partly to overlap.

The hydration (hydrolysis) of β-UO_3 produced from ammonium uranate, and that of amorphous UO_3, was studied in the liquid and vapour phases of water. The infra-red spectra of the initial and amorphous UO_3 samples were the same as those reported by Hoekstra [11].

The β-UO_3 sample was hydrolised in distilled water for various periods, with continuous agitation. The products were filtered, washed with acetone, dried in vacuum at room temperature and stored in a desiccator with silica gel. The DTG curves for the original material and for samples hydrolised for different periods are shown in Fig. 11.

So long as the water content of each sample does not exceed that required by the composition $UO_3.0.66H_2O$, dehydration occurs in a single step. It will be seen from the DTG curve that dehydration at 110 °C involves the maximum change in weight. The DTG curve, however, is not symmetrical, the second half being flattened and the dehydration rate decreasing with increasing temperature to end at 400 °C. An endothermic effect is involved, and the DTA and DTG peak temperatures are equal. Considering the rather low DTG peak temperature, this water can be attributed to poor water bonding; all the water can be removed, but only over a broad temperature interval.

The conversion of UO_3 to U_3O_8 at 610 °C is a single stage process up to 0.66 water per uranium atom. The decomposition of oxygen has a similarly high endothermic effect with DTA and DTG peaks occurring at the same temperature.

As soon as the water content per uranium atom in the sample exceeds 0.66, the decomposition step characteristic of the fully hydrolysed $UO_3.2H_2O$ composition manifests itself; this is assumed to correspond to three different dehydration and two oxygen decomposition processes.

The thermal decomposition characteristics are best seen on the DTG curve of a fully hydrolysed $UO_3.2H_2O$ sample (Fig. 12). It is apparent from this curve that the two water molecules per uranium atom are removed in three steps. Loss of water occurs at 120 °C at a point of inflexion, whereas at 160° and 350 °C it definitely takes place at a DTG peak. On the TG curve, the steps corresponding to the first two peaks are seen to merge. The DTG curve nevertheless makes it possible to determine the change in weight involved in each of the individual stages of decomposition. The elimination of water corresponding to the inflexion point at 120 °C on the DTG curve amounts to about 0.33 mole, and that up to the DTG minimum after the second peak to 1.0 mole, while the loss calculated from the DTG minimum following the third peak is 0.66 mole per uranium atom. On the other hand, the shapes of the DTG curves for samples with various contents of water show the gradual superimposition of two other dehydration peaks on the first one on the DTG curve at 102 °C, but extending almost up to 400 °C as the water content increases. The loss of water reflected by the 160 °C DTG peak actually sets in above 120 °C, with the result that the two peaks are still distinct. For samples with a higher water content, the second stage sets in earlier (close to the 120 °C peak) and the first stage in water removal cannot manifest itself except at the point of inflexion. The abrupt DTG peak at 160 °C results from the superposition of nearly all the seond half of the first peak and all of the second peak. By plotting the components of the resultant peak at 160 °C, a second stage is obtained, starting at about 110 °C and ending at about 220 °C. The third stage of dehydration is superimposed on the trailing edge of the first stage. This is apparent also since the first half of the third stage is flattened, and even exhibits, around 300 °C, a slight inflexion. Consequently, the third stage in water removal starts at about 300 °C and ends at 420 °C.

The areas bounded by the peaks thus plotted, shown by the dotted line on the DTG diagram in Fig. 12, are nearly equal. This means that dehydration per uranium atom occurs in three steps, with 0.66 mole water lost at each step. It can be inferred from this that $UO_3.2H_2O$ is not a monomer, but a trimer or a whole-number multiple thereof. Assuming a trimer, two H_2O molecules are removed per decomposition step; but they are present in different forms and with different bond strengths.

With the onset of the three dehydration steps, the oxygen also is progressively removed, in two steps. For samples of composition $UO_3.2H_2O$, the DTG peak corresponding to the first loss of oxygen appears at 530 °C, the second at 630 °C. The two steps involve opposite changes in enthalpy: the DTA curve for the first loss indicates low exothermic, the second high endothermic, effects. It can be inferred from the thermogravimetric curve that two-thirds of the oxygen is lost in the first step and one-third in the second. Relating this to the specific loss of 1/3 oxygen atom per atom of uranium, the two steps correspond to losses of 1/9 and 2/9 of an oxygen atom respectively.

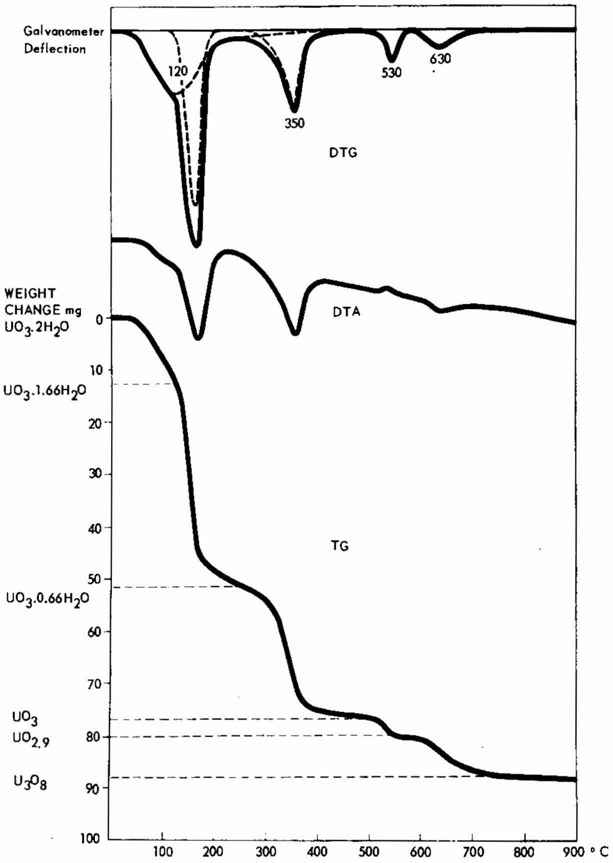

Figure 12. Complete derivatogram for $UO_3.2H_2O$ sample

The composition and thermal decomposition of the system UO_3-H_2O-NH_3 was also investigated. $UO_3.2H_2O$ was used as the starting material and subsequently combined at varying mole ratios with an ammonium hydroxide solution. Filtering and washing with acetone gave final products with compositions in agreement with Cordfunke's results [12].

As the $NH_4.OH$ concentration of the solution was increased, the composition of the solid compounds varied according to the formula $UO_3.(2-x)\,H_2O.xH_2O$. A high NH_3 to UO_3 mole ratio (> 80) yielded a product with a $NH_3{:}UO_3$ mole ratio close to 0.66, with maximum ammonium content.

The derivatograms of the individual products indicate progressive variation. With initially low ammonium content, the derivatogram is similar in shape ot the $UO_3.2H_2O$ curve, while with increasing ammonium content the decomposition peak corresponding to the loss of two oxygens turns gradually into a peak representing the loss of one oxygen atom observed for β-UO_3. The loss of ammonium sets in with intense exothermic effect in the temperature range of the third water removal step.

The thermal decomposition of ammonium uranates produced by direct ammonium hydroxide precipitation from uranyl nitrate was also studied. In one set of experiments the separation was performed at various, but during precipitation constant, pH values, while in another case precipitation at constant end pH was practised. In these cases the decomposition curves were even more intricate, since the nitrate contamination could not be removed from the samples and produced additional, separate peaks on the derivatogram.

At low pH (~3.5) precipitation, even the $UO_{2.9}$ peak characteristic of the decomposition of amorphous UO_3 and $UO_3.2H_2O$ could be identified on the derivatogram. For products precipitated at higher pH, oxygen is lost in a single step.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/450 Hongrie

Progrès récents dans le traitement des minerais

par E. Szabó *et al.*

Les auteurs indiquent les principes physiques à la base des méthodes de pondération des lectures de radiamètres, fondées sur l'effet photoélectrique, l'induction et les effets diélectriques; ils décrivent les radiamètres construits d'après ces principes. Les procédés ainsi mis au point permettent de réduire le nombre des fractions granulométriques traitées par des méthodes radiométriques, et améliorent l'efficacité de la séparation.

Les auteurs décrivent les essais expérimentaux de méthodes d'abattage et de triage ayant pour objet d'obtenir la granulométrie optimale pour le triage radiométrique; ils donnent des exemples de l'application des résultats de laboratoire à l'échelle industrielle.

Lorsque des minerais d'uranium contenant des carbonates sont soumis à une attaque sulfurique, il se produit une coprécipitation de sulfate de calcium et d'uranium à partir de la phase liquide. On peut éviter les pertes d'uranium qui en résultent en traitant au préalable le minerai par flottation, pour réduire sa teneur en carbonate. Le concentré de carbonate obtenu par flottation peut être traité efficacement par lessivage alcalin. Le concentré qui contient moins de carbonate et plus de silicate est alors attaqué à l'acide sulfurique. Cette double attaque permet de séparer sensiblement plus d'uranium que l'attaque simple à l'acide sulfurique. Le coût des agents chimiques est également abaissé. L'économie réalisée couvre les frais d'installation et d'exploitation de l'atelier de flottation.

Les auteurs ont étudié certains solvants d'extraction qui semblaient convenir pour la purification de solutions obtenues par élution à partir de résines échangeuses d'ions. Ils ont déterminé les isothermes de l'extraction, ainsi que les effets des ions en phase liquide (sulfate, chlorure, acide chlorhydrique, etc.) sur la vitesse d'extraction. Ils ont établi les conditions optimales d'extraction et examiné la possibilité de procéder à une seconde extraction, à partir de la phase organique.

Au cours d'expériences de laboratoire, on a constaté que les mélanges de diéthyl-2-hexylphosphate et de tributylphosphate étaient les solvants d'extraction les plus satisfaisants. Pour la seconde extraction, les meil-

leurs résultats ont été obtenus avec une solution de carbonate d'ammonium.

Un mélangeur-décanteur à gravité et à contre-courant a été construit à l'échelle du laboratoire pour étudier la purification des concentrés d'uranium. On peut obtenir ainsi des pastilles d'oxyde d'uranium de pureté nucléaire à 95 % de la densité théorique.

On a étudié les effets des conditions de précipitation et de calcination des uranates d'ammonium sur la composition et les propriétés physiques des produits.

Des recherches fondamentales ont été effectuées sur la structure des uranates d'ammonium et des trihydroxydes d'uranium, ainsi que sur leur décomposition sous l'effet de la chaleur. Les auteurs ont étudié la formation, la composition et les propriétés thermochimiques des systèmes $UO_2(NO_3)_2$-NH_3, UO_3-H_2O et UO_3-H_2O-NH_3. A partir d'études par les infrarouges et par thermo-analyse différentielle, ils ont établi de nouvelles relations entre les structures des trihydroxydes d'uranium et des uranates d'ammonium et leur décomposition sous l'effet de la chaleur.

A/450 Венгрия

Успехи в области переработки венгерских урановых руд

Э. Сабо *et al.*

Описываются физические принципы весовой коррекции, основанной на фотоэффекте и индукции, а также конструкции радиометров с весовой коррекцией. Данный метод позволяет сократить число фракций, подвергаемых радиометрической сортировке, и повысить коэффициент извлечения металла.

Излагаются экспериментальные исследования буровзрывных работ и сортировки с целью получения оптимальных размеров кусков для радиометрической сортировки. Сообщается о промышленном внедрении лабораторных результатов.

При сернокислотной переработке урановых руд, содержащих карбонатные минералы, из жидкой фазы выпадает в осадок сернокислый кальций, захватывающий часть урана. Выпадение осадка, сопровождающееся потерей урана, можно предотвратить путем уменьшения содержания карбонатов в руде флотацией. Полученный в результате флотации карбонатный продукт можно эффективно перерабатывать меньшим содовым выщелачиванием. Флотационные хвосты с меньшим содержанием карбонатов и большим содержанием силикатов можно затем перерабатывать меньшим сернокислотным выщелачиванием. Применение совместного выщелачивания значительно повышает извлечение урана по сравнению с методом только сернокислотной переработки исходной руды. Стоимость реагентов также снижается. Уменьшается стоимость монтажа и эксплуатации флотационной установки.

Исследованы свойства некоторых экстрагентов или их смесей, пригодных для очистки технического регенерата. Определены их экстракционные изотермы, изучено влияние на экстракцию ионов (сульфата, хлорида, соляной кислоты и др.), находящихся в водной фазе. Определены оптимальные условия экстракции. Изучена возможность реэкстракции из органической фазы.

Лабораторные исследования показали, что неплохими экстрагентами являются смеси ди-2-этилгексилфосфата и трибутилфосфата. Для реэкстракции наиболее подходит раствор углекислого аммония. В настоящее время готовятся полузаводские испытания.

Для исследований процессов очистки урановых концентратов сконструирован лабораторный многоступенчатый смеситель-отстойник гравитационного типа. В этом аппарате можно получать гранулы UO_2 реакторной чистоты 95% теоретической плотности.

Изучено влияние условий осаждения и кальцинирования уранатов аммония на состав и физическое состояние полученного продукта.

Проведены основные исследования структуры и термического разложения уранатов аммония и триоксигидратов урана. Изучены образование, состав и термическое поведение систем $UO_2(NO_3)_2$—NH_3, UO_3—H_2O и UO_3—H_2O—HN_3. Установлены новые зависимости между структурой и термическим разложением триоксигидратов урана и уранатов аммония на основе дифференциального, термогравиметрического и термического анализа.

A/450 Hungria

Resultados recientes en el tratamiento de los minerales de uranio húngaros

por E. Szabó *et al.*

Se examinan los fundamentos físicos de los métodos utilizados para ponderar las lecturas radiométricas, basados en un efecto fotónico, en pulsadores inductivos y en efectos dieléctricos, y se describen los correspondientes radiómetros empleados. Siguiendo los métodos expuestos es possible disminuir el número de fracciones de tamaños de grano que se someten al enriquecimiento radiométrico, y mejorar el rendimiento del proceso.

Se describen las investigaciones sobre las técnicas de voladura y de clasificación que permiten obtener la distribución de granos óptima para la clasificación radiométrica, y la aplicación de los resultados obtenidos en el laboratorio a la producción en gran escala.

En el tratamiento con ácido sulfúrico de los minerales de uranio que contienen componentes carbonatados, el precipitado de sulfato cálcico que se separa de la fase líquida contiene una cantidad de uranio considerable. Se puede evitar esta pérdida de uranio disminuyendo el contenido de carbonatos en el mineral mediante flotación. La lixiviación alcalina del producto carbonatado obtenido por flotación, da buen rendimiento. Mediante el tratamiento, por ácido sulfúrico, del mineral empobrecido en carbonatos y la lixiviación alcalina de los productos carbonatados, es posible conseguir un considerable aumento en la producción de uranio, si se compara con el método de lixiviación directa con ácido sulfúrico del mineral de partida. También disminuye el gasto de los reactivas. Los ahorros que así se realizan cubren los gastos que supone la instalación y funcionamiento de la fábrica de flotación.

Se han investigado las propiedades de algunas sustancias extractoras puras o en mezclas, que parecían adecuadas para la purificación de los eluidos de resinas cambiadoras de iones. Se han determinado las isotermas de extracción y se ha estudiado la influencia de los iones que se encuentran en la fase acuosa (fosfatos, cloruros, ácido clorhídrico, etc.) sobre la velocidad de extracción. También se han fijado las condiciones óptimas para ésta y se ha estudiado la posibilidad de reextracción de la fase orgánica.

Los experimentos de laboratorio han puesto de manifiesto que las mezclas de fosfato de di-2-etilhexilo con fosfato de tributilo constituyen los agentes de extracción más satisfactorios. Para la reextracción, lo más conveniente es una disolución de carbonato amónico.

Se ha construído un extractor por gravedad en contracorriente del tipo mezclador-sedimentador en escala de laboratorio para estudiar la purificación de concentrados de uranio. A partir de éstos se pueden obtener pastillas de UO_2 de pureza nuclear de 95 % de densidad teórica.

Se ha estudiado la influencia de las condiciones de precipitación y calcinación de los uranatos de amonio sobre la composición y las propiedades físicas del producto obtenido.

Se han llevado a cabo investigaciones básicas acerca de la estructura y la descomposición térmica de los uranatos de amonio y de los hidratos de trióxido de uranio. Se ha estudiado la formación, la composición y el comportamiento térmico de los sistemas $UO_2(NO_3)_2 — NH_3$, $UO_3 — H_2O$ y $UO_3 — H_2O — NH_3$. Datos obtenidos mediante estudios con rayos infrarrojos y termoanálisis diferencial han permitido establecer nuevas relaciones entre la estructura y la descompo sición térmica de los trihidróxidos de uranio y los uranatos de amonio.

Reactor grade uranium from UAR monazite by newer technologies

By M. Y. Farah *

Chemical processes for treating monazite have both advantages and disadvantages and are, in general, directed towards separating the major constituents, rare earths [1] or thorium [2,3]. Since thorium utilization is slow to be realised, interest has justifiably turned again towards monazite's uranium content. The sulphuric acid process suffers from incomplete separation during the subsequent thorium and rare earth fractionation, and leads to rapid plant depreciation from corrosion effects; while in the alkali process [4] very fine grinding is required, a drawback also encountered in chlorination and reduction methods [5], and necessitates replacement of rotating parts of grinding mills every fortnight [6]. Vibromills, suggested by some workers [7], are still used only on a small scale. Some preliminary trials undertaken in this laboratory to optimise alkali attack on unground placers resulted in a 32% efficiency, only when the sand to sodium hydroxide ratio was 1:1.5 and 90% when 1:3; on sodium hydroxide recycling, there was some loss of uranium in the filtrate. The approach was not therefore pursued.

The present investigation introduces two newer approaches which make use of the advantages of both processes, namely:

(*a*) Omitting ore dressing and grinding operations;

(*b*) Stripping the phosphates and overcoming the overlapping effects;

(*c*) Reducing the dilution, neutralisation or recycling operations;

(*d*) Obtaining directly a high-purity product, or eventually using a single solvent for the direct refining of leach liquors.

The two methods are: (i) $CaCO_3$ heat-treatment followed by HCl leaching, and ion exchange fixation of complex chlorides and (ii) extraction by trilaurylamine of the rare earth bearing monazite sulphate digests.

SINTERING-HCl LEACHING AND ION-EXCHANGE URANIUM FIXATION APPROACH

This investigation was described before [8] and has now been developed fully. It consists in carbonate-oxidation sintering of the run-of-mine sands and in fact continues the geochemical processes by which tetravalent thorium was able to get inside the monazite lattice during crystallisation of the rare earth phosphates. Both anionic and cationic defects are again exploited following Hume-Rothery's rule of 15% deviation in ionic radii [9] for solid solutions. Calcium because of its favourable dimension and its affinity for phosphate is used to crack the monazite, whilst the chloride ion serves as a binding agent in this solid state interaction. Calcium carbonate was chosen because of its simultaneous thermal decomposition, leading to dilatation of the crystal cracks by gaseous diffusion of the carbon dioxide.

EXPERIMENTAL

Laboratory samples of unground monazite assaying between 50 and 98% were obtained by heavy media separation, using methylene iodide, and electromagnetic sorting by the Franz isodynamic separator. For subsequent experiments on ½ kg monazite, the concentrate was obtained by one of the versatile techniques developed in the UAR laboratories [10],

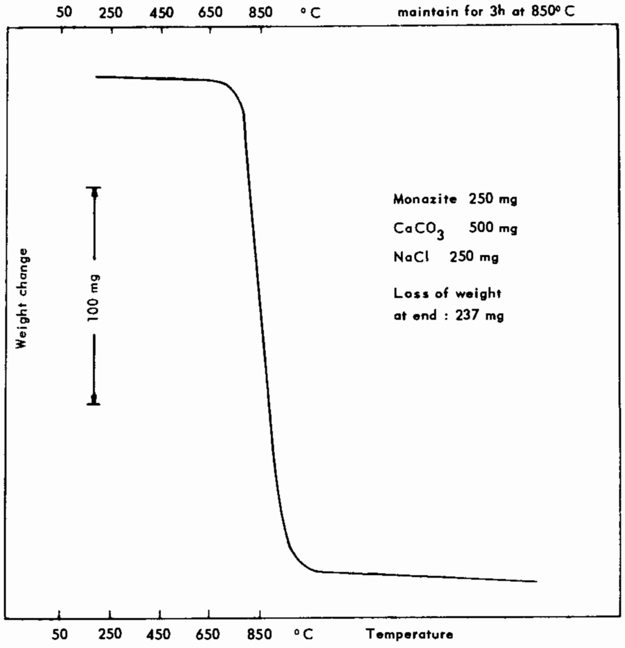

Figure 1. Example of thermogravimetric experiment

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namely (*a*) screening-electromagnetic-tabling; (*b*) flotation using amines or carboxylates; (*c*) flotation using sulphonates while activating by oxalate; (*d*) flotation whilst modulating with boiled starch. In each sintering experiment the sands were moistened with 5-10% by weight of chloride which could be obtained from recycled washings of resin columns. The sand was then intimately mixed with twice its weight of calcium carbonate, the mass dried and introduced into the muffle furnace. For the thirty exploratory runs on the thermobalance, quantities weighed were quarter or half-grams of sand. Both Rosetta and Madagascar sands were used, as well as precipitated calcium carbonate, Meudon white, magnesium carbonate, geobertite, dolomite, chalk, calcite, fluorite, etc., as fluxes; pyrolusite and sodium or calcium chloride were used as exidants or binders. The extent of sintering was followed by heating gradually at the rate of ten degrees centigrade per minute on an automatic thermobalance ADAMEL model, for the range 150 to 1 050 °C, then under isothermal conditions in the open atmosphere (Fig. 1). The samples were shock cooled then carefully scrubbed and quartered. For mineralogical examinations a Leitz binocular and Richter petrographic microscope were used, followed by Krumbein and Pettijohn counting techniques [11]. Another alternative consisted in examining the extent of leaching within 15 minutes in 4 times the weight of sand of boiling 1:1 hydrochloric acid, appropriate corrections being made for zircon, ilmenite and garnet.

RESULTS AND DISCUSSION

Figure 2 (*a*, *b*) and Table 1 illustrate the development of the heat-treatment process and its effect on monazite leaching for various fluxes and recorded temperatures and also the optical and colour variations on sintering. It is evident that optimum results are obtained in experiment 21 (Table 1), in which sintering was carried

Table 1. Studies on sintering of monazite

Experiment No.	Conditions	Sintering temperature °C	Duration of constant temperature stage (Hours)	Observations
1	Monazite alone	1 050	—	0.5% wt loss at 500 °C
2	As above but twice heating and shock cooling	850	—	Segregation of inclusions, red dots appear.
3a	1: 1 monazite/NaCl	850	0.33	Peripheral obliteration
3b	As 3a	850	3	7.2% wt loss; rusty coloured melt left
3c	1: 2 monazite/NaCl	815	1	No wt loss; 80% of sand is leachable
4	1: 1 monazite/NaF, followed by quenching	850	0.33	Complete fusion
5	1: 1 monazite/CaF_2, heating	1 050	1	4.2% wt loss at 370-550 °C
6	1: 1: 1 monazite/NaCl/NaOH heating up, then at constant temperature	1 050	1	7.5% wt loss at 250 °C; 11.2% wt loss at 370 °C; 19.4% wt loss at 1 045 °C; Fusion complete at end
7	1: 2: 1.5 monazite/NaCl/NaOH	450	3	5% wt loss brick sinter, almost completely soluble in nitric acid
8	As 7	250	5	Cracking more or less pronounced
9	1: 2 monazite/NaOH	250	—	Good attack, more or less leachable
10	1: 1: 1 monazite/CaO/NaCl	1 050	2.5	7.9% wt loss at 400 °C; 9.1% wt loss at 650 °C; 37.7% wt loss at 1 045 °C; complete attack; chlorides partly volatilize
11	1: 2: 1 monazite/chalk/NaCl	1 050	3	Complete attack, mass leachable
12d	As 11	815	1.5	23% wt loss as CO_2; 4% wt loss for NaCl flash
12b	1: 1: 1 monazite/chalk/Nacl	815	1.5	50% of placers obliterated; 99% are leachable in 1: 1 HCl
13a	1: 2 monazite/precipitated calcium carbonate	825	2	29% wt loss
13b	1: 2 monazite/calcite	825	2	3/4 grains attacked
14	1: 2 monazite/geobertite	425	4	1/3 grains cracked
15	1: 2 monazite/dolomite	900	3	36% wt loss; 1/3 grains attacked
16	1: 1: 1: 1 monazite/NaCl/$MgCO_3$/$CaCl_2$, heating up to 400 °C then constant at 900 °C	400 900	1 1	1/3 grains attacked 25.3% wt loss, cracking complete
17	1: 1: 1 monazite/MnO_2/$MgCO_3$	600	3	1/3 grains attacked
18	1: 1: 1 monazite/MnO_2/$CaCO_3$	950	3	90% grains attacked
19	1: 1: 1: 1 monazite/MnO_2/NaCl/$CaCl_2$	660	5	All grains cracked but resist leaching
20	1: 2: 1 monazite/calcite/NaCl	850	2	Complete cracking and dissolution of sintered grains in 1: 1 HCl or in concentrated nitric acid
21	1: 2: 0.05-0.1 monazite/$CaCO_3$/NaCl	815	2	Complete cracking and dissolution
22	1: 2 monazite/$Ca_3(PO_4)_2$	950	2	½ grains attacked; ¼ dissolve in 1: 1 HCl
23	1: 2: 1 monazite/$Ca_3(PO_4)_2$/NaCl	825	3	1.5% wt loss and 1/3 grains attacked

Figure 2. *a* : 50 % monazite, mounted 1.772, petro x 100, before heat treatment; *b* : Same, after heat treatment

out for 1.5 hours at 815 °C, using a calcium carbonate: monazite: NaCl weight ratio of 2 : 1 : 0.1, independent of grain size, provided careful homogenisation is ensured. As carbon dioxide can be recovered, the re-use of precipitated calcium carbonate could render the operation economic in subsequent exploitation.

During the heat treatment stage, a series of interactions occur which have not been explained completely. Probably they include conversion of rare earth phosphates into carbonates, which decompose in the order praseodymium, cerium, samarium, neodymium, lanthanum [12]. Dimorphism, double salts and solid solutions are believed also to occur. Petrographic mountings show (Fig. 2) the appearance before and after sintering. Taking cerium as an example the reaction can be represented as follows:

$$3CaCO_3 + 2CePO_4 \longrightarrow Ca_3(PO_4)^2 + Ce_2(CO_3)^3$$

the latter meanwhile decomposes above 500 °C, to give

$$Ce_2(CO_3)^3 \longrightarrow 2CeO_2 + 3CO_2,$$

so that around 800 °C, when all the chalk decomposes,

$$3CaCO_3 \longrightarrow 3CaO + 3CO_2,$$

there would be a cumulative gas diffusion from calcium and rare earth carbonates. Moreover, to this dilating effect, contraction of tetravalent cerium (1.02 Å) formed from decomposing cerous carbonate (1.18 Å) also results in the appearance of brick-red dots of ceric oxide, with subsequent rupture of the crystal and friability of the sand. This series of autocatalysed kinematic reactions leads to complete cracking of the monazite. It is worth mentioning that attack of monazite by perchloric acid and nitrate attack of monazite, which also are oxidation methods [13], proceed six times faster than sulphuric acid leaching. The sintered mass becomes extremely soft on cooling, and does not stick to the container walls.

Table 2 shows also that to render the sintering approach selective, zircon and ilmenite could remain unattacked; garnet, however, shows exception. Nevertheless, the sintering treatment could thus be equally as advantageous as the sulphuric acid attack, since extraneous minerals remain unattacked and the extra expense of upgrading middlings to 98% could be avoided. This would constitute a second advantage over the alkali process, after omitting grinding. The oxidised monazite could be used as an inorganic ion exchanger similar to zirconium phosphate [14] or as a catalyst, since cerium phosphate has proved valuable in this field [15].

EXTENDED PROCESS

The above considerations were sufficiently encouraging to warrant extending the sintering approach to a complete process (Fig. 3). After many trials it was evident that the best method would involve scrubbing the cooled mass with two to three times its own weight of water containing 5-10% the sand weight of sodium hydroxide, keeping the temperature at 60 °C, then decanting the lime-bearing phosphate. Unless this measure is adopted, 1% uranium and 2% rare earths are liable to get entrained in the overflow.

Table 2. Comparative studies on zircon, ilmenite and garnet

Experiment No.	Conditions	Sintering temperature °C	Duration of constant temperature stage (Hours)	Observations
24	1: 2: 0.1 zircon/$CaCO_3$/NaCl	1 050	2	30% wt loss, all grains cracked
25	Same as 24	825	2	30% wt loss; rare zircon grains crack or dissolve in HCl
26	1: 2:0.1 ilmenite/chalk/NaCl	1 050	3	30% wt loss, all ilmenite crack
27	Same as 26	825	2	No ilmenite cracking or leachable in HCl
28	1: 2: 0.1 garnet/$CaCO_3$/NaCl	825	2	¼ garnet grains only cracked and are leached in HCl

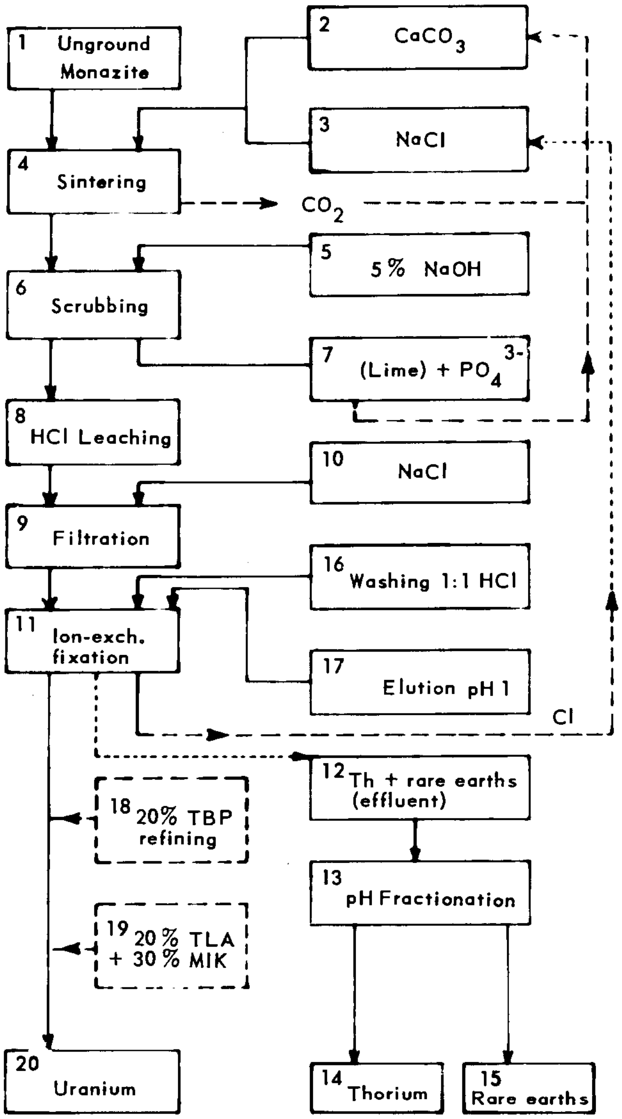

Figure 3. Flowsheet of extended process

In the proposed method, four-fifths of the phosphates are also skimmed off with the dross, and the residual amount scarcely affects [16] the exchange capacity of the anionic strong base resin subsequently used for uranyl chloride complex fixation. Dissolution was effected in 4-5 times the sand weight of 1:1 HC, using a galvanic couple and trace fluorides to enhance leaching within fifteen minutes and to control the redex potential to 0.4 volt. After filtering, solid NaCl was added to about 5.8 molarity. The clear feeds assayed usually 1-2 g uranium per litre, with phosphate about 0.2*M*. The resin in-pulp technique was tried, followed by subsequent phosphate elimination at pH 1.8, but 200 ppm iron, 0.1% thorium and up to 1% cerium, lanthanum and neodymium were still left in the uranium eluate. To minimise such contaminants, ascending and descending fixations were preferred, provided washing with 2.5 bed volumes 1:1 HCl was ensured.

The recommended fixation: washing: elution ratios were 4: 4: 1, by this means a four-column system, (3 for adsorption and 1 for elution) was feasible. Figure 4 illustrates the fixation of five litres of monazite chloride feed on a column containing 180 ml resin. In practice the column was considered fully loaded when the effluent uranium was 80% of the head strength. Recovery was always around 98.5%. Elution was achieved using HCl at pH 1; regeneration was effected weekly.

Spectrographic analyses were made of yellow cake simulating fractions obtained by ammonia precipitation (pH 6.5) of eluates, the inferred purity being comparable with that of nuclear grade material, i.e. iron 500 ppm, aluminium, manganese 50-100 ppm, titanium 20-50 ppm, yttrium 20-50 ppm, boron 20 ppm, lead 20 ppm, ytterbium 10 ppm (with respect to dry uranium oxide). Only samarium gadolinium and cerium sometimes assayed 0.2-0.5%. It is clear that controlled washing by some means above 2.5 bed volumes could remove these rare earths. However, a second alternative was to use the chloride eluate diluted to volume by concentrated HCl or saturated with sodium chloride. 20% TBP (tributylphosphate) or 20% TLA (trilaurylamine) + 30% MIK (methylisobutylketone-hexone) in white spirit diluent were used. With a maximum of four stages and scrubbing with extra uranium, a re-extract of nuclear purity, assying 40-50 gU/l is obtainable with separation factors, for U/Th, Ce^{III}, Zr of 10^3, 10^3 and 10^2, respectively, Rare earth traces were within the specification and the intermediate yellow cake stage had

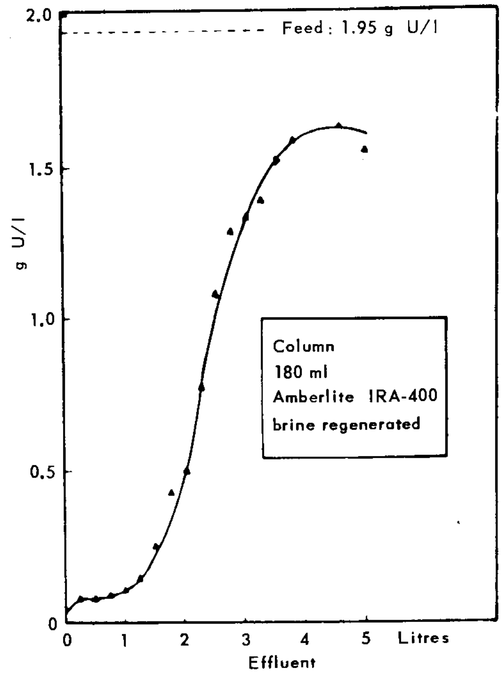

Figure 4. Fixation chromatogram of uranyl chloride complex on Amberlite IRA-400

been avoided thus economising in nitric acid, which is expensive, provided the valencies. Ce^{III}, Fe^{II} and U^{VI} were observed.

Versatile reducers were also tested for the production of high purity eluates, followed by wet precipitation to produce the dioxide fuel material or the tetrafluoride by evaporation from the fluoride eluted.

DIRECT EXTRACTION OF URANIUM BY TRILAURYLAMINE FROM MONAZITE SULPHATE DIGESTS CONTAINING RARE EARTHS

The extraction of uranium from sulphate solution can be performed either by the Dapex or the Amex process. The first implies the use of organophosphorus extractants [17]; it has been adapted for UAR monazite extraction of thorium [18] and of uranium [19]. The second, the Amex process, deserves special attention as it makes use of a single alkylamine. It was first proposed by Crouze [20] then by Kawamura [21] who used Primene-JM-T for isolating nuclear grade thorium. The mechanism of uranium extraction was later established by Allen [22], Boirie [23] and Verstgen [24]. In a second extension of the method, Crouze and Brown [25] used a 0.05 molar tri-iso-octylamine sulphate solution in eight stages at a pH of 0.1 and at an organic aqueous phase ratio of 1.3: 1 to enhance quick phase separation [26]; later introductions at Oak Ridge were better scrubbing methods, controlled pH stripping, and the use of ammonium carbonate or calcium nitrate to strip in-tank solutions to refineries, thus avoiding dust hazards and the expense of precipitating yellow cake [27, 28].

The aim of the present investigation is to re-examine the possibility of obtaining high nuclear purity uranium from rare earth bearing monazite sulphate digests at a pH of 1.15, thus optimising partition coefficients and avoiding contamination. TLA was used for the purpose at an optimum ratio of aqueous to organic phase, thereby achieving good decontamination and eliminating multi-stage scrubbing introduced by Japanese workers.

INVESTIGATION TECHNIQUES

TLA was obtained from the Usine Rhône-Poulenc. 0.1 and 0.05 molar solutions were prepared by measuring 66 or 33 ml amine, adding 51 or 25.5 ml secondary octanol and bringing to 1 or 0.5 litre. Before use, every amine was re-equilibrated by shaking for fifteen minutes with 25 or 12.5 ml $4N$ sulphuric acid.

The batch equilibrium isotherms and partition coefficient measurements were carried out by shaking aliquots until equilibrium was attained for various organic to aqueous ratios and determining the uranium concentration in both phases. Fluorimetric or X-ray fluorescent methods were used depending upon the concentration range; the first employing a Caratom model, and in the second a Philips assembly. The characteristics of the latter were: X-tube 48kV and 24 mA, plateau 1 750 V and multiplication factor 16 [29]. When quenching difficulties were encountered in fluorimetry, an ethyl acetate [30] extraction was also necessary or partition chromatography was used.

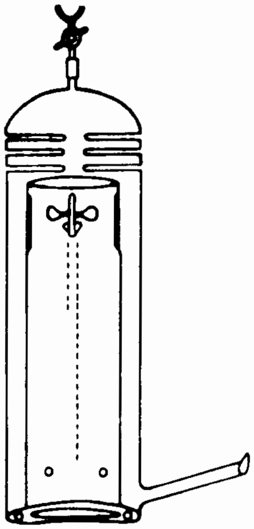

Figure 5. Unit chamber of mixer-settler assembly

The mixer-settler assembly, of a cascade type, was kindly put at our disposal by the SERAC Laboratories at Fontenay-aux-Roses, CEA. Figure 5 shows a single unit. The organic phase falls under gravity and the aqueous phase is pumped, countercurrently, by means of a diaphragm mechanism. Flow rates were controlled by capillary level meters and the interface controlled by submerged electrode relays.

The average uranium content of a typical monazite extract obtained by digesting sand with liquor in the ratio 1:10 (weight) was around 320 mg/l uranium; after adjusting to the desired pH, usually 1.15. The filtered liquor was always refiltered before a run because fine crystals precipitate on ageing.

CONCLUSIONS

(*a*) Some exploratory measurements were undertaken on pure uranyl sulphate at various concentrations of H_2SO_4, using $0.1M$ TLA and an organic to aqueous phase ratio of 1: 1. The results are shown in Table 3.

It should be noted that some analytical uncertainties in the concentration of very weak solutions analysed by fluorimetry, particularly in the steep increase of the curve, were encountered, so that values at the higher concentrations should be more reliable. In fact, preliminary measurements made on natural 50% monazite solutions, gave partition values around 14-15 for liquors containing 120 mg/l of uranium and $0.23M$ in H_2SO_4.

Table 3. Partition coefficients of pure uranyl sulphate solutions in TLA

Feed concentration mg/l U	Sulphuric acid	Distribution coefficient
800	pH 1.0	900
1 200	1.0	360
1 400	1.0	360
2 000	1.0	100
6.2	0.23*M*	30 (?)
23.0	0.23*M*	75
30.1	0.23*M*	58
62.0	0.23*M*	205 (?)
232.0	0.23*M*	60
2 232.0	0.23*M*	30
5 760.0	0.23*M*	8.3
11.8	1.33*M*	6.4 (?)
24.0	1.33*M*	9.2 (?)
53.5	1.33*M*	10.9
100.3	1.33*M*	13.5
223.0	1.33*M*	8.7
2 325.0	1.33*M*	7.0

(*b*) As the average composition of natural liquors, with respect to uranium, is 10 to 12 times the thorium content and about 80 to 100 times the rare earth content, some tests were carried out on synthetic liquors simulating actual digests analysing 230 mg/l uranium, 4.285 g/l thoria and 16.5 g/l Ce_2O_3 at two acidities, namely 0.23*M* and 1.33*M* sulphuric acid. These solutions gave partition coefficients of 0.028, 0.0046, 0.024 and 0.024 for thorium and cerium respectively, from which a decontamination factor around 2 000 (i.e., 2 143, 2 500, 1 891, etc.) was deduced.

(*c*) The results obtained when actual monazite digests were examined in separating funnels are reported in Table 4, from which it is evident that at optimum loading, for a sand-to-liquor ratio of 1 :10, the uranium should not exceed 0.674 mg/l per stage. Even by three-fold co-current cascading no more than 0.795 mg/l uranium was attained and not more than 1.103 mg/l when a 0.2*M* TLA solution was employed. By minimising the acidity to pH 0.5, a value of 1.176 was obtained; while at pH 1.0 (Fig. 6, curves *c* and *d*), still higher loadings were possible with 0.1*M* TLA than with the 0.05*M* TOA (curves *a* and *b* obtained by Crouze, and reproduced for comparison). Since the slope of the isotherm apparently increased, it was hoped that fewer stages would be permissible.

(*d*) Figure 7 is an example of the parallel study of the effect of pH variation on TLA extraction of uranium at 0.05*M* and 0.1*M* solvent solutions; the study was extended to the weaker 0.05 molarity because occasionally low grade monazite leaches, low in uranium, are unavoidable. Details of the extraction

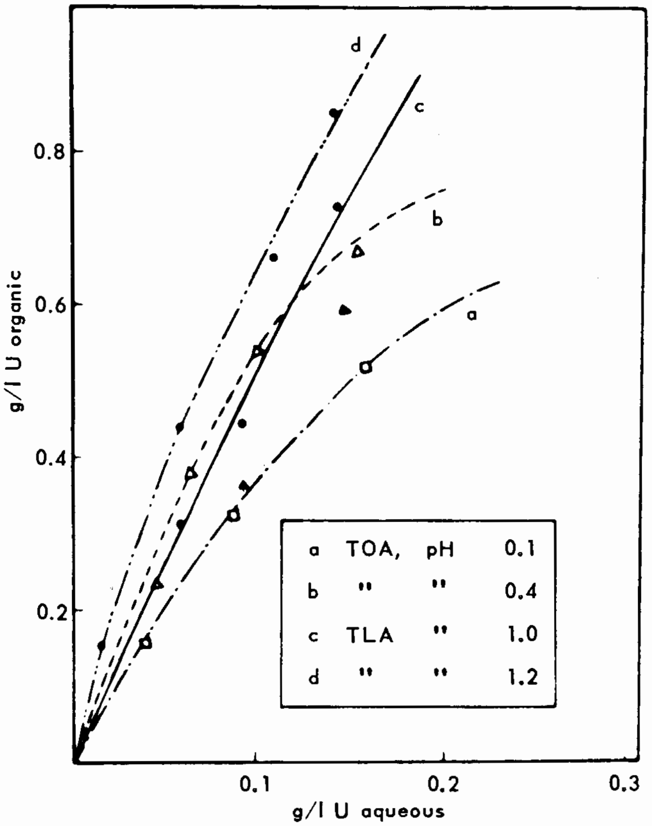

Figure 6. Comparison of TOA and TLA at various pH values

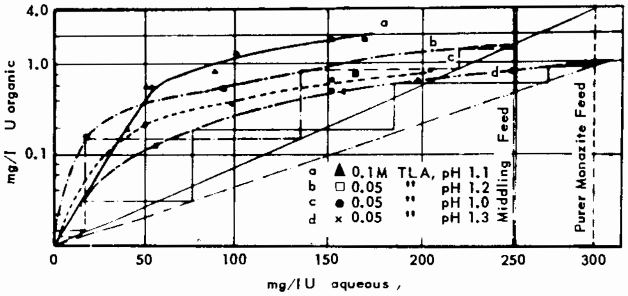

Figure 7. McCabe-Thiele diagram at various pH values and various amine molarities

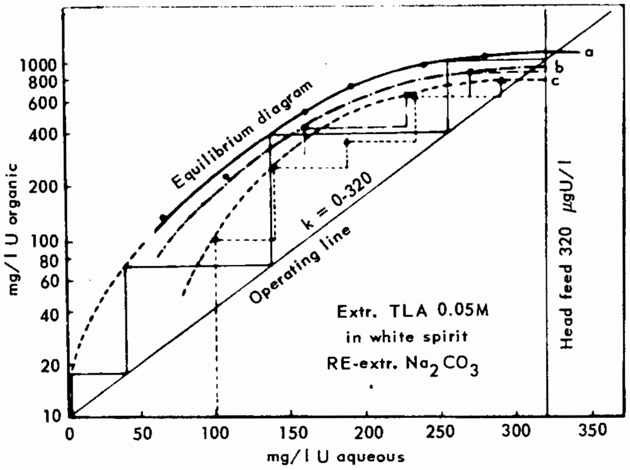

Figure 8. Continuous bench-scale, mixer-settler extraction diagrams and resaturation for completion

Table 4. Partition coefficients for uranium extraction from actual monazite feeds at high acidities

Uranium concentration mg/l	Sulphuric acid molarity	Organic to aqueous ratio	U found org/aq. mg/l U	Distribution coefficient
110.6	0.23	1:1	103/7.6	13.5
110.6	0.23	1:4	408/13.0	31.0
110.6	0.23	1:9.6	674/44.8	13.5
192.6	0.90	1:1	135/57	2.4
192.6	0.90	1:2	170/107	1.5
192.6	0.90	1:3	178/132	1.3
192.6	0.90	1:5	228/146.4	1.5
192.6	0.90	1:10	270/165	1.8

Table 5. Distribution coefficients on actual feeds as function of pH value variation

Curve number	Uranium in feed mg/l	pH	Solvent (TLA) molarity	Organic to aqueous ratio	U found org/aq. mg/l U	Distribution coefficient
Fig. 7 curve *a*	230	1.1	0.1	1: 1	191/39	4.9
	230	1.1	0.1	1: 2	335/60.5	5.5
	230	1.1	0.1	1: 3	499/52.2	9.6
	230	1.1	0.1	1: 5	718/86.4	8.3
	230	1.1	0.1	1:10	1 286/101.2	12.3
	230	1.1	0.1	1:20	1 635/1 483	11.0
Fig. 7 curve *b*	308	1.2	0.05	1: 0.5	144/20	7.2
	308	1.2	0.05	1: 1	263/45	5.8
	308	1.2	0.05	1: 2	425/95.5	4.5
	308	1.2	0.05	1: 5	708/166	4.3
	308	1.2	0.05	1:15	2 060/171 (?)	?
Fig. 7 curve *c*	272	1.0	0.05	1: 1	223/49	4.6
	272	1.0	0.05	1: 2	352/96	3.7
	272	1.0	0.05	1: 3	356/153	2.3
	272	1.0	0.05	1: 5	596/153	3.9
	272	1.0	0.05	1:15	970/207.3	4.7

procedure for the optimum cases (curves *a*, *b*, *c*), are shown in Table 5.

From the results obtained at constant temperature, it was deduced that extraction around pH 1.1 with 0.05*M* TLA would be equally applicable to all digests assaying between 230 and 320 mg uranium per litre; accordingly a thorium stripping step seemed to be compulsory and the work with liquors containing only rare earths was preferable. Therefore it seemed feasible to reduce the number of theoretical stages (Fig. 7) from eight as used by Crouze, to four or five. This is in good agreement with the work of Rames [31] with LA1 and XE 204 (Rohm and Haas), as also with TFA (General Mills Inc. (pH 1.1)). At the higher pH 1.3 (curve *d*), turbidity was inevitable and hence the feed rate was lowered. In fact the amine used for this series had aged and was effectively only 0.025*M*. It is not improbable, also, that the thirty second contact time used and recommended by Wells [32] for TOA, was insufficient.

(*e*) The above results in terms of continuous operation necessitated working with 5 kg batches of monazite, bringing each batch to 30 litres volume, stripping thorium by the addition of 1.5 litre ammonia 25 °B, leaving overnight and filtering (the final pH was alway around 1.15). The uranium concentration of a representative batch was found to be 322 mg/l. One portion (10 litres) was subjected to separating funnel equilibration and another portion (20 litres) to a bench scale mixer-settler run. The amine used, of 0.05*M*, had not aged. Figure 8, curves *a* and *c*, represent the results from analyses of both phases for a batch (*a*) and a continuous run (*c*) respectively. The simultaneous analysis of a 1 litre fraction of raffinate proved that equilibrium was attained after four hours; the organic solvent was fed in at a rate of 500 ml/h and the aqueous at 1 500 ml/h. It should be noted when interpreting these results that the contactor efficiency was only 70-80% theoretical. Indeed when the contents of the first, second and third stages were equilibrated at the end of the run with original feed, their respective points were enhanced, as shown in curve *b*. Another mixer-settler design satisfying such needs could prove more efficient. However when the one-stage washed, two-stage re-extracted uranium (using 9% sodium carbonate) was treated with sulphuric acid to expel CO_2 and uranium subsequently precipitated at pH 6.5, the spectrographic analysis inferred: barium and manganese 20 ppm, ytterbium 10 ppm, aluminium and iron 100 ppm; only thallium, gadolinium and cerium assayed between 500 and 1 000 ppm. The last three were 8.0, 0.5 and 0.5% in the original work of Crouze.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/454 République arabe unie

Préparation d'uranium de pureté nucléaire à partir des monazites de la RAU par des procédés nouveaux

par M. Y. Farah

Le procédé acide tout comme le procédé alcalin servant à séparer de l'uranium et du thorium de pureté nucléaire ou diverses terres rares d'un haut degré de pureté présentent des inconvénients : i) fractionnement assez long en présence des phosphates; ii) broyage excessif avant la lixiviation alcaline; iii) nécessité d'employer plusieurs solvants organiques pour raffiner tant le thorium que l'uranium avant d'atteindre la pureté nucléaire, et cela par des méthodes coûteuses, lentes et compliquées.

Le mémoire décrit deux nouvelles techniques :

a) Frittage à la craie, attaque chlorhydrique et fixation de l'uranium par échange d'ions sous forme de complexe de chlorures, suivie de réduction par voie humide en dioxyde d'uranium ou de fluoration.

Cela est une modification du brevet français, où :

i) Le broyage et la préparation de la monazite à 98 % sous forme de poudre passant au tamis 325 sont remplacés par un frittage à 825 °C à l'aide de plusieurs fondants, en particulier la craie;

ii) Après lavage du produit fritté, on attaque la monazite avec de l'acide chlorhydrique dilué par un volume équivalent d'eau;

iii) On sature la solution avec du sel commercial et on ajuste le potentiel à 0,4 V;

iv) On fixe les complexes de chlorures d'uranyle sur une résine échangeuse à base forte;

v) On lave la colonne pour éliminer le thorium et les terres rares avec 2,5 fois son volume de HCl 1/1, puis on élue l'uranium à pH 1 au moyen de HCl ou de fluorure;

vi) On réduit l'éluat par des réducteurs variés et on précipite l'oxyde d'uranium qui sera utilisé comme combustible;

vii) On raffine enfin les éluats de chlorure directement au moyen de TBP ou de trilaurylamine-méthylisobutylcétone (TLA/MIK).

b) Extraction d'uranium de pureté nucléaire directement par la trilaurylamine sur les jus d'attaque de monazite chargés en terres rares.

Cette seconde technique est une modification originale du procédé AMEX :

i) On ajuste les jus sulfatés d'attaque de monazite à pH 1,1 par différents procédés pour extraire la majeure partie du thorium en laissant leur charge de terres rares;

ii) On extrait ensuite l'uranium au moyen de sulfate de trilaurylamine tout en définissant les paramètres, les conditions optimales d'extraction, en traçant les isothermes et en déduisant la cinétique du système et le nombre d'étages théoriques suivant les diagrammes de McCabe et Thiele;

iii) On présente les résultats des essais discontinus de même que ceux obtenus en continu sur une batterie de mélangeurs-décanteurs en vue du raffinage de l'uranium, en donnant également les résultats des analyse spectrographiques et leur degré de coïncidence avec les spécifications.

A/454 OAP

Новые способы получения реакторно чистого урана из монацита ОАР

М. Я. Фарах

Как кислотный, так и щелочной процесс извлечения реакторно чистого урана, тория или отдельных редкоземельных элементов высокой чистоты страдают такими недостатками, как длительный процесс расщепления в случае наличия фосфатов, высокая степень измельчения перед щелочным выщелачиванием, необходимость использования редких растворителей при очистке тория или урана для достижения реакторной чистоты с помощью дорогостоящих и сложных методов.

В докладе описываются два новых способа:

1. Спекание с мелом, выщелачивание соляной кислотой, ионообменное извлечение в виде хлоридного комплекса с последующим мокрым восстановлением до двуокиси урана или фторированием.

Этот способ представляет собой модификацию французского патента,

a) вместо операции дробления и измельчения 98% монацита до порошка — 325 меш производится спекание при 825° C с различными флюсами, в частности с мелом;

b) извлеченная спеченная масса выщелачивается равным объемом HCl (1 : 1);

c) полученный раствор насыщается технической поваренной солью и его э. д. с. доводится до 0,4 *в*;

d) с помощью сильноосновной ионообменной смолы извлекается уранилхлоридный комплекс;

e) для удаления тория и редкоземельных элементов через колонку пропускается 2,5 колоночных объема HCl 1 : 1 и затем уран элюируется соляной кислотой или фторидом при pH = 1;

f) восстановление подходящими восстановителями и мокрое осаждение двуокиси урана, используемой в качестве ядерного топлива;

g) окончательная очистка хлоридных элюатов, например ТБФ или ТЛА в МИБК.

2. Прямая экстракция реакторно чистого урана трилауриламином из монацитовых щелоков, содержащих редкоземельные элементы.

Этот способ представляет собой оригинальную модификацию амекс-процесса, при котором

a) сернокислые щелока после сернокислотной обработки монацита доводятся различными средствами до pH = 1,1, чтобы отделить основную массу тория, удерживая в жидкости только редкоземельные элементы;

b) после этого уран экстрагируется сернокислым трилауриламином при определенных оптимальных условиях с одновременным определением параметров. Представлена изотерма, а также изучена кинетика в данной системе и определено число теоретических тарелок по методу Мак-Кейба — Тиле;

c) представлены данные по очистке урана, полученные на периодическом и непрерывно действующем смесителе-отстойнике лабораторного масштаба, а также подробно описана методика спектрографического анализа.

R/454 República Árabe Unida

Uranio de calidad nuclear a partir de monacita de la RAU por tecnologías nuevas

por M. Y. Farah

Para la separación de uranio y torio de calidad nuclear, o de tierras raras individuales de pureza elevada, los procesos ácido y alcalino presentan los inconvenientes de :

un fraccionamiento largo en presencia de fosfatos;

una molienda muy fina antes de la lixiviación alcalina;

la necesidad de emplear varios disolventes para la purificación del uranio o del torio para alcanzar una calidad de pureza nuclear, con métodos caros y muy complicados.

Esta memoria describe das nuevos procedimientos :

a) Sinterización con yeso, lixiviación con ácido clorhídrico y fijación del uranio, como complejo cloruro, por intercambio de ion, seguida luego por la reducción, por vía húmeda a dióxido de uranio o por la fluoruración.

Es una modificación de una patente francesa en la que :

i) la molienda y la preparación de la monacita hasta que el 98 % es inferior a 325 mallas se sustituye por la sinterización a 825 °C empleando distintos fundentes, especialmente yeso;

ii) después de lavar el sinterizado, la monacita se lixivia con un volumen 1:1 de HCl;

iii) luego se satura el líquido con sal común y se ajusta el potencial a 0,4 voltios;

iv) se fija el complejo de cloruro de uranilo sobre una resina de cambio iónico fuertemente básica;

v) se lava la columna con 2,5 volúmenes de lecho de HCl 1:1, para separar el torio y las tierras raras, eluyendo luego el uranio con ácido clorhídrico o fluoruro a pH 1;

vi) luego se reduce el uranio con distintos reductores y se precipita, en húmedo, el producto combustible como dióxido de uranio;

vii) como alternativa se pueden purificar los eluídos de cloruro por TBP o por TLA/MIK.

b) La extracción directa, con trilaurilamina de uranio de calidad nuclear a partir de líquidos estériles de tierras raras procedentes del ataque de monacita.

Es una modificación original del proceso AMEX :

i) en la que los líquidos procedentes del ataque de la monacita por sulfatos se ajustan a pH 1,1 de distintas formas, para precipitar la mayor parte del torio manteniendo su contenido de tierras raras;

ii) luego se realiza una extracción del uranio con trilaurilamina, se dan los parámetros controlantes, las condiciones óptimas, las isotermas, así como las investigaciones sobre la cinética del sistema y el número de etapas teóricas según los diagramas de McCabe-Thiele;

iii) para el refino del uranio se presentan los datos de laboratorio en escala discontinua y continua, de mezcladores-sedimentadores, así como los análisis espectrográficos que indican en qué medida se satisfacen las especificaciones.

Prospecting for and dressing of uranium ore in the Federal Republic of Germany, progress in methodology and new results

By H. Closs *

During the years 1958 and 1959, uranium prospecting, largely supported by public finance in the Federal Republic of Germany, experienced a period of relatively strong intensity [1].

From 1961 to 1963, however, the interest in uranium prospecting tapered off due to overcapacity on the world market, only to be increased again at present as a result of the EURATOM report [2]. In the first phase of the programme, a large number of geological possibilities was investigated. In the crystalline basement the well-known concepts of the formation of uranium deposits were taken as a basis, whilst for the work in sediments paleogeographical aspects played a prevalent part in determining areas to be investigated.

To-day's most promising deposits, including those actually being mined, can be regarded as chance findings or the result of extended exploration rather than discoveries arising from scientific considerations, if a very general classification of rock types or provinces of mineral deposits are considered only as a guiding motive for prospecting.

The first stage of the prospecting consisted of establishing a general survey of the chances of finding uranium in the Federal Republic of Germany. In the present stage, the most promising districts have been studied with particular intensity.

Up to now no associated elements or mineral associations have been found in the crystalline basement which could be regarded as truly reliable indicators for uranium deposits, although Co, Bi, F, Zn etc. are frequently encountered in places of higher uranium concentrations. In the sediments, paleogeographic considerations have certainly pointed in the right direction for the finding of large quantities of uranium, but they have not led to any deposits with concentrations of economical interest. This does not mean that scientific predictions derived from a known general geological situation are entirely worthless, but nowadays more reliance is placed on fortuitous finds than in earlier times. Methods capable of rapidly prospecting large areas in a routine fashion are therefore of most interest [3].

The Federal Republic does not contain any large deposits of world-wide interest. Those discovered so far are only useful to our country in view of the present stage of development in reactor technology. Nevertheless the general experience gained in prospecting work may assist in reducing the element of chance in the search for uranium deposits.

PROSPECTING IN CRYSTALLINE REGIONS

In a tin- and tungsten-bearing carboniferous granite (Rudolfstein near Weissenstadt, Fichtelgebirge), torbernite was found on joints in considerable concentrations and quantities.** Since this granite contains uraninite [4, 5], the probability of the formation of the deposit from uraniferous hydrothermal fluids was obvious. The torbernite encountered at a depth of 50 m was interpreted by some experts as a secondary formation in the roof of a deposit, by others as a primary concentration due to special conditions. It was agreed that at greater depths higher contents and larger quantities of uranium, perhaps in other ore minerals, might be expected [6]. Torbernite was found at depths down to 200 m, though to a decreasing extent. Absolute dating of the torbernites from 50-200 m depth furnished the explanation for this negative result of the investigations, as the torbernites were found to belong to the tertiary period (15-18 million years). Therefore, a primary ore formation was out of the question, since at that time relevant volcanic events had not taken place; the uranium concentration is due to lateral secretion of weathering solutions which have descended to the surprisingly great depth of nearly 300 m. If in this case continuous absolute datings had been made simultaneously with the sinking of the shaft, the mining could most probably have been stopped at an earlier stage and considerable investment could have been saved.

In another granitic region in the western part of the Bohemian Massif (Falkenstein Granite), a scintillometer test** yielded indications of several uranium

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** Work carried out by Eisengewerkschaft Maximilianshütte.

enrichments. In the weathering zone high uranium concentrations (prevailingly uranium micas) of more than 1 kg/t with a total of 10 to 20 tons of U_3O_8 were found. Absolute datings on samples revealed very young ages (6-8 million years), a fact pointing clearly to secondary formations in the weathering cycle. But higher ages (70 to 80 million years) were also obtained which encouraged further examination, especially as intensive mineralogical examinations in the weathered material yielded preliminary indications of a primary uranium mineralization [7, 8]. After several drillings, 500 samples were investigated by microscopic, polarographic and X-ray spectral and structural analyses. After very contradictory predictions, intensive examinations led to the following conclusions: The granitic region is crossed by a fracture zone of up to 50 m width with sericitization and strong chloritization. The latter does not run completely parallel to the uranium enrichment, because the uranium mineralization has developed prior to the chloritization through early ascending solutions. Subsequent to the uranium mineralization, a substantial addition of magnesium and iron took place and, as a result of chlorite formation at the expense of the granite, a potassium-aluminium loss occurred, which in combination with desilification in the region near the surface, led to the formation of sericite. These processes took place at temperatures of about 300 to 400 °C and, therefore, this type of deposit is to be assigned to the pyrometasomatic to hydrothermal range. While such features render the distribution of uranium ore irregular, the width of the dyke-shaped prospect, the certainly primary nature of the ore formation, and uranium concentrations of up to 5 kg/t of several metres encourage continued investigation. Only a combination of various methods of prospecting and research yielded this result.

It was shown that the area west of the Bohemian Massif could be considered as promising for uranium deposition and that there was reason to assume that up to three or more different intrusions of granite had taken place. Their importance for uranium enrichment may not be uniform. Therefore, it is now planned to cover the area with a grid of absolute age datings by the rubidium-strontium and potassium-argon methods and, if possible, also by the uranium-lead method using zircon. Perhaps a clarification of the age relationships in this area may be helpful for uranium prospecting (this plan was in part the subject of a EURATOM Research grant). Even now a few rubidium/strontium age determinations have suggested that the principal phase of the varistic-carboniferous orogeny with which the intrusion of granites was connected must be older (about 300 million years) than has been assumed.

In the extreme west of the Bohemian Massif (Wölsendorf), prospecting dealt very intensively with pitchblende-bearing fluorite dykes [9, 10]. Here attempts to find trace elements which could be used as indicators for uranium enrichments in the immediate and more distant vicinity of known uranium deposits were made. After preliminary investigations using optical spectrography, bismuth appeared most promising, as other elements, such as cobalt, nickel, silver etc., were practically non-existent. A rapid chemical method for the detection of very small bismuth concentrations was developed (20% error at 0.5 ppm, 10% at 100 ppm) and ample sample material was investigated. This showed that although high uranium concentrations were always associated with higher bismuth concentrations, bismuth enrichments were found, which were by no means associated with parallel uranium enrichments.

Therefore, in this mineral assemblage which has a certain similarity to that of Joachimsthal, bismuth cannot be considered a reliable indicator for uranium, and thus bismuth aureoles cannot be used as an aid to uranium prospecting.

The occurrence at Ellweiler on the Nahe river, SE of Trier, of a deposit of approximately 100 t of U_3O_8 down to a depth of about 100 m which is being mined at present, is also situated in a fracture zone of a crystalline massif, a permian porphyry (Porphyry of Nohfelden) [11]. This deposit was discovered through scintillation measurements without recourse to scientific predictions. This deposit was at first considered to be of secondary origin and it was expected that it would become impoverished with increasing depth. A first revision of this assumption was due to a systematic analysis of fractures which traverse the deposit in various densely populated systems. Correlations of uranium enrichments in the fractured porphyry with the fracture systems were discovered. A thorough mineralogical investigation followed during which a great abundance of secondary uranium minerals including several new ones, such as ellweilerite and paulite, as well as several primary minerals of one or more hydrothermal stages, were found. Thus the correctness of the results of the fracture analysis was confirmed. Examples of primary minerals are uranium pitchblende and probably primary coffinite. A speciality were highly uraniferous hydrocarbons for which hydrothermal origin is assumed [12, 13].

During the prospecting for the Ellweiler deposit radon measurements of the ground air and geochemical investigations proved to be very valuable. The latter showed mainly that samples from underneath a young cover of weathering products contained far more information than samples which were taken near the surface. Both methods indicated a probable dyke-shaped outline for the deposit and therefore indirectly a primary origin. As a consequence of various investigations over several years, deep mining is now being carried out at Ellweiler. Absolute dating of the deposit has not been possible so far because of the high content of non-radiogenic lead.

At present, the Ellweiler deposit has an annual production of approximately 10 t of U_3O_8. The concentration of the ore fluctuates between 300 and 1 000 ppm U_3O_8. The ore serves mainly for technical experiments in the dressing plant at Ellweiler and as an addition to richer ores.

It was hoped that, on the basis of the experience described thorough structural and geochemical investigations in the entire porphyry complex would yield several other deposits of the same type. However, it now appears likely that primary concentrations in other places were later redissolved by hydrothermal action and carried away. This example again shows the difficulty of specific prediction even when they are made on the basis of a good knowledge of the local geological setting.

In the southern Black Forest [14, 15, 16, 17] a deposit was found in a granite SE of Freiburg on the southern slope of the Feldberg massif (Menzenschwand). Pieces of highly radioactive black rock were found in a diluvial moraine. After this discovery systematic surveys by the Gewerkschaft Brunhilde were started from a helicopter and by ground crews. This led to the exposure of a highly concentrated uranium occurrence after several metres of till had been dredged away. Large parts have uranium contents of 10-15 kg/t. The ore consists almost exclusively of pitchblende and a little coffinite. Associated minerals are hematite and manganese oxide, occasional magnetite, small amounts of various sulphides and some arsenides of iron, copper, nickel, and traces of lead selenides. Gangues are chert, quartz, fluorite and baryte. This makes it a deposit of the iron-baryte formation type which is generally considered as very promising for large uranium deposits. The age of the deposit has been determined* as 229.4 ± 3.3 million years. Hahn-Weinheimer *et al.* [18] give an age of 218 ± 10 million years for the granite containing the deposit by the rubidium-strontium method (total rock) that means that within the limits of error the deposit is syngenetic with the granitic intrusions.

The survey of the deposit is not very advanced yet. Estimates of the yield lie between 1 000 and 3 000 tons U_3O_8, which are worthwhile exploiting.

The Menzenschwand deposit is situated on the fringe of a granite complex near a gneiss. Several other uranium enrichments not yet investigated have been found near the contact. This makes it appear possible that the granite is especially promising for uranium in the contact zone (see below Geochemical prospecting).

PROSPECTING FOR URANIUM IN SEDIMENTS

As the most productive deposits in the world are of a sedimentary nature, promising sediments and localities which appeared favourable from a paleogeographic point of view were investigated. The varistic (permo-carboniferous) cycle of granite or porphyry formation associated with the well-known orogeny in Central Europe appeared to be a possible source for direct or indirect uranium concentration. This equally concerns physico-chemical precipitation of uranium in sediments as an enrichment in detrital formations which had their source area in the varisticum (as well as reworked uranium in detrital sediments).

At the time of the carboniferous coal formation (Ruhr and Saar areas), the basement of the varisticum was either not yet eroded to such an extent that economically useful uranium concentrations could be formed in the coal substance, or the areas, i.e., the amounts of coal substance, were too large, so that the content of the uraniferous solutions was spread very widely preventing the formation of deposits.

In the lower Zechstein of central and northern Germany, marine sediments were formed in the regions of the former varistic mountains. All these sediments are typical of anaerobic facies of stagnant waters: black shales with sulphides of iron, copper, zinc, vanadium, bismuth, silver, etc., the so-called *Kupferschiefer*. As low grade copper ores have been mined from these horizons for a long time, the conditions of sedimentation and of the supply of metalliferous weathering solutions from the remainder of the varistic mountains were rather well known. This knowledge could be taken into acount during the prospecting. The slags of copper smelting works were also tested. Uranium contents of 100 ppm and more were frequently found. Thus, uranium reserves of the order of 100 t U_3O_8 could be calculated for relatively small areas, but economically useful enrichments were not found.

The variegated sandstone of the lower Triassic [19] consists of a continental detrital sequence, mainly of red rocks, with intermittent occurrences of marine water ingressions [20, 21]. Gamma-log measurements in boreholes through these horizons revealed little variation from the maximum radioactivity (22). Small concretions of heavy metals with high contents of lead, copper, vanadium and uranium were also frequently found [23, 24]. Therefore, the entire sequence was thoroughly investigated. Only one of the many investigations is mentioned briefly because it deviates strongly from the general pattern. North of the town of Göttingen, west of the Harz Moutains, a marine-shale horizon in the middle variegated sandstone (Hardegsen clay) proved especially uraniferous [25]. Detailed geologic mapping and a few shallow drillings determined the extent and the properties of the hori-

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* Bundesanstalt für Bodenforschung, Hannover, Wiesenstr. 1.

zons. A bay-shaped area of deposition about 40 km wide and 50 to 60 km long with a thickness of 0-10 m was found. A petrographic investigation showed that the detritus came mainly from an area of paleozoic sediments and igneous rocks to the South, i.e., from an area which was promising for primary uranium content. Subsequently, the sedimentological character of the deposits was analysed in detail with the aim of determining the hydrodynamic mode of formation. It appeared probable that in the past the water level changed seven times from low to relatively high with a few areas being dried up occasionally. Spectral and subsequent chemical analyses for U, Zn, Cu, Pb, C and CO_2 and autoradiograms were made on systematically selected samples. The evaluation of all data showed that uranium was deposited syngenetically with the finest clay suspension, only during periods of higher water level when preferential precipitation of heavy metals took place. Zinc prevails in sediments of shallow water while lead was precipitated mainly in deep water. However, no uranium enrichments of economic value were found on the basis of this study although uranium contents of up to 700 ppm were encountered locally and the total uranium content is considerable.

As far as the geological environment is concerned, the two examples mentioned so far are very similar. Both cases are conducive to the formation of uranium deposits, but the amounts of metal brought in were not large enough either due to the great distance from the source area or due to unfavourable erosional conditions there. It would be premature and over pessimistic to consider this result as indicating that the uranium available in the primary source area is small and therefore to consider the chances of finding uranium deposits in the crystalline regions poor.

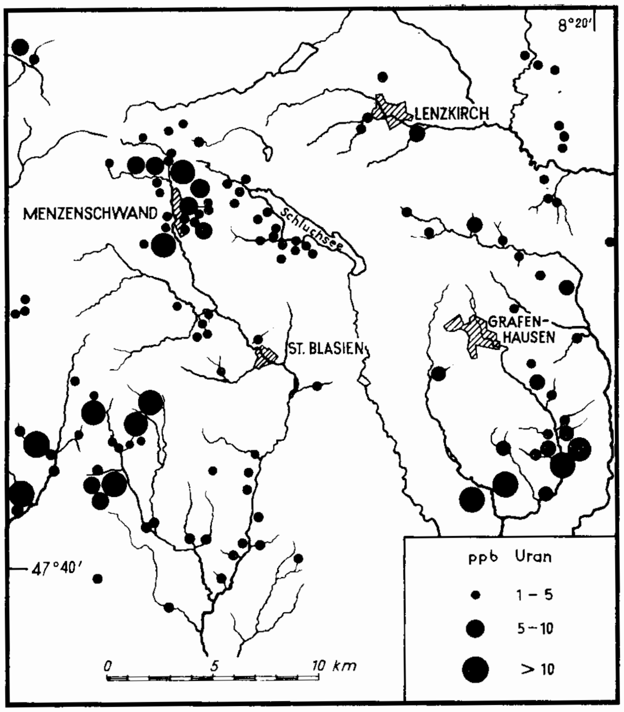

Figure 1. Geochemical prospecting for uranium (Black-Forest) in waters of creeks and springs
(U-contents < ppb not indicated)

As was shown above, the Bohemian Massif as a whole must be considered as promising with respect to uranium. Therefore, care was taken to investigate the most closely situated sediments. Indeed considerable enrichments of radioactive matter were found in places in the Triassic, especially in those sediments containing arkose [26, 27], but deposits of economic value were not found. Near the Bohemian-Bavarian crystalline Massif some lignite deposits were formed during the Tertiary. Solutions bringing uranium from the basement came into contact with these formations of the upper Miocene to form uranium enrichments [28, 29]. At 300 ppm, these may be of economic value so long as they are contained in the lignites which can be burnt. But these reserves totalling about 150 t of U_3O_8 were not exploitable in spite of the possibilities for easy strip mining (cf. Mineral dressing).

From these and other examples it can be concluded that predictions on economic enrichments of uranium in sediments cannot at present be considered as more than basic guide lines for prospecting, even in geologically well-known areas, such as the Federal Republic of Germany. Here, too, direct scientific means are not sufficient for reaching a quick decision but it is necessary to employ routine geophysical and/or geochemical methods before the actual scientific evaluation.

GEOCHEMICAL AND GEOPHYSICAL PROSPECTING

In our country, with its well-known meteorological conditions, geochemical prospecting for uranium in rivers and springs has proved useful especially after periods of protracted dryness during the summer months [30, 31]. An example of such a survey is shown in Fig. 1.

In the vicinity of the Menzenschwand deposit mentioned above, high uranium concentrations are found in waters. But it is to be expected that due to local features in the water circulation or water chemistry not all areas of high uranium concentrations will give information on deposits. If one can be sure that no large areas of importance are missed by this method, this type of survey cannot be overestimated as a preliminary to more detailed work. This method has already been reported in literature [32, 33, 34]. In the areas staked out by water prospecting, geochemical prospecting of soils and bedrocks and eventual radiation measurements and detailed geological investigations follow. Depending on the type of programme, the geochemical prospecting is preceded by an airborne survey.

The analyses were carried out as follows. The traces of uranium in the water samples are co-precipitated with iron hydroxide. The uranium is dissolved with hot nitric acid from these precipitates as well as from soil or rock samples. It is then extracted from the acid with tributylphosphate and separated from most of the other elements. After re-extraction of the uranium using ammonium acetate solution, the polarographic determination in strong sulphuric-perchloric solution is carried out on a cathode-ray polarograph. This type of analysis for uranium has the advantage that uncontrolled interference by other elements is eliminated. The limit of detectability was 1 ppm U for soils and rocks and 0.1 ppb U for waters.

Optimization of this process was achieved by carrying out the various steps of the operation (drying, grinding, filtration, shaking, polarography) in sets of 30 samples in an assembly-line array. One unskilled worker and one expert can produce 90 analyses including sample preparation in one 8-hour day.

A 4-ton laboratory truck was developed for field work. It is equipped with a modern laboratory fume hood, glow and drying furnaces, apparatus for water analysis, a 12 kV-220 V generator and air-conditioning. It can be used anywhere a source of water is available. An example of its application was the processing of 1 200 water samples from an area of 1 000 km² in the southern Black Forest in 20 days (for a section of this area see Fig. 1). In areas of consistently higher uranium content, a programme of analysing 4 500 soil and rock samples for uranium followed over the next three months. This led to the discovery of uranium enrichments of up to 2 000 ppm in the soil which were hitherto unknown. The economic-geological investigation of this area is still going on.

The equipment of the mobile laboratory was versatile to allow for rapid analyses for other elements, for example copper, which might yield useful hints as to the origin of newly discovered uranium enrichments. This approach has been tested not only in Germany but also in the High Andes in Peru under very difficult conditions.

A few years ago, we still believed that geochemical prospecting was best employed as a complement to a radiation survey. To-day we prefer this method for fast surveys whenever air-borne surveys are impossible due to the terrain. But geochemical prospecting can also be recommended in combination with an air-borne survey.

In spite of the great value of radon measurements in prospecting, some limitations of this method are worth mentioning [35]. Weathering at times produces a layer of low permeability at a depth of a few decimetres. Calculations and experimental work have shown that, below such a layer, the radon concentration can easily rise because of low diffusion rates and then may be erroneously interpreted as an indication of a uranium deposit or some special structure.

Moreover, it is a well-known fact that absolute age dates may, in spite of correct treatment and measurement, have values which geologists reject as erroneous. An example of this are the ages ranging from 0 to 180 million years, which were measured in the laboratories of the Bundesanstalt für Bodenforschung on samples from deep mines in late varistic fluorite dykes on the edge of the Bohemian Massif, even pitchblendes of various ages were among them. Therefore, great care must be taken to investigate the samples mineralogically prior to the absolute dating. On the other hand, the variety of ages obtained on samples from a certain deposit may give information on the occurrence and frequency of special events, which may have had an influence on the deposit.

MEASURING EQUIPMENT FOR PROSPECTING

For air-borne surveying, a fully transistorized air-borne scintillometer was designed and constructed in the laboratories of the Bundesanstalt für Bodenforschung. The unit consists of a 5 in diam by 5 in high NaI (Tl) crystal and its electronic control unit. The lower energy barrier for the detecting of gamma-rays can be varied within wide limits by means of high voltage and discrimination adjustments. Recordings is by means of a Varian compensation recorder. An accessory unit makes possible digital recording for the simultaneous registration of additional data such as flight altitude, aeromagnetic data etc. Double marks can also be registered for the exact co-ordination of measurement pattern and topography. The entire unit consists of three parts with a total weight of 35 kg, and thus is very adaptable and suited for incorporation in any airplane.

Prospecting experiences of the Gewerkschaft Brunhilde showed that a portable radiometer should not exceed 1 000 g in weight to be convenient for routine fieldwork. By employing printed circuits and transistors, smaller and lighter units could be developed without sacrificing sensitivity. It was also found convenient to design the units for one-hand operation to render possible the carrying, switching and changing of ranges by one hand. To lower the costs of daily use, the units were equipped with batteries which do not require servicing.

A variety of instruments are used for the various tasks such as mining control of a deposit, monitoring of transport vehicles, field prospecting, concentration measurements on ore samples and monitoring for the purpose of protection against radiation. The Gewerkschaft Brunhilde has constructed a number of types where the weights vary between 300 and 800 grammes.

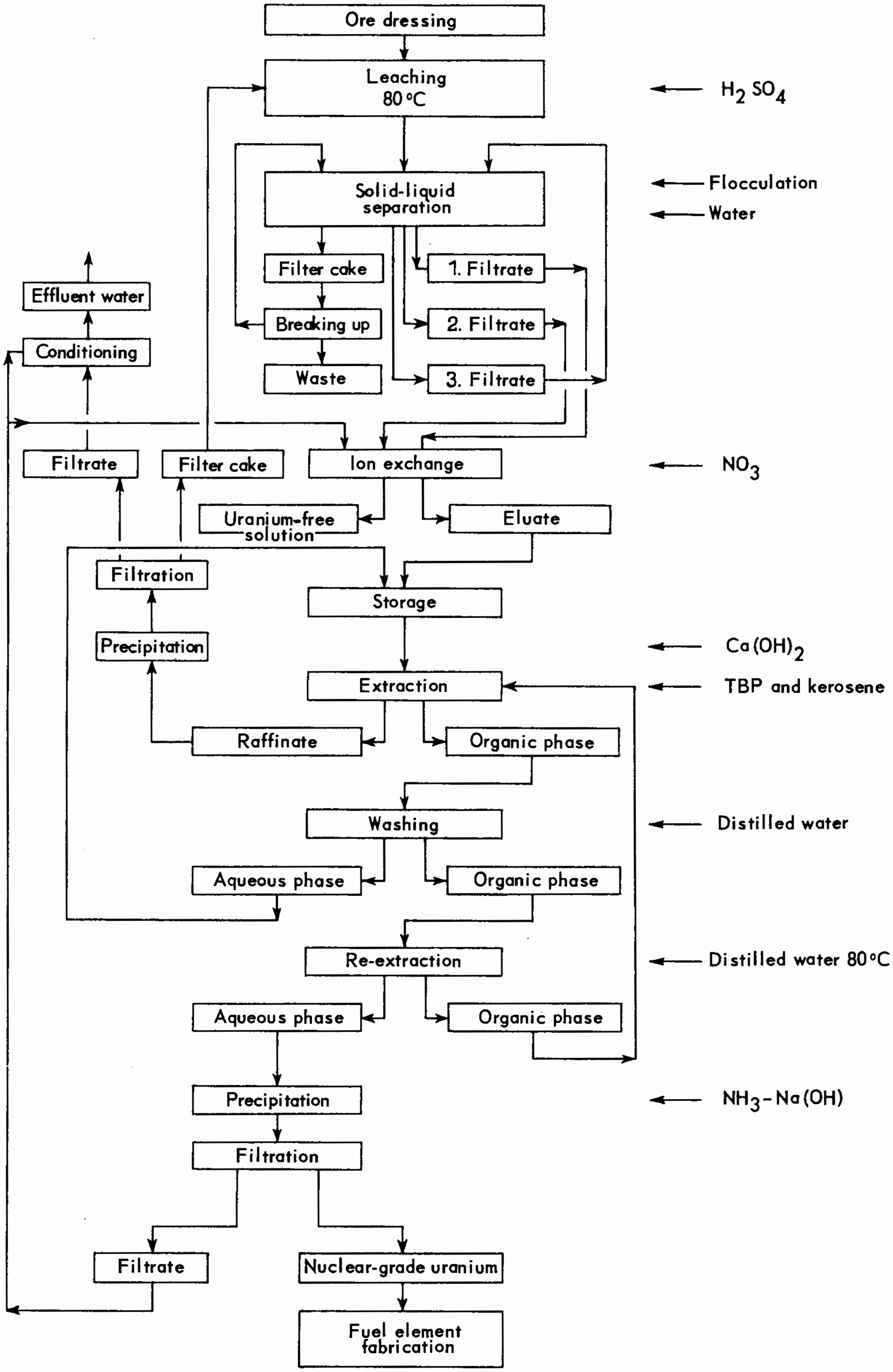

Figure 2. Flow-diagram for dressing uranium ore to nuclear-pure uranate using ion-exchange and liquid-liquid extraction

EXPERIENCES IN MINERAL DRESSING

Uranium and lignite (Wackersdorf, Oberpfalz/Bavaria)

Laboratory investigations* aimed at preparing a mineral dressing procedure have shown that uranium is present in the lignite as a uranium-iron complex of humic acid. There was no proof that the uranium was adsorbed or held in inorganic compounds. A slightly basic extraction brought up to 95% of the uranium into solution. An attempt to concentrate the uranium by combustion of the material led to technical difficulties because of the high clay and water content. Moreover, the combustion temperature had to be kept below 700 °C to avoid strong sintering. On the other hand, combustion at low temperatures showed that a greater fraction of the clay would enter the subsequent solution.

Uranium and fluorite

In the fluorite dykes mentioned above, uranium was found in considerable amounts. The extraction of the uranium ore was only acceptable if the valuable fluorite was not rendered useless. Detailed mineralogical and physico-chemical investigation showed that up to 900 ppm UO_2 were present in the fluorite lattice. This, however, is not a solid solution but rather an incorporation of more or less large molecular groups [36]. These lattice disturbances influenced the cleavage. This explains why about 60-80% of the total uranium content could be extracted by leaching from the ground fluorite (grain size smaller than 0.2 mm). During the usual flotation of fluorite using oleic acid, pitchblende partly enters the fluorite fraction and partly the waste [37]. After grinding the material to the grain size required for fluorite flotation (about 0.1 mm), an enrichment of 65% of the uranium content of the ore in 10 to 15% of the original material was achieved by making use of the density difference. But the loss of uranium in this type of flotation appeared to be too high [38].

To obtain a maximum yield of uranium, leaching had to be done prior to the fluorite flotation. Preliminary experiments have shown that acid as well as basic leaching in weak concentrations can be applied without influencing the present fluorite flotation method. It is only necessary to increase the amount of flotation media, especially that of the oleic acid.

Ellweiler pilot plant

The Ellweiler pilot plant was constructed with Government support by the Gewerkschaft Brunhilde in the years 1958/59. It began production in 1960. Its design has been described in detail [39]. A great number of dressing experiments for various ores have been performed and improvements of dressing processes are now being developed. Recently a combination of ion exchange and liquid-liquid extraction has been developed using the plant for the production of nuclear-pure solutions and uranates on a technical scale directly from the ore. The uranium is dissolved out of the ore with sulphuric acid and subsequently collected on strongly basic anion exchange columns. The columns are eluted with acidic sodium nitrate solution from which the uranium is extracted with tributylphosphate and petroleum. It is re-extracted with hot pure water and then precipitated as nuclear-pure uranate. A flow diagram of the technical process is shown in Fig. 2.

The extraction of heavy metals, particularly uranium, from lowgrade ores by means of chlorine gas has recently been reported [40]. Chlorine is passed through the ore at 1 100 °C and the uranyl chloride is drawn from the furnace together with the chlorine gas and, cooling to 450 °C, separated as uranium oxide. To make this expensive process economically acceptable, it is necessary to make use of the chlorides of the other heavy metals as well, as there as those of Fe, Mn, V, Ti, etc.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/478 République fédérale d'Allemagne

Prospection et préparation de minerai d'uranium dans la République fédérale d'Allemagne, progrès en méthodologie et nouveaux résultats

par H. Closs

Le progrès technique en matière d'appareils de mesure des rayonnements a suivi, en Allemagne, la tendance générale des techniques de mesure. Ainsi a-t-on, par exemple, déjà fait d'importants progrès dans l'enregistrement et le traitement numériques des données obtenues par des mesurages aériens. La prospection géochimique de l'uranium à l'aide de laboratoires mobiles a été à tel point perfectionnée qu'une petite équipe mobile peut examiner 1 500 échantillons de sol ou d'eau par mois. A l'aide des méthodes modernes de la minéralogie, y compris l'analyse de structure et l'analyse aux rayons X, on a pu faire, d'après les affleurements, des prédictions sur les associations minérales à des profondeurs plus grandes. De même, des déterminations par diverses méthodes d'âge absolu de minerais et de roches constituent, conjointement avec la spectroscopie à rayons gamma, un autre moyen important pour l'appréciation de la genèse des gisements. Particulièrement dans la Forêt-Noire méridionale, la prospection a donné d'excellents résultats; on y a découvert dans les filons de quartz-hématite rouge-baryte des dépôts contenant de la pechblende. Dans une grande partie des dépôts on a trouvé des concentrations de plus de 1 % d'uranium. Étant donné les prix actuellement extrêmement bas sur le marché mondial des gâteaux d'oxyde d'uranium, on a cherché à abaisser les prix de revient de la préparation des minerais riches et des minerais pauvres par des recherches et études technologiques intensives. Ces études ont été faites à l'usine de traitement d'Ellweiler en utilisant des minerais provenant de dix gisements. Ce n'est que récemment qu'on a soumis à des essais finals un procédé permettant, par une combinaison d'échange d'ions et d'extraction liquide-liquide, la production de solutions et d'uranates nucléaires purs au cours du traitement du minerai d'uranium.

A/478 ФРГ

Разведка и обогащение урановых руд в Федеративной Республике Германии: прогресс в методологии и новые результаты

Г. Клосс *et al.*

За техническим усовершенствованием радиометров в ФРГ последует общий прогресс в методах геофизических измерений. Так, например, в значительной степени совершенствуется цифровая регистрация и обработка данных, полученных в результате аэрограмма-съемки. Геохимическая разведка урана с помощью передвижных лабораторий усовершенствована до такой степени, что небольшие полевые партии могут проводить в месяц до 1500 анализов почвы и воды. Современные методы минералогических исследований, в том числе рентгенографический и структурный анализы, позволили предсказывать по поверхностным выходам характер минеральных ассоциаций на значительных глубинах. Определения абсолютного возраста руд и пород различными методами, наряду с проведением гамма-спектроскопии, оказались важными вспомогательными средствами для определения генезиса месторождений. Особенно успешными оказались поиски в южной части Шварцвальда, где было открыто месторождение настурана в кварц-гематит-баритовых жилах. Содержание урана в рудах этого месторождения по большей части превышает 1%. Ввиду исключительно низкой цены уранового концентрата на мировом рынке в настоящее время были проведены широкие исследования и технические разработки по снижению себестоимости обогащения богатых и бедных руд. На обогатительной установке в Эльвейлере проведены технологические исследования руд десяти различных месторождений. Совсем недавно проводились завершающие опыты по обогащению урановой руды комбинированным методом ионного обмена и жидкостной экстракции, позволяющим получать чистые растворы и ураннаты.

A/478 República Federal de Alemania

Prospección y concentración de mineral de uranio en la República Federal de Alemania, progresos en metodología y nuevos resultados

por H. Closs

El progreso técnico de los aparatos detectores de radiaciones en Alemania ha seguido las tendencias generales de las técnicas de medidas. Así, por ejemplo, se encuentran muy avanzados los sistemas digitales de registro y elaboración de datos, recogidos en medidas tomadas desde aviones. La prospección geoquímica de uranio con laboratorios móviles ha progresado tanto que un pequeño equipo de campo puede efectuar hasta 1 500 análisis de suelos y aguas por mes. Los métodos modernos de mineralogía, incluyendo los análisis por rayos X y estructurales, han logrado que, a partir de los afloramientos superficiales, se puedan precedir las asociaciones minerales a mayores profundidades. Las determinaciones de edad absoluta en minerales y rocas por varios métodos, junto con la espectroscopía gamma, ha demostrado ser un medio auxiliar importante para estimar la génesis de los yacimientos. Ha tenido un éxito particular la prospección de la parte meridional de la Selva Negra, donde se descubrió un yacimiento con pechblenda en filones de hematites-barita-cuarzo. Se encontraron leyes mayores de 1 % de uranio en zonas extensas del yacimiento. Debido a los precios mundiales extremadamente bajos del concentrado, la investigación se dirigió principalmente a tratar de conseguir una disminución de los costes de la concentración de minerales ricos y pobres. Se han realizado investigaciones con minerales procedentes de 10 yacimientos distintos en la instalación de concentración de Ellweiler. Hace poco tiempo que fueron realizados los ensayos finales de un método que permite la recuperación de soluciones de pureza nuclear y uranatos en el curso del tratamiento del mineral, mediante una combinación de las técnicas de extracción por intercambio de ion y líquido-líquido.

Developments in thorium production technology

By K. J. Bril and P. Krumholz *

The thorium industry started at the beginning of this century using monazite as raw material and producing thorium nitrate mainly for the incandescent gas-mantle industry. During the period between the two world wars this thorium market disappeared progressively. Since the advent of the atomic era, and although some non-nuclear applications of thorium did develop, the revival of the thorium market still awaits the future development of atomic power generation programmes. However, prospects of using thorium in power reactors seem hopeful enough to justify and stimulate research to develop thorium technology further. In this paper the recent developments in the processing of thorium bearing ores and in the production of nuclear grade thorium oxide are reviewed with special reference to industrial and pilot plant experience in Brazil.

MINERAL RESOURCES

The known reserves of low cost thorium (5-10 US$/lb ThO_2) in Western countries were recently reported to be only about 5×10^5 tons of ThO_2 [1] and Kaplan *et al.* [4] give an account of thorium mineral resources in the USSR. Thus, there is little doubt that the long range nuclear fuel supplies for power production will depend chiefly on the low grade sources [2]. A comprehensive bibliography containing numerous references to the mineralogy, prospecting, exploration and reserves of thorium has recently been released [3]. The list of thorium bearing minerals exceeds 100, among which about 60 contain over 1% of thorium. However, besides monazite, which is the most important source of thorium, thorianite, brannerite and to a lesser extent thorite, are the only thorium minerals which are commercially exploited. In the particular case of monazite dressing plants [5], their installed capacity throughout the world greatly exceeds the present production rate, and the tendency in several countries is to reduce production even further [6].

THE PREPARATION OF THORIUM CONCENTRATES

The starting material for the production of nuclear grade thorium is generally a more or less rich thorium salt concentrage. This situation will certainly prevail, at least in the near future, because of the existence of important thorium stockpiles accumulated mainly as a result of monazite processing. The development of solvent extraction technology and the continuing search for more selective solvents however, make it probable that this intermediate step could some day be omitted [7].

In Table 1 references to recent papers relating to processing of thorium raw materials are listed together with a brief description of the processes. Attempts to recover high cost thorium (up to 500 US$/lb of thorium + uranium) from low grade resources have also been considered.

Numerous methods for the treatment of monazite have been reviewed [5]. The relative advantages of the many flowsheets which have been proposed still remain open to discussion. Industrial practice is based either on H_2SO_4 or NaOH breakdown. Cost comparison of both methods [7-9] gives a slight advantage to the H_2SO_4 process. However, due credit has not been given to the values of the rare earths and Na_3PO_4. Because it gives a high quality thorium concentrate at an early stage of the process and because the rare earths can be obtained practically free from thorium and phosphate, the caustic soda breakdown of monazite is particularly useful where further purification of thorium and/or splitting of the rare earths into the individual elements is considered.

Brazilian practice of thorium recovery from monazite

Chemical processing of monazite started in Brazil in 1948. The actual production capacity is 3 000 tons of monazite per year. The process is based upon the caustic soda breakdown. Several years' experience with large scale operation have led to many improvements of the original process [10].

Monazite is processed as a + 98.5% concentrate. It contains about 64% of rare earth oxides, 5.5-6.5% of ThO_2 and 0.15-0.35% of U_3O_8. The high purity of the sand used greatly improves the performance of the chemical processing [11-12]. The monazite is ground to 99% minus 300 mesh. The attack with caustic soda (about 55 wt%) is carried out under a pressure of several atmospheres and at 170 °C. This results in a readily controllable operation. NaOH is used in an excess of about 100% over the theoretically necessary

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Table 1. Chemical processing of thorium raw materials

Raw material	Breakdown agent	Main process steps and references
Monazite	H_2SO_4	Selective pptn. of Th: as basic phosphate by NH_3 [18, 19], MgO [20, 21], electrolytically [21]; as pyrophosphate [22, 23]; as oxalate [24-26]; as sulfate [24, 25, 27]. Caustification and TBP extn. [18, 23] or basicity sepn. [20].
		Selective pptn. of rare earths as double sulfates [28-32], or anhydrous sulfates [33]. Th recovered as oxalate [28-31], as fluoride [33]. Caustification followed by basicity sepns.
		Selective extn. of Th by amines [34-37], esters of H_3PO_4 [34, 38], other solv. [34], cellulose [24, 25, 40, 41]; ion exchange resins [43, 44].
		Total pptn. with oxalate [8, 19, 45] or fluoride [46]. Caustification or calcination; TBP extn. [8] or basicity sepns. [20].
	NaOH	Selective leaching of rare earths [39] in HCl [13, 47]. Crystn· of $Th(SO_4)_2$ from HCl [47], H_2SO_4 [13, 16]. Dissoln. in HNO_3 and TBP ext.
		Total dissoln. in HCl [47-53] or HNO_3 [49]; basicity sepn. [55]; TBP extn. [49, 56]; ion exchange sepns. [42, 57].
		Ce oxidation; selective dissoln. of 3+ rare earths; reductive dissoln. of Ce; Th recovery as basic salt [15, 16].
	Miscellaneous	Pressure digestion with aq. NaOH [13, 107]; fusion or sintering with NaOH [52], Na_2CO_3 [52, 58], CaO [52], CaO + $CaCl_2$ [59], Na_2SO_4 + C [60]. Chlorination and fract. distn. [27, 61, 62].
Uranothorianite	HNO_3	Pptn. as sulfate or oxalate; caustification and TBP extn. [63].
		TBP extn.; U separation by oxalate pptn. or pre-extn. with dilute TBP [63-65].
Thorite	H_2SO_4	Extn. with amines; NaCl stripping; pptn. with oxalate or soda ash [75].
	HNO_3	Concn. by pptn. with NaOH; TBP extn. [25, 66].
Blind River ores	H_2SO_4 [67]	Extn. of U-barren liquors with esters of H_3PO_4 [25, 34], amines [25, 34, 68], ion exchange resins [69].
		Extn. of leach liquors with amines [34, 70].
Granites, etc. . .	H_2SO_4	Extn. with primary amines [71-74]; stripping and purification with trioctylphosphine [73f].

amount. The hydroxides of thorium and rare earths are suspended in water and separated from Na_3PO_4 and excess NaOH by filtration. After crystallization of Na_3PO_4, the mother liquor is concentrated. About 50% of the recovered NaOH is recycled.

Addition of reducing agents (e.g. glucose) during the caustic soda attack prevents the oxidation of cerium, thereby avoiding difficulties experienced by other workers [49, 54] during the dissolution of the bulk of rare earths.

The process followed in the separation of thorium from rare earths depends upon the form in which the latter are required by the consumer. If rare earth chlorides are required the mixed hydroxides are suspended in water to give a final rare earth concentration of 300 g/l, and the rare earth chlorides are leached selectively, at 70 °C by the addition of HCl (final pH about 4.5). Thorium recovery is quantitative and that of uranium nearly complete. The decontamination factors of thorium from the rare earths and phosphate are of the order of 100 [11, 13].

A satisfactory separation of thorium from rare earths cannot be obtained by selective leaching with H_2SO_4. Thus, if the rare earths are to be recovered as sulfates, or double sulfates, the mixed hydroxides are suspended in water to give a final total oxide concentration of 80 g/l and dissolved completely with H_2SO_4 at 45 °C. Thorium hydroxide is thrown down with NH_3 until a final pH of 6 is reached. Co-precipitated rare earths are leached with dilute HCl.

An alternative flowsheet has been devised for the possibility of a commercial outlet for cerium free rare earths and/or for the separation of the individual members of this group. The mixed hydroxides of thorium and rare earths are either dried and subjected to air oxidation of cerium [14], or suspended in water and the cerium is oxidized with Cl_2 [15]. Cerium-free rare earths are leached with HCl. Separation of thorium from cerium is carried out by dissolution in the presence of a reducing agent (methanol, glucose, SO_2, etc.), followed by selective precipitation of thorium with ammonia.

The crude thorium cake obtained according to one of the above processes is next submitted to leaching with a $Na_2CO_3/NaHCO_3$ mixture. In this operation, 70-80% of the uranium content is dissolved and recovered after filtration as sodium diuranate. At the same time chlorides are largely removed.

The final crude thorium hydroxide has the composition given in Table 2. For some time a technical grade $Th(SO_4)_2$ has been produced starting with this material. Details of this process have been published elsewhere [16].

Table 2. Typical composition[a] of crude thorium hydroxide (dry basis)

	Concentration		Concentration
ThO_2	58%	Li	200 ppm
Ln_2O_3[b]	5-7%	Mo	5 ppm
Fe_2O_3	3%	As	60 ppm
TiO_2	0.5%	SiO_2	4%
PbO	0.3%	P_2O_5	1.7%
U_3O_8	0.5%	F	0.5%
Cd	50 ppm	Cl	100 ppm
V	200 ppm	B	25 ppm
Insoluble in $4N$ HNO_3 : 24%			

[a] Except for silica the analysis refers to that part of thorium hydroxide which is soluble in $4N$ HNO_3.

[b] Ln_2O_3 stands for total rare earth oxides. According to the monazite composition [11], about 5% of Ln_2O_3 consists of rare earths with high thermal neutron cross sections: Sm, Eu, Gd and Dy.

PREPARATION OF NUCLEAR PURITY THORIUM OXIDE

Published specifications of nuclear purity are rather scarce for thorium. It is generally necessary to maintain samarium, europium, gadolinum and dysprosium (i.e. the rare earths having very high thermal neutron cross sections) below 0.05 ppm each. If breeding of ^{233}U is considered, the ^{238}U content of thorium should be as low as possible and preferably about 1 ppm [17]. The purification process starting with a raw material having a composition similar to that given in Table 2 must thus ensure a decontamination factor of 10^5 for the rare earths and 10^4 for uranium.

Methods used (or proposed) for the large-scale production of nuclear grade thorium are all based on solvent extraction, although processes involving ion exchange [7, 66, 76, 78] are currently being studied. Tributylphosphate (TBP) is the most popular solvent used. However, great efforts are being made to find and employ better solvents [80-89], in particular because of the need for the reprocessing of irradiated fuels [79, 90, 106, 108]. Further improvement of solvent extraction separations may be expected from the studies of synergistic effects [95-98] and from a systematic investigation of diluents [99].

The TBP processes have been studied in several countries i.e. France [63, 64], India [47, 91], United Kingdom [20, 24, 56, 66], Brazil [92, 93], etc. The recent monograph of Cuthbert gives a comprehensive account of the USA practice. The present discussion will be confined to the production of nuclear grade ThO_2 from monazite concentrates.

According to the UK practice described by Jamrack [66], uranium is separated first by extraction from nitrate solution with 5% TBP in xylene [94]. Next, thorium is separated from the rare earths and other impurities by extraction with 40% TBP in xylene. Each cycle of operations requires 9 extraction, 5-6 scrubbing and 5 stripping stages. Thorium stripping is performed with $0.02N$ HNO_3. The final product is obtained by denitration, oxalate precipitation or precipitation with NH_3 according to the required properties of the ThO_2. A similar process has been investigated in India [91].

According to the USA process as developed at the Battelle Memorial Institute [48, 49, 51], the separation of uranium is performed after the extraction of thorium nitrate into TBP by using selective stripping of thorium and a backwash of eventually stripped uranium. In order to secure further decontamination from uranium, thorium is precipitated as oxalate. The alternative developed at Ames [8, 9, 19], starts with a feed produced via oxalate precipitation, from which most of the uranium has been already eliminated.

Brazilian pilot plant experience in the preparation of nuclear purity thorium oxide

The flowsheet established for the production of nuclear grade ThO_2 (see Fig. 1) differs in several respects from current practice:

(*a*) Thorium is extracted from a low acidity feed;

(*b*) Thorium is extracted from non-clarified solutions (slurries containing up to 150 g/l of solids), using active carbon to prevent emulsion formation [100];

(*c*) Thorium is stripped from the solvent by extractive precipitation of $Th(SO_4)_2$ [101];

(*d*) A separate step for the decontamination of thorium from uranium is eliminated, the selectivity of the extractive precipitation being sufficiently high;

(*e*) About 60% of HNO_3 is recovered and recycled into the dissolution process.

The difficulties of obtaining filterable suspensions by dissolving crude thorium hydroxide in HNO_3 are well known and have led many workers to attempt the direct extraction of slurries with TBP. The reported results have not been fully satisfactory [104, 105]. A thorough study of the conditions of the dissolution and the use of active carbon to prevent emulsion formation permits a novel approach to the problem of slurry extraction.

The efficiency of the separation of thorium from uranium by precipitation of $Th(SO_4)_2$ can be greatly increased if precipitation is carried out directly

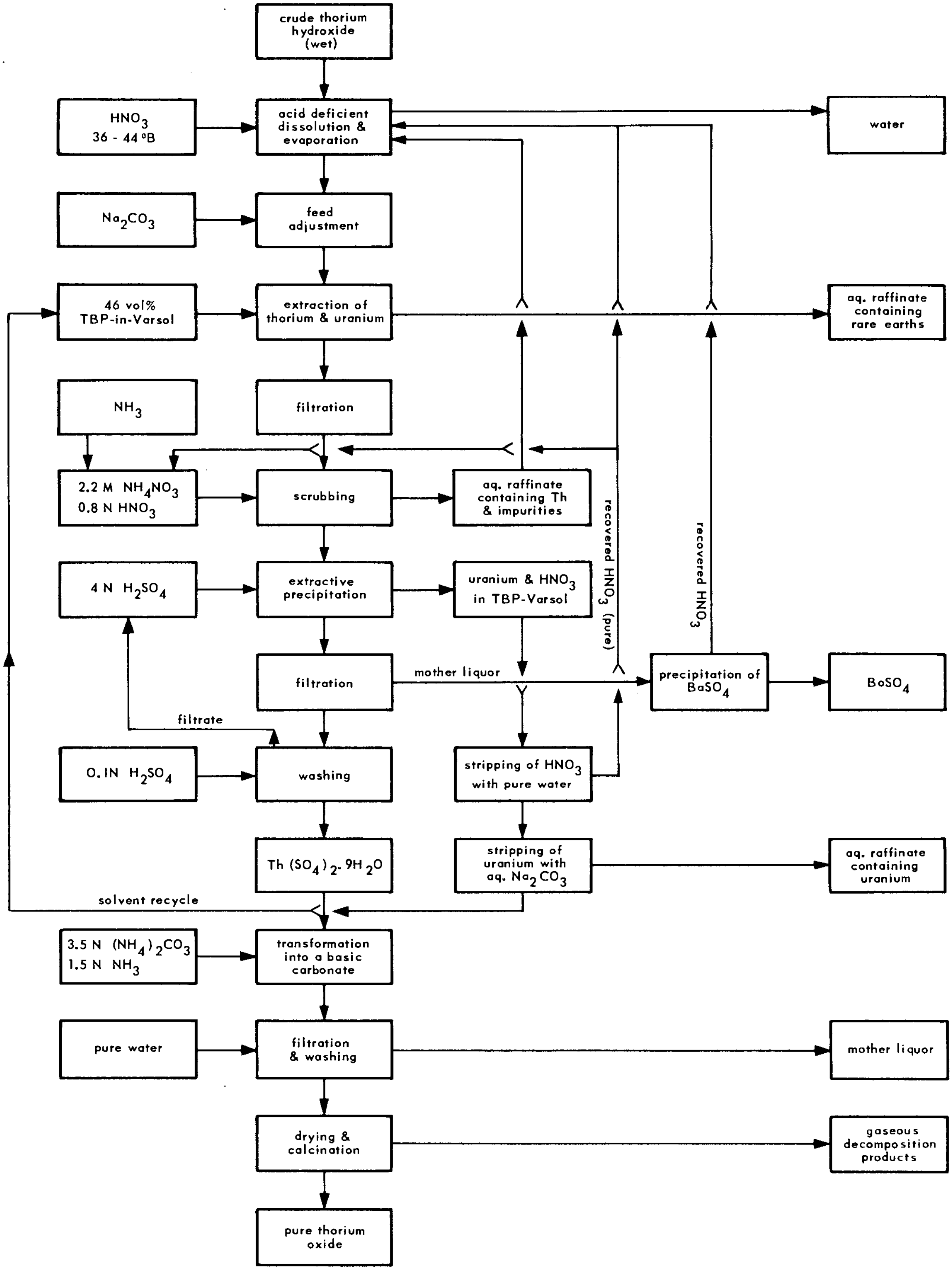

Figure 1. Flowsheet for the production of nuclear grade thorium oxide

from TBP. The resulting high nitrate concentration and the presence of the organic phase allow the uranium concentration in the aqueous phase to be held at very low levels, which decreases co-precipitation by a factor of up to 100 as compared with the extent of co-precipitation of uranium in pure aqueous solutions [101, 102].

Feed preparation

About a third of the wet crude thorium hydroxide is introduced into the aqueous solution coming from the scrubbing stage (see Fig. 1). Next, recovered nitric acid and crude thorium hydroxide are introduced alternately. Acid-deficient conditions are maintained while the suspension is boiled down* to 350 g/l of ThO_2. Fresh HNO_3, 36-44 °B, is added to give a free acidity of 2-2.5*N*. The mixture is digested for 6 hours at a temperature near the boiling point. Na_2CO_3 is added to reduce the free acidity to 0.8*N*. The final suspension contains about 280 g/l of ThO_2, 2.2*M* $NaNO_3$ and 100-150 g/l of solids.

Purification of thorium by solvent extraction

For reasons discussed elsewhere [93] the solvent used is a mixture of 46 vol% of TBP and 54 vol% of Varsol (trade name of a paraffinic naphthal fraction). The diluent was treated with H_2SO_4 to eliminate most of the non-saturated and aromatic hydrocarbons. With the particular solvent mixture used, separation into a TBP-rich and a diluent-rich phase occurs at a thorium concentration of about 130 g/l at 30 °C.

It is well known that the distribution coefficients of many elements decrease very significantly as the thorium concentration in TBP approaches the saturation limit [7]. In order to take full advantage of this effect it was decided to operate at high thorium concentrations in TBP.

Starting with a feed containing 280 g/l of ThO_2 and maintaining the concentration of ThO_2 in the organic phase at 125-126 g/l, the extraction yield of thorium was 98 and 99% in 4 and 5 stages respectively. At a concentration of 120 g/l the extraction yield increases to 99 and 99.5% respectively. At the same concentration of the salting agents the extraction of thorium in pure solutions should exceed 99.8% in all these cases. The observed decrease of extraction yield in real systems is due to the complexing action of fluorides and phosphates.

The efficiency of decontamination of thorium from rare earths has been followed by using europium as a tracer. Europium can be readily determined polarographically, even in the presence of a great excess of thorium. Furthermore, the decontamination factor, $D_{\mathrm{Eu}}^{\mathrm{Th}}$, gives a fairly conservative estimate for the efficiency of thorium separation from the other elements of this group, because, as shown earlier [92], the separation factor $K^{\mathrm{Th}}/K^{\mathrm{Eu}}$ is one of the lowest for the rare earth elements. The knowledge of the experimental variation of K^{Eu} with thorium concentration in TBP [93] (see Fig. 2) allows a fairly correct prediction of the behaviour of the system. It has thus been found, in accordance with the expected values, that at 125 g/l of ThO_2 in TBP, $D_{\mathrm{Eu}}^{\mathrm{Th}}$ in the extraction section is about 120 and that the decontamination from the total rare earths is even better.

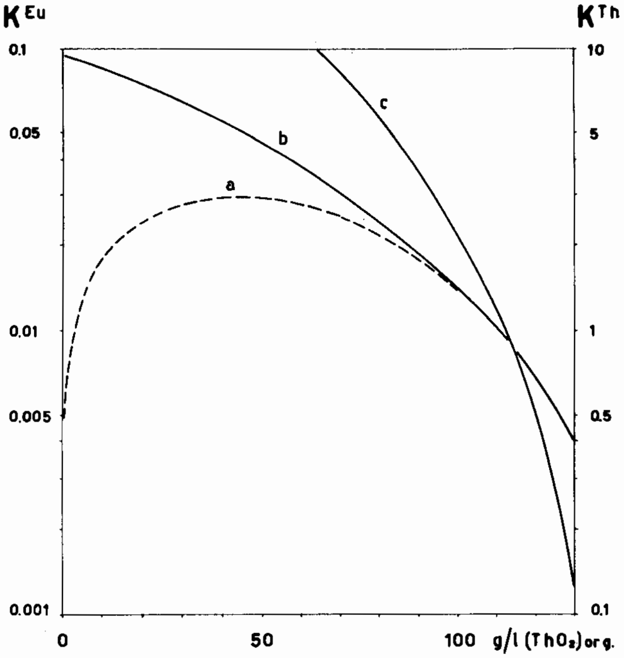

Figure 2. Variation of distribution coefficients of thorium (K^{Th}) and europium (K^{Eu}) with the concentration of thorium in 46 vol% TBP in Varsol

Most of the published results have been obtained in a battery of glass mixer-settlers having a useful volume of 1 liter per stage. The experiments have been scaled up to a 10 l stainless steelmixer-settler. Maintaining water-in-oil emulsions was found to be preferable. Using a solvent containing 0.2-0.5 g/l of active carbon no stable emulsions were formed and entrained TBP was controlled to within 0.2-0.3%. Preliminary experiments with continuous operation of the mixer-settlers have been successful.

The TBP leaving the extraction section is filtered through diatomaceous earth in order to remove any colloidal impurities and coalesce traces of entrained aqueous phase. The filtered solution is scrubbed with 2.2*M* $NH_4NO_3 + 0.8N\ HNO_3$. In view of the high decontamination achieved in the extraction step, the scrubbing section need only secure a decontamination of 10^3 for the rare earths. From the known equilibrium data [93], it may be inferred that starting with a

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* Evaporating this slurry to 220 l/100 kg ThO_2, introducing it into 105 l of 36 °B HNO_3 at 70-90 °C, diluting to ~ 400 l and digesting for 3 hours at 90 °C, results in readily filterable solutions.

solution containing 120-125 g/l of ThO_2, such decontamination can readily be achieved in three stages, using an aqueous/organic ratio of about 0.1. This fact has been confirmed experimentally using the battery of discontinuous mixer-settlers.

The performance of pulsed columns during the scrubbing operation is rather puzzling. It appears that D^{Th}_{Eu} does not vary with thorium concentration in TBP in the manner to be expected from theoretical considerations. Thus, in a 2 in pulsed sieve-plate column (total height 2 m, working height 1.2 m) [103], at thorium concentrations above 110 g/l, D^{Th}_{Eu} decreases with increasing thorium concentration in TBP. At 110 g/l of ThO_2, the values of the height equivalent to a theoretical stage are about 50 cm whereas at 125 g/l the values increase to 2 m. The net effect is a 5-fold *decrease* of D^{Th}_{Eu}. A similar effect has been found during the separation of uranium from thorium [103].

Among the elements listed in Table 2, only arsenic, boron, molybdenum and vanadium have appreciable distribution coefficients (0.01-0.03) [93]. Even for these elements a three stage scrubbing system provides sufficient decontamination. Due to the decomposition of TBP the only element not behaving in a predictable manner is phosphorus.

Extractive precipitation of thorium sulfate

The organic solution is now introduced with vigorous stirring into a small excess of $4N$ H_2SO_4. $Th(SO_4)_2$ precipitates readily and is filtered off. Depending upon the temperature of precipitation the aqueous mother liquor still contains 3-10 g/l of ThO_2. After elimination of sulfates by precipitation of $BaSO_4$, the resulting $\sim 3N$ HNO_3 is recycled into the dissolution process (see Fig. 1). $Th(SO_4)_2$ is washed with some dilute H_2SO_4 and the filtrate is used to prepare the solution of $4N$ H_2SO_4.

The organic phase, which still contains 2-5 g/l of ThO_2, is contacted with a fresh portion of $4N$ H_2SO_4. TBP, which thus becomes practically free from thorium, is poured off. A fresh portion of loaded TBP is introduced into the remaining acid and a new cycle of the extractive precipitation started.

The extractive precipitation of $Th(SO_4)_2$ results in a D^{Th}_{U} as high as 2×10^4 [101]. In the concentration range of 10 — 100 ppm the decontamination factors for Na, K, Ca, Ni, Co, Cu, Zn, Cd, Cr, Fe, Mo and Ti are of the order of 100, for boron of the order of 10^3. Lead and rare earths are decontaminated by a factor of 10, phosphorus by a factor of 5 [102]. Despite being small, the D^{Th}_{P} achieved during the extractive precipitation is particularly valuable.

Thorium is recovered with a yield of 96-97%. It has an uranium content of about 1 ppm.

Experiments were performed in a 15 l stainless steel vessel. $Th(SO_4)_2$ has been easily filtered with a cake height of 20-30 cm. Finally the crystals were washed with a small amount of alcohol in order to remove any traces of adhering TBP.

The only difficulty so far experienced was the formation of crusts on the walls of the precipitation vessel. It is believed that this problem can be overcome by recycling a greater amount of the $Th(SO_4)_2$ slurry to provide a greater surface for crystallization.

Preliminary experiments of a continuous extractive precipitation have been successfully performed using a stirred column.

Recovery of uranium and nitric acid

The thorium-free TBP still contains about 30% of the original HNO_3 and practically all the uranium. HNO_3 can be selectively stripped with water and part of it recirculated to the dissolution process (see Fig. 1). Only 40% of the total acid required for the dissolution of the crude thorium hydroxide needs to be fresh HNO_3 if the acid recovered from the $Th(SO_4)_2$ mother liquor is taken into account.

Uranium is finally extracted with Na_2CO_3 and recovered as sodium diuranate. The extraction with Na_2CO_3 serves a dual purpose, since the solvent is regenerated at the same time.

Transformation of $Th(SO_4)_2$ into basic carbonate

The transformation of $Th(SO_4)_2$ into basic carbonate is performed at 70 °C by introducing a solution of $3.5N$ $(NH_4)_2CO_3$ and $1.5N$ NH^+_3, into an aqueous slurry of $Th(SO_4)_2$. After extensive washing, the moist basic carbonate contains about 30-35% of ThO_2 and 100-150 ppm of SO_4^{2-}. Calcination at 900 °C, 1 100 °C and 1 250 °C lowers the SO_4^{2-} content to 75, 25 and 10 ppm respectively (i.e. down to 3 ppm of sulphur).

The purity of a typical sample of thoria is illustrated in Table 3.

Table 3. Typical analysis of pure thorium oxide

Impurity	Concentration ppm	Impurity	Concentration ppm
U	1	Ln_2O_3[b]	1
B[a]	0.2	Fe	1
Cd	0.1	Ni	1
Si	4	Pb	1
P	5-10	Cu	1
Zn	1	Mo	0.5

[a] The B content does not reflect the real efficiency of the process, since Pyrex glass has been used in some steps of the process.

[b] Ln_2O_3 stands for total rare earth oxides.

The production of ThO_2 via the basic carbonate process promises to result in a very readily sinterable thoria [77].

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/484 Brésil

Développements récents dans la technologie de la production du thorium

par K. J. Bril et P. Krumholz

Les développements récents dans le traitement des minerais de thorium et dans la production d'oxyde de thorium de qualité nucléaire sont passés en revue, en particulier en ce qui concerne l'expérience acquise au Brésil à l'échelle industrielle et à l'échelle de l'usine pilote.

Du point de vue de la production de thorium, le procédé alcalin de traitement de la monazite, utilisé au Brésil à l'échelle industrielle depuis 1948, offre un avantage considérable en comparaison avec les autres techniques. En particulier, le rendement est pratiquement de 100 %, les facteurs de séparation du thorium d'avec les terres rares et le phosphate sont de l'ordre de 100, et le thorium est obtenu sous une forme bien appropriée à une purification finale par extraction aux solvants. On présente les conditions d'exécution permettant d'obtenir des résultats satisfaisants dans de bonnes conditions économiques.

La purification du thorium par extraction au moyen de solvants est discutée, tout particulièrement en relation avec les problèmes suivants : *a*) extraction des solutions non filtrées, *b*) décontamination du thorium par séparation des terres rares, *c*) séparation du thorium d'avec l'uranium.

On décrit l'expérience acquise à l'échelle pilote, dans un système de mélangeurs-décanteurs, sur l'extraction des solutions non filtrées. La formation d'émulsions pendant l'extraction des solutions non filtrées du produit brut de thorium, résultant de l'attaque alcaline de la monazite, est éliminée par l'emploi de charbon actif comme agent désémulsifiant.

Une décontamination satisfaisante du thorium par séparation des terres rares, qui constituent l'impureté principale (10 %) dans le concentré brut de thorium, présente un aspect particulier lorsque l'opération de lavage est faite dans des colonnes d'extraction pulsées. L'augmentation de la concentration du thorium dans le tributylphosphate améliore les facteurs de séparation à un étage entre le thorium et les terres rares; cependant, dans une colonne pulsée, on remarque une diminution du facteur de séparation avec une grande augmentation résultant de la hauteur du plateau théorique.

On obtient des séparations très nettes du thorium d'avec l'uranium par l'emploi d'un procédé basé sur l'extraction et la précipitation simultanée; ce procédé consiste à mettre en contact une solution de nitrate de thorium dans le solvant organique avec de l'acide sulfurique à 20-30 %. Le thorium est en même temps extrait et précipité sous forme de sulfate de thorium, qui reste entièrement en phase aqueuse. On peut atteindre des facteurs de séparation thorium-uranium allant jusqu'à 20 000 en une seule opération. Une décontamination appréciable du thorium par élimination de beaucoup d'autres éléments accompagne cette séparation. Un avantage particulier du procédé consiste dans une récupération facile de l'acide nitrique, qui peut être recyclé dans le processus initial de dissolution du concentré de thorium brut.

Après transformation du sulfate de thorium en carbonate basique, on obtient par calcination un oxyde de thorium de haute pureté.

А/484 Бразилия

Развитие технологии производства тория

К. Дж. Бриль, П. Крумгольц

Рассмотрены развитие методов переработки торийсодержащих руд за последнее время и производство ядерночистой окиси тория; особое внимание уделено опыту работы промышленной и полузаводской установки в Бразилии.

Процесс щелочного расщепления монацита, используемый в Бразилии с 1948 года в промышленном масштабе, имеет большие преимущества перед другими методами с точки зрения извлечения тория. В частности, в этом процессе удалось добиться практически количественных выходов; коэффициенты разделения тория от редких земель и фосфата составляют порядка 100; торий получается в форме, очень удобной для очистки экстракцией растворителем. Описаны рабочие условия, позволяющие получать удовлетворительные результаты при удовлетворительной экономике.

При обсуждении очистки тория экстракцией растворителем особое внимание уделено: *а*) экстракции шламом, *b*) очистке тория от редких земель и *с*) выделению тория и урана.

Сообщается об опыте, накопленном в полузаводском масштабе, по экстракции шламом в смесителях-отстойниках. Образование эмульсии при экстракции нефильтрованных растворов необработанных ториевых продуктов, получаемых при щелочной обработке монацита, предотвращается благодаря использованию активированного угля в качестве деэмульгирующего агента.

Удовлетворительная очистка тория от редких земель, составляющих основную массу (10%) примесей в необработанном ториевом продукте, представляет своеобразные проблемы, если операция промывки осуществляется в пульсирующих экстракционных колоннах. С увеличением концентрации тория в трибутилфосфатном растворителе улучшается коэффициент разделения тория и редких земель для одной ступени, но в импульсной колонне наблюдается уменьшение коэффициента разделения, соответствующее большему увеличению высоты, эквивалентной одной теоретической ступени.

Высокоэффективное разделение урана и тория достигается за счет использования процедуры экстракции — осаждения, которая проводится путем контактов раствора нитрата тория в органическом растворителе с 20—30%-ным раствором серной кислоты. Торий одновременно экстрагируется и осаждается в виде сульфата, который целиком остается в водной фазе. При работе на одной ступени были получены коэффициенты разделения тория и урана вплоть до 20 000. В то же время достигается значительная очистка тория от многих других элементов. Дополнительным преимуществом экстракционного осаждения является возможность легко восстанавливать азотную кислоту, которая может быть возвращена в цикл в процессе первоначального растворения необработанного ториевого концентрата.

После превращения сульфата тория в основной карбонат можно путем обжига получить окись тория высокой чистоты.

A/484 Brasil

Avances en la tecnología de la producción del torio

por K. J. Bril y P. Krumholz

Se resumen los recientes avances en el tratamiento de minerales que contienen torio y en la producción de óxido de torio de pureza nuclear, con especial referencia a la experiencia adquirida en planta piloto e industrial en el Brasil.

El tratamiento alcalino para el ataque de monacitas, tal como se practica en el Brasil desde 1948 en escala industrial, presenta, desde el punto de vista de la recuperación del torio, considerable ventaja sobre otros métodos. En particular, los rendimientos son prácticamente cuantitativos, los factores de separación del torio de las tierras raras y fosfato son del orden de 100, y se obtiene el torio en una forma muy adecuada para la purificación por extracción con disolventes. Se presentan, asimismo, las condiciones de trabajo que permiten obtener resultados satisfactorios en buenas condiciones económicas.

Se discute la purificación del torio por extracción con disolventes con especial referencia a: *a*) extracción de la pulpa, *b*) descontaminación del torio de las tierras raras y *c*) separación de torio y uranio.

Se da a conocer la experiencia en planta piloto con extracción de la pulpa en mezcladores-decantadores. La formación de emulsiones en la extracción de soluciones no filtradas del producto crudo de torio, procedentes del ataque alcalino de monacitas, se impide usando carbón activo como agente antiemulsionante.

La descontaminación satisfactoria del torio de las tierras raras, que constituyen la principal impureza (10 %) en el producto crudo de torio, plantea algunos problemas peculiares si la operación de lavado se lleva a cabo en columnas de pulsación. Incrementando las concentraciones de torio en el disolvente fosfato de tributilo mejoran los factores de separación en un solo contacto de torio-tierras raras, pero en una columna de pulsación se observa una disminución del factor de separación correspondiente al gran aumento de las alturas equivalentes de la etapa teórica.

Se consigue una separación de alta eficiencia de torio-uranio usando un procedimiento de extracción-precipitación, que consiste en poner en contacto la solución de nitrato de torio en el disolvente orgánico con una solución de ácido sulfúrico de 20-30 %. El torio es simultáneamente extraído y precipitado como sulfato, el cual permanece íntegramente en la fase acuosa. Se obtienen factores de separación de torio-uranio de hasta 20 000 en una operación en una sola etapa. Al mismo tiempo se logra una apreciable descontaminación del torio de otros muchos elementos. Una ulterior ventaja de procedimiento de extracción-precipitación es la fácil recuperación de ácido nítrico, el cual puede reciclarse en el proceso original de la disolución del concentrado crudo de torio.

Después de la transformación del sulfato de torio en carbonato básico, se obtiene por calcinación un óxido de torio de alta pureza.

Prospecting and mining of nuclear raw materials in Portugal

By R. Cavaca*

This paper describes the practical iesults achieved in the metropolitan territory of Portugal and its overseas provinces of Angola and Mozambique, in the field of prospecting and mining nuclear raw materials.

It is not necessary to make an extended reference to the prospecting methods adopted since they have been the subject of papers previously presented at Geneva meetings in 1955 and 1958 and, since then, such methods have not undergone significant modifications.

The main radioactive ores, uranium and thorium ores, will be examined separately from other nuclear raw materials, beryllium, tantalum and zirconium because the methods used for studying them and their genetic characteristics are distinct.

As a result of some research parallel to the exploring operations the former provisional metallogenic classification has been adjusted to classify adequately the most important uraniferous ore deposits in this country.

The data concerning reserves will be grouped regionally with a view to future exploitation programmes.

The available economic data, either unitary costs for prospecting operations or costs of production, will be given when properly documented.

METROPOLITAN TERRITORY OF PORTUGAL

Radium and uranium

The discovery of radium by M. and P. Curie was followed in Portugal by active prospecting for uranium-radiferous ore deposits and most of the production was then used on research work supervised by those scientists.

In 1909 the exploitation at Rosmaneira, the earliest uranium and radium Portuguese mining concession, lying to the east of the granitic massif of Serra da Estrela, was started.

From 1909 to 1923, prospecting proceeded intensively, using the rudimentary means then available, with 94 claims by the end of this period. Although some of the most important Portuguese uranium-radiferous deposits were found during this period, the fact is that most of the discoveries were plain supergenic occurrences of secondary mineralization, sometimes rather spectacular but without important reserves.

Prospecting activities declined after 1923, the number of concessions remaining constant at about its maximum figure of 98. These activities declined even more sharply after 1931, the number of concessions having been reduced to 61 and 52 by 1936 and 1955, respectively, through abandonment of some concessions. In the meantime, private prospectors recorded more than 83 uraniferous occurrences, most of them of no economic value at all, as had happened before with some of the earliest concessions. Such was the situation when the government took the decision of holding all national territory as a reserve in favour of the State.

Up to the advent of the atomic era, marked by the devastating effect of nuclear explosions and the prodigious pacific applications of atomic energy, the exploitation of Portuguese uraniferous ore bodies was carried out exclusively with a view to producing radium and was subject to several vicissitudes as happens frequently with mining activities.

During the earliest period (1908-1910), Portuguese ores, concentrated by hand-picking, were exported to France and processed at the Nogent plant.

As the transportation charges weighed heavily on the cost of radium, some plants were built in Portugal for the preparation of concentrates or pure salts and, later on, of radiferous barium sulphate. This was the situation prevailing from 1910 to 1926.

Some mines were closed in 1913 when the exploitation started at Urgeiriça, which came to be considered later as one of the most important European uraniferous deposits. A plant for the preparation of radium was built there, using a more efficient and economical method than the ones formerly employed.

Although exploitation of the Urgeiriça mine was considered to be economically viable, its radium production ceased between 1923 and 1930 as it was unable to meet the competition from Congolese ores, due to the prices fixed for the latter.

The exploitation at Urgeiriça mine, still exclusively for the production of radium ore, was resumed on a

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Table 1. Treatment of uranium ores in Urgeiriça mine

Chemical treatment	Ore		Yield of chemical treatment %	Obtained U_3O_8	
	Tons	% U_3O_8		Tons	% U_3O_8 in concentrates
Plant	485 000	0.30	84-89	1 278	12-24
Natural leaching	70 000	0.11	55-75	47	8-12
Total/average	555 000	0.276	85	1 325	15-20

moderate scale from 1931 to 1938 and, more intensively, from 1939 to 1944.

The ore production during these periods of activity may be estimated at 25 000 tonnes of high grade ore, 0.50 % to 1.5 % U_3O_8, obtained by hand-picking and pre-concentration. The production of radium is estimated at about 50 grammes.

Production costs as reported by A. Ingles (1929) and Lepierre (1931) were, respectively, £4 000 and £4 500 per gram of radium, while commercial values, as reported by the same authors, were about £14 000 and £12 000. On the whole, exploitation was not accompanied by prosperity, owing to the vicissitudes that affected it.

The exploitation at Urgeiriça mine was resumed in 1949, this time however for the production of uranium which earlier had been a mere by-product with limited application and demand and hardly any commercial value at all.

A chemical treatment plant was built at Urgeiriça in 1950-1951 with an annual capacity of 125 tons of U_3O_8. The process was based on the treatment of the ore with sulphuric acid followed by precipitation of uranium by magnesia.

As a result of laboratory and pilot scale testing, a new method named "natural leaching" was developed. This process was essentially an attack of low grade ore by sulphuric acid resulting from the oxidation of pyrites present in the ore or added in adequate proportions, followed by the precipitation of U_3O_8 by magnesia. This method was adopted in five plants built from 1953 to 1959, at Urgeiriça, Rosmaneira, Bica, Valinhos and Vale de Arca. It was a method of particular interest for economical processing close to the mine of low grade ores which would not bear transportation costs to the Urgeiriça plant.

The exploitation of Portuguese uraniferous ores and their concentration by methods referred to above became a rather important business owned by one corporation,* its rights being assured at the time over more than 50 mining concessions.

From 1951 to April 1962, the exploitation and chemical treatment of ores proceeded continuously and regularly in 16 mines, 7 with a major potential. Urgeiriça and Bica supplying 75 % of the total production, and the remaining 25 % coming from small exploitations or mining exploration.

On the whole, 555 000 tons of ore were extracted, having an average grade of 0.276 % U_3O_8. Treatment was as shown in Table 1.

Production costs were influenced by several factors, of which the most important ones are the size of deposits, facilities for mining extraction, physical and chemical characteristics of the ores including their grades and transportation charges to the plant. For most of the mines, these costs were quite acceptable and amongst the cheapest prevailing at the time.

Table 2 contains data concerning seven of the most important mines, which account for 94.4 % of the total production.

Table 2. Cost of U_3O_8 contained in concentrates

(USA dollars per pound of U_3O_8)

Mines	Years	% of total production	Cost including amortization						Total cost		
			Drilling	Mining exploitation	Ore transportation	Chemical treatment	Taxes	General expenses	Chemical treatment	Natural leaching	Chemical treat. plus natural leaching
Urgeiriça . . .	1951-62	54.2	—	2.19	0.03	1.58	0.17	0.47	4.45	2.24	4.41
Id. Aluvião . .	1959-62		0.02	1.03	0.03	2.12	0.17	0.22	3.59	2.73	3.58
Bica	1953-62	20.2	0.28	2.38	0.89	1.70	0.15	0.40	5.81	3.31	5.61
Vale de Arca. .	1957-62	7.0	0.15	1.90	0.91	1.56	0.15	0.30	4.96	6.35	5.00
Carrasca . . .	1953-60	4.2	0.13	1.95	0.54	1.09	0.16	0.31	4.17	4.55	4.17
Valinhos . . .	1956-62	4.2	0.47	6.41	0.08	1.56	0.17	1.05	9.75	2.99	8.61
Reboleiro . . .	1951-55	2.3	0.48	7.90	0.76	2.36	0.16	1.58	13.24	—	—
Rosmaneira . .	1951-58	2.3	1.63	13.76	1.14	1.94	0.13	2.38	20.98	2.45	17.69

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* Companhia Portuguesa de Rádio, Lda.

By the end of the second period of Portuguese uranium mining activity an over-all production of 1 325 tons of U_3O_8 was reached, which though limited by the resources, started when the prospects for world reserves were less promising than at present.

The whole production was sent to the USA and the UK through the Combined Development Agency, due to a firm desire to co-operate with countries having traditionally friendly connections with Portugal.

All mines and plants under the control of the former concessionnaire were transferred to the Junta de Energia Nuclear in June 1962. Work is proceeding now on mining reconnaissance work and development and exploitation between the 380 metre and 460 metre levels at the Urgeiriça mine, where there are still important ore reserves already partially defined by drilling. At present, the chemical treatment plant is being modernized to produce higher grade U_3O_8 concentrates.

In 1955, the Junta de Energia Nuclear set up a prospecting programme for uranium in the Portuguese metropolitan territory. The earliest phase of this programme was practically completed in 1959 and consisted essentially of:

(*a*) Expeditious and economical preliminary radioactive reconnaissance;

(*b*) Air-borne and car-borne scintillometric surveys over areas geologically favourable to the occurrence of uraniferous mineralization;

(*c*) Systematic radiometric prospecting following a grid which was progressively more dense in areas selected as the most favourable and almost exclusively in the provinces of Beiras and Alto Alentejo, together with a detailed geological survey.

The geological and radiometric surveys were conducted with a double objective of discovering and selecting uraniferous occurrences bearing in mind their metallogenic types and economical importance. It was shown that the mineralization is essentially conditioned by the tectonic nature of some regions in this country.

It was found that the uraniferous occurrences can often be examined through their outcroppings or by trenching or rudimentary mining work. However, in most cases the structures causing the mineralization do not result in outcrops or only in very small outcrops, since they are covered with residual weathering deposits thick enough to prevent useful results being obtained from geological and radiometric surveys. The complex structures and characteristics of mineralization distribution of the ore bodies hardly show up on surface. Such elements can actually be defined only through drilling and mining exploration according to individual deposit characteristics.

Where geological and radiometric classical surveyings are not accurate enough or where structural problems present too much complexity, electrical prospecting has been applied and has helped to solve some important structural problems.

The broad outline of the prospecting work was planned according to the interest of different regions of the country from the knowledge acquired previously by private prospecting for radium and uranium. Thus, the prospecting began in the uraniferous areas of Nelas, Trancoso, Guarda, Belmonte and Sabugal, later on extending to areas where some radioactive indications were already known or where a favourable geological facies was shown.

The radiometric prospecting methods, during different stages, covered the following regions:

(*a*) Granitic and crystalline massifs of northern and central parts of the country;

(*b*) Contact aureoles of ante-Ordovician metasediments with metamorphosising granites;

(*c*) Continental formations of Permian-Carboniferous and in the Tagus River tertiary basin.

The extent of several prospecting operations and their unit costs are briefly shown in Table 3.

The major concentrations of Portuguese uraniferous ore deposits correspond to highly tectonized regions formed either by monzonitic Hercynian granites or by ante-Ordovician metasediments, located:

(*a*) West, north and east of Serra da Estrela in the great belt involving this stable granitic massif;

(*b*) In the metamorphic contact zone surrounding the Castelo de Vide granitic massif and within the same massif.

A total amount of 342 ore bodies and occurrences of varying importance was reported. From the point of view of their metallogeny, those deposits can be grouped according to the following types.

Epithermal vein deposits

(*a*) Siliceous epithermal veins with gangue predominantly of jasper and chalcedony, mineralized with pitchblende, secondary uraniferous minerals and sulphides enclosed in Hercynian granites.

These comprise 72 deposits of which Boavista, Borrega, Bica, João Antão and Urgeiriça are the most important.

(*b*) Siliceous epithermal veins with gangue predominantly of white or smoked quartz, zoned growing and frequent crystallizations in geodes, mineralized with pitchblende, secondary uranium minerals and sulphides enclosed in Hercynian granites or along their contact zones with ante-Ordovician metasediments.

These comprise 53 deposits of which Cruz da Faia, Cunha Baixa, Freixiosa, Pinhal do Souto, Reboleiro and Tarabau are the most representative.

(*c*) Epithermal veinlet systems, hardly siliceous, mineralized with pitchblende secondary uraniferous minerals and iron sulphides, in highly tectonized zones enclosed in Hercynian granites or in contact metamorphic rocks.

Table 3. Prospected areas

Adopted methods of surveying	Covered areas	Unitary costs (escudos)	Observations
Photogeology	21 354 km^2	30 per km^2	Scales 1/25 000 and 1/50 000
Geological survey	12 066 km^2	233 per km^2	—
Scintillometer survey:			
Air-borne	4 184 km^2	378 per km^2	Ground clearance, 100 m flight-lines distance of 400 m
Car-borne	49 613 km^2	28 per km^2	Density of routing 1 221 km per km^2
Radiometric prospecting on ground:			
General	16 952 km^2	350 per km^2	Grid from 200 to 300 m
Regional	1 947 km^2	772 per km^2	Grid 25 × 50 m
Semi-regional	130 km^2	6 045 per km^2	Grid from 5 × 25 m to 5 × 50 m
Local	1 146 ha	396 per ha	Grid from 2 × 4 m to 1 × 1 m
Subsurface reconnaissance:			
Trenches	61 271 m	26 per m	—
Wagon-drilling	70 600 m	38 per m	—
Core drilling	149 500 m	209 per m	With drilling done by C.P.R. Lda.
Electrical prospecting	1 900 m	550 per m	—

These comprise 54 deposits of which Alto do Gorgo, Barroca Funda, Nisa, Palheiros de Tolosa and Senhora das Fontes are the most important.

Alteration and lixiviation deposits

(*a*) Impregnation of secondary uraniferous minerals in quartz-limonitic breccias in the wallrocks of white-quartz veins or in granitic breccias. These comprise 120 deposits, the largest number of all, of which Barregão, Freixinho, Ribeira do Ferro and Sacouto are the most important.

(*b*) Impregnation of uraniferous secondary minerals in altered granites. Only one deposit of this type, Meada, has significant reserves; there are three more occurrences of little interest.

(*c*) Impregnation of uraniferous secondary minerals in altered zones of doleritic dykes. These comprise 20 deposits of which A-do-Cavalo, Prado Velho and Quinta das Seixas are the most important.

(*d*) Impregnation of secondary uraniferous minerals in metamorphic contact rocks. These comprise 18 deposits almost all with a relative high potential, those of Ázere, Cótimos, Cunha Baixa, Mato da Póvoa, Nisa and Senhora das Fontes deserve special mention.

(*e*) Impregnation of uraniferous secondary minerals in recent alluvial deposits. Only one small deposit of this type is known, adjacent to the Urgeiriça vein deposit.

Notwithstanding the preponderancy of epithermal vein deposits, both in number (62 % of total) and in actual reserves (68 % of total), other metallogenic types are also well represented. Those formed by impregnation in schists include a small number of deposits (5.3 % of total) but correspond to 24 % of all reserves defined up to now.

Impregnations in more or less brecciated wallrocks of barren white quartz veins, though numerous (35 % of the total) contain hardly 5 % of estimated reserves.

Cameron suggests that the uraniferous veins in the province of Beiras are contemporary with the upheaval of Serra da Estrela and are related to the medium or upper-Oligocene. Cerveira considers them to be later than the formation of the doleritic dykes which Tadeu sets at the initial phases of Alpine movements.

Recent age determinations of pitchblende samples from Urgeiriça and Reboleiro, done by Horne and Stieff and Stern date the primary uraniferous mineralization down to medium or upper-Cretaceous (respectively 83 million years according to former author and 60 to 100 million years according to latter authors).

Up to now all attempts to relate the distribution of uraniferous mineralization, either in vein or in impregnation deposits, to the structural, mineralogical and petrological conditions of shearing zones and to the type of alteration of host rocks, has not led to definite practical conclusions. An extremely irregular distribution can be noted in all Portuguese deposits, which does not follow any known laws, though in some cases, a predominance of higher grade ores in the junction zones of certain structures and an intensive hematitization of host rocks is revealed.

These circumstances have conditioned in some degree the reconnaissance methods adopted for the definition of ore reserves, taking into consideration the statistical analysis of obtained results in the earlier phases of our activities.

Of all deposits and occurrences (342) referred to above, only 120 have been investigated so far. They were selected from amongst the most promising.

For vein deposits, diamond drilling reconnaissance is in progress with holes at distances of 25 to 30 metres at levels between 25 and 160 metres. A reconnaissance with a wagon-drill following a close grid (10 × 10 metres), is being carried out on the extensive impregnation deposits in schists. Additional mining work at 40 deposits has been done to obtain more accurate data on mineralization distribution by exploration and systematic sampling. This work will also give a more accurate interpretation of the surface indications of structural features, and of the estimation of reserves from drilling results.

The reconnaissance work being carried out on some of the most important Portuguese ore deposits, Nisa, Cunha Baixa, Urgeiriça, Pinhal do Souto and Palheiros de Tolosa, will be completed by the end of 1964. A systematic study, in accordance with the pattern mentioned above is still required on more than two hundred uraniferous deposits. Special attention should be devoted to the schistous complex of Ázere which, notwithstanding its low grade (0.10% U_3O_8), is likely to contain important reserves.

Therefore the data resulting from reconnaissance work up to April 1964 are provisional and are certain to be a great deal below the real uraniferous potential of the country.

Present reserves estimated for the metropolitan territory of Portugal are about 3 260 000 tons of certain and probable ore with an average content of 0.184% U_3O_8, corresponding to 6 000 tons of U_3O_8.

If preliminary geological and radiometric prospecting costs are not taken into account (and logically they should be spread over total reserves yet to be defined), the weighted average incidence of the cost of drilling reconnaissance work, is US$ 0.06 per pound of U_3O_8.

The regional distribution of these reserves is shown in Table 4 which shows a possible arrangement of the several centers of production with a view to reducing the cost of transportation to the treatment plants. Future production costs of U_3O_8 can not be anticipated at this time.

Table 4. Distribution of uranium reserves in Portugal

Regions	Ore		Reserves tons of U_3O_8
	Tons	% U_3O_8	
Bragança	8 200	0 195	16
Coimbra	32 600	0 187	61
Viseu	1 158 300	0 193	2 236
Guarda	539 500	0 216	1 165
Castelo Branco	173 600	0 186	322
Portalegre	1 347 800	0 163	2 200
Totals	3 260 000	0 184	6 000

Beryllium, niobium and tantalum

Beryllium occurrences, exclusive of Hercynian granites outcropping in the north of the country, consist of beryllium mineralization in granitic pegmatites, which are mineralogically and morphologically irregular, sub-vertical and up to 15 metres in width. The essential elements are the ones common to pegmatites. The more common ancillary elements, are: beryl, cassiterite, wolframite, molybdenite, phosphates of uraninite and triphilite groups, iron sulphides, tourmalines and columbite-tantalites.

Scattered throughout Braga, Castelo Branco, Guarda, Vila Real and Viseu regions, there are at present 17 beryllium mining concessions, of which 9 were claimed exclusively for this element and the remaining for lithium, tin, tungsten, niobium, tantalum and others. The earliest concessions date from 1935 and the newest one from 1957. The deposits discovered last have been worked as quarries, the beryllium being a by-product of quartz, feldspar and kaolin exploitations. The production also sometimes contains cassiterite, columbite-tantalites, wolframite, mica and, rarely, lithiofilite. Beryllium is concentrated by handpicking to a product with 10% to 12% of BeO.

The production of industrial beryllium, a small one because of the low demand, was about 1 500 tons from 1951 to 1963.

Prospecting for beryllium in pegmatites has been done privately and may be considered complete. However, beryllium may occur under mineral species difficult or impossible to identify at sight. It would therefore be advisable to conduct a systematic study in this country, using beryllometers, of wolframite, sheelite, molybdenite, manganese fluorite mines and their wastes, of quartz veins enclosed in granites whether apparently mineralized or not, ferruginous skarns (with tungsten, molybdenum and fluorine), coals and other geological formations already considered in other parts of the world as possible beryllium sources.

Niobium and tantalum, in addition to associating with beryllium as referred to above, also occur together with cassiterite in pegmatitic and quartz veins, enclosed in metamorphic micaceous schists, in the basement complex contacting the Hercynian granites. Nearby these primary deposits, eluvial and alluvial deposits may be found, certainly of small tonnage but frequently containing useful minerals chiefly cassiterite and columbite-tantalite.

There are 23 niobium and tantalum mining concessions in the regions of Braga, Guarda, Viana do Castelo, Vila Real and Viseu, of which 7 are exclusively for tantalum or tantalum plus niobium, 4 for these elements plus beryllium, and the remaining 12 for niobium and tantalum plus tin, tungsten, titanium and lithium.

The production of concentrates of columbite-tantalites, from 1951 to 1963, was only about 23 tons, a portion of which came from recovery of tin mining wastes.

The production of beryllium, niobium and tantalum could be substantially increased if demand reached a higher level and caused an interest in such mining exploitation.

ANGOLA

The indications of radioactive mineralization known up to the present are not numerous. The following deserve particular attention:

(*a*) The phosphate formations of Cabinda on account of its uranium content;

(*b*) The ring structures of the so called Volcanic Belt of Angola on account of its abundant and varying thorium, niobium and zirconium mineralization contained either in carbonatites and eruptive rocks or in their adjacent eluvial deposits.

Other occurrences were discovered, although without economical interest, and may be grouped as follows.

(*a*) Pegmatite formations in Alto Dande and Lucala;

(*b*) Quartz-cupreous vein at Caquete;

(*c*) Alluvial deposits of the Planalto de Benguela, on which we will comment briefly.

Some radioactive indications were detected in 1950 in the pegmatitic area of Alto Dande belonging to the basement complex, in the contact of pegmatites with their enclosing gneisses which were caused by the accidental occurrence of uranimite, autunite and torbernite.

Radioactivity, detected in 1953 in the region of Lucala, was caused by the presence of complex minerals, samarskite and euxenite, in graphic pegmatites intersecting the gneissic granites and gabbros of the basement complex. Radiometric surveys and trenching have shown the limited extent of anomalies and the scarceness of uraniferous mineralization.

An extensive quartz vein is known in Caquete, with copper and gold sporadically associated with occasional torbernite. Prospecting did not confirm the persistence of radioactive mineralization.

Some radioactive indications attributed to monazite, were also found in 1953 in the auriferous concentrates of alluvia proceeding from some Cunene river tributaries (Samboto, Cassongue and Chivira) on the Benguela Plateau.

The phosphate deposits of Angola are scattered, with some regularity, along the coastal zones of Cabinda and Sul do Zaire, the former ones being better known. They are scattered through a NW-SE zone, probably corresponding to a structural direction. There are several levels of phosphates which are discontinuous and of lenticular morphology, with characteristics differing from place to place. Barren intercalations sometimes divide the phosphated complex into thin beds and are frequently found.

The reported age of some deposits is Maestrichtian, others are Eocene. They are covered by argillaceous sands with beds of rolled pebbles (Pleistocene).

The deposits studied in detail up to now, Cambota, Chibuete Chivovo and Mongo-Tando, are very large, from 2 to 5 kilometres long and 3 to 10 metres wide. The measured reserves amount to 16.5 million tons and the possible reserves to 10 millions tons.

High radioactivity which was registered over these formations, was caused either by the presence of uranium fixed by the iron and manganese hydroxides existing in the phosphates, or by the frequency of torbernite in well individualized lamellae.

Chemical analysis of phosphate samples collected from locations with higher radioactivity revealed uranium contents of between 0.08 and 0.20% of U_3O_8, which is considerably higher than the ones reported by Nininger, Butler, Lenoble, Salva, Zigler and Yrigoyen in similar formations from other parts of the world.

Should the persistence of uraniferous mineralization and grades be confirmed throughout the deposits, which may be expected from the reconnaissance already done, the uraniferous reserves corresponding to the Cabinda deposits will be very high, between 15 000 and 30 000 tons of U_3O_8.

Laboratory research for the possible recovery of uranium from phosphates is being carried out and, in the near future, a large wagon-drill reconnaissance programme will be started with a view to defining exactly the uraniferous potential of these deposits.

The ring structures, in the Benguela Plateau, first referred to by Giesecke (1955), are about 300 kilometres long and lie along a SW-NE direction, going through west of Nova Lisboa, and were named the Volcanic Belt of Angola by that author. Eleven such structures have been recognized with diameters of between 1 and 10 kilometres, of circular shape, generally prominent over the enclosing older formations (basement complex and granitic massif), and possibly related with great fractures. Their volcanic character is shown by volcanic rocks, tuffs and brecciae, frequently associated with carbonatites. The age of this volcanic activity seems to be Karroo and is probably contemporary with similar formations of Southwest Africa.

Iron mineralization has been known since the most remote times in some of the structures (Andulo and Bailundo) and varying mineralizations of manganese, titanium, niobium, tantalum, rare earths, thorium, gold, silver, apatite, florite and barite have later been recognized; uranium has not been found so far.

Among the structures studied in more detail, the more important ones are Bailundo, Longonjo and Capula, formed by two concentric rings, essentially comprising, inwardly, carbonatites and syenitic intrusions disposed circularly, and outwardly, volcanic brecciae, tuffs and highly altered syenites. There are large bodies of titaniferous hematites and magnetite regarded as resulting from replacements in the carbonatites.

The radioactive mineralization, probably related to carbonatites, is represented by complex minerals of niobium, tantalum rare earths and thorium it being generally considered that the pyrochlore is the mineral principally responsible for the radioactivity.

The content of ThO_2 plus rare earths is between 0.10 and 5.85%.

In the immediate proximity of these first two structures, large eluvial deposits were formed, constituted from residuals of carbonatite alterations in which dense minerals were naturally concentrated. For a deposit adjacent to the Longonjo structure, the reserves were estimated to be 4.5 millions of tons containing 0.37% of Nb_2O_5 and 2.5% of ThO_2 plus rare earths.

The Cânata structure corresponds to a large depression contrasting with peripheral elevations which bestows its typical morphology on that structure. Although the petrographical constitution is comparable to the preceding structures and the mineralization identical, the radioactive indications are less pronounced.

In the alluvia of the Cubal and Balombo Rivers, relatively important concentrations of ilmenite and zircon were recognized and probably result from the weathering of the Sulima ring structure.

At the present stage of our knowledge, it is not possible to give definite figures for reserves of nuclear raw materials existent in the Volcanic Belt of Angola. However, provisional figures given by a private enterprise working in this area are given in Table 5. These figures will be adjusted after exploration operations to be conducted by the Junta de Energia Nuclear.

Table 5. Probable reserves of nuclear materials in Angola

Location	Nb tons	Zr tons	ThO_2 tons
Longonjo	10 800	—	41 850
Cubal and Balombo Rivers	—	16 000	—

MOZAMBIQUE

In Mozambique there are important deposits both of radioactive ores and of beryllium, niobium, tantalum, and other typical elements of pegmatitic formations. However, no economical deposit of pitchblende or its derived minerals has been found yet.

The more common radioactive minerals known at present are davidite, alanite, pyrochlore, samarskite, euxenite, polycrase, monazite and zircon.

Davidite occurs predominantly in the Tete region in quartz-ankeritic veins generally enclosed in gabbro rocks. These veins contain a varying mineralization which includes davidite with about 7% of U_3O_8 and magnetite, ilmenite, rutile, molybdenite, pyrite and chalcopyrite.

The Mavuzi * mine lies in the most representative davidite ore body. The possible reserves were assessed at 80 000 tons of ore with 0.1% U_3O_8. However, production has been small for lack of a market. Thus, from 1949 to 1957 400 tons of davidite were produced, and there has been no production at all since 1957.

Pyrochlore occurs in carbonatite formations, lying in the Tete region, some of them (the Salamabidua and Muambe hills) defining typical ring structures.

The remaining uranium-thoriferous products referred to above occur in several pegmatitic areas located in the Tete and Zambézia regions, in concentrations suitable for economic exploitation.

Monazite and zircon occur also in coastal deposits of generally radioactive dense sands, between the Rovuma, and Zambesi rivers. All these deposits are recent and consist of beach sands and dunes. Those of Pebane, Portinho, Lagoa, Gorai, Idugo, Tanino and Manaepa are particularly interesting and are estimated at 4 million tons of mineralized sands. Their thickness is about 4 metres although it is irregular, and they are sometimes 400 metres long. These sands have a characteristic mineralogical composition with a high content of dense opaque minerals, always more than 50%, among which ilmenite is predominant. They also contain monazite (0.24 to 2.40%) zircon (1.56 to 5.6%) and rutile (0.2 to 2.2%) which are considered of economic interest, as well as quartz in irregular concentrates and several other minerals characteristic of sands, all of them in small percentages. Radioactivity is caused almost exclusively by thorium contained in monazite.

Air-borne prospecting (radiometry and magnetometry) was conducted over 4 selected areas totalling 30 000 km². The selection was done in relation to the following geological structural characteristics:

(*a*) Continental formations of the Karroo system representing conglomeratic beds rich in carbonaceous matter and with frequent cross-bed structures;

(*b*) Rocks in granitic-gneissic complexes;

(*c*) Rocks belonging to the gabbro-anortositic complex, related to zones where good radioactive indications had been previously registered;

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* Concession made to the Companhia de Urânio de Moçambique.

(*d*) Highly tectonized metasediments related to gneisses and old granites.

The flight directions were selected on the basis of the results of photogeologic interpretation.

As a result of the interpretation of the field work, it was concluded that the radioactive anomalies, however numerous, are mostly small and caused by thorium though some are related to uranium and, possibly, to potassium-40. Although a discriminatory method was adopted, based on the energy level, the results are not conclusive. The intensity of the anomalies depend on several factors and do not give an indication of absolute values on regions where metallogenic characteristics are not yet well known.

Thus, so far as radioactive mineralization is considered, it would seem premature to reach any conclusions about the practical scope of these surveys. But as the possibility of the occurrence of pitchblende and related minerals is not excluded, it is intended to proceed with radiometric and geochemical prospecting in selected zones, on the basis of these surveys.

Beryllium, niobium and tantalum occur predominantly in pegmatites located in the Zambézia region, one of the world's most important pegmatitic centers, so far as the frequency and dimension of pegmatites or their mineralization are concerned.

These pegmatites, scattered throughout several pegmatitic fields, were discovered around 1930. Their exploitation, initially for mica, was considerably expanded in 1944, for the production of beryllium and columbite-tantalites. From the geological point of view, this region is essentially constituted of two pre-Cambrian series, intensively metamorphized, locally crossed over by basic and granitic intrusions.

The most important pegmatitic fields of Zambézia are those of Alto Ligonha, followed by those of Mutala, Mocuba, Marropino, Mugeba, Ile and Nauela, the latter three having predominantly radioactive mineralization. These pegmatitic fields are distributed around granitic intrusions in sometimes well defined tectonic zones.

The pegmatites of Zambézia may be grouped as homogeneous or heterogeneous from the point of view of their structure. The former are usually barren while the latter are rich in useful minerals and present varying facies as regards their zoning and mineralization. Beryllium and columbite-tantalites are the most valuable products.

Beryllium and columbite-tantalites are undoubtedly the products with a high industrial value and correspond to a high economic potential. Beryllium occurs mainly in the zone of large feldspars in perfect crystals and in irregular masses. It may also be found in the quartz nucleus and quartz-muscovitic zones. The production of beryllium from 1956 to 1963 was 7 822 tons with grades of from 11.5 to 13% of BeO.

Columbite-tantalites also occur preferentially in the zones of large feldspars (predominantly columbite and tapiolite) and of lithic minerals (predominantly tantalite, manganotantalite and microlite). The global production of columbite-tantalites, from 1956 to 1963, was 985 tons of concentrates, sometimes exceeding a grade of 80% Ta_2O_5.

There are estimated reserves for only some of the most important deposits. The activity of the last few years and the large number of unexplored pegmatites indicate excellent prospects for beryllium, niobium and tantalum.

A beryllometer and conventional radiometric portable equipment were used in prospecting for these pegmatites.

ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/501 Portugal

Prospection et exploitation de matières premières nucléaires au Portugal

par R. Cavaca

La première découverte de gisements uranifères au Portugal métropolitain a eu lieu en 1909. Elle a été suivie d'une période d'intense activité de prospection et d'exploitation en vue exclusivement de la production de radium. Cette activité a toutefois varié avec le prix de revient et les conditions de l'offre et de la demande.

Une extraction totale d'environ 25 000 tonnes de minerai de haute teneur (0,50 à 1 % de U_3O_8) a été enregistrée de 1910 à 1944. La production de radium provenant de ce minerai s'est élevée à environ 50 grammes.

L'avènement de l'âge atomique a conduit à l'exploitation de certaines mines d'uranium. La production de U_3O_8, a atteint 1 325 tonnes pour la période s'étendant de 1960 à 1962.

Un vaste programme de prospection radiométrique systématique a été mis en œuvre à partir de 1955; il a porté sur les faciès géologiques favorables, c'est-à-dire tous les massifs granitiques hercyniens, tous les complexes schisteux anté-ordoviciens contigus à ces

massifs, et les formations continentales de l'autunien et du miocène-pliocène.

De nombreux dépôts et gisements uranifères de divers types métallogéniques ont été identifiés. Parmi eux prédominaient des gîtes filoniens aux gangues plus ou moins complexes, jusqu'alors les seuls connus et exploités; ces gîtes étaient caractérisés par des imprégnations superficielles de métaux secondaires dans le pourtour métamorphique de quelques massifs granitiques. Ces dépôts semblaient ouvrir des perspectives favorables.

Ces travaux ont été suivis à partir de 1959 par l'exploration systématique par sondages et par travaux miniers des gisements les plus importants. Celle-ci se pousuivra selon les prévisions jusqu'à la fin de 1965.

Les réserves nationales ne pourront être déterminées avec certitude qu'après la conclusion de ces travaux d'exploration. Dans l'état actuel des connaissances, on ne peut qu'indiquer un chiffre préliminaire des réserves du Portugal métropolitain, à savoir 6 000 tonnes de U_3O_8 dans des minerais ayant une teneur moyenne de 0,20 %.

La possibilité d'obtenir du béryllium, du niobium et du tantale dans le Portugal métropolitain fait l'objet d'une discussion.

Des relevés aériens radiométriques et magnétiques ont été faits au Mozambique en 1961 et 1962, sur quatre emplacements choisis selon leurs caractéristiques géologiques et structurelles. Ceux-ci comprennent les formations du complexe de base, roches ignées, système Karoo et carbonatites, ayant au total 24 000 km².

On a enregistré un nombre élevé d'anomalies, généralement d'amplitude réduite, imputables à des minerais complexes d'uranium et de thorium, avec prédominance de ce dernier. On entreprendra sous peu l'étude systématique de ces anomalies.

Les gisements bien connus de Tete, qui se situent près d'un de ces emplacements, ont une minéralisation réfractaire (davidite et samarskite) découverte en 1947. Leur production totale de 1949 à 1959 s'est élevée à 388 tonnes. Des travaux complémentaires y sont actuellement en cours pour la détermination des réserves.

Les champs de pegmatite du district de Zambézia ont été étudiés en 1963, en ayant comme objectif de coordonner tous les éléments géologiques, métallogéniques et économiques concernant les importants gisements qui ont été découverts depuis 1940. Leur minéralisation est riche et variée, les minerais prédominants étant le béryl et les colombo-tantalites dont la production entre 1956 et 1963 s'est élevée à 7 822 et 985 tonnes respectivement. Les calculs qui permettront de définir l'ordre de grandeur des réserves sont actuellement en cours.

Le mémoire fournit aussi des données provisoires sur les dépôts existant en Angola.

А/501 Португалия

Разведка и добыча ядерного сырья в Португалии

Р. Кавака

Первое урановое месторождение в Португалии было открыто в 1909 году. За этим последовал период его интенсивной разведки и разработки исключительно для производства радия в зависимости от менявшихся конъюнктурных условий стоимости производства, спроса и предложения.

С 1910 по 1944 годы было в общей сложности добыто около 25 000 *т* богатой руды с содержанием от 0,50 до 1,00% урана. Производство радия из этой руды составило около 50 *г*.

С наступлением атомного века началась разработка месторождения для получения урана. С 1950 по 1962 годы было добыто 1325 *т* урана в виде закиси-окиси.

С 1955 года началось осуществление систематической программы радиометрической разведки всех геологически благоприятных фаций, а именно: всех герцинских гранитных массивов, прилегающих к ним сланцевых комплексов доордовикского периода и континентальных формаций, относящихся к отенитскому и миоцено-плиоценовому ярусам.

Обнаружены многочисленные рудопроявления и урановые месторождения различных металлогенических типов. Преобладающими среди них были жильные месторождения с тем или иным комплексом жильных минералов (до последнего времени был известен и разрабатывался только такой тип месторождений) и вкрапленностью вторичных металлов в зоне контактного метаморфизма некоторых гранитных массивов. Эти месторождения оказались весьма перспективными.

В 1959 году были начаты систематические разработки наиболее важных месторождений с помощью бурения и подземных работ. Предполагается, что они будут продолжаться до конца 1965 года.

Подсчитать запасы с определенной степенью точности можно будет только по окончании этих разведочных работ. На основании известных данных в настоящее время предварительная оценка запасов Португалии (метрополия) может составить 6000 *т* урана в рудах со средним содержанием 0,20%. Обсуждается возможное присутствие бериллия, ниобия и тантала в Португалии (метрополия).

В 1961—1962 годах в Мозамбике были проведены аэрогамма-поиски и аэромагнитная разведка четырех районов, отобранных по их геологическим и геологоструктурным характеристикам. Они представлены свитами фундамента, изверженными породами, системой Карру и карбонатитами на общей площади 24 000 *км*².

Зарегистрировано значительное количество аномалий, как правило с небольшими амплитудами, которые можно приписать комплексным рудам, содержащим уран и торий с преобладанием последнего. Вскоре будет начато систематическое изучение этих аномалий.

Известные месторождения Тете, расположенные недалеко от этих районов и имеющие тугоплавкую минерализацию (давидит и самарскит), были открыты в 1949 году. За период 1949—59 годов добыча на них составила 330 т урана. В настоящее время проводится подсчет запасов.

В 1963 году были исследованы пегматитовые районы округа Замбези, в целях обогащения всех геологических, металлогенических и экономических данных по важнейшим месторождениям, которые были открыты, начиная с 1940 года. Минерализация их интенсивна и разнообразна. Преобладающими минералами являются бериллий и колумбито-танталовые минералы. Добыча их с 1956 по 1963 год составила соответственно 7822 и 985 т. В настоящее время производится подсчет запасов.

A/501 Portugal

Prospección y minería de materias primas nucleares en Portugal

por R. Cavaca

El primer depósito uranífero del territorio metropolitano portugués fue descubierto en 1909. Esto fue seguido por una prospección y explotación minera intensivas, exclusivamente para la producción de radio, sujeta a las condiciones variables de costes de producción, oferta y demanda.

De 1910 a 1944 fueron extraídas cerca de 25 000 t de mineral de ley alta (0,50 % a 1,00 % de U_3O_8) y la producción de radio ascendió a unos 50 g.

La minería para la producción de uranio comenzó con el advenimiento de la era atómica, siendo la producción entre 1950 y 1962 de 1 325 t de U_3O_8.

En 1955 comenzó un programa de prospección radiométrica sistemática con el que se cubrieron todas las áreas geológicas favorables, a saber: todos los macizos graníticos hercinianos, los complejos de pizarras pre-ordovicienses adyacentes y las formaciones continentales pertenecientes al Autuniense y Mioceno-Plioceno.

Se identificaron muchos yacimientos uraníferos de variada metalogenia. Entre éstos predominaban los yacimientos filonianos con ganga más o menos compleja — siendo éstos hasta entonces los únicos yacimientos que se habían reconocido y explotado — y con impregnaciones superficiales de metales secundarios sobre las aureolas metamórficas de algunos macizos graníticos. Estos depósitos ofrecían perspectivas favorables.

En 1959 se continuó esta labor con la exploración sistemática de los yacimientos más importantes por medio de sondeos y trabajos de interior. Se espera que estos trabajos continúen hasta fines de 1965.

No será posible determinar las reservas de uranio con precisión antes de la conclusión de este trabajo. Sobre la base de los actuales conocimientos, una estimación preliminar de las reservas en la metrópoli portuguesa puede situarse en 6 000 t de U_3O_8 en minerales de una ley aproximada de 0,20 %.

Se examina la disponibilidad del berilio, el niobio y el tántalo en Portugal (territorio metropolitano).

Se hicieron prospecciones aéreas radiométricas y magnéticas en Mozambique durante 1961 y 1962, cubriendo cuatro áreas elegidas de acuerdo con sus características geológicas y estructurales. Estas comprenden, Series Basement, rocas ígneas, Sistema Karoo y carbonatitas, totalizando 24 000 km².

Se registraron un gran número de anomalías, teniendo en general pequeñas extensiones, lo cual puede ser debido a minerales complejos de uranio y torio, en los que predomina este último. El estudio sistemático de estas anomalías será iniciado pronto.

Los bien conocidos yacimientos de Tete, ubicados en la vecindad de una de estas áreas, contienen mineralización refractaria (davidita y samarskita) encontrada en 1947. La producción total desde 1949 a 1959 ascendió a 388 t. Se trabaja ahora en la determinación de las reservas.

Las áreas pegmatíticas del distrito de Zambezia han sido prospectadas en 1963 con vistas a una coordinación de todos los datos geológicos, metalogénicos y económicos concernientes a este importante yacimiento descubierto en 1940. Su mineralización es rica y variada. Los minerales predominantes son berilo y columbita tantalita. La producción desde 1956 a 1963 ascendió a 7 822 y 985 t, respectivamente. Se está preparando una estimación del orden de magnitud de las reservas.

Se facilitan también datos provisionales sobre los yacimientos disponibles.

Chemical treatment of uranium ores at the mines in a semi-mobile plant

By J. Freire de Andrade, H. Carreira Pich and F. Marques Videira *

A few small dispersed deposits are found in the uraniferous area of the district of Guarda, in the north-east of Portugal, containing about 10 to 50 tonnes of uranium each.

Following the prospecting and mining development of that region, the need arose in 1957 to study a process for uranium recovery from these ores. On the one hand, most of the ores would not bear transportation costs to the only existing uranium chemical treatment plant, at Urgeiriça. On the other hand, the relatively small reserves and the dispersion of the deposits did not justify the building of a conventional plant in that area. For this reason, studies were directed to developing a process for uranium recovery at the mines, the main purpose being the simplification of the conventional process, so that the equipment might be easily carried from mine to mine. In such a way transportation costs of the ore could be avoided.

A solution to this problem was urgently required since it was also necessary to deal with the ores which were being removed as a result of the prospecting work in several mines.

Among the apparently suitable solutions to this problem, natural leaching seemed to be worth considering. This process has been developed by Companhia Portuguesa de Radium since 1953, and considerable experience has already been acquired [1]. The process was being applied at the mines for the recovery of uranium from low grade ores. It is based upon the oxidation by air of existing or added pyrites in the presence of moisture. Under these conditions, ferric and sulphate ions, responsible for the oxidation and dissolving of the uranium are produced [2, 3].

However, this process was slow. About 12 months were required for recovering 60 to 70 per cent of the uranium. Furthermore, large terraces were necessary for the leaching of the ore, thereby increasing investment costs per mine. As the composition of the liquors changes considerably during leaching, ion exchange or solvent extraction processes for uranium recovery could not be considered, unless the uranium solutions from different stages of the leaching were mixed, in order to obtain an homogeneous liquor. Because the concentration of salts in solution was rather high, direct precipitation produced a low grade concentrate.

As a general rule, the slow natural leaching process seems to be more suitable for the treatment of low grade ores from large mines, which are close to a conventional chemical treatment plant which can absorb the small amounts of liquors or low grade concentrates produced by the process.

However, natural leaching has the advantage of requiring a reduced amount of equipment, since the bulky operations, typical of chemical treatment plants, such as milling, conventional leaching and thickening, are eliminated. It was considered advisable, therefore, to study a process which could benefit from the simplicity of the natural leaching technology, although it was early recognised that research should be directed to faster leaching.

LABORATORY EXPERIMENTS

Materials and experimental conditions

The following ores were studied:

Ore A, (Forte Velho ore) ferruginous, quartzeous, weathered granitic rock with torbernite mineralization;

Ore B, quartzeous, ferruginous, rather clayey granitic rock, mainly mineralized by autunite;

Ore C, quartzeous, kaolinized, granitic rock with autunite mineralization;

Ore D, basic doleritic highly weathered rock with autunite mineralization;

Ore E, clayey graphite, tourmaline shale with autunite mineralization.

The following processes have been tried:

(*a*) The ore was impregnated with a sulphuric acid solution and left for different periods of time to *cure*. After the cure the ore was sprinkled with water or with a very dilute sulphuric acid solution to remove soluble uranium;

(*b*) The ore was sprinkled with sulphuric acid solution and rinsed with water or with a very dilute sulphuric solution to remove soluble uranium.

In the first process advantage is taken of the strong dissolving power of a rather concentrated sulphuric acid solution absorbed in the solids. Also, during the

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* Laboratório de Física e Engenharia Nucleares, Sacavém.

cure, good conditions for the oxidation process are provided by air circulation.

In the second process, as the ore is being sprinkled, a permanent extraction of uranium is carried out. Capillarity leaching developed in France [4] is similar to this process. However we have adopted higher acid concentrations and flow rates and therefore shorter treatment periods.

In the first stage of the experimental work, several ores were treated to compare these two processes and to make a rough evaluation of their technical and economical possibilities. The main parameters examined were sulphuric acid consumption, leaching time and ease of percolation through the various ores, ground to particles of less than ½ in diameter. Leaching was carried inside columns of 40 cm diameter and 60 cm high.

The treatment of Forte Velho ore was systematically studied in the second stage of the experimental work since that mine would be the first one to be exploited. Columns 20 cm in diameter were employed in this case. Although the cure process appeared to be more efficient it is more difficult to apply in practice, as it involves the mixing of the ore with a rather concentrated sulphuric acid solution. For this reason, the cure process was not considered for the systematic study of the Forte Velho ore.

Sprinkling was performed by means of a nozzle, the flow rate being about 100 l hr^{-1} m^{-2}. Uranium concentration, pH and total content of dissolved salts in leach liquors were always checked during the tests.

Results and conclusions

From the first set of preliminary experiments the following conclusions were drawn:

(*a*) About 60 to 70 per cent of the uranium was recovered in a week, when coarse ores ground to minus ½ in were treated with 15 to 50 kg of sulphuric acid per tonne of ore;

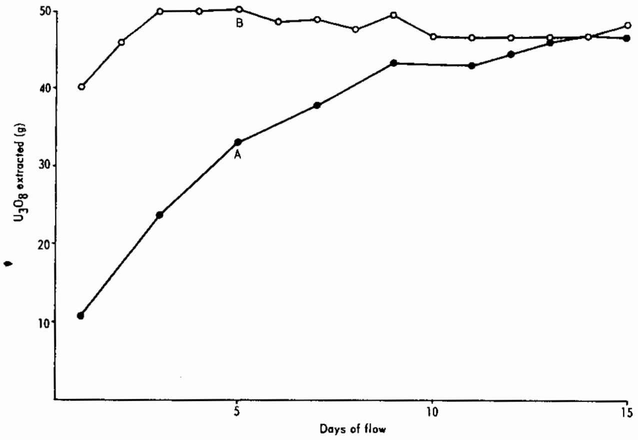

Figure 1. Forte Velho ore. Effect of cure
A: Uranium in the leach liquor;
B: Uranium in the leach liquor plus the uranium in the solution wetting the ore

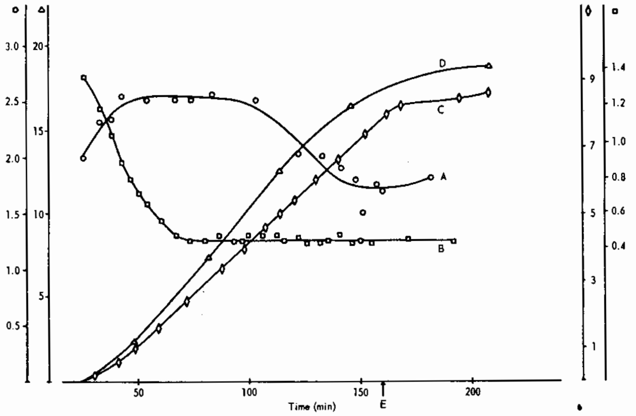

Figure 2. Forte Velho ore. Single stage leaching with a 5 per cent sulphuric acid solution
A: Uranium concentration (g/l); B: pH;
C: Total volume (l); D: Total U$_3$O$_8$ extracted (g);
E: Sprinkling end point

(*b*) In most cases the uranium was dissolved during the cure or during the first contact with the acid sprinkling solution, the following leaching stages being carried out for rinsing purposes only. This result is clearly shown in Fig. 1. The total dissolved uranium was calculated assuming that the solution still impregnating the ore had the same uranium concentration as the last fractions of the leach liquor obtained;

(*c*) To a certain extent, the cure process leads to a higher extraction of uranium than the sprinkling process;

(*d*) Recycling through fresh ores of leach liquors having high quantities of free acid resulted in higher recoveries.

The treatment of Forte Velho ore was studied in greater detail after these preliminary experiments. It was found that, in single stage leaching, the uranium concentration of the leach liquor rises at the beginning of the leaching, then reaches a plateau before decreasing. It was also found that an interruption of the acid sprinkling was always followed by an increase in the uranium concentration of the leach liquor. These results for single stage leaching of Forte Velho ore, using 25 kg of sulphuric acid per tonne of ore in a 5% (wt/vol) solution are shown in Fig. 2. Taking into consideration the pH curves there is evidence that, during the leaching, the uranium extraction and acid consumption are as follows:

(*a*) The uranium dissolving rate and acid consumption are rather high at the beginning;

(*b*) Later on, the uranium dissolving rate decreases and the pH of the leach liquor becomes constant.

It seems advisable, therefore, to interrupt sprinkling when the uranium concentration begins to fall and to leave the acid solution impregnating the ore to carry on leaching. It was found that at least 12 hours' contact time was necessary. The effect of this interruption becomes more evident when the leaching is

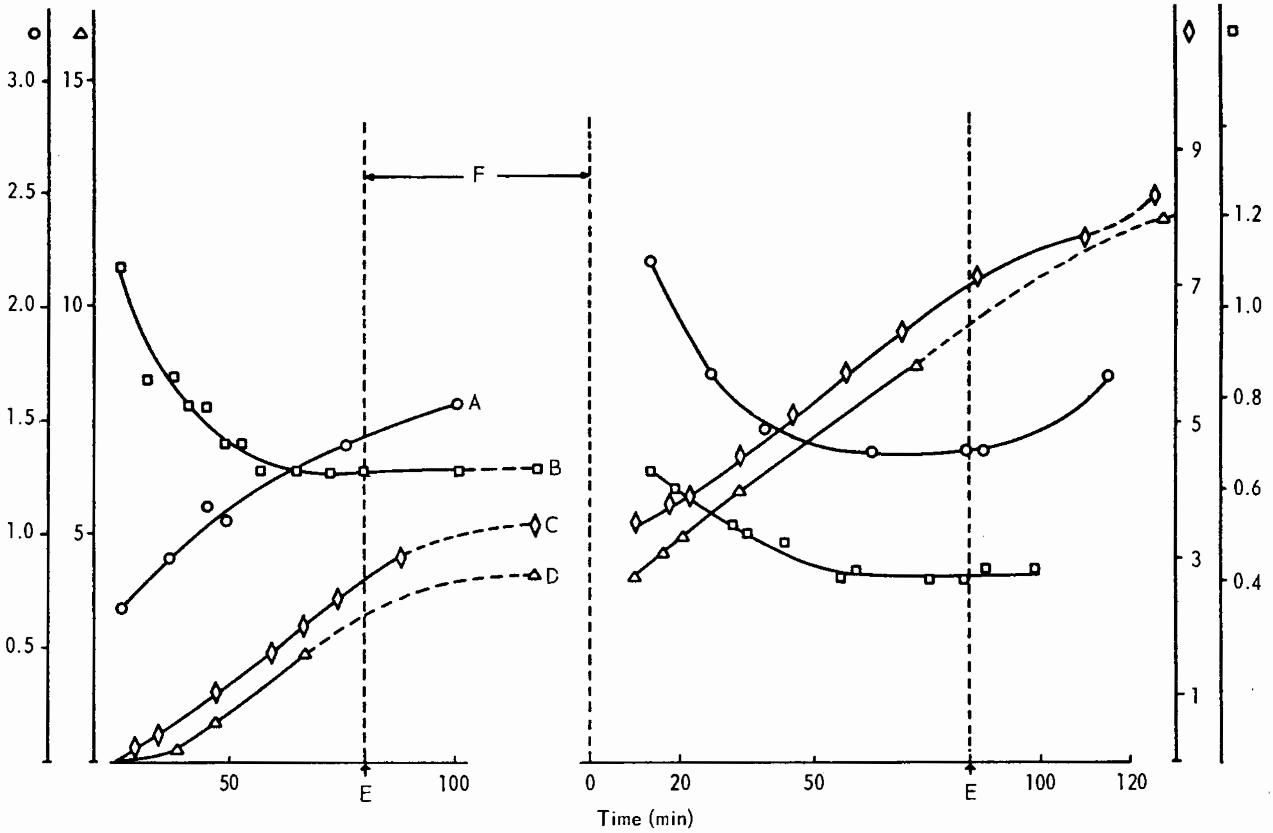

Figure 3. Forte Velho ore. Two stages of leaching with a 5 per cent sulphuric acid solution
A: Uranium concentration (g/l); B: pH; C: Total volume (l); D: Total U_3O_8 extracted (g); E: Sprinkling end point; F: 24 hours' contact time

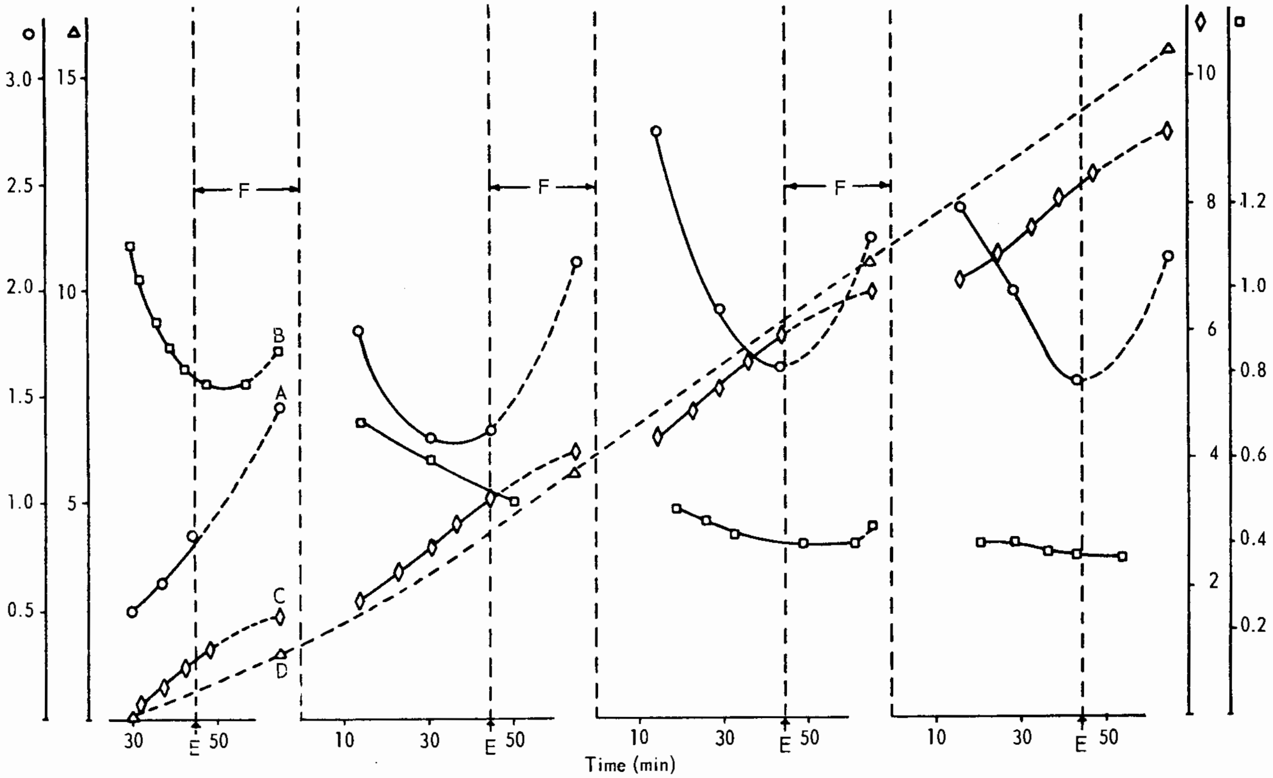

Figure 4. Forte Velho ore. Four stages of leaching with a 5 per cent sulphuric acid solution
A: Uranium concentration (g/l); B: pH; C: Total volume (l); D: Total U_3O_8 extracted (g); E: Sprinkling end point; F: 22 hours' contact time

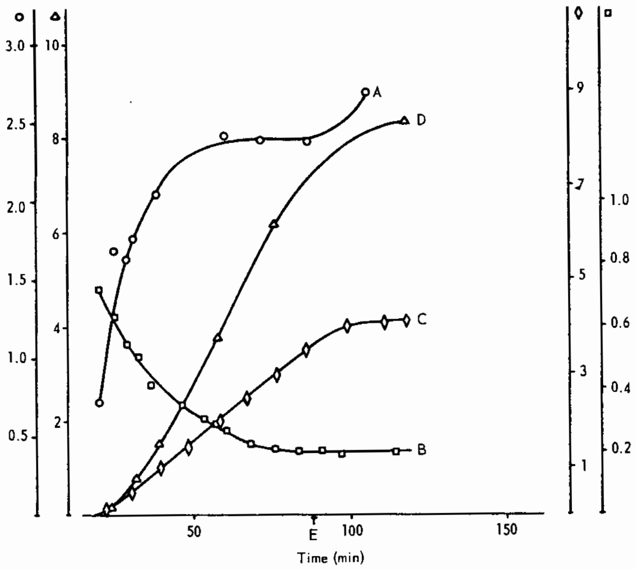

Figure 5. Forte Velho ore.
Single stage leaching with a 10 per cent sulphuric acid solution
A: Uranium concentration (g/l); B: pH; C: Total volume (l); D: Total U_3O_8 extracted (g). E: Sprinkling end point

performed in several stages. The results of 2 and 4 leaching stages are shown in Figs. 3 and 4.

When a 10% sulphuric acid solution is employed, the shape of the curves is quite different, as shown in Fig. 5. This is probably due to the small volume of leaching solution used.

Following these experiments, the influence of the important leaching parameters on uranium recovery, namely, acid concentration, acid consumption, number of leaching stages, and column height, was studied in a systematic way. The results are shown in Tables 1 and 2.

Table 1. Tests on 20 kg columns 50 cm high

Effect of the number of leaching stages.
Quantity of acid: 25 kg per tonne of ore.

Acid solution concentration %	U_3O_8 extraction % Number of leaching stages 1	2	4
5	58.5	64.3	71.2
10	64.2	66.5	60.0

Effect of the quantity of sulphuric acid.
5% acid solution concentration.
Single stage leaching.

Quantity of acid per tonne of ore kg	U_3O_8 extraction %
15	40.0
20	52.0
25	58.5
50	83.2

Table 2. Tests on 80 kg ore columns 1.8 m high

Effect of the number of leaching stages,
Quantity of acid: 25 kg per tonne of ore.

Acid solution concentration %	U_3O_8 extraction % Number of leaching stages 1	2	4
5	83.7	83.5	88.9
10	82.0	78.6	76.2

Effect of the quantity of sulphuric acid.
5% acid solution concentration.
Four leaching stages.

Quantity of acid per tonne of ore kg	U_3O_8 extraction %
15	72.3
20	80.9
25	83.5
50	84.8

Effect of the acid concentration.
Quantity of acid: 25 kg per tonne of ore.
Four leaching stages.

Acid concentration %	U_3O_8 extraction %
3	74.3
5	88.9
10	76.2

The effect of recirculating the leach liquors was also studied. It was found that some of the liquors resulting from leaching with a 5% acid solution were still rich in free acid. Thus, the richest ones were recycled through fresh ore which, later on, was also leached with a 5% acid solution. With this procedure, 79 to 82% uranium recovery was obtained, with an acid consumption of about 17.5 kg per tonne of ore.

The laboratory results lead to the following main conclusions:

(*a*) The sulphuric acid sprinkling process has given reasonable uranium recoveries with fairly low acid consumptions. Therefore testing this process on a pilot plant scale is justified;

(*b*) There is an increase of uranium recovery with column height resulting from the longer contact time between the ore and the acid solution;

(*c*) It is convenient to carry the leaching in several stages with interruptions of at least 12 hours;

(*d*) Acid consumption is less than 25 kg per tonne of ore, when a 5% acid solution is used on ore ground to minus ½ in;

(*e*) Recycling of acid leach liquors can increase the uranium recovery and diminish the acid consumption;

(*f*) When the Forte Velho ore is leached under these conditions, uranium recovery reaches about 80%.

These conclusions and the experimental laboratory results were used for the design of a semi-mobile pilot plant.

Uranium recovery from leach liquors

To recover the uranium from the leach liquors the following three methods were available:

(*a*) Precipitation by means of lime or magnesite;
(*b*) Solvent extraction;
(*c*) Ion exchange.

As a high grade concentrate was required, the direct precipitation method could not be considered. Preference was not given to the solvent extraction method due to the changing characteristics of leach liquors. Therefore because of these characteristics, and taking into consideration the experience previously gained by the authors, the ion exchange method was chosen.

The strongly basic ion exchange resin, Zerolit FF, was selected. Its main characteristics were analysed after several adsorption cycles, using the liquors obtained during the leaching tests. It was found that the resin lost about 12% of its initial capacity, which is considered to be normal. The shape of the leakage curves did not vary significantly and the resin ashes had a low percentage of silica and no traces of resin poisons.

SEMI-MOBILE PLANT

Plant description

Leaching is performed in a set of six cells where the ore is heaped up after crushing to minus ½ in by means of a jaw crusher and a roll crusher. The cells are made of bricks, covered with cement and lined with an asphaltic product, each one able to contain 90 tonnes of ore, corresponding to 2 m useful height. During the charging of the cells, the ore is watered in order to facilitate solid-liquid contact and to avoid the formation of dust, 50 to 200 litres of water per tonne of ore being necessary for this purpose.

Nozzle sprayers are used for sprinkling the leaching and washing solutions. They are geometrically arranged 2 m above the ore. The leaching solutions are prepared by injecting concentrated sulphuric acid into a water flow with the aid of two dosing pumps. Leaching is initiated by the recycling of the acid leach liquors from previous treatments and is continued by sprinkling, in 3 or 4 stages, with a fresh 5% sulphuric acid solution. The ore is finally washed several times with water or with a dilute sulphuric acid solution. The flow rate of the leaching and washing solutions is about 100 l hr^{-1} m^{-2}. The acid consumption is about 25 kg per tonne of ore with a uranium content of the order of 0.2% U_3O_8. The leach liquors are collected and mixed in six tanks of 45 m^3 capacity, built in granite protected by an asphaltic product.

Sodium hydroxide is added to these tanks to adjust the pH of the liquor which is then filtered in a sand filter before entering the ion exchange columns, each holding 500 l of Zerolit FF resin (3 columns in adsorption and 1 in elution). Backwashing of the resin is carried out in a special column of a larger volume and diameter, the resin being transferred to and from this column by hydraulic means. In this way it is possible to have shorter columns for adsorption and elution which can be easily transported when transferring the plant to another mine.

Eluting solutions are prepared and stored in a set of four 3 m^3 tanks. The dilute uranium eluate is recycled as eluting solution. The richer effluent is pumped to a fifth tank where the uranium is precipitated, in a single stage, with sodium hydroxide, and filtered in a filter press. Part of the filtrate is returned to the eluant make up system. The other part is bled off in order to avoid the build up of ions, such as sulphate and phosphate in the eluting solution. As the pregnant liquor is rather rich in phosphate ions, it was necessary to raise the volume of the eluting solution.

After filtration the yellow cake is washed in the filter press with water and dried in a small stove. The barren liquors are sent to a small natural dam and there neutralized with lime.

The plant has a working capacity of about 35 tonne of ore per day and has been in operation since May 1962.

Cost of equipment and consumption of reagents

The total cost of the plant was about 1.7 × 10^6 Escudos (ca. 59,000 Dollars). The value of the mobile equipment is about ¾ of the total cost. The remainder is lost whenever the plant has to be moved and it corresponds mainly to the civil engineering and installation costs. The consumption of reagents is given in Table 3.

Table 3. Average consumption of reagents per tonne of ore

Process	Reagent	Consumption
Leaching:	sulphuric acid	27.9 kg H_2SO_4
Ion exchange		
pH adjustment:	sulphuric acid	0.26 kg H_2SO_4
	sodium hydroxide	5.3 kg NaOH
elution:	nitric acid	3.3 kg HNO_3
	sodium hydroxide	0.08 kg NaOH
resin washing and transfer:	sulphuric acid	0.17 kg H_2SO_4
Precipitation:	sodium hydroxide	2.4 kg NaOH
Barren liquors neutralization:	lime	3.5 kg

It should be mentioned that, in this plant, ores resulting from the prospecting work on other mines, have been treated. This justifies the slightly higher acid consumption on leaching, in relation to the laboratory results obtained for the Forte Velho ore.

The possibility of reducing the sodium hydroxide consumption, used for the pH adjustment of the ion exchange pregnant liquor, is being investigated.

Characteristics of the concentrate

It was found that the uranium grade of the concentrate is closely dependent on the washing. With an efficient washing, the uranium grade in the dried concentrate is of the order of 75% U_3O_8. Analytical results on the concentrate are given in Table 4.

Table 4. Analysis of the uranium concentrate produced in 1962

Impurity	Concentration
Halogens (Cl + Br + I)	Not detected
Nitrogen.	0.81% NO_2
Sulphur	1.25% SO_3
Phosphorus	4.86% P_2O_5
Silicon.	0.80% SiO_2
Aluminium.	1.04% Al_2O_3
Iron.	2.14% Fe_2O_3
Magnesium.	0.01% MgO
Calcium	0.36% CaO
Copper	Traces
Sodium	8.00% Na_2O
Potassium	0.46% K_2O
Cadmium	14 ppm CdO
Uranium.	76.66% U_3O_8

Behaviour of the ion exchange resins

The behaviour of the ion exchange resins has been systematically checked. Their capacity and nitrogen contents have been periodically analysed, the results are shown in Table 5. It can be seen from these results (and from the loading and elution curves), that the resin is in good condition and that a caustic regeneration does not yet appear to be necessary.

Table 5. Ion exchange resins capacity and nitrogen content

Time months	Total uranium passed through the resins kg U_3O_8	Nitrogen content % on basis of dried resin-chloride	Resin capacity for nitrate meq. per g of dried resin-chloride
0	—	5.72	4.02
4	1 148	5.45	3.62
7	2 987	—	3.25
10	4 222	5.19	3.58
15	8 710	—	3.31
21	12 430	5.24	3.41

Phosphate interference in the elution

Elution becomes rather difficult due to the high concentration of the phosphate ion in the leach liquor. The analysis of the pregnant liquor gave results within the following figures:

Uranium.	0.3 — 0.7 g/l U_3O_8
Iron	0.4 — 1.0 g/l Fe
Phosphate	0.3 — 0.8 g/l PO_4^{3-}

If all the iron were oxidised, the molar ratio Fe/PO_4^{3-} would still be very low. As a result, a considerable amount of phosphate is adsorbed by the resin, the elution curves becoming less sharp and the uranium being more difficult to remove. Although the volume of the eluting solution equals 12 bed volumes, the uranium concentration in the last fractions of the eluate is sometimes as high as 1 to 2 g/l U_3O_8 (Fig. 6 curve a).

Attempts were made to eliminate this interference. Two processes were employed.

Increasing the filtrate bleed off. A 25% filtrate bleed off had been foreseen initially. An increase of this volume to 3 bed volumes greatly favoured the elution (Fig. 6 curve b).

Increasing the eluate solution acidity. The elution is normally performed with a 0.3*N* HNO_3 and 0.7*M* $NaNO_3$ solution. An increase of the nitric acid concentration to 0.5*M* (total nitrate 1.1*M*), greatly improved the elution (Fig. 6 curve c).

These improvements are, however, counterbalanced by an increase in the reagent consumption. Elution costs rose about 70% in the first case, and 30% in the second case.

Immersion leaching

Recently, the ore has also been processed by immersion leaching. The advantages of immersion over sprinkling are:

(*a*) A longer contact time between the ore and the leaching solution;

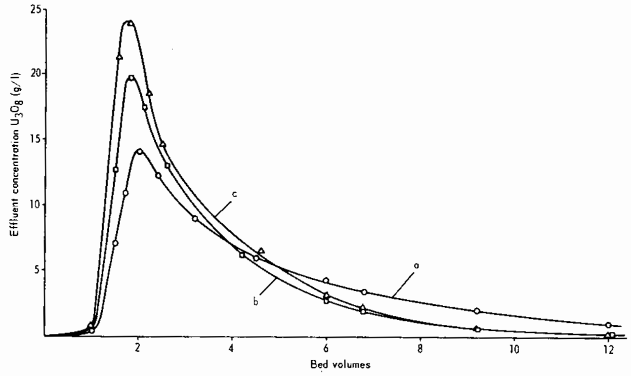

Figure 6. Elution curves

a: Eluant 0.3*N* HNO_3, 0.7*M* $NaNO_3$ 1 ½ bed volume purge; b: Eluant 0.3*N* HNO_3, 0.7*M* $NaNO_3$ 3 bed volume purge; c: Eluant 0.5*N* HNO_3, 0.6*M* $NaNO_3$ approx. 1 ½ bed volume purge (*b*) An easier access of the acid to the whole solid;

(*c*) A more uniform solid-liquid contact.

On the other hand, this process has the following disadvantages:

(*d*) A faster attack on the cell linings;

(*e*) The access of the fresh leaching solution to the ore, is not continuous, as happens when the acid solution is sprinkled over the ore;

(*f*) A greater danger of the ore becoming impermeable;

(*g*) The quantity and the concentration of the acid are closely dependent on the void volume of the ore.

For uranium recovery, both processes seem to give similar results.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/503 Portugal

Traitement chimique de minerais d'uranium auprès des mines, dans une installation semi-mobile

par J. Freire de Andrade *et al.*

Dans la région uranifère du nord-est du Portugal se trouvent quelques petits gisements épars ayant des réserves d'uranium de 10 à 50 tonnes par gisement, situés à des distances considérables de la seule installation industrielle portugaise de traitement chimique de l'uranium. La construction d'une installation fixe pour le traitement de minerais dans la région n'est pas justifiable, en raison de la dispersion des gisements et de l'importance relativement réduite des réserves. Aussi a-t-on entrepris l'étude d'un procédé simple et économique pour la récupération de l'uranium auprès des mines, avec un équipement réduit pouvant être transporté facilement d'une mine à l'autre.

Les études ont été orientées en vue de réduire ou d'éliminer les grosses opérations de broyage et de séparation solide-liquide. On a essayé de faire le traitement après broyage grossier. Après des études de laboratoire, deux procédés de traitement ont été essayés :

a) Imprégnation du minerai par une solution sulfurique et, après des périodes de temps variées, arrosage du minerai avec de l'eau pour entraîner l'uranium solubilisé;

b) Arrosage du minerai avec une solution d'acide sulfurique; ensuite, arrosage avec de l'eau pour entraîner l'uranium solubilisé.

Les deux méthodes ont été appliquées avec succès à plusieurs types de minerais, exception faite des minerais basiques et peu perméables. En particulier, une étude très détaillée a été faite concernant le traitement du minerai de Forte Velho, principalement composé d'une roche granitique altérée, avec minéralisation de torbernite. Les essais au laboratoire à l'aide de petites colonnes de minerai broyé à moins de 0,5 pouce ont permis, pour un lot à 0,2 % de U_3O_8, d'atteindre des rendements d'environ 80 %, la consommation d'acide sulfurique ne dépassant pas 25 kg par tonne de minerai traité. Les résultats ont suggéré qu'il y avait avantage à faire recirculer les liqueurs d'attaque encore riches en acide à travers des minerais frais et à employer des colonnes plus hautes permettant d'augmenter le temps de contact entre le minerai et la solution sulfurique.

D'après ces différents essais, on a créé une installation pilote de traitement de minerais ayant une capacité d'environ 35 tonnes par jour. Elle est constituée essentiellement par :

a) Une installation de broyage de minerai à moins de 0,5 pouce;

b) Une batterie de cellules où ce minerai est entassé et arrosé;

c) Une batterie de bassins permettant de recueillir les liqueurs d'attaque et de régler le pH;

d) Une installation de colonnes échangeuses d'ions;

e) Un équipement pour la précipitation et la filtration du concentré.

Cette installation a commencé de fonctionner en mai 1962. Le rendement d'extraction d'uranium est d'environ 75 % malgré les variations fréquentes des caractéristiques et des teneurs des minerais employés. Des concentrés contenant environ 75 % de U_3O_8 sont obtenus.

Des éléments concernant l'équipement et le coût d'exploitation de l'installation sont indiqués. On a donné aussi des renseignements concernant quelques problèmes soulevés par son exploitation, dont les suivants :

a) Comportement des résines échangeuses d'ions;

b) Tentatives d'élimination de la perturbation causée par l'ion phosphate dans l'élution;

c) Emploi du procédé d'immersion du minerai dans une solution sulfurique.

A/503 Португалия

Химическая переработка урановых руд на рудниках в полупередвижной установке

X. Фрейра-де-Андраде *et al.*

В ураноносном районе на северо-востоке Португалии открыто несколько небольших разбросанных месторождений урана с запасами металла от 10 до 50 *т*, расположенных на значительном расстоянии от единственного в стране уранового гидрометаллургического завода. Относительно небольшие запасы и разбросанность месторождений не оправдывают строительства нового завода в этом районе. В связи с этим были проведены исследования по изысканию экономичного процесса обогащения урановых руд в аппаратуре, которая могла бы легко перевозиться с рудника на рудник.

Задача исследований заключалась в сокращении или исключении таких сложных операций, как измельчение и фильтрация. Испытывалась переработка руд после крупного дробления. В порядке лабораторного изучения были испытаны два способа переработки:

1. Руду замешивали с раствором серной кислоты и затем промывали водой для удаления растворенного урана.

2. Руду опрыскивали раствором серной кислоты и затем промывали водой для удаления растворенного урана.

Оба эти способа были проведены с обещающими результатами на нескольких типах руд, за исключением щелочных и водонепроницаемых руд.

В частности, весьма детально исследовалась переработка руды месторождения Форте-Вельхо, которое сложено главным образом эродированными гранитными породами с торбернитовой минерализацией. При лабораторных исследованиях этой руды, содержащей 0,17% урана, раздробленной до минус 12,5 *мм* и помещенной в небольших колоннах, достигнут коэффициент извлечения металла 80%, при расходе серной кислоты не выше 25 *кг* на тонну руды. Отмечены также преимущества рециркуляции богатых кислых растворов через свежую руду и применения длительности контакта руды с кислотой.

На основании этих опытов была запроектирована полупромышленная установка производительностью 35 *т* руды в сутки. В систему аппаратов установки входят:

а) оборудование для измельчения руды до минус 2,5 *мм*,

b) группа камер, в которые руда загружается, обрабатывается кислотой и промывается водой;

c) группа емкостей для сбора растворов после выщелачивания и регулировки pH;

d) группа ионообменных колонн;

e) оборудование для осаждения и фильтрации концентрата.

Эта установка работает с мая 1962 года. Коэффициент извлечения урана составляет около 75%, несмотря на частые изменения вещественного состава и содержания урана в руде. Урановый концентрат содержит около 65% металла.

Приводятся детальные данные по оборудованию и эксплуатационным расходам. Рассматриваются также некоторые вопросы, связанные с работой установки, а именно:

a) поведение ионообменных смол;

b) способы избежать влияния фосфатов при регенерации;

c) переработка руд погружением в сернокислотный раствор.

A/503 Portugal

Tratamiento químico de minerales de uranio a bocamina en una instalación semimóvil

por J. Freire de Andrade *et al.*

En la región uranífera situada al noreste de Portugal, lejos de la única instalación industrial de tratamiento químico de uranio existente en el país, se encuentran dispersos unos pocos yacimientos pequeños, cada uno de los cuales tiene alrededor de 10 a 50 t de uranio. Las reservas, relativamente pequeñas, y la dispersión de los yacimientos no justificaría la construcción de una fábrica convencional en dicha región. Por esta razón los estudios se orientaron a la elaboración de un proceso económico de concentración del uranio, con equipo que se pudiese trasladar fácilmente de una mina a otra.

Se realizaron estudios con el fin de reducir o eliminar las operaciones que requerían mucho volumen, tales como la molienda y la separación líquido-sólido. Se ensayó el tratamiento de los minerales después de una trituración gruesa. Se realizaron estudios a escala de laboratorio, investigando los dos procesos siguientes:

a) El mineral se impregnaba con una solución de ácido sulfúrico y después de periódos de tiempo diferentes, se lavaba con agua para separar el uranio disuelto.

b) La mena se regaba con solución de ácido sulfúrico y luego con agua para extraer el uranio soluble.

Estos dos procesos se aplicaron a varios tipos de menas con resultados alentadores, con excepción de las menas alcalinas e impermeables.

En particular se estudió con gran detalle el tratamiento del mineral de Forte Velho, que consta fundamentalmente de roca granítica alterada y con mineralización de torbernita. En los experimentos de laboratorio se obtuvo una recuperación del 80 % del uranio, con un consumo de ácido de 25 kg/t de mena, a partir de un mineral que tenía el 0,2 % de U_3O_8 triturado a menos de ½ in y colocado en columnas pequeñas. Los resultados también sugirieron las ventajas de recircular, a través de mineral nuevo, los líquidos más ricos en ácido, y el emplear columnas más altas con el fin de aumentar el tiempo de contacto entre el mineral y la solución ácida.

Basados en estos experimentos se proyectó una planta piloto de 35 t/día. La instalación comprende fundamentalmente:

a) Equipo para la trituración de la mena a menos de ½ in;

b) Un conjunto de celdas donde se almacena, se riega con ácido y con agua;

c) Un conjunto de depósitos para recoger los líquidos de lixiviación y ajustar el pH;

d) Columnas de cambio de ion;

e) Equipo para la precipitación y filtración del concentrado.

Esta instalación lleva funcionando desde mayo de 1962. La recuperación del uranio ha sido de aproximadamente el 75 % a pesar de las variaciones frecuentes de las características y leyes de las menas de uranio que se han tratado. El concentrado de uranio contiene aproximadamente el 75 % de U_3O_8.

Se mencionan detalles sobre el equipo y los costes de operación. También se hace referencia a algunos problemas relacionados con la operación de la fábrica tales como:

a) Comportamiento de las resinas de cambio de ion;

b) Tentativas para eliminar las interferencias de los fosfatos en la elución;

c) Tratamiento de los minerales por inmersión en soluciones de ácido sulfúrico.

A new technique for upgrading Australian thorium resources

By A. W. Wylie and E. S. Pilkington *

PRODUCTION POTENTIAL

Although workable thorium deposits comparable with the complex oxide and silicate ores of the Canadian uranium fields have not yet been discovered in Australia, thorium is found as monazite in many localities of the Commonwealth [1, 2]. High grade concentrates of this mineral are recovered as a by-product of industries processing beach sands for ilmenite, rutile and zircon. The Bureau of Mineral Resources, Geology and Geophysics [1, 3] reports the latest production statistics for monazite:

	1961	1962	1963[a]
Queensland	156	167	57
New South Wales	152	162	320
Western Australia	362	570	1 150
Total, tons	670	899	1 527

[a] For nine months

It is difficult to infer a reliable figure for the production capacity of the industry, as plant may be used only intermittently to upgrade accumulated stocks of lower grade concentrates. Assessment of reserves is equally difficult as these are intimately associated with life-expectancy of the beach sand industry as a whole [4]. New producers entering the industry should, however, assure production of monazite at a level at least equal to that for 1963 for some years to come. There may be some increase in production in later years, but a tapering off by 1980 is expected to follow exhaustion of high grade reserves of beach sand minerals and the opening-up of lower grade deposits [4].

Most of the recent production of monazite has been exported, the average f.o.b. price in 1962 being £41.2/ton for a grade containing not less than 60% combined thorium and rare earth oxides [1].** The thorium content of a number of Australian monazites is variable [2] but for most beach sand concentrates it lies between 5 and 7.5% thorium oxide.

It is feasible to recover at least 80% of the thorium in a high grade beach sand concentrate on a technical scale [5]. If it is assumed that the full 1963 level of production applies to a 6% concentrate, then Australian production of thorium as oxide could, if required, approach 100 tons per annum. Present indications are that this output would be more than sufficient to satisfy the needs of a future power programme based on nuclear reactors of the type under study by the Australian Atomic Energy Commission [6].

Thorium costs

An important factor in deciding on a suitable extraction process is the cheapness of sulphuric acid in Australia compared with the cost of reagents such as sodium hydroxide and hydrochloric acid. Reagent costs are therefore lowest for processes utilising sulphuric acid provided end-products of comparable quality are obtained, and for the production of crude thorium hydroxide they should not exceed 9 to 10 shillings (Australian) per lb of thorium oxide. This cost is exceeded in many processes which have been proposed in the literature. There would be a further charge in all processes for refining the above product to nuclear grade. Various direct and indirect conversion costs cannot be estimated for any process until a likely scale of operation is established.

Some reduction in process costs should follow from the scale of production of by-products such as various rare earth and sodium salts.* In favourable circumstances this could lead to a drastic reduction in such costs or even to the reversal of the role of product and by-product. These considerations also affect the scale of operation desirable. However, it is a matter of conjecture whether any significant demand for large quantities of such by-products exists at present in Australia or its export markets, and the present investigations have been conducted on the basis of extracting thorium at lowest possible reagent cost without undue dependence on the sale of by-products.

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** Units used throughout this paper are: 1 long ton = 2 240 lb = 1 016 kg; £1 (Australian) = £0.796 (British) = $2.23 (USA).

* Authors of some processes have not always described how to recover by-products. Before comparisons can be made, additional stages must be added to these processes and costs adjusted accordingly.

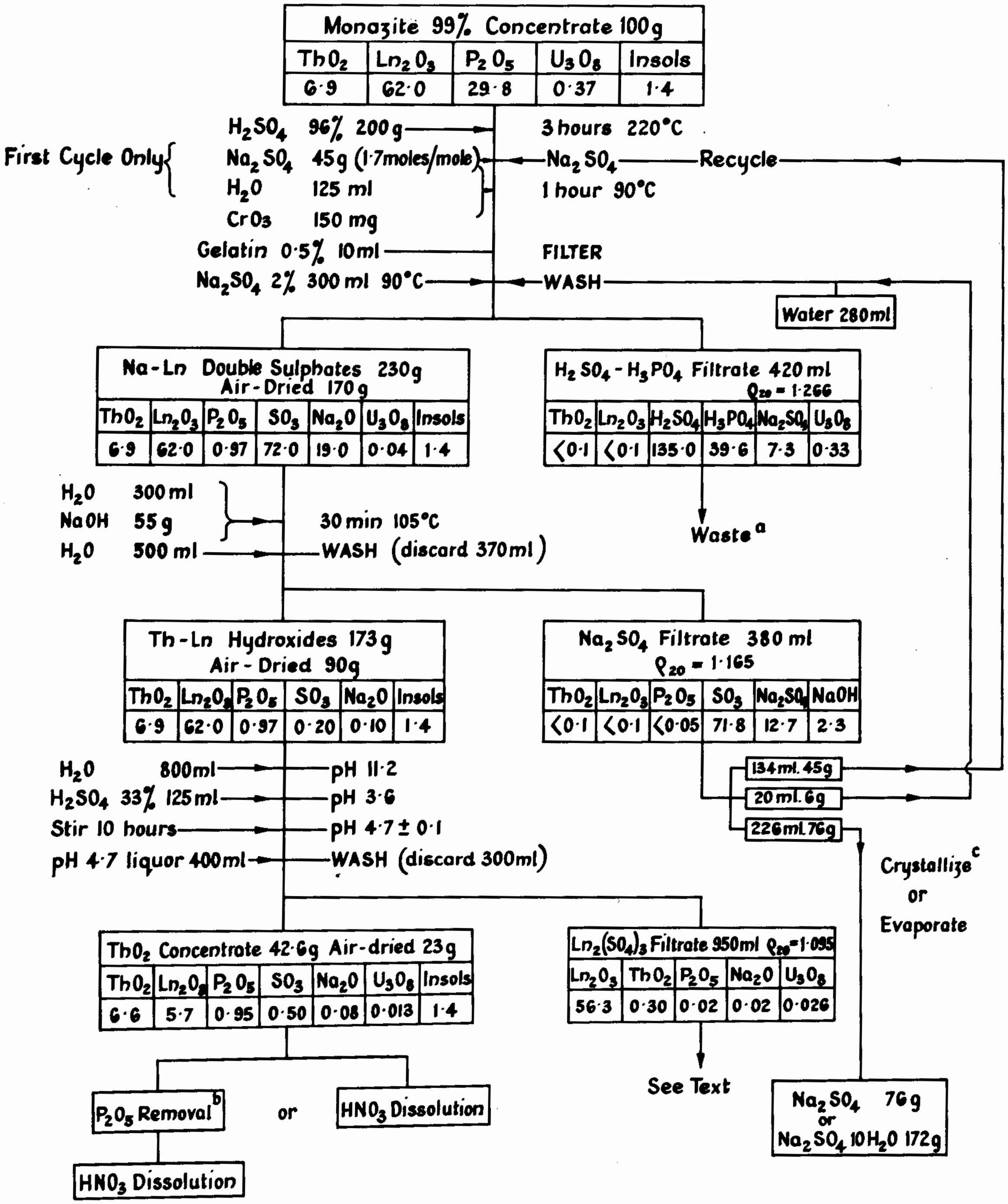

Figure 1. Flowsheet of process

(*a*) Or uranium recovery if warranted; (*b*) Optional step — see text; (*c*) Or used to precipitate sodium rare earth sulphates free from thorium

CHEMICAL EXTRACTION OF THORIUM

Various processes proposed up to 1958 for the extraction of thorium from ores and mineral concentrates [7, 8, 9] have been critically reviewed by Wylie [10]. In a more recent development due to Crouse, Brown [11, 12] and others [13], the amine liquid-liquid extraction process has been applied to the separation of thorium from liquors obtained by decomposing monazite with sulphuric acid. In all these processes the thorium produced must be further refined by solvent extraction to obtain material of nuclear grade. Tributylphosphate-thorium nitrate systems have been favoured for this purpose [16, 17, 18].

In an earlier sulphuric acid process designed chiefly to yield rare earth hydroxides for conversion to glass polishing powders, Pilkington and Wylie [14, 15] and Urie [5] proposed to recover thorium from monazite in two approximately equal fractions, one associated with rare earths and the other with "waste" sulphuric and phosphoric acids. Conditions have now been found for channelling all thorium into a single rare earth fraction, leaving the bulk of the uranium in the waste acid solution and thus greatly simplifying the whole process. Rare earths and thorium are later separated by a simple and economic process leaving a crude thorium concentrate in laboratory yields exceeding 94%.

The principal features of this simplified process are, firstly, the quantitative co-precipitation of thorium with rare earths by means of recycled sodium sulphate liquor; secondly, conversion of the double sulphate precipitate to hydroxides; and finally, the selective leaching of the hydroxides with sulphuric acid to separate thorium from the rare earths. Further refining by chemical means is considered unjustifiable and the hydroxide concentrate may be treated with excess nitric acid to obtain thorium nitrate solutions suitable for refining to nuclear grade material by either of the solvent extraction techniques developed by Menzies and Rigby [16] from earlier work by Audsley and co-workers [17, 18].

Description of process

Stage 1. Decomposition of monazite. Unground monazite sand, preferably a high grade concentrate similar in composition and grain size to the material previously described, is decomposed with 96% sulphuric acid at 220 °C. The 2 : 1 weight ratio of acid to sand representsthe minimum quantity of acid required to obtain a stirrable paste at the end of the 3 hour digestion period. Decomposition of monazite is virtually complete [14].

Stage 2. Co-precipitation of sodium rare earth double sulphate and thorium sulphate. For maximum elimination of phosphoric acid and recovery of over 99% thorium and rare earths, the pasty mixture of sulphates containing phosphoric acid and excess sulphuric acid is cooled to 50 °C and vigorously stirred into a cold concentrated solution of sodium sulphate recycled from Stage 3. A suitable uranium oxidant is added beforehand to avoid co-precipitation of uranium(IV) with rare earths and thorium. Although the amount of sodium sulphate recommended (Fig. 1) is only slightly in excess of that found in the precipitate, Table 1 shows that high yields of thorium can be obtained provided a high sulphate concentration (i.e., low precipitation volume) is maintained. In addition, phosphate contamination of the double sulphate is minimised (Table 1). A temperature of 90 °C should be maintained for approximately 1 hour and the precipitate filtered hot to ensure a virtually quantitative yield of thorium. Filtration is rapid if 0.5% gelatin solution is added to the suspension to flocculate colloidal silica.

Stage 3. Conversion of mixed sodium rare earth and thorium sulphates to mixed rare earth and thorium hydroxides. The mixed double sulphates are heated with a 10% excess of 15% sodium hydroxide solution. Exothermic decomposition forms a dense, easily settling form of mixed hydroxides. Heating at boiling point should be continued for 30 minutes to complete

Table 1. Effect of precipitation volume on yield of thorium co-precipitated with sodium rare earth sulphates

Conditions : 100 g sand decomposed; paste stirred into various volumes containing 45 g of sodium sulphate; immediate filtration after 1 h at 90 °C

Solution volume, ml	Weight ratio of sulphuric acid: monazite sand			
	2 : 1		2.8 : 1[a]	
	ThO_2 Yield %	P_2O_5[b] content %	ThO_2 yield %	P_2O_5[b] content %
500	86	1.50	94	1.33
250	97	1.10	98	0.53
125	99	0.60	99	0.27[c]

[a] Ratio formerly used [14].
[b] In air-dried material.
[c] Phosphate elimination from thorium, 99%.

the reaction and improve filtration properties. The relic structure of the hydroxide particles has been described [14]. To prevent oxidation of cerium(III) to cerium(IV), which follows thorium in the process, the filter cake should be kept covered with water or blanketed with nitrogen. Alternatively a little sulphurous acid should be added to the wash water and the filter cake immediately leached as described in the following section.

The filtrate from Stage 3, with the addition of the prescribed quantity of wash water (Fig. 1), contains sodium sulphate at a concentration of 340 g/l. It is kept above 32 °C to prevent crystallisation and recycled in part as shown in Fig. 1. The bulk of the remainder is evaporated to recover sodium sulphate in anhydrous or hydrated form, or used as described in Stage 4.

Stage 4. Selective leaching to remove thorium from mixed hydroxides. The filter cake of mixed hydroxides is slurried with cold, 33% sulphuric acid at a pulp density of 130 g/l (9% solids). The acid requirement is 85% of that needed for complete dissolution. The pH is allowed to fall over a period of several hours to a near equilibrium value of 4.7 ±0.1 at 20 °C. The semi-gelatinous thorium "hydroxide" filters slowly from the solution of rare earth sulphates. It should be washed by dispersion in water, the first wash being at pH 4.7. The over-all yield of thorium is 96%, quantitative recovery being possible only at the expense of the quality of the product. A typical washed concentrate loses approximately 50% in weight on drying in air. In terms of anhydrous oxides its composition is:

	ThO_2	Ln_2O_3*	U_3O_8	Na_2O	P_2O_5	SO_3	Acid insoluble**
Wt%	38	44	0.07	0.5	6.0	3.0	9.0

The air-dried material dissolves readily in concentrated nitric acid to give feed solutions approximately 1 *M* in thorium and 3-4 *M* in nitric acid as required for the selected refining process [16]. Any yellow colour due to inadvertent oxidation of cerium(III) to cerium (IV) should be discharged by small additions of 10% hydrogen peroxide to the hot solution.

Alternative chloride route. The more expensive chloride route can be followed if there is sufficient demand for by-product rare earth chlorides. The acid requirement is now 95% of theoretical and the final pH should be adjusted as before. The thorium concentrate, obtained in 95% yield, contains less sulphate ($\simeq$ 1%) than the product of the all-sulphate route, but is otherwise similar in composition. Chloride ion in the washed product is less than 0.1%.

Products and yields

Thorium product. From 100 lb high grade monazite concentrate containing 6.9 lb thorium oxide, 6.6 lb thorium oxide is obtained by either the sulphate or chloride routes. This oxide is in the form of a crude hydroxide suitable for further purification by an established process. The over-all yield of thorium is thus 95-96%, and Urie [5] has shown that pilot plant yields in a similar process equal 90% of those obtained in the laboratory.

By-products

Sulphate route. The concentrated rare earth sulphate solution filtered from the final thorium concentrate (Fig. 1) is free from major impurities including phosphate. It contains 56 lb rare earth oxides, equivalent to a yield of 90%. This solution is well suited for use as a feed solution in processes designed to separate rare earths by use of ion exchange resins [19], or solvent extraction with long chain alkylamines [20]. Alternatively, it could be treated with the 77 lb sodium sulphate otherwise available as a by-product of the process (see Fig. 1) to obtain high yields [14] of easily filterable sodium rare earth double sulphates containing only traces of thorium.

Chloride route. The rare earth chloride solution filtered from the final thorium concentrate may be evaporated to a syrup and cooled. Mixed chlorides of the following composition (in terms of anhydrous oxides) solidify as hexahydrates:

	Ln_2O_3	ThO_2	Na_2O	P_2O_5	SO_3
Wt%	>99	0.5	0.03	0.03	0.05

There is no significant difference in yield of rare earths between the chloride and sulphate routes.

Thorium-free rare earths. If required, the major proportion of the rare earth by-products can be obtained free from all traces of thorium, irrespective of which leach acid is used in Stage 4. For this, selective leaching should be halted when approximately 75% of the total rare earth oxides have been dissolved, and the suspension filtered to obtain a thorium-free product. Leaching of the thorium fraction is continued as before. The second and smaller rare earth fraction will, unavoidably, contain a higher proportion of thorium than quoted in the preceding paragraph.

Reagent consumption and costs

Reagents required per 100 lb monazite concentrate are 200 lb 96% sulphuric acid, 86 lb 33% sulphuric acid, and 55 lb sodium hydroxide as a solution of appropriate concentration. If the more expensive chloride route is justified because of a demand for by-products in chloride form, 110 lb hydrochloric acid would be needed in place of 86 lb 33% sulphuric acid. In either case adoption of the optional phosphate

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* Oxides of the lanthanons.

** Silica and undecomposed beach sand minerals such as zircon, rutile, etc.

removal stage (*q.v.*) would require an addition of 12-15 lb sodium hydroxide.

Cost of these reagents per lb thorium oxide is approximately 9s 4d for the sulphate route. For monazite purchased at £40 (Australian) per ton, total raw material and reagent costs therefore total 14s 1d to 15s 2d per pound of thorium oxide. Rare earth oxides are available in a concentrated sulphate solution or as sodium double sulphates at 1s 6d per pound of oxide.

This thorium is significantly cheaper in reagent cost than that produced by the French alkali process [21], (19s 6d per lb thorium oxide), and recent versions of the sulphuric acid process [22, 23]. It is almost identical in reagent cost with thorium produced by the process of Crouse and Brown, but the process described is considered to offer considerable advantage over the latter process with respect to flexibility and potential returns from disposal of by-products.

DISCUSSION

Co-precipitation of thorium with rare earths. The partial co-precipitation of thorium with mixed sodium lanthanon sulphates has been known for some time [14], the extent of co-precipitation depending on experimental conditions. The discovery of conditions for achieving quantitative co-precipitation of thorium has greatly facilitated subsequent processing. The quantity of sodium sulphate added, *viz.*, 1.7 moles per mole of Ln_2O_3, is much smaller than formerly used to precipitate the rare earths and may be compared with the composition of the air-dried precipitate, which is approximately 1.6 Na_2SO_4, $Ln_2(SO_4)_3$, 2.3 H_2O and 0.07 $Th(SO_4)_2$.

Phosphate content of products. The phosphate content of the double sulphate product is less than a third of that obtained in the earlier process. As phosphate strongly complexes thorium, and may cause its precipitation at low acidities, separation of 97%-98% of the total phosphate in a single operation notably facilitates subsequent purification of thorium by solvent extraction. Up to 20% of phosphate* can be tolerated in the refining process of Menzies and Rigby [16]. The thorium concentrate prepared in this work contains 10-13% of phosphate and may therefore be dealt with satisfactorily.

If greater flexibility of operation is required for the refining process it may be obtained by reducing the phosphate content of the final product to 1-2%. This can be accomplished most simply by digesting the crude thorium hydroxide concentrate in a closed vessel with sufficient 50% sodium hydroxide at 140-150 °C to form a stirrable slurry. Approximately twice the theoretical requirement of sodium hydroxide to convert all basic oxides to hydroxides is needed and the expense of this operation can only be justified if equivalent economies result from improved operation of the refining process.

Selective leaching with sulphuric acid. Selective leaching of mixed thorium and rare earth hydroxides with sulphuric acid has occasionally been proposed in the literature but seldom applied in practice, in contrast to the use of hydrochloric acid. The separation offers no technical difficulties if adequate time is allowed for an equilibrium state to be approached. Simple control measures can be devised to prevent loss of thorium exceeding 4-5%.

Problems of carbonate leaching processes. The relatively high cost of sodium hydroxide in Australia has stimulated investigation of processes designed either to replace sodium hydroxide or to leach sodium pentacarbonate selectively from sodium rare earth sulphates. Use of sodium carbonate in place of sodium hydroxide is technically feasible in Stage 3 of the process just described, but is complicated by formation of double sodium rare earth carbonates. Sodium carbonate must be removed from these before separating rare earth salts by selective leaching and no significant economy of operation can ultimately be achieved.

The principal drawback to selective leaching of sodium rare earth sulphates with aqueous sodium carbonate is the low recovery of thorium. Although thorium can be quantitatively recovered from the resulting sodium thorium pentacarbonate solution by precipitation as a high grade hydroxide concentrate* the over-all yield of thorium does not exceed 80 ± 5% however the process is carried out. Experiment showed that this was caused by co-precipitation of thorium in the lattice structure of the double sodium rare earth carbonates produced from the simple carbonates formed initially. Thus initially:

$$1.5\ Na_2SO_4,Ln_2(SO_4)_3 + 3Na_2CO_3 \longrightarrow Ln_2(CO_3)_3 + 4.5\ Na_2SO_4,$$

with a similar equation holding for thorium sulphate. The resulting thorium carbonate dissolves in excess reagent to give sodium thorium pentacarbonate. Co-precipitation then occurs:

$$\underset{\text{(soln.)}}{Na_6Th(CO_3)_5} + \underset{\text{(solid)}}{Ln_2(CO_3)_3} + \underset{\text{(soln.)}}{1.6\ Na_2CO_3}$$
$$\rightleftharpoons \underset{\text{(soln.)}}{Na_6(Th,Ln)(CO_3)_5} + \underset{\text{(solid)}}{1.6Na_2CO_3, (Ln,Th)_2(CO_3)_3}$$

The unsatisfactory yield of thorium obtained in attempts to leach sodium thorium pentacarbonate from mixed thorium and rare earth hydroxide is also attributed to the same basic cause.

Role of uranium. The role of uranium(IV) and uranium(VI) in precipitation of sodium rare earth and

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* Expressed as wt $P_2O_5 \times 100/\text{wt}\ (ThO_2 + Ln_2O_3)$.

* $ThO_2 : Ln_2O_3 : P_2O_5 = 1 : 0.4 : 0.04$ by wt.

thorium sulphates has been previously investigated [24]. Since adequate decontamination of thorium from uranium can be achieved by solvent extraction if the initial uranium to thorium ratio in the feed solution is reduced to the levels investigated by Menzies and Rigby, an oxidant is added to the sodium sulphate liquor used in Stage 1 of the present process. Uranium (IV) is then converted to uranium(VI) and 90% of the total uranium passes into the waste acid liquor. It may be recovered, if required, by extraction with a suitable tertiary amine. Omission of an oxidant would cause a high proportion of the uranium to pass into the thorium concentrate.

A further separation of two-thirds of the residual uranium occurs during the leaching operation of Stage 4, making the over-all separation of uranium in the process approximately 97%. Decontamination of thorium from uranium in the refining process should therefore offer little difficulty.

CONCLUSIONS

Present indications are that sufficient thorium could be obtained from Australian production of monazite to supply the needs of a nuclear power programme based on reactors of a type now under development in Australia.

An inexpensive, sulphuric acid-based process has been developed to produce a crude thorium hydroxide concentrate suitable for solution in nitric acid and subsequent refining to nuclear grade thorium by a preferred solvent extraction process.

The extraction process devised channels all thorium and rare earths into a single sodium double sulphate product, leaving phosphate and uranium in a waste acid solution. The double sulphates are converted to hydroxides which are then selectively leached to produce a thorium concentrate with thorium, rare earth and phosphorus oxides in the weight ratio 1 : 1 : 0.1. There is a useful preliminary decontamination of thorium from uranium, and rare earth salts are useful by-products.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/521 Australie

Une nouvelle technique de valorisation des ressources de thorium en Australie

par A. W. Wylie et E. S. Pilkington

L'Australie ne disposant pratiquement d'aucun gisement exploitable de thorium qui puisse être comparé au minerai d'oxyde et de silicate des régions uranifères du Canada, le thorium s'obtient localement à partir de la monazite. Les réserves totales de ce minerai ne sont pas connues avec précision, mais la production s'est rapidement accrue grâce au développement des industries s'occupant de l'extraction de l'ilménite, du rutile et du zircon à partir des sables de plage. En 1962, la production de monazite raffinée a été de 899 tonnes, provenant principalement des installations de traitement de l'ilménite en Australie occidentale. Le reste est venu de la Nouvelle-Galles du Sud et du Queensland. La presque totalité de cette production, y compris

les réserves accumulées de concentrés, a été exportée en Europe et aux États-Unis comme produit à haute teneur contenant 95 % et davantage de monazite.

L'extraction du thorium à partir de la monazite n'a pas été réalisée commercialement en Australie. Cependant, il existe de nombreuses possibilités de le faire avantageusement si la Commission de l'énergie atomique australienne continue à s'intéresser aux cycles de combustion Th-^{233}U et Th-^{239}Pu ou si d'autres débouchés intéressants se présentent. Plusieurs procédés d'extraction inutilement compliqués ont été proposés. D'autre part, plusieurs procédés abrégés ne donnent ni un produit suffisamment pur, ni un rendement satisfaisant. On propose ici un procédé acide simplifié permettant d'obtenir un concentré de thorium en effectuant un nombre limité d'opérations avec des quantités minimales de réactifs peu coûteux. Le rendement en thorium est supérieur à 95 %. Le concentré contient un poids approximativement égal de terres rares sous la forme de carbonates ou d'hydroxydes. En le dissolvant dans l'acide nitrique on obtient une solution-mère de nitrates se prêtant à l'extraction par le tributylphosphate comme solvant, procédé de raffinage nécessaire à la production du thorium de qualité nucléaire.

Les phases principales du procédé sont les suivantes : 1) coprécipitation totale du thorium avec les terres rares au moyen d'une solution recyclée de sulfate de soude; 2) conversion du précipité de sulfates doubles en carbonates doubles par l'action d'une solution de carbonate de soude; 3) lixiviation sélective des carbonates mixtes au moyen de l'acide sulfurique ou d'un autre acide afin de séparer le thorium d'avec les terres rares. Au besoin, la teneur en phosphate du concentré de thorium résiduel peut être diminuée par un traitement à la soude caustique.

Les sels des terres rares sont des sous-produits de valeur et on fait observer que, n'importe où, le choix entre ce procédé et le procédé alcalin le plus rentable dépend dans une large mesure du profit que l'on peut retirer de la vente des sous-produits et de la forte différence de prix qui favorise l'usage de l'acide sulfurique en Australie.

A/521 Австралия

Новый метод обогащения ториевых руд в Австралии

А. У. Уили, Э. С. Пилкингтон

Поскольку Австралия по существу не располагает промышленными месторождениями тория, сравнимыми с запасами окисленных и силикатных руд урановых месторождений Канады, торий приходится получать из монацитов. Общие запасы этого минерала точно не известны, однако добыча его быстро возрастает по мере развития переработки прибрежных песков с целью получения ильменита, рутила и циркона. В 1962 году было добыто 899 *т* обогащенного монацита, в основном на заводах, производящих ильменит в Западной Австралии. Остальная часть была получена в Новом Южном Уэльсе и Квинсленде. Почти вся эта продукция вместе с накопленными запасами концентрата была вывезена в Европу и США в виде высококачественного продукта, содержащего свыше 95% монацита.

В Австралии не предпринималось попыток организовать извлечение тория из монацита в промышленном масштабе. Однако имеется достаточное количество установок, чтобы делать это рентабельно, если у Комиссии по атомной энергии Австралии сохранится заинтересованность в топливных циклах Th — U^{233} и Th — Pu^{239} или появятся другие выгодные возможности сбыта. Предложено много сложных технологических схем извлечения тория и много упрощенных процессов, не дающих, однако, дешевого продукта соответствующей чистоты. В настоящее время предлагается упрощенный «кислотный» процесс, в результате которого при небольшом числе операций с использованием минимальных количеств недорогих реагентов получается ториевый концентрат. Извлечение тория превышает 95%. В концентрате содержится приблизительно одинаковое по весу количество редкоземельных элементов, в виде карбонатов или гидроокисей. После его обработки азотной кислотой получается соответствующий раствор нитрата для процесса жидкостной экстракции трибутилфосфатом, позволяющего рафинировать торий до ядерной чистоты.

Основными особенностями этого процесса являются: 1) количественное соосаждение тория с редкоземельными элементами рециркулирующим раствором сульфата натрия; 2) превращение бисульфатного осадка в бикарбонат обработкой содовым раствором; 3) селективное выщелачивание смешанных карбонатов серной или другой кислотой для отделения от редкоземельных элементов. Содержание фосфата в получающемся ториевом концентрате может быть при необходимости снижено обработкой концентрированной каустической содой.

Получаемые соли редкоземельных элементов представляют собой ценные побочные продукты. Отмечается, что выбор для любого завода этого процесса или наиболее конкурентоспособной «щелочной» технологии может зависеть в значительной степени от прибыли, получаемой в результате продажи побочных солей и колебаний рыночных цен на химикаты. Исходя из последнего фактора, в Австралии предпочтительнее использовать серную кислоту.

A/521 Australia

Un nuevo procedimiento para incrementar la importancia de las reservas australianas de torio

por A. W. Wylie y E. S. Pilkington

Al no existir en Australia depósitos explotables de torio comparables a los de minerales de óxido y de silicatos de los campos uraníferos canadienses, el torio local debe obtenerse a partir de la monacita. Las reservas de este mineral no se conocen con precisión, pero la producción se ha incrementado rápidamente con el crecimiento de las industrias de tratamiento de arenas de playa para la obtención de ilmenita, rutilo y circón. En 1962 se produjeron 899 toneladas de monacita refinada, procedente la mayor parte de las instalaciones de tratamiento de ilmenita del oeste de Australia, el resto de Nueva Gales del Sur y de Queensland. Casi toda esta producción, junto con reservas acumuladas de concentrado, fue exportada a Europa y a los Estados Unidos en forma de producto de alto contenido, con más del 95 % de monacita.

La extracción de torio a partir de la monacita no se ha intentado en Australia a escala comercial. Sin embargo, existen instalaciones capaces de realizarla en condiciones económicas si la Comisión Australiana de Energía Atómica mantiene su interés en los ciclos de combustible Th-^{233}U y Th-^{233}Pu, o bien si surgen otras salidas comercialmente atractivas. Para esta extracción, algunosde los procesos propuestos son innecesariamente complicados, mientras que muchos otros procesos simplificados, no conducen a un producto de puerza adecuada con rendimiento económico. En esta memoria se propone un nuevo proceso acido simplificado en el que se produce un concentrado de torio después de un corto número de pasos con cantidades mínimas de reactivos baratos. La producción de torio es superior al 95 % (del contenido). El contenido en los concentrados aproximadamente iguala, en peso, al de tierras raras en forma de carbonatos e hidróxidos. Después de disolverse en ácido nítrico, se suministra una solución apropiada de nitrato para el proceso de extracción con fosfato de tributilo como solvente, proceso necesario para separar el torio hasta alcanzar la pureza nuclear.

Las características principales del proceso son: *a*) precipitación cuantitativa simultánea del torio con tierras raras por medio de una solución reciclada de sulfato sódico; *b*) conversión del precipitado doble de sulfatos en precipitado doble de carbonatos mediante el tratamiento con una solución de carbonato sódico; *c*) lixiviación selectiva de los carbonatos mezclados con una lechada de sulfúrico ó de otro ácido para separar el torio de las tierras raras. El contenido en fosfato del concentrado residual de torio puede disminuirse, si interesa, tratándolo con hidróxido sódico concentrado.

Las sales de tierras raras son subproductos valiosos; se señala que la elección, en un lugar dado, entre este proceso y el más competitivo proceso alcalino puede estar determinada en gran parte por el aprovechamiento de los subproductos y la marcada diferencia de precios que favorece el uso del ácido sulfúrico en Australia.

Aplicación de la lixiviación en pilas *(heap-leaching)* en el tratamiento de minerales argentinos

por A. M. Cecchetto, R. C. Coppa, R. Del Boca, A. Licha y P. N. Stipanicic *

Dentro del territorio argentino existe un número de depósitos uraníferos, en los que a causa de la incidencia desfavorable de diversos factores no se hace posible la concentración económica de la totalidad o parte de sus minerales por debajo de 8 US $/lb U_3O_8, aplicando los métodos convencionales de procesamiento, por lo que los mismos no resultarían aprovechables en el presente. Al respecto, se distinguen tres casos fundamentales:

a) Yacimientos de volúmenes discretos o grandes, con menas de baja ley, las que no soportan los costos de tratamiento ni la amortización de las plantas clásicas;

b) Yacimientos con menas de ley normal o aún altas y aptas para su proceso por las vías convencionales, pero cuyas reservas no justifican la instalación de plantas en sus cercanías, a la vez que sus distancias hasta los centros de concentración impiden su transporte, por la fuerte incidencia de los fletes;

c) Yacimientos parcialmente aprovechables en sus sectores con leyes normales, cuyas menas soportan los gastos de explotación minera, transporte y procesamiento convencional, pero en los que se hace necesario dejar en mina cantidades importantes de uranio, contenido en minerales de baja ley, los que no pueden hacerlo si inciden los tres factores citados en toda su extensión.

Ejemplos típicos del primer caso lo constituyen los yacimientos de los distritos Tinogasta (Catamarca) y Punilla (Córdoba), en los cuales las reservas uraníferas alcanzan cifras de consideración, pero sus minerales, por su baja ley, no resultan económicamente aprovechables en la actualidad, ya que no pueden soportar los costos totales de procesamiento.

En la tabla 1 se incluyen algunos de los yacimientos uraníferos argentinos que quedarían comprendidos en los casos citados en *b*) y *c*). Sus minerales, entre el costo del flete y el precio propio, entrarían en la planta más cercana con un valor tan elevado que dejarían a veces un margen insuficiente para su concentración económica y otras, lo impedirían directamente, salvo que se recurriera a explotar en forma muy selectiva los sectores más ricos de los respectivos depósitos, dejando en los mismos cantidades apreciables de uranio sin extraer.

Así, varios yacimientos con leyes normales, como los distritos Sierra Cuadrada y Río Chico, en Chubut (« Sierra Cuadrada », « Cañadón Gato », « Cañadón Kruger », etc.); Rahueco y Chihuidos, en Neuquén (« La Primera », « María Teresa », etc.); Jachal, en San Juan (« Cerro Aspero », « La Cuesta », etc.) y « San Roque », en La Rioja, no podrían ser explotados en el presente, pues sus respectivos minerales llegarían a las plantas más cercanas con un valor complexivo por flete y costo propio, oscilante entre 10 y 22 dólares por kg de U_3O_8 recuperable, aún para el caso de menas con tenores uraníferos elevados (p. ej., « María Teresa », con 0,39 % U_3O_8).

En otro grupo de yacimientos, como los de los distritos Sañogasta (« San Victorio », « Santa Brígida», etc.) y Guandacol (« Sonia », « La Martita », « Urcal », etc.) en La Rioja; San Isidro (« Soberanía », etc.) en Mendoza y Comechingones (« Estela », etc.) en San Luis, sólo resultarían aprovechables los minerales más ricos, con leyes por lo general superiores a 0,2 % U_3O_8, debiendo dejarse en mina, sin extraer, volúmenes importantes de uranio, contenido en menas con tenores discretos y aún normales (0,1 a 0,2 % U_3O_8).

Finalmente, otro ejemplo típico lo constituyen los depósitos del grupo Huemul, en Mendoza (« Huemul », « Agua Botada », « Arroyo Seco », etc.), los que abastecen de mineral a Planta Malargüe, con ley media de entrada a la misma de 0,18 % U_3O_8. Para alcanzar tal contenido, el tenor de corte mínimo en boca mina no puede bajar de 0,06 % U_3O_8, lo que obliga a desechar proporciones elevadas de material ya extraído con valores que oscilan entre 0,04 y 0,06 % U_3O_8, o bien dejar de explotar paños enteros del yacimiento, con leyes del mismo orden.

Los casos anteriores movieron a la Gerencia de Materias Primas de la CNEA a buscar una solución a los problemas citados, tendiendo a posibilitar no sólo el aprovechamiento económico de los minerales de yacimientos alejados o de baja ley, sino también la de permitir una explotación más integral y orgánica de los mismos y de otros que poseen reservas apreciables con tenores marginales, al lado de las actual-

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* Comisión Nacional de Energía Atómica.

Tabla 1

Yacimiento		Planta concentración		Costo kg U_3O_8 recuperable en mineral entrado planta (en US $)		
Minas	Ley % U_3O_8	Distancia km	Rto. %	Flete	Valor mineral	Costo total
San Victorio, etc. (La Rioja)	0,1	470	85	6,60	3,90	12,50
	0,15		90	5,40	4,25	9,65
	0,25		90	3,25	4,25	8,50
San Roque (La Rioja)	0,175	430	70	7,15	5,50	12,65
La Martita, etc. (La Rioja)	0,15	580	85	9,15	4,45	13,60
	1,0		95	1,25	5,00	6,25
Cerro Aspero, etc. (San Juan)	0,15	750	90	9,75	4,25	14,00
	0,25		90	5,85	4,25	10,10
Soberanía, etc. (Mendoza)	0,15	650	90	6,50	4,25	10,75
	0,22		90	4,40	4,25	8,65
Estela (San Luis)	0,1	620	90	8,45	3,90	12,35
	0,15		94	5,40	4,05	9,45
	0,28		95	2,85	4,05	6,90
La Primera, etc. (Neuquén)	0,165	400	90	14,25	4,25	18,50
María Teresa, etc. (Neuquén)	0,15	400	90	15,70	4,25	19,95
	0,39		90	6,00	4,75	10,75
Cañadón Gato, etc. (Chubut)	0,15	2 450	90	15,15	4,25	19,40
Sierra Cuadrada (Chubut)	0,15	2 570	90	17,85	4,25	22,10

Nota: En los costos de los fletes inciden no solamente las distancias sino también las ubicaciones geográficas y topográficas de los yacimientos, la calidad de los caminos, cercanías a las rutás principales, etc.

mente recuperables. La situación de estos depósitos argentinos se relaciona, por otra parte, con un hecho indiscutible y perfectamente fundamentado por varios autores [1-3] sobre la necesidad creciente de recurrir a minerales de uranio, que por sus características, ubicación de sus yacimientos o por su baja ley, no permiten un tratamiento por el clásico método de agitación.

La tecnología a aplicar, en líneas generales, se orientó en la Argentina según dos sentidos: *a*) eliminación de la incidencia del costo del transporte; *b*) máxima reducción de los costos totales de procesamiento.

Sobre tales bases quedó sentada la absoluta necesidad de que el procesamiento, total o parcial, se hiciese en las minas o en sus cercanías y que en la etapa de lixiviación debería reducirse al máximo la incidencia de cuatro factores que afectan fundamentalmente a los costos de producción: grado de molienda, consumo de reactivos, consumo de energía y amortización de equipos de alto precio. Desde un principio, se consideró que dos variantes ofrecían soluciones posibles al problema: *a*) lixiviación del mineral *in situ*, dentro de la mina; *b*) lixiviación del mineral en pilas.

El primer sistema tiene posibilidades de aplicación muy limitadas, y por el momento sólo se lo piensa ensayar en algunos sectores del yacimiento « Don Otto », en Salta, para recuperar el uranio de sectores con baja ley, cuyos minerales no soportan los costos de explotación minera.

Por dicho motivo, se prestó especial atención al segundo camino, el de la lixiviación en pilas, al que se dedicó un grupo de trabajo, creado al efecto: el Departamento de Lixiviación Natural de la Gerencia de Materias Primas, el cual comenzó a estudiar y ensayar el comportamiento a la lixiviación en pilas de un número elevado de minerales uraníferos argentinos, sea bajo tratamiento ácido, alcalino o mediante sales hidrolizables, investigando en cada caso la influencia de diversos factores, como se detalla más adelante.

METODO APLICADO

Consideraciones físico-químicas

Son conocidas las condiciones básicas que rigen el proceso de la lixiviación y que se han definido así [4]: *a*) las substancias a extraer deben quedar expuestas; *b*) las partes expuestas de las substancias han de ser accesibles al agente lixiviante; *c*) debe producirse el transporte de las substancias desde los lugares expuestos al seno de la solución lixiviante.

Salvo el tercero, estos criterios son de naturaleza física, debiéndose notar que la movilidad de los componentes desde puntos expuestos en la superficie de una partícula se puede hacer efectivo por convección (extracción por agitación), mientras que el transporte desde puntos interiores de la partícula se efectúa generalmente por difusión.

El método de lixiviación en pilas es una aplicación característica de extracción sólido-líquido basada en el último concepto. Pero la definición de los parámetros adecuados que caractericen los aspectos físicos de este tipo de lixiviación es un problema aún no completamente esclarecido.

En principio, hay que considerar el equilibrio que se tiende a alcanzar durante la operación y la velocidad con que se llega al mismo, en función de los diversos factores que pueden afectar a una y otra. Estos factores pueden ser: la porosidad, la superficie específica, la permeabilidad, la difusibilidad y la tensión superficial. La determinación de los dos primeros (porosidad y superficie específica) permitirían asimilar este caso al escurrimiento laminar de un fluído a través de una capa porosa, entrando en el dominio gobernado por la ecuación de Kozeny-Carman [5].

El conocimiento que se posee sobre la interfase líquido-sólido es escaso y por ello el mecanismo primario del cambio de fase de un soluto presente inicialmente en forma sólida, del cual depende la cinética del proceso, permanece oscuro, haciendo imposible el desarrollo de una teoría general para esta operación, similar a las que se establecen para el intercambio líquido-líquido o líquido-gas. Además, la aplicación de las ecuaciones de difusión conduce a resultados dudosos debido a la influencia de otras fuerzas, como p.ej. la capilaridad.

Puestos en la necesidad de obtener datos valederos para su utilización en escala productiva industrial, esta primera etapa de estudios se encaró en la Argentina en función de su aplicabilidad inmediata, pero permitió, no obstante ello, evidenciar ciertas observaciones interesantes.

Glosario de términos adoptados

Con el objeto de uniformar una terminología que defina el concepto de ciertos factores empíricamente adoptados y de algunos estados que rigen la operación, se estableció el siguiente glosario:

1. *Lixiviación en pilas:* es el equivalente a la expresión anglo-sajona *heap-leaching* y a la expresión francesa *lixiviation en tas*. No define el mecanismo de la operación, sino la conformación geométrica del sistema.

2. *Velocidad de percolación:* es el volumen de líquido que atraviesa una sección de la pila en la unidad de tiempo. Se expresa en litros por hora y por metro cuadrado (l/h m^2).

3. *Velocidad de circulación:* es el volumen de líquido que circula a través de cierta masa de mineral en la unidad de tiempo. Se expresa en litros por día y por tonelada (l/d t).

4. Volúmenes de soluciones que intervienen en la lixiviación:

a) *Volumen total* (V_t): es igual a la suma de los volúmenes circulante, humectante y empapante ($V_t = V_c + V_h + V_e$);

b) *Volumen circulante* (V_c): es la cantidad de líquido al exterior del sistema;

c) *Volumen humectante* (V_h): es la cantidad de líquido que retiene una pila una vez drenado el volumen empapante. Corresponde a la « humedad máxima » que retiene el mineral en las condiciones de la experiencia o del proceso;

d) *Volumen empapante* (V_e): es la cantidad de líquido circulando en el interior de la pila mientras se realiza un riego constante. Corresponde al volumen de solución distribuído en los espacios intergranulares del mineral.

5. *Neutralización:* período comprendido entre el comienzo de la acidificación y el momento en que los líquidos de salida alcanzan pH 3,0.

6. *Extracción:* período que se extiende desde el momento en que los líquidos de salida acusan pH 3,0 hasta que se alcanza la máxima solubilización del uranio presente en el mineral.

7. *Lavado:* período definido por el desplazamiento de la solución fértil empapante mediante soluciones frescas, hasta llegar en la solución de salida a la mínima concentración compatible con la economía del proceso *.

TECNOLOGÍA

Como se ha dicho, hay una necesidad mundial creciente de recurrir a minerales de uranio que por sus características, ubicación de sus yacimientos o por su baja ley no permiten su beneficio económico por el método clásico de extracción sólido-líquido con agitación. Para estos casos adquiere singular importancia la definición de un método de lixiviación que reduzca cuatro factores que inciden notoriamente en los costos de producción: grado de molienda, consumo de reactivos, consumo de energía y amortización de equipos. A la vez, si el objetivo es llegar a un preconcentrado intermedio, se deben regular las condiciones de tratamiento a fin de alcanzar la mayor selectividad de extracción con respecto al uranio, ya que reduciendo la incorporación de elementos extraños se obtiene una mayor ley en dicho metal en el producto intermedio. La tecnología a aplicar en el método de la lixiviación, sea en columnas o en pilas, es la siguiente:

El mineral, reducido al grado óptimo de granulometría y dispuesto según cierta forma geométrica, es regado desde la superficie superior por la solución lixiviante. El riego se realiza mediante la formación de un espejo de líquido y la velocidad de circulación se regula con una capa de arcilla de espesor variable.

La solución que se difunde a través de la masa de mineral, en el transcurso de recirculaciones sucesivas neutraliza, en primer término y tratándose de lixiviación ácida, la alcalinidad del mineral y luego

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* Evidentemente, no hay una delimitación neta entre los tres períodos con relación al grado de extracción del uranio. Se adoptan estas definiciones al solo efecto de una mejor interpretación de la evolución del proceso.

inicia la extracción neta del uranio y parte de los elementos acompañantes.

Cuando la solución lixiviante llega a la carga máxima en uranio, definida por el máximo rendimiento de extracción obtenible, se separa del sistema y se precipita con lechada de cal.

Ensayos en escala de laboratorio

Un primer ensayo exploratorio se realiza en columnas de vidrio de 0,50 m de altura y 0,05 m de diámetro. Demostrada la aptitud del mineral para ser tratado por este método, se pasa al primer ensayo riguroso en columnas de 2,00 m de altura y 0,30 m de diámetro.

A continuación se detallan algunos ejemplos de ensayos efectuados sobre minerales de yacimientos argentinos.

« *Estela* » (San Luis)

Mena de ganga ácida, constituída por un granito brechoide, en partes muy meteorizado y atravesado por venas de fluorita fétida. La especie uranífera dominante es uranofano, la cual impregna en delgadas capas el granito y la fluorita. Los datos corresponden al caso extremo de una recuperación de escombreras con ley 0,032 % U_3O_8. El mineral, triturado a 10 mm, de modo tal que se obtiene un 50 % entre mallas 2 y 5 Tyler, se trató durante 140 días con solución de ácido sulfúrico a pH 2, manteniendo una velocidad de percolación de 15 l/h m². El rendimiento de extracción fué de 87,5 % en U_3O_8.

« *Los Adobes* » (Chubut)

La mena está constituída por un sedimento arenoso conglomerádico, con cemento silíceo y minerales amarillos de uranio (uranofano, schroeckingerita y fosfuranilita), que tapizan los granos menores. La muestra, con una ley de 0,16 % U_3O_8, triturada a 10 mm, fué sometida a dos tratamientos comparativos:

a) Con ácido sulfúrico en solución a pH 1,5;

b) Con sulfato ferroso incorporado en la masa del mineral, en una relación del 4 % de $SO_4Fe \cdot 7\,H_2O$ y regado con agua.

En este ensayo orientativo, los rendimientos de extracción alcanzaron al 85 y 75 %, respectivamente, para los dos casos señalados (figura 1).

« *Palo Quemado* » y « *María Teresa* » (Neuquén)

Caracterizados como menas complejas de uranio, vanadio y cobre. La mineralización de uranio consiste principalmente en carnotita, a la que se asocian minerales carbonatados de cobre, volborthita, hematita, jarosita y materia carbonosa.

Elementos	« Palo Quemado »		« María Teresa »	
	Ley	Rto.	Ley	Rto.
U_3O_8	0,14 %	90,0 %	0,33 %	91,0 %
CuO.	3,21 %	96,7 %	0,69 %	93,2 %
V_2O_5	2,74 %	27,0 %	4,50 %	22,3 %
Granulometría . . .	75 % entre M 5 y 50		80 % entre M 5 y 50	
Velocidad percolación.	10 l/h m²		10 l/h m²	
Tiempo tratamiento.	160 días		135 días	
Solución lixiviante .	SO_4H_2 a pH 1,0		SO_4H_2 pH 2,0 (60 días) SO_4H_2 pH 1,0 (75 días)	

« *Don Otto* » (Salta)

La mena está constituída por material areniscoso y lutítico. El componente psamítico se integra con granos

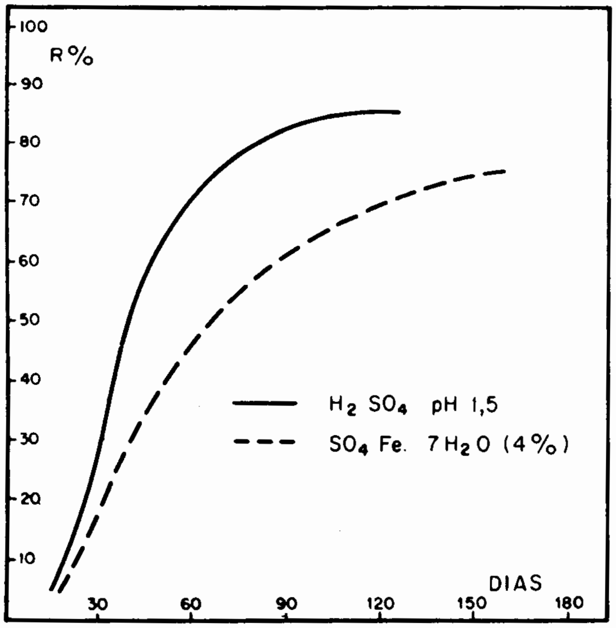

Figura 1. Ensayos comparativos de mena de « Los Adobes »

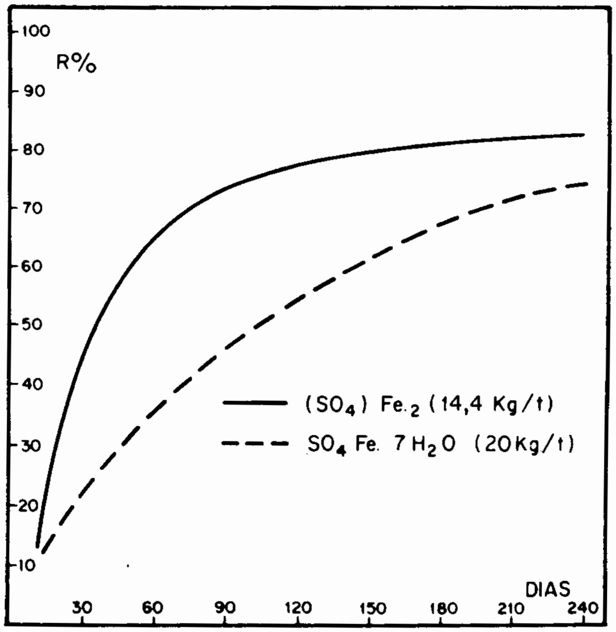

Figura 2. Ensayos comparativos de mena de « Don Otto »

de cuarzo cementados por material arcilloso y el lutítico está constituído por arcilla levemente compactada en forma de láminas. Las especies minerales son: meta-autunita, tyuyamunita, schroeckingerita y carnotita.

En la figura 2 se reproducen los resultados de dos ensayos comparativos: *a*) incorporando sulfato ferroso en la masa del mineral, a razón de 30 kg de $SO_4Fe \cdot 7\ H_2O$/t; *b*) incorporando sulfato férrico a razón de 21,6 kg de $(SO_4)_3Fe_2$ por tonelada de mineral, regando en ambos casos con agua.

Los rendimientos de extracción para los dos casos señalados fueron de 82 y 74 %, respectivamente. Estos resultados abren favorables perspectivas para el reemplazo del ácido sulfúrico, de difícil y costoso acarreo hasta el yacimiento « Don Otto », por materias sólidas productoras de ácido por hidrólisis en el seno de una pila.

Ensayos en escala piloto

La realización del ensayo en esta escala permite definir con razonable exactitud las condiciones óptimas de operación. La experiencia se lleva a cabo en una columna de 4 m de altura y 1,30 m de diámetro, que en la parte inferior posee un lecho filtrante de 0,30 m de espesor, constituído por capas sucesivas de grava de 2 y 1 pulgada, arena gruesa y fina. Un depósito superior permite mantener el riego constante de la columna durante 24 horas. Un depósito colector en la base reúne los líquidos de drenaje: cada 24 horas se reajusta el pH y por bombeo se lo envía nuevamente al depósito superior para repetir el ciclo. Cuatro embudos colectores dispuestos en el seno del mineral a distintas alturas permiten recibir muestras de líquido.

Se reproducen los resultados del ensayo que se efectuó sobre el mineral del yacimiento « Don Otto », cuya composición es la siguiente:

Pérdida por calcinación	2,2 %
U_3O_8	0,165 %
P_2O_5	0,195 %
Al_2O_3	16,0 %
CaO	2,0 %
Fe_2O_3	1,7 %
SiO_2	72,0 %

Condiciones de operación:

Tiempo de tratamiento . . . . . . (neutralización y extracción).	206 días
Consumo de ácido sulfúrico. . . .	18 kg/t
Volumen total de líquido	229 l/t
Relación sólido-líquido.	4,4/1

Rendimientos:

a) Por fracción granulométrica:

7% mayor de 22,6 mm (0,33% U_3O_8)	87, 9%
38% entre 22,6 y 4 mm (0,22% U_3O_8)	90,0 %
55% menor de 4 mm (0,12% U_3O_8)	90,9 %

b) Por altura de columna:

Hasta 1 metro.	94, 0%
Hasta 2 metros	88,5 %
Hasta 3 metros	87,3 %
Hasta 4 metros	87,3 %

Como solución lixiviante se empleó en principio ácido sulfúrico a pH 1,5 y a partir de los 125 días a pH 1,2. Un pH mayor no es aconsejable en razón de la interferencia del fósforo presente en la especie mineralógica.

El sistema de riego adoptado (recicle permanente de la solución con ajuste de pH), permitió alcanzar una concentración en U_3O_8 de hasta 7 g/l. El tiempo de tratamiento es susceptible de ser reducido a 180 días si se lo inicia directamente a pH 1,2 y si simultánemente se abrevia el período de neutralización aplicando la máxima velocidad de percolación admitida por el sistema (30 l/h m^2), hasta llegar a pH 3,0 en los líquidos de salida.

En la curva que representa el consumo de ácido en función del tiempo se evidencía un hecho interesante: en el período de extracción se revela aparentemente una condición de equilibrio indicada por la relación « kilogramo de ácido consumido por tonelada y por día », y que para este caso específico resultaría igual a 0,08 kg/t día, aproximadamente.

Esta condición estaría ligada con la tendencia a mantenerse constante la diferencia de los pH de entrada y de salida de los líquidos durante el período de extración, para condiciones estables de percolación. La misma podría der el valor de la relación « acidez-velocidad de circulación-tiempo de contacto ». Es posible que este concepto indique una constante para cada tipo de mineral, definida como su capacidad para ser extraído en función del tiempo.

Con el objeto de establecer una relación más ajustada entre los resultados de un ensayo experimental y los de una pila de producción, es conveniente ampliar el criterio de representación gráfica: *a*) graficando las variables físico-químicas del proceso en función del tiempo, como control de las condiciones de trabajo del proceso; *b*) graficando las variables químicas puras en función de los kilogramos de ácido consumido por tonelada de mineral, como observación de las condiciones químicas del proceso. El factor « kg/t » aparece en el sistema 1 como curva operativa y en el sistema 2 como coordenada. Este factor relaciona los dos sistemas.

La figura 3 es un ejemplo de representación según el segundo criterio, y corresponde a la evolución de los valores de concentración, rendimiento y pH de salida en función de los kilogramos de ácido sulfúrico por tonelada de mineral consumidos por el sistema.

Con los datos obtenibles de estas curvas es relativamente sencillo predecir en forma aproximada la composición del precipitado cálcico en cualquier momento de la operación. Para ello, basta aplicar la

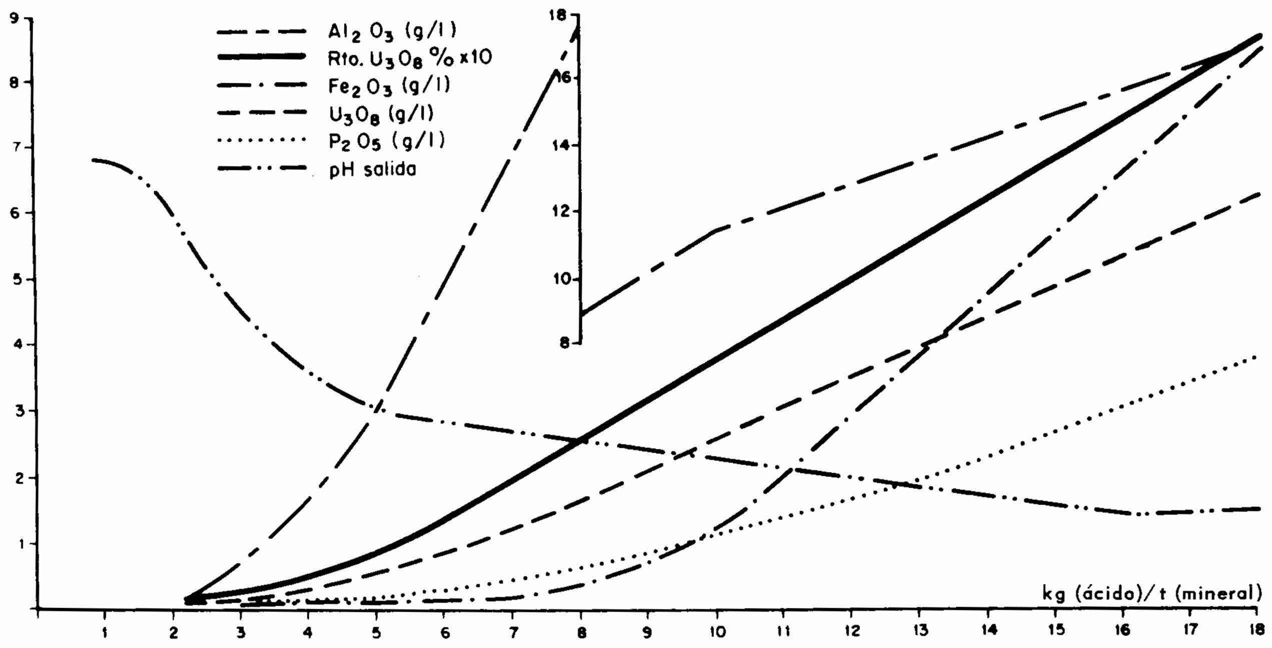

Figura 3

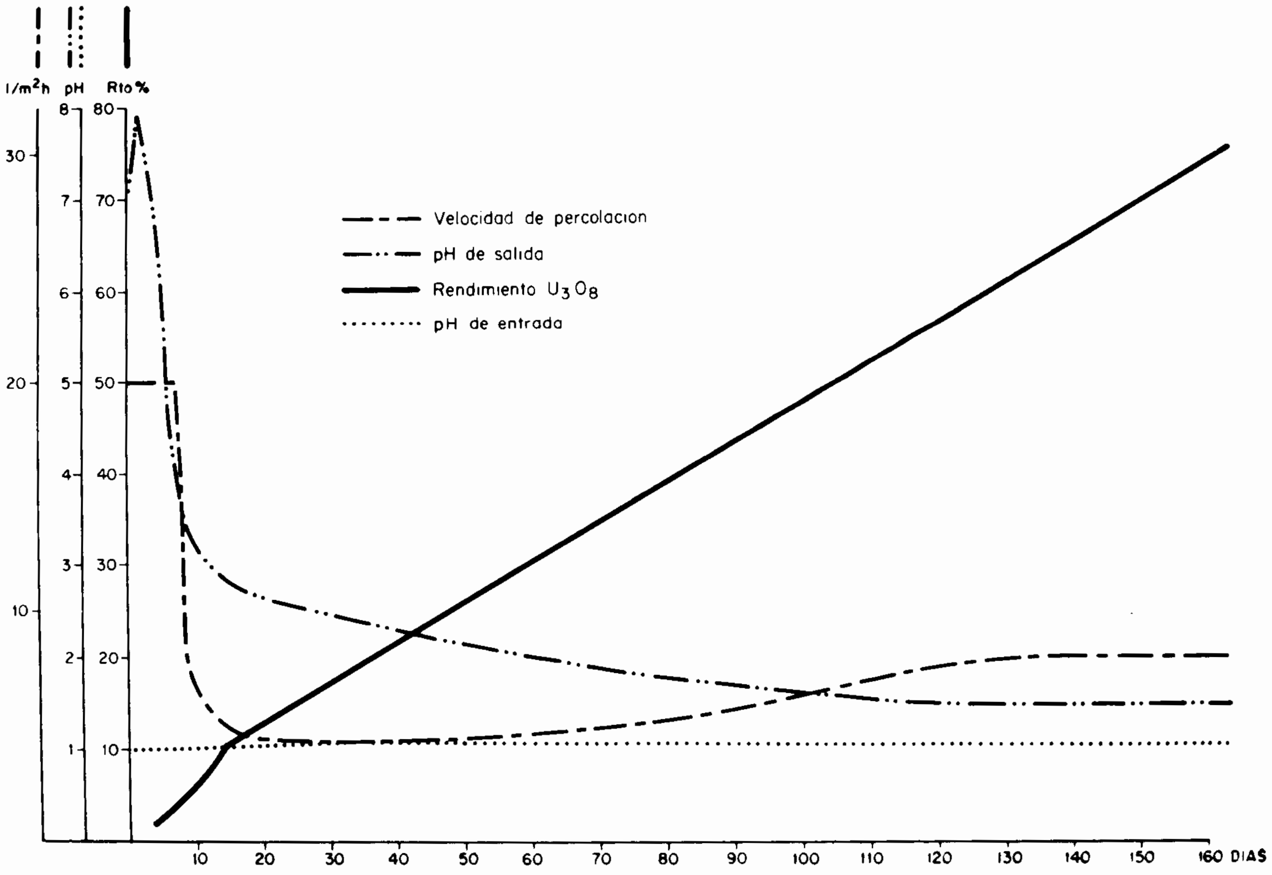

Figura 4. Evolución promedio de la operación

fórmula que se acompaña, en la cual los símbolos entre paréntesis expresan « concentración en g/l », y cuya resolución da por resultado los gramos de preconcentrado cálcico seco a obtener por litro de solución a precipitar:

$$Ps = 1{,}7(U_3O_8) + 5{,}0(Al_2O_3) + 3{,}5(Fe_2O_3) + (P_2O_5) + 1{,}4)SO_4H_2 \text{ libre})$$

Ensayo en escala experimental

Se realiza para verificar la repetición de los datos ofrecidos por el ensayo piloto. Consiste en el funcionamiento de una pila de 700 toneladas de mena, de forma tronco-piramidal, con dos de sus lados limitados por el talud natural del mineral y los otros dos por un cerco perimetral, tal como se describe más adelante.

La conclusión más importante que permitió establecer este ensayo es la influencia del talud. Este sector prismático triangular no se humecta uniformemente y las soluciones que provienen del cubo central migran por la parte inferior del talud hacia los bordes de la pila, desde donde ascienden por la cara exterior, se evaporan y precipitan sales de uranio cristalizadas.

DESCRIPCIÓN DE UNA INSTALACIÓN PRODUCTIVA INDUSTRIAL

El objetivo de esta primera instalación fué el tratamiento de 36 000 toneladas del yacimiento « Don Otto », con una ley media de 0,15 % U_3O_8.

El mineral, groseramente triturado (30 % entre 12 y 50 mm y 70 % de 12 mm), se dispuso sobre planchadas impermeabilizadas y con suave declive hacia uno de los ángulos, con una capacidad de carga de 2 000 toneladas cada una y con una altura media de 4 metros. La impermeabilización se obtuvo disponiendo bandas de fieltro asfáltico sobre la superficie lisa de la planchada, superponiendo los bordes de las bandas y soldándolas con asfalto fundido. Se depositaron luego capas sucesivas de asfalto fundido hasta alcanzar un espesor de 5 mm, distribuyendo finalmente arena muy fina para lograr una mayor consistencia. El cerco perimetral se construyó con parantes de madera, reforzados con puntales a 45°. Para unir los parantes se dispusieron 5 filas horizontales de rieles decauville en desuso. Sobre los rieles y hacia el interior de la pila se extendió tejido de alambre de malla rómbica de 1,5 pulgadas y finalmente, sobre el tejido, se colocaron sucesivamente bandas de fieltro asfáltico, con superposición de 10 cm entre dos contiguas y sin adhesivo entre ellas. Entre dos pilas consecutivas no existe ningún elemento de separación. Entre la superficie impermeabilizada de la planchada y el mineral apilado se dispuso un lecho filtrante de cantos rodados, que permite el drenaje de los líquidos. Estos se colectan en tanques de fibro-cemento recubiertos con pintura asfáltica.

En definitiva, cada pila tiene una forma paralepipédica, de 36 metros de largo, 8 metros de ancho y una altura media de 4 metros. El conjunto de las 18 pilas apareadas constituyen una instalación de 144 metros de largo por 36 metros de ancho.

La solución lixiviante se vierte sobre la superficie de cada pila, regulándose la velocidad de percolación mediante una capa de arcilla de espesor variable, dispuesta sobre el mineral. La solución circula a través del mineral y se colecta en la base de la planchada, donde el lecho de cantos rodados facilita el drenaje normal. En el tanque colector se ajusta el pH de la solución y se recircula por bombeo a la superficie de la pila.

Este ciclo (percolación, ajuste de pH, bombeo, percolación) se repite sucesivamente hasta obtener la máxima solubilización del uranio presente en el mineral. En ese momento, se desplazan del sistema las soluciones ricas mediante lavados con soluciones frescas a pH 1,2. Las soluciones se precipitan con lechada de cal y el producto, escurrido y seco, se despacha como preconcentrado cálcico a la planta de refinación sita en Córdoba. Para este caso particular del mineral del yacimiento « Don Otto », la evolución promedio de la operación está representada sintéticamente en la figura 4.

CONCLUSIONES

El método de la lixiviación en pilas, cuando es factible de ser aplicado, presenta las siguientes ventajas:

1. Una economía del 35 % en las amortizaciones de equipo respecto a una planta convencional, considerando solamente las etapas de preparación física y lixiviación del mineral.
2. Una economía del 20 % en el consumo de reactivos (ácido sulfúrico) respecto al de la planta convencional, aún incluyendo el ácido necesario para la redisolución del preconcentrado.
3. Una economía del 35 % en el consumo de energía, respecto al de una planta convencional.
4. Una mayor selectividad en la lixiviación, al trabajar con débil acidez, lo que evita la incorporación de impurezas, hecho inevitable en las plantas clásicas, donde se trabaja con concentraciones elevadas de ácido.
5. Reduce sensiblemente, de 50 a 100 veces, el costo del flete, pues suplanta el transporte del mineral de baja ley por el de un preconcentrado con alto tenor.
6. Posibilita el aprovechamiento de los minerales de yacimientos muy distantes o de difícil acceso, en los cuales el costo del transporte de los mismos es muy elevado.
7. Posibilita el aprovechamiento económico de minerales de uranio de baja ley, y permite además

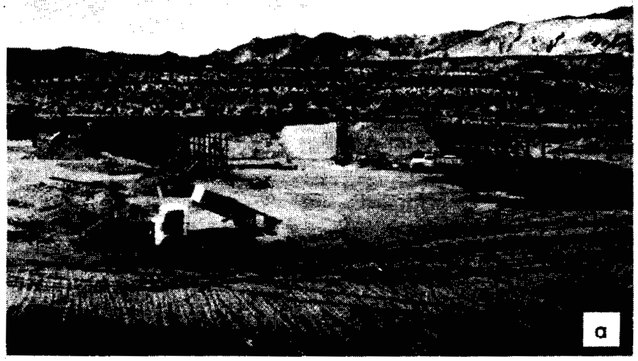

Figura 5a. Vista general de la estación de lixiviación « Don Otto », cargada con 17 000 t de mineral

Figura 5b. Vista lateral de las pilas, mostrando detalles del cerco perimetral, tanques de ácido sulfúrico, tanques colectores de soluciones y bombas para movimiento de líquidos

Figura 5c. Vista de los tanques colectores de soluciones y bombas para movimiento de líquidos

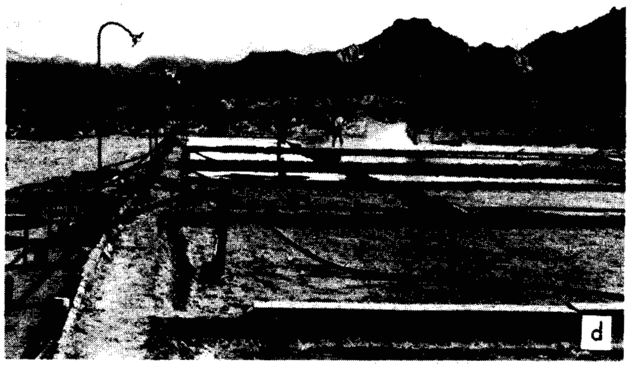

Figura 5d. Vista de la superficie superior de las pilas, mostrando en la parte posterior el espejo de riego

una explotación minera más integral de los yacimientos, al hacer factible una disminución de la ley de corte. Inclusive, puede transformar en útil el mineral de escombreras.

8. La posibilidad de utilización de reactivos sólidos productores de ácido por hidrólisis (sales ferrosas o férricas), disminuye los inconvenientes y costos del transporte de drogas corrosivas líquidas.

9. Permite una mayor simplicidad en las operaciones y medio de control, factores que pueden revestir importancia en relación con la calidad de mano de obra y supervisión disponibles en algunos lugares.

10. Permite la utilización de materiales rústicos y baratos, obtenibles generalmente en las zonas de operación.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/768 Argentina

Application of heap-leaching to the processing of Argentine ores

By A. M. Cecchetto *et al.*

The great area of Argentina and the scattered distribution thereon of numerous uranium ore bodies possessing special characteristics has made it necessary to study the possibility of applying heap-leaching as an economic method of ore processing.

The need to attempt processing with unconventional methods arises from the presence of various unfavourable factors, such as:

(*a*) The existence of deposits of reasonable size but low grade, whose ores do not justify the cost of transport to distant processing centres and whose low uranium content makes the installation of a conventional processing plant an uneconomic proposition;

(*b*) The existence of many uranium ore bodies of medium, normal or even high grade, but of insufficient size to justify setting up conventional concentrating plants, added to the considerable freight costs entailed in transporting to the processing plant;

(*c*) The existence of deposits from which normal grade ores can be obtained by selective working methods but which, fail to extract appreciable quantities of uranium present in marginal or low grade ores, so that the deposits are not fully exploited.

The paper briefly reports the results of heap-leaching trials carried out with various Argentine uranium and copper-uranium ores, on both laboratory and semi-pilot plant scale, more particular attention being devoted to the results for one typical ore, that from the Don Otto deposit (Salta Province).

The study for this special case includes:

(*a*) General considerations regarding the method;

(*b*) Laboratory tests using 1-metre columns;

(*c*) Intermediate-stage tests using 4-metre columns;

(*d*) Results of treating an experimental heap of 700 tons of ore;

(*e*) Description of a production plant for the treatment of 36 000 tons of ore.

The method adopted can be summarized as follows: the coarsely-milled ore is placed on a water-proofed platform tilted slightly towards one corner. The parallelepipedal heap of ore, with vertical sides held in place by a suitable surround, has a horizontal top surface. The leaching solution is poured over the surface of the heap and the percolation rate is controlled by a layer of clay of variable thickness on top of the ore. The solution circulates through the mass and collects at the level of the platform, where a pebble bed facilitates normal drainage, thence passing into a collecting tank. Here the pH of the solution, which has been partially neutralized during its passage through the ore, is adjusted and the solution is then pumped to the top of the heap. This cycle (percolation-pH adjustment-pumping-repercolation) is repeated until the maximum quantity of uranium has been leached out of the ore, after which the rich solutions are removed by washing with acid water. The uranium-bearing liquids are then recovered by precipitation with milk of lime and, after drying, the lime preconcentrate is sent to a plant for final purification.

A/768 Argentine

Application de la lixiviation en tas (heap-leaching) pour le traitement des minerais argentins

par A. M. Cecchetto *et al.*

La grande extension du territoire argentin, et la distribution irrégulière des nombreuses manifestations uranifères, avec caractéristiques spéciales, ont obligé à étudier les possibilités de l'application des méthodes de lixiviation en tas (heap-leaching) en vue d'un traitement économique de ces minerais.

Le besoin d'essayer de concentrer ces minerais par des méthodes non classiques est dû à plusieurs facteurs défavorables, entre lesquels on peut mentionner principalement :

a) L'existence de gisements relativement grands mais pauvres, dont les minerais ne justifient pas le coût du transport jusqu'aux centres de traitement éloignés, dont la basse teneur en uranium ne justifie pas non plus l'installation d'une usine classique de traitement qui puisse fonctionner de manière rentable.

b) L'existence des nombreux gisements uranifères, à teneurs moyennes normales, et même élevées qui, étant trop petits, ne permettent pas d'installer des usines classiques de traitement d'une part et, d'autre part, sont trop éloignés des centres de traitement existants en raison de quoi leur transport devient trop onéreux.

c) L'existence de gisements d'où l'on peut extraire un minerai à teneur normale grâce à une exploitation sélective, mais où restent des quantités appréciables d'uranium en concentrations marginales ou basses, qu'il est impossible d'utiliser intégralement.

Le mémoire rend compte succinctement des résultats des essais de lixiviation en tas réalisés avec différents minerais argentins d'uranium ou de cuivre et uranium, aussi bien en laboratoire que dans des instal-

lations semi-pilotes, avec une analyse plus détaillée des résultats correspondant à un minerai caractéristique, celui du gisement Don Otto (province de Salta).

L'étude de ce cas spécial s'est faite selon le plan suivant :

a) Études d'ordre général sur la méthode appliquée;

b) Essais de laboratoire avec colonnes de 1 m;

c) Essais à l'échelle moyenne, en colonnes de 4 m;

d) Résultats de l'opération sur un tas expérimental de 700 t;

e) Description d'une installation pour le traitement de 36 000 t de minerai.

La méthode adoptée peut être décrite rapidement de la manière suivante : Le minerai grossièrement concassé est déposé sur un dallage imperméable présentant une pente très douce vers l'un des angles. Le tas de minerai à la forme d'un parallélépipède à des faces latérales verticales, maintenues sur son périmètre et à face supérieure horizontale. La solution de lixiviation est versée sur la surface du tas, le débit de percolation étant réglé au moyen d'une couche d'argile d'épaisseur variable disposée sur le minerai. La solution circule à l'intérieur du tas et est collectée à la base du dallage, où se trouve un lit de gravier qui permet un drainage normal. De là elle est conduite à un bassin collecteur. Dans ce bassin, on ajoute le pH de la solution partiellement neutralisée pendant son passage à travers le tas de minerai puis on renvoie la solution à la surface du tas. Ce cycle (percolation-ajustement du pH-pompage-percolation) est répété jusqu'à la dissolution maximale de l'uranium contenu dans le minerai. Ensuite les solutions riches sont déplacées au moyen d'un lavage à l'eau acidulée. Les liqueurs uranifères sont traitées par précipitation à la chaux et le préconcentré, une fois sec, est expédié à une usine pour le traitement final.

A/768 Аргентина

Применение кучного выщелачивания для переработки аргентинских руд

А. М. Чекетто *et al.*

Большая территория Аргентины и разбросанное расположение на ней многочисленных урановых залежей, имеющих разнообразные характеристики, потребовали изучить возможности кучного выщелачивания руд как дешевого способа их переработки.

Необходимость прибегнуть к необычной технологии была вызвана целым рядом неблагоприятных факторов, среди которых следует указать главным образом на следующие.

a. Наличие довольно крупных, но бедных по содержанию металла месторождений, руду которых невыгодно перевозить до удаленных перерабатывающих центров, а строительство на месте обычного гидрометаллургического завода также нерентабельно потому что стоимость переработки такой бедной руды не могла бы уложиться в экономичные рамки.

b. Наличие многих урановых месторождений со средним и даже с высоким содержанием урана в рудах, но настолько небольших по запасам, что организация перевозки их к существующим заводам так же была бы невыгодной.

c. Наличие месторождений, позволяющих добывать руды с нормальным содержанием урана, посредством селективной разработки, но с оставлением значительных количеств бедных руд, то есть с условием неполной отработки этих месторождений.

В настоящем докладе сообщаются основные результаты опытного кучного выщелачивания, проведенного с несколькими типами урановых и медно-урановых аргентинских руд как в лабораторном, так и в полупромышленном масштабе; особое внимание уделено результатам испытания типичной руды с месторождения «Дон-Отто» (в провинции Де-Сальта).

Исследования этого особого случая включают:

Общие соображения относительно применяемого метода.

Лабораторные испытания в колоннах высотой 1 *м*.

Промежуточные испытания в колонне высотой 4 *м*.

Результаты обработки экспериментальной кучи 700 *т*.

Описание промышленной установки для переработки 36 000 *т* руды.

Принятый метод может быть вкратце изложен следующим образом:

Крупнодробленая руда помещается на водонепроницаемой платформе, сделанной с небольшим уклоном в направлении одного из углов. Параллелепипедообразная куча руды, удерживаемая по периметру вертикальными стенками, имеет горизонтальную верхнюю поверхность. Выщелачивающий раствор подается на эту поверхность кучи, и скорость его просачивания контролируется слоем глины различной толщины сверху руды. Раствор просачивается через толщу кучи и стекает по поверхности платформы, где слой гравия обеспечивает нормальный дренаж; затем раствор собирается в коллектор. В коллекторе регулируется pH раствора, подвергаемого частичной нейтрализации во время просачивания через руду; затем раствор снова подается на поверхность рудной кучи. Этот цикл (просачивание, регулирование pH, выкачивание, просачивание) повторяется до максимального выщелачивания урана из руды. После этого обогащенные ураном растворы вымываются подкисленной водой и подвергаются осаждению урана известковым молоком; после обезвоживания и сушки карбонатный грубый концентрат отправляется на завод для окончательной рафинировки.

Técnicas de prospección aérea radimétrica y emanométrica terrestre aplicadas en la República Argentina

por C. T. Friz, J. L. Gamba, R. J. A. Jemma, K. Marinkeff y C. G. M. Martínez *

PROSPECCIÓN AÉREA RADIMÉTRICA

Yacimientos radiactivos

En la República Argentina, los primeros trabajos de prospección aérea destinados a la búsqueda de yacimientos radiactivos se iniciaron a mediados del año 1958. A partir de dicha fecha, y como consecuencia de los resultados obtenidos, el método se fué aplicando en forma progresiva, hasta llegar al año 1960, en que pasó a ser utilizado con carácter regular y en forma casi exclusiva para el reconocimiento y prospección de amplias zonas con interés uranífero. Las ventajas del sistema, juntamente con las características naturales del país, demostraron que en áreas previamente seleccionadas, la prospección aérea resulta altamente eficaz por su rapidez y economía.

El perfeccionamiento alcanzado en el desarrollo de instrumental y equipos, en las técnicas operativas de campaña y en la interpretación de los registros en gabinete, permiten afirmar que aplicando correctamente este método, el hallazgo de un depósito uranífero depende casi exclusivamente de la presencia de afloramientos próximos a la superficie.

Instrumental y equipos

El instrumental y equipos utilizados no difieren en general de los ya clásicamente usados en otros países y están constituídos por un escintilómetro de gran sensibilidad, un radioaltímetro, registradores gráficos para las unidades anteriores y una cámara fotográfica aérea de registro continuo, sincronizada con aquellos y suplementada con un sistema de marcación de la película. En los trabajos que así lo exigen, se utilizan radiofaros para la orientación de los vuelos y además equipos transceptores especiales para la comunicación entre avión y superficie.

El escintilómetro aéreo transistorizado MP 10 fué desarrollado y construído en la Gerencia de Materias Primas de la CNEA y diseñado específicamente para la utilización aérea. Se usa con uno o dos cabezales provistos de cristales de INa activados con Tl, de 5 in de diámetro por 2 in de espesor. El amplificador permite variar las escalas de tiempo entre 0,05 y 1,5 segundos y los rangos son 250, 500, 1 000, 5 000 y 10 000 cuentas por segundo. El error entre las distintas escalas es inferior a 5 %, teniendo en cuenta que sus rangos oscilan entre 250 y 10 000 cuentas por segundo.

A los efectos de contar en todo momento con la distancia entre el avión y la superficie del terreno y poder aplicar el factor de corrección correspondiente a la pérdida de radiactividad que se produce por la absorción del aire interpuesto entre la fuente emisora y el detector, se instala un radioaltímetro del tipo AN-APN-1 que permite la exacta medición de la altura de vuelo.

Las lecturas correspondientes al escintilómetro y radioaltímetro se grafican en forma sincrónica en un registrador doble, continuo, que permite así efectuar las correcciones correspondientes. Los registradores electromecánicos utilizados poseen una constante de tiempo acorde con la sensibilidad del equipo, son totalmente transistorizados, de doble banda rectilínea y poseen tres rangos de sensibilidad (10 V, 1 V y 100 mV).

A los efectos de referir los valores obtenidos en el vuelo a puntos reales del terreno, se acopla al instrumental de detección una cámara aérea de registro continuo, suplementada con un sistema de marcación de accionamiento automático y/o manual. Se obtiene en esa forma una banda fotográfica del terreno, que se puede aplicar sobre el fotomosaico o sobre los planos topográficos, posibilitando una mayor exactitud en la ubicación de los puntos con interés.

Para lograr una correcta orientación de las líneas de vuelo, en los trabajos de prospección detallada con malla preestablecida, se recurre al empleo de la navegación radioeléctrica, utilizándose radiofaros y radiobalizas diseñados y construídos también en la Gerencia de Materias Primas de la CNEA, de acuerdo con las necesidades propias de este tipo de tareas.

Para ayudar a corregir los efectos de deriva, controlar la verticalidad del pasaje del avión sobre los puntos de referencia y otras necesidades operativas de campaña, se asegura un contacto permanente entre el avión y personal auxiliar de tierra, agregando

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* Comisión Nacional de Energía Atómica,

una etapa modulada a los radiofaros y dotando de receptores VHF a las unidades móviles.

El material de vuelo lo constituyen las clásicas avionetas Cessna 180-182 o Piper PA 18, cuyas características (alta maniobrabilidad, velocidad de crucero, costos de operación y mantenimiento, etc), se ajustan a los requerimientos propios de esta técnica de prospección.

Técnicas aplicadas

Reunida toda la documentación existente de la zona a sobrevolar y de acuerdo con los antecedentes que se tengan de cada una de ellas, se inician los trabajos con algunos vuelos de reconocimiento, los que permitirán ajustar los límites de la zona y determinar el tipo de vuelo que se aplicará en cada caso. Se hacen líneas de vuelo con equidistancias que varían entre los 1 000, 500 o 250 m según el carácter de la prospección, expeditiva, regular o detallada, respectivamente y en los casos que la topografía así lo exija, se realizan vuelos de ladera. La altura de vuelo utilizada es de 75 m, término medio.

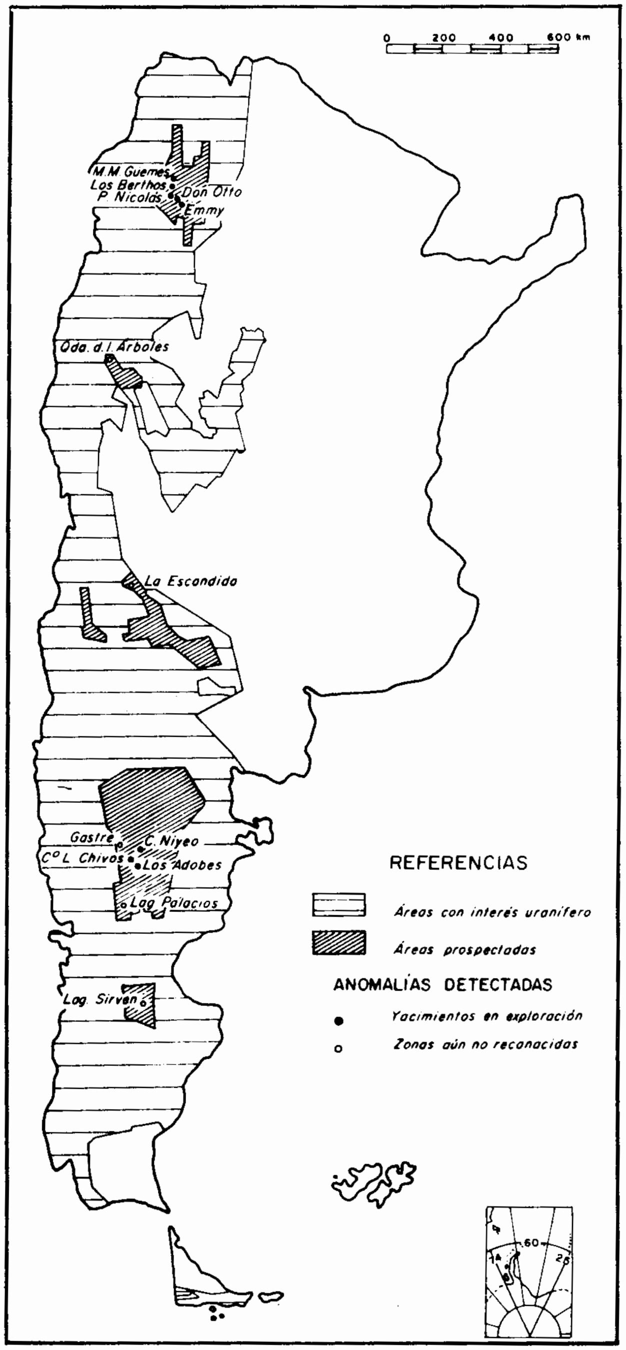

Figura 1. Prospección aérea en la República Argentina

Toda la documentación obtenida (registros radimétricos, altimétricos, fotografía, etc) se elabora diariamente por el personal en campaña, efectuando las correcciones correspondientes y volcando en los planos adecuados los resultados, para su posterior examen y análisis.

Resultados

Las áreas sometidas a trabajos de prospección aérea fueron previamente seleccionadas de acuerdo con sus características y posibilidades, en las que la geología juega como principal factor en la elección de las prioridades asignadas a cada una de ellas. En esta forma se delimitaron 395 000 km^2 con posibilidades uraníferas de interés inmediato, discriminadas en la siguiente forma: 115 000 km^2 con prioridad I, 130 000 km^2 con prioridad II y 150 000 km^2 con prioridad III.

Hasta el presente, se cubrieron 75 000 km^2 de áreas con prioridad I y II, para lo que fué menester utilizar más de 2 000 h de vuelo (figura 1). Como consecuencia de estos trabajos se descubrieron 550 anomalías de las cuales se recomendaron 250 para su revisión en superficie, habiéndose constatado en 50 de ellas la existencia de acumulaciones uraníferas de variada importancia, muchas de las cuales revisten interés económico, como las correspondientes a los yacimientos « Don Otto », « Emmy », « Pedro Nicolás », « Pepe Luis », « Los Berthos », « M. M. de Güemes », etc en la provincia de Salta, « La Escondida » en Mendoza y « Los Adobes », « Cerro Chivo », « Carhue Niyeo », etc, en Chubut.

Radimetría aérea en relación con cuencas petrolíferas

En base a los antecedentes mundiales disponibles sobre la aplicación de la radimetría aérea como método de exploración para la delimitación de cuencas petrolíferas [1-6 y 8], la CNEA realizó algunos trabajos tendientes a ensayar y desarrollar este método y determinar prácticamente los reales alcances y resultados que del mismo podrían esperarse.

Tal como se consigna en la bibliografía respectiva, la utilización del método radimétrico en la exploración de estructuras petrolíferas, se basa en la redistribución zonal de los elementos radiactivos sobre las acumulaciones de hidrocarburos en profundidad. Esta redistribución obedecería, en todos los casos, a las condiciones geoquímicas creadas por la presencia de los hidrocarburos en el subsuelo, hecho que desequilibra el ordenamiento primitivo, modificando o alterando las condiciones del ambiente geoquímico original, ya sea por migración de gases o líquidos hacia la superficie, ya sea creando tensiones superficiales, etc. En el caso de los radiactivos, este hecho se registra en forma directa con las mediciones radimétricas.

Los citados cambios en el ritmo normal de los fenómenos geoquímicos de superficie tienen lugar específicamente en las zonas relacionadas con las acumulaciones de hidrocarburos en profundidad y no gravitan en las áreas circundantes, donde los procesos de equilibrio geoquímico continúan sin ser afectados, resaltando por ello las diferencias enumeradas anteriormente.

La interferencia que otros factores pueden tener en la determinación de las anomalías resultantes, hacen en muchos casos difícil la interpretación de los resultados.

Basándose en la información acumulada durante los últimos años [2, 5-8] se ha constatado que los yacimientos petrolíferos se reflejan en superficie con un registro irregular de radiación gamma, pues encima de los mismos la intensidad radiactiva es menor que el « fondo general » de la zona circundante o *back ground* regional. En muchos casos, los bordes o límites del campo petrolífero se corresponden perfectamente en superficie con un « halo » radiactivo, en el que se registran actividades superiores a la normal. Las zonas anómalas así delimitadas coinciden con gran aproximación con los límites de las acumulaciones de hidrocarburos.

Trabajos efectuados

Los trabajos que se realizaron en la Argentina abarcan una superficie de 5 000 km², distribuídos en tres regiones distintas del país (provincias de Neuquén, Salta y Santa Cruz), cubriéndose sectores productores de hidrocarburos y extendiéndose en parte hacia otros cyuas posibilidades no eran totalmente conocidas, de manera que pudiera apreciarse el rendimiento del método. Es así, como quedaron incluídos en ellas diversos yacimientos controlados por condiciones geológicas y estructurales variables, lo que permitiría una información diferencial y comparativa para cada caso.

En todas las etapas previas del trabajo fué necesario considerar y conciliar las exigencias inherentes a la técnica del método a utilizar, con las reales posibilidades, operativas en campaña. Las características estructurales y geológicas fueron también consideradas y primaron en la decisión final cuando se estudiaron los diferentes factores que podían gravitar en ese sentido.

Dada la exactitud requerida, fué indispensable contar con el instrumental en condiciones óptimas de operación y calibración, motivo por el cual se debió asegurar un buen mantenimiento electrónico y estricto control de los equipos.

Los vuelos se ejecutaron con una separación lateral de 500 m, asegurados con un apropiado apoyo radioeléctrico y control fotográfico. En cada zona se elaboró la correspondiente carta de isorradiactividad relativa, la que se obtuvo corrigiendo los valores sistemáticamente y normalizándolos mediante métodos estadísticos, que permitieron eliminar las variaciones ajenas a la radiactividad del terreno. Obtenida esta información, se analizó la amplitud de la diferencia entre los valores mínimos y máximos registrados, estableciéndose así el fondo relativo y determinando a su vez la zona de « alzas » y « bajas », con los gradientes respectivos.

Además del mapa isorradio, se confeccionaron algunos perfiles radimétricos, los que cortando estructuras petrolíferas conocidas, pusieron de relieve la información suministrada por el método.

Resultados

Los trabajos que se cumplieron hasta el presente permiten demostrar que, en principio, este método de prospección para acumulaciones petrolíferas es capaz de brindar resultados positivos, ya que del total de la superficie estudiada surgió a grandes rasgos la delimitación de áreas favorables en ciertos casos, eliminación de zonas desfavorables en otros, y también coincidencias con estructuras ya conocidas. Como es lógico, dado el carácter expeditivo del presente estudio, aparecen también sectores en los que los resultados radimétricos (por influencia de factores diversos) divergen con las condiciones geológico-estructurales que se tenía de ellos.

En una próxima etapa y mediante un estudio complementario, la CNEA investigará cada uno de los factores superficiales lo cual permitirá interpretar el papel que en conjunto desempeñan. Con tal motivo, se programaron una serie de nievos trabajos de campaña, sobre las mismas áreas, pero en sectores más reducidos, que contemplan entre otros : levantamiento radimétrico aéreo con discriminación de las energías del U, Th y K, levantamiento ionométrico terrestre, levantamiento geoquímico, perfiles radimétricos terrestres, corrección por interpretación geológica, etc.

Con toda esta información, se tratará de determinar qué grado de exactitud puede alcanzar el levantamiento radimétrico aéreo para la búsqueda de acumulaciones de hidrocarburos.

PROSPECCÍON EMANOMÉTRICA TERRESTRE

Como complemento de la prospección radimétrica aérea, se aplicó en numerosas manifestaciones uraníferas y con buenos resultados, el método emanométrico. La primera utilización del método data del año 1948, en el que se aplicó durante el estudio del yacimiento uranífero « Soberanía », en la provincia de Mendoza. Posteriormente, la emanometría se convirtió en uno de los métodos de rutina para complementar la información previamente obtenida con prospecciones radimétricas aéreas y terrestres.

Las correspondientes observaciones de campo se realizaron con electrómetros de Ambronn, efectuándose las determinaciones de radón del aire telúrico sobre perfiles adecuadamente espaciados o sobre reticulados con malla de 25 × 10 m, según el problema que se deseaba resolver.

La prospección emanométrica se reveló como muy conveniente, tanto para los casos en que la mineralización abarca franjas de considerable extensión, como para la determinación de cuerpos más regulares, que estuviesen sustraídos a una observación geológica directa, por cuanto es capaz de proporcionar casi de inmediato y a un costo operativo reducido datos de ponderable interés.

Se enumeran, a título informativo, algunos casos donde el mismo evidenció la conveniencia de su aplicación.

Yacimiento «Rodolfo»

Este yacimiento uranífero, ubicado en la provincia de Córdoba, fué prospectado en su sector austral sobre 6 km de extensión mediante 28 perfiles emanométricos de 150 m de largo (término medio), orientados de E-O, es decir, normales a la corrida de la faja mineralizada, que acusa un buzamiento promedio de 40° E y que en gran parte está cubierta por acarreo moderno.

Las mediciones mostraron en casi todos los perfiles dos máximos bien definidos, coincidiendo el que aparecía en la mitad oriental de cada perfil, con los bancos mineralizados que había reconocido el laboreo superficial. Algunas labores de comprobación, que se efectuaron en el sector sur del yacimiento, indicaron que la anomalía evidenciada en la mitad occidental de los perfiles, correspondía a un banco mineralizado desconocido hasta entonces y que pertenecía a un nivel inferior de la serie sedimentaria, igualmente mineralizado (figura 2). Este banco, que posteriormente fué reconocido con perforaciones sobre una longitud de 2 km, permitió inferir, en base a estos resultados, la continuidad de la mineralización hasta el extremo norte de la zona bajo prospección, lográndose de esta manera un sensible incremento de las reservas del depósito uranífero.

Región de Cañadón Gato-Krueger

En la exploración geofísica de esta región del Chubut, se aplicó la emanometría como método directo de prospección por minerales de uranio. Paralelamente, para localizar las intrusiones basálticas que acompañan las grietas mineralizadas, se usó el método de perfiles de resistividad obtenidos mediante sondeos eléctricos horizontales (método de la *traînée*).

Tanto para las mediciones emanométricas como para las de resistividad, se trazaron 31 perfiles, con separación de 250 m aproximadamente entre ellos, a la vez que las estaciones sobre cada perfil se espaciaron 10 m. Para las determinaciones de resistividad aparente del terreno se eligió una profundidad constante de 20 m, realizándose además, sobre un mismo perfil, algunas mediciones para profundidades de 10 y 40 m.

El análisis comparativo de las curvas de descarga electrométrica y las de resistividad, manifestó un incremento en los valores a medida que se pasa del sector norte de la zona mineralizada al del centro, alcanzándose máximos emanométricos y de resistividad que afectan la misma estación o dos adyacentes. Esto permitió la suposición de la existencia de concentraciones de mineral de uranio a lo largo de líneas definidas (diques basálticos, grietas tensionales, etc). El desplazamiento que se observa a menudo entre los máximos emanométricos y los de resistividad sobre un mismo perfil, indicaría que la mayor difusión del radón corresponde a zonas de contacto entre formaciones litológicas de alta resistividad (intrusiones basálticas) y otras de resistividad baja (arcillas o areniscas arcillosas mineralizadas). Esta suposición se vió confirmada en varios perfiles, donde los registros emanométricos y de resistividad más elevados, coincidieron con afloramientos o destapes en que aparecieron las mencionadas formaciones litológicas. Las anomalías recomendadas fueron luego ratificadas mediante perforaciones.

Yacimiento «Los Adobes»

Un ejemplo típico de prospección emanométrica de detalle destinada a localizar un cuerpo mineralizado de dimensión reducida, lo ofrece la investigación que se efectuó en el Cañadón La Orientala (Chubut), sobre una anomalía puesta de manifiesto por radimetría aérea

El plan de estudio geofísico de la zona anómala comprendió, en primer término, la prospección radimétrica, mediante escintilómetro, de un área de 3 × 5 km. La segunda etapa consistió en la prospección emanométrica y de resistividad de la superficie previamente delimitada por la escintilometría, y en la cual se había efectuado, además, un reconocimiento geológico preliminar, mediante algunos destapes y un pique de exploración, con el cual se atravesó un banco uranífero de 10 m de potencia.

Se efectuaron determinaciones de ensayo del radón telúrico en las inmediaciones del pique, de manera que los valores de descarga electrométrica pudiesen relacionarse experimentalmente con el tenor del mineral y con el espesor y la naturaleza litológica de la cubierta estéril que lo ocultaba. Luego, en la zona a prospectar y con una separación de 50 m, se trazaron 12 perfiles de 200 m de longitud promedio, perpendiculares al supuesto banco mineralizado, con lo que se cubrió un área de aproximadamente 10 Ha. Posteriormente, en la zona de mayor interés, se hizo necesario intercalar otros perfiles, a fin de posibilitar una mejor correlación de los valores emanométricos registrados y de delimitar el área anómala mediante curvas que correspondiesen a descargas del electrómetro, equivalentes 50, 100, 250 y 500 milivoltios por segundo. Esto permitió definir la continuidad del cuerpo, bajo una cubierta estéril de hasta 10 m con la curva de 100 mV/s y las zonas de mayor concentración con las curvas de 250 y 500 mV/s (figura 2).

Sobre los mismos perfiles se efectuaron también mediciones de resistividad (sondeos eléctricos horizontales) a la profundidad constante de 20 m, con el fin de tratar de correlacionar los valores de resistividad con la mineralización y la litología del área prospectada. Se pudo constatar, de esta manera, que los valores de ϱ comprendidos entre 50 y 100 Ωm caracterizan las formaciones conglomerádicas portadoras de uranio, ya que coinciden en su mayor extención con las áreas en que se registraron valores de dispersión eléctrica superiores a los 100 mV/s, pero sin definir en forma neta la zona mineralizada de la estéril.

« *Cuesta de Huaco* »

A 40 km al norte de la ciudad de Jáchal (San Juan), en la « Cuesta de Huaco », se había localizado una manifestación uranífera en sedimentos parcialmente aflorantes La prospección se efectuó en el área que se consideraba de mayor interés y en la cual se había realizado, con anterioridad, un estudio geológico y un levantamiento radimétrico. Después de ensayos ejecutados en las cercanías de labores bien conocidas (con el objeto de establecer alguna relación entre los valores de descarga y la distancia de la masa mineralizada), se realizaron las mediciones emanométricas que pusieron de manifiesto interesantes anomalías, cuya distribución se correlacionaba perfectamente con lo que ya se conocía acerca de la mineralización en el área.

En base a las correlaciones puestas en evidencia, se determinó como valor límite de las zonas mineralizadas, el que correspondía a una dispersión eléctrica equivalente a una descarga de 90 milivoltios por segundo, de manera que la curva que unía los puntos con dicho valor permitió delimitar el área de interés, que se extiende hacia el noroeste, fuera de la zona reconocida con labores.

Los sucesivos trabajos de exploración minera confirmaron las conclusiones a que se había arribado con el levantamiento emanométrico, resultando que la curva de 90 mV/s correspondía, efectivamente, a la demarcación de la zona mineralizada y otra débilmente impregnada o estéril.

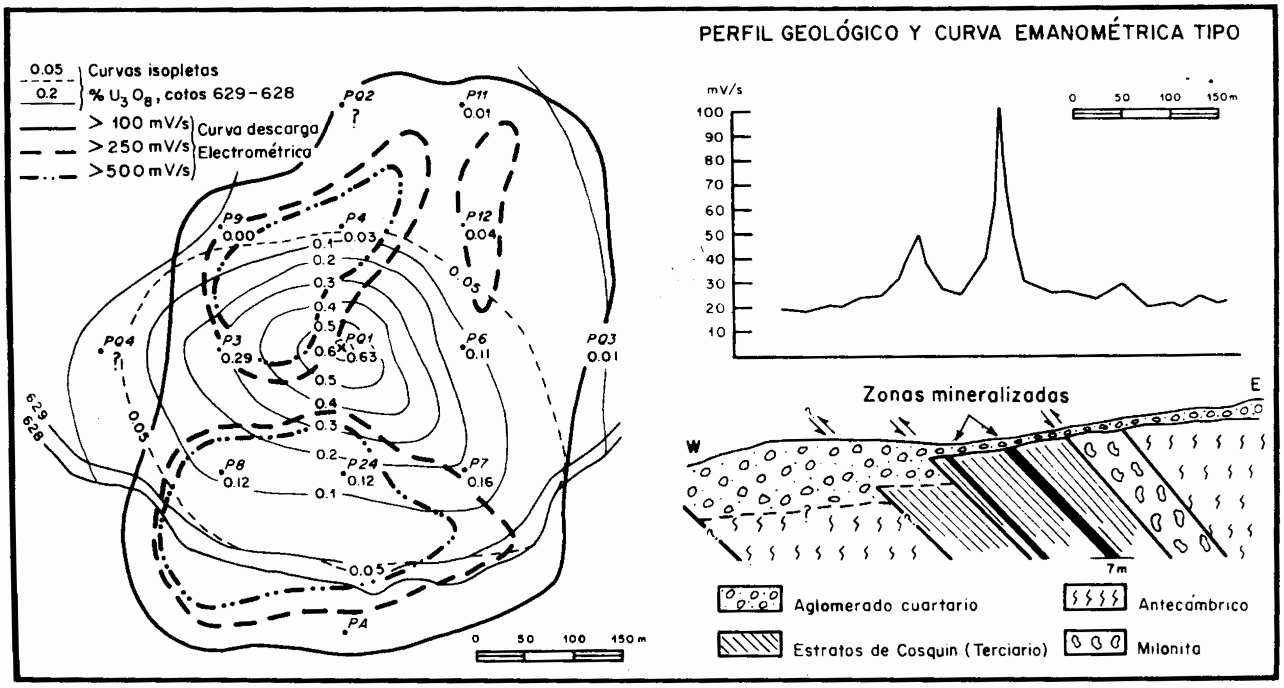

Figura 2. Prospección complementaria en anomalías detectadas desde el aire
A la izquierda, yacimiento Los Adobes, provincia de Chubut. A la derecha, yacimiento Rodolfo, provincia de Córdoba

Este método emanométrico como todo geofísico, tiene lógicamente sus alcances y limitaciones y debe combinarse adecuadamente con ellos para tratar de obtener una información resultante que permita la interpretación más exacta posible del caso que se estudia. Naturalmente, es susceptible de mejorar sus técnicas, y por ello, la CNEA estudia el empleo de instrumental de mayor precisión (electrómetros de alta sensibilidad selectiva, registadores con cristal de radiación α, etc).

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/838 Argentina

Radiometric aerial and emanometric ground prospecting methods in Argentina

By K. Marinkeff *et al.*

Radiometric aerial prospecting

Sporadic aerial prospecting for radioactive ore deposits began in Argentina in the middle of 1958. Since 1960 the method has been applied systematically and, thanks to its greater economy and speed, has come to be used almost exclusively, in preference to ground prospecting, for the surveying of extensive uranium-bearing areas.

Up to the present 75 000 km² have been prospected, in various regions, and 550 radioactive anomalies have been discovered, 250 of which have been selected for surface examination. Fifty of these have already been investigated and found to contain uranium contents of varying amounts and, in many cases, of economic value.

The techniques and instruments used in Argentina are essentially similar to those current in other countries.

The authors describe the features of the instruments and the improvements made to them, and the methods used in field operations, for interpretation and correction of records and for preparation of the final data.

Mention is also made of a radiometric aerial prospecting trial over oil-bearing areas, covering 5 000 km², in three separate regions of the country (Salta, Neuquén, Santa Cruz), and of the modifications made to the method for this purpose. The aim was to eliminate, by means of geological interpretation supported by geochemical analysis, the errors due to recording radiation from thorium and potassium.

Emanometric ground prospecting

Along with the application of the radiometric aerial prospecting technique, there has recently been a revival of the use of electrometers for the detailed prospecting of uranium deposits, because of the ease of application of the emanation method, the speed of field operations, and the larger volume of data obtained.

The National Atomic Energy Commission has carried out emanometric prospecting with Ambronn electrometers in various parts of Argentina.

The authors quote examples of the use of this method to investigate the continuity of uranium mineralization including the Rodolfo (Córdoba), Los Adobes (Chubut) and Cuesta de Huaco (San Juan) deposits, and to direct trial drillings and logging in areas where the mineralized strata lay under a thick alluvial cover. Subsequent exploratory work (drilling and mining) has confirmed the results obtained with this method.

A/838 Argentine

Techniques de prospection aérienne radiométrique et émanométrique terrestre appliquées en République Argentine

par K. Marinkeff *et al.*

Prospection aérienne radiométrique

Vers la moitié de 1958 commencèrent dans la République Argentine les premières opérations (non régu-

lières) de prospection aérienne, pour la recherche des gisements de minerais radioactifs. A partir de 1960, ces mêmes opérations ont été poursuivies de façon régulière et le procédé est maintenant utilisé de manière presque exclusive; il remplace la prospection terrestre dans la reconnaissance de grandes zones d'intérêt uranifère, étant moins onéreux et plus rapides.

Jusqu'à présent 75 000 km² ont été prospectés dans divers secteurs et l'on a découvert 550 anomalies, dont on a retenu 250, par suite de leur importance, pour les contrôler en surface. On a contrôlé 50 d'entre elles et on a toujours constaté l'existence d'accumulations uranifères d'importance variable, dont beaucoup présentent un intérêt économique.

Les techniques et les appareils utilisés ne diffèrent pas sensiblement de ceux qui sont employés dans d'autres pays.

Dans le mémoire, les auteurs traitent des caractéristiques et des perfectionnements apportés aux appareils ainsi que des méthodes utilisées dans toute la phase opérative de la campagne pour l'interprétation et la correction des données enregistrées et pour l'établissement du rapport final.

On fait aussi mention d'un essai de prospection aérienne radiométrique en relation avec des districts pétroliers qui a été effectué dans trois zones distinctes du pays (Salta, Neuquén, Santa Cruz) sur une superficie de 5 000 km², et de la nouvelle tendance que l'on donnera à la méthode à cet effet, en essayant d'éliminer des enregistrements l'activité du thorium et du potassium, grâce à des corrections fondées sur l'interprétation géologique et la géochimie.

Prospection émanométrique terrestre

Parallèlement à l'application de la méthode de prospection aérienne radiométrique, on est revenu, pendant les dernières années, à l'emploi des électromètres dans la prospection détaillée des gisements d'uranium, en raison de la facilité d'application de la méthode émanométrique, de la souplesse des opérations sur le terrain et de la plus grande quantité de renseignements que l'on obtient.

La Comisión Nacional de Energía Atómica a procédé à des prospections émanométriques avec des électromètres d'Ambronn dans différentes régions de l'Argentine.

On donne des exemples dans lesquels l'application de la méthode émanométrique a permis d'éclaircir des problèmes de continuité de la minéralisation en uranium, comme dans les cas des gisements Rodolfo (Córdoba), Los Adobes (Chubut), Cuesta de Huaco (San Juan), et d'orienter les sondages de recherche et d'échantillonnage dans les zones où les couches minéralisées se trouvaient sous une épaisse couverture alluvionnaire. Des études ultérieures (sondages et travaux miniers) ont confirmé les résultats obtenus avec cette méthode.

A/838 Испания

Аэрогамма-поиски и эманационная съемка при поисках радиоактивных руд

К. Маринкеф *et al.*

Аэрогамма-поиски

Отдельные аэрогамма-поиски месторождений радиоактивных руд стали проводиться в Аргентине с середины 1958 года. С 1960 года этот метод стал применяться систематически и благодаря большей экономичности и быстроте сделался почти исключительным методом, заменившим пешеходные радиометрические поиски при геологической разведке крупных ураноносных районов.

К настоящему времени аэрогамма-поисками обследовано 75 000 *км*² в различных районах страны, и обнаружено 550 радиоактивных аномалий, из которых 250 отобраны для наземного изучения. Пятьдесят из них уже обследованы; подтверждено, что они содержат уран в разных концентрациях во многих случаях промышленного значения.

Методы и аппаратура, применяемые в Аргентине, по существу аналогичны используемым в других странах.

В работе описываются особенности аппаратуры, применявшейся в полевых условиях, методы интерпретации и коррекции регистрационных записей и подготовки окончательных данных.

Кроме того, уделено внимание опытным аэрогамма-поискам в нефтеносных районах, покрывшим 5000 *км*² в трех различных областях страны (Салта, Ньюквен, Санта-Круз), и изменениям этого метода, с тем чтобы путем геологической интерпретации совместно с геохимическим анализом устранить ошибки, возникающие при регистрации излучений тория и калия.

Эманационные съемки

Вместе с применением аэрогамма-поисков недавно вновь стали использоваться электрометры для детальных поисков урановых месторождений вследствие простоты применения эманационной съемки, быстрого осуществления полезных работ и большего объема получаемых данных.

Национальная комиссия по атомной энергии провела в различных районах Аргентины эманационную съемку с электрометрами Амбронна.

бурения и каротажа в районах, где минерализированные участки перекрыты мощными аллювиальными отложениями. Последующие разведочные работы (бурение и горные выработки) подтвердили результаты, полученные с помощью этого метода.

В работе приводятся примеры использования эманационной съемки для изучения непрерывности уранового оруденения, включая разведку месторождений «Родольфо» (Кордоба), «Лос-Адобес» (Чубут) и «Куеста-де-Хако» (Сан-Хуан), и для непосредственного поискового

Uranium resources and recovery process in Japan

Atomic Fuel Corporation

PART 1. URANIUM RESOURCES IN JAPAN*

DEVELOPMENTS SINCE THE SECOND GENEVA CONFERENCE

Development of prospecting for uranium deposits

The results of the reconnaissance over the whole country to discover new uranium deposits are as follows.

In massif regions, mostly granitic and metamorphic rocks, indications of uranium mineralization occur in many hypogenic metallic ore deposits. Some have been prospected by underground workings, but none is exploitable economically.

The uranium deposits in sedimentary rocks in Japan fall into two types, namely, syngenetic deposits in clay slate and chert of the Paleozoic or Mesozoic Era and epigenetic deposits in Neogene Tertiary sedimentary rocks overlying granites.

The syngenetic type of deposit in clay slate has been found in more than twenty localities. All are closely related to the bedded manganese deposits. Ore bodies of this type that have been discovered cannot at present be regarded as uranium resources, because they are of small scale and low grade. In addition to these, however, continuous uranium occurrences have been discovered in widely extending chert and argillaceous rocks, so that geologically large scale deposits, though the grade is low, can be expected.

Another type of sedimentary deposit in Neogene Tertiary sedimentary rocks of which those of the Ningyo-togé area is typical is distributed from Hokkaido to South Kyushu as shown in Fig. 1. At present, emphasis is on prospecting for deposits of this type which afford promise of economic development.

In the Ningyo-togé area, several deposits have been found as well as many radioactive anomalies, in addition to the deposits reported at the Second Geneva Conference [1]. The most remarkable of these is the high grade ore body with average grade of 1% U_3O_8. The mineralized layer is several decimetres thick and extends for 8 000 m². The extent of uranium distribution in the Ningyo-togé area ranges approximately 20 km from north to south and 20 km from east to west.

Ore reserves

Ore reserves in Japan, estimated at the beginning of the fiscal year 1964 (1 April), are as follows:

	Proven	Probable	Possible
Ore (t)	1 144 000	280 000	1 900 000
Grade (% U_3O_8) .	0.061	0.053	0.064
U_3O_8 content (kg)	693 000	150 000	1 200 000

URANIUM DEPOSITS IN NEOGENE TERTIARY SEDIMENTARY ROCKS

Outline of geology

The characteristics of the uranium deposits in Neogene Tertiary sedimentary rocks are summarized in Table 1.

The principal uranium-bearing layer is comprised mainly of conglomerate and sandstone whose principal components are derived from granites. The uranium mineralization is controlled mostly by the

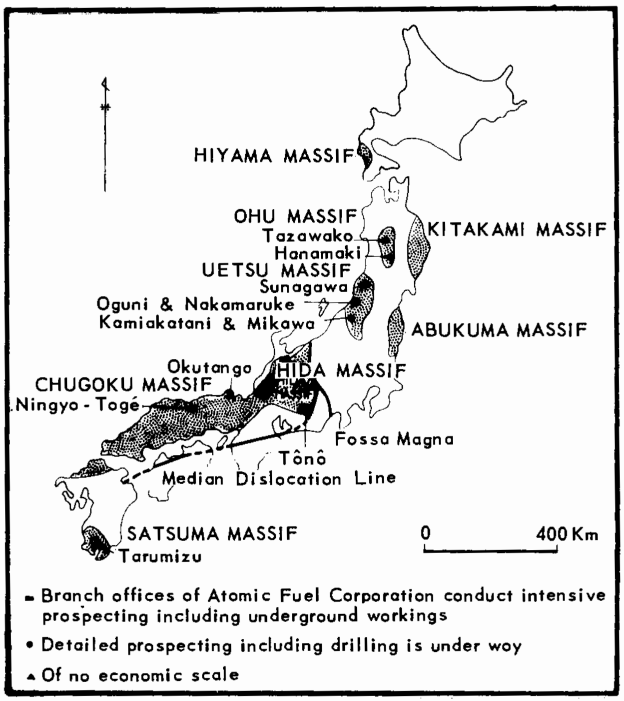

Figure 1. Promising regions for uranium prospecting and distribution of uranium deposits in Neogene Tertiary sedimentary rocks in Japan

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* M. Sato, H. Misawa, F. Togo.

Table 1. Characteristics of uranium deposits in Tertiary sedimentary rocks in Japan[a]

	Host rocks			Overlying impermeable layers	Principal uranium minerals	Characteristic associated materials
	Lithologic feature	Environment of deposition	Age			
Nyngyo-togé:						
Nyngyo-togé Mine.	Conglomerate, Sandstone	Nonmarine	Lower Pliocene	Lava, Argillaceous rock	Ningyoite, Atunite	Pyrite, Limonite, Gypsum, Kaolinite
Togo Mine . .	Conglomerate, Sandstone, Tuffaceous clay, Tuff	Nonmarine	Lower Pliocene	Lava, Tuffaceous rock	Uraninite, Ningyoite, Coffinite, Uranophane, Beta-uranophane, Autunite	Pyrite, Montmorillonite, Carbonaceous matter (locally)
Okutango . .	Conglomerate, Sandstone, Coaly shale, Tuff breccia	Nonmarine	Middle Miocene	Lava, Tuffaceous rock	Coffinite, Autunite, Uranocircite	Pyrite, Calcite, Zeolite, Carbonaceous matter
Tono	Conglomerate, Sandstone, Tuffaceous sandstone	Nonmarine	Middle Miocene	Argillaceous rock	Coffinite, Uranocircite, Autunite	Pyrite, Calcite, Carbonaceous matter
Tarumizu . . .	Conglomerate, Sandstone, Tuff	Nonmarine	Pliocene?	Welded tuff	Yellow mineral (not identified)	Hydrated halloysite
Kami-Akatani & Mikawa . .	Sandstone, Coaly shale	Nonmarine	Middle Miocene	Lava, Tuffaceous rock	Uraninite, Coffinite	Pyrite, Calcite, Carbonaceous matter
Nakamaruke .	Sandstone	Nonmarine	Middle Miocene	Argillaceous rock	Autunite	Apatite
Oguni	Conglomerate, Sandstone, Tuff breccia	Nonmarine	Middle Miocene	Argillaceous rock	Coffinite, Autunite Uranocircite	Pyrite, Limonite, Carbonaceous matter
Sunagawa . .	Conglomerate	Marine	Middle Miocene	Tuffaceous rock	Not identified	Pyrite, Calcite, Carbonaceous matter
Tazawako . .	Conglomerate, Tuff breccia	Nonmarine	Lower Miocene	Lava, Tuffaceous rock	Coffinite	Pyrite, Carbonaceous matter
Hanamaki . .	Conglomerate, Sandstone, Tuff breccia	Nonmarine	Lower Miocene	Lava, Tuffaceous rock	Coffinite, Uranophane, Autunite	Hematite, Chlorite, Calcite, Kaolinite, Carbonaceous matter

[a] Basement: Granite.

paleotopography of the basements, the deposits generally occurring at the basal parts of sedimentary rocks deposited on the basement depression. The depression is sometimes shaped like a paleostream, channel or sometimes it is a wider basin. Typical examples are shown in Figs. 2 and 3.

Characteristics of uranium mineralization

The characteristics of uranium mineralization are as follows:

(*a*) All uranium ore deposits were formed after the sedimentation of the host rocks;

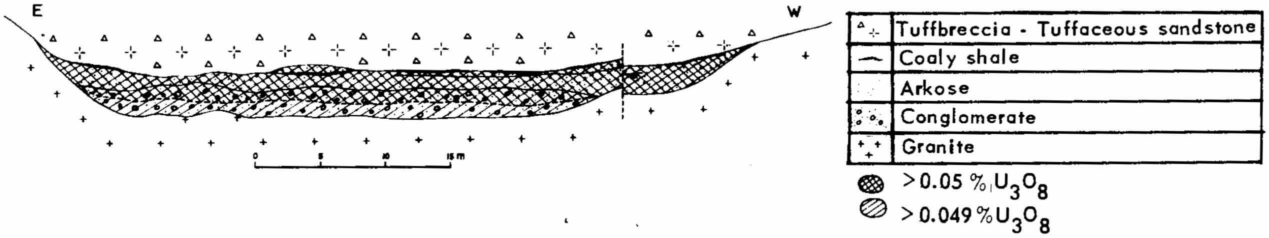

Figure 2. Geologic cross section of the Kannokura No. 2 ore body

(*b*) It is believed that primary uranium minerals were precipitated by reduction under conditions such that there was stagnant ground water;

(*c*) The geochemical properties of solutions containing uranium have the regional peculiarities reflected in the species of uranium minerals, parageneses and distribution of minor elements;

(*d*) There is wide support for the supergene hypothesis [2] for the origin of uranium in the deposits but the hypogene hypothesis of origin is also supported as for example for the genesis of the sandstone type deposits of the Colorado Plateau.

Developments in prospecting techniques

Prospecting for uranium deposits in Japan is being done under co-operation by the Geological Survey of Japan and the Atomic Fuel Corporation.

The noteworthy developments in prospecting techniques are (*a*) the success of the seismic method for inferring the structure or the location of the depression of basements covered with thick formations [3, 4], (*b*) the use of paper chromatography for simple and speedy semi-quantitative determinations in geochemical prospecting [5], and (*c*) combined application of geochemical and electrical resistivity methods to locate the boundary between sedimentary rocks and granite in soil covered regions.

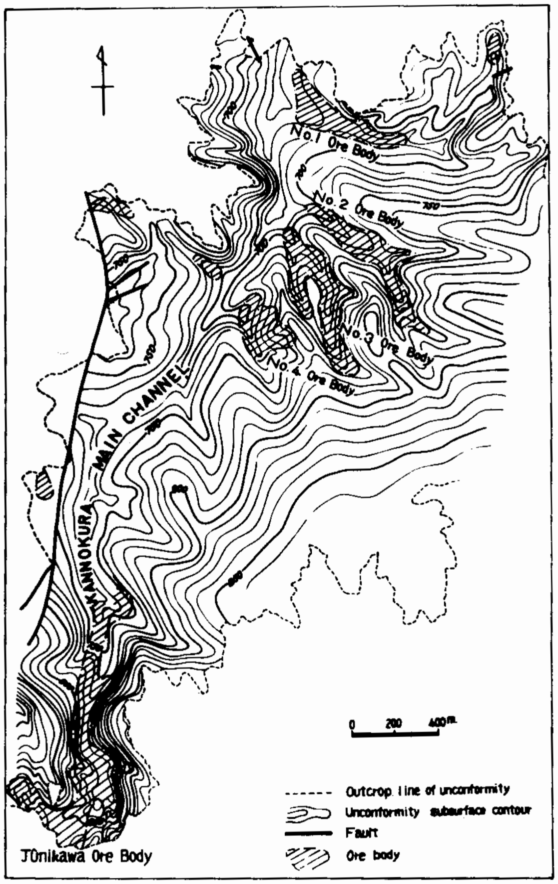

Figure 3. Contour map of the unconformity in the Kannokura area of Ningyo-togé, showing its channel structure

ORES OF THE NINGYO-TOGÉ URANIUM DEPOSITS AND THEIR MILLING PROPERTIES

Properties of uranium

The following characteristics of the uranium ores are important in connection with mining and milling.

Firstly, the uranium ores in this area comprise principally soft and loosely cemented conglomerates or young sandstones.

Secondly, uranium minerals occur as fine-grained crystals (of several microns) which cement voids of the arkose and matrices or cracks of the gravels of the conglomerate, or form a skin-like coating on the surface of gravels. This is one of the most favourable properties for the contact between leaching solutions and uranium minerals. In view of the relation between grade and grain size of the ore, these modes of uranium occurrence prove that it is quite natural for uranium minerals to concentrate in fine-grained ore fractions. Uranium distribution through the mineralized layer is considerably heterogeneous and uranium contents range from $0.0n\%$ to $n\%$ U_3O_8.

Thirdly, the major constituent minerals of the ores are rock-forming minerals such as quartz and feldspar and their resultant products [6]. The ores bearing remarkably high clay mineral contents (locally up to 70%) cause some difficulty in the milling process; however, these ores represent only a small percentage of the total ore reserves. No conspicuous sulphide minerals are present but pyrite associates with the ores. Traces of carbonate minerals are detected only in the oxidized zone. The principal uranium minerals are ningyoite in the unoxidized and autunite in the oxidized zones. In addition coffinite, uraninite, uranophane and beta-uranophane occur locally as principal ore minerals, and boltwoodite, carnotite, weeksite, ranquillite, torbernite and other unidentified secondary uranium minerals are also found. Though uranium is present in the tetravalent state, ningyoite, hydrated calcium uranous phosphate, is easily soluble in acid, because of the tube-like vacancy in the crystal structure [7]. Fourthly, as indicated by the mineral composition, any elements troublesome in the chemical treatment or elements with high neutron absorption cross section are only minor constituents in the geochemical sense and in practice can be neglected.

Wet screening and washing test

The results of wet screening and washing analyses of unoxidized ores (including partly oxidized ores) have shown that weight-distribution of fractions is approximately even, but grade-distribution is uneven

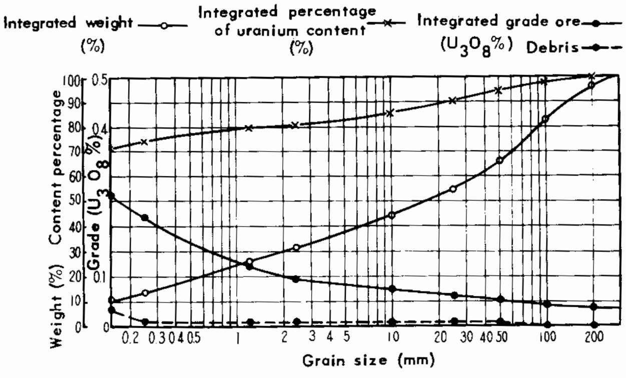

Figure 4. Results of wet screening analyses of the unoxidized ores of the Ningyo-togé mine

(Fig. 4) and uranium minerals are concentrated in parts where the grain is finer than 0.15 mm. The uranium content of the concentrate is 0.26% U_3O_8 and is 6.6 times higher than that of crude ores, 0.04% U_3O_8. When the slime passing through a 0.15 mm diam screen is recovered, the weight of the concentrate is 10.8%, that is one tenth that of the crude ore. The waste contains only 0.013% U_3O_8, and may be neglected. The percentage recovery of U_3O_8 contained in the concentrate is 71.7%.

Hydraulic mining test

The characteristics of the ores which are beneficial for washing and screening should make it possible to raise the productivity of the mining and milling process. Hydraulic mining is now being tried out in the gallery of the Ningyo-togé mine, as it utilizes these properties and is one of the most efficient methods of exploiting low grade uranium ores (Fig. 5). This method consists of the following:

(*a*) Face excavation by high pressure water;

(*b*) Separation of gravels and matrices by washing and excavating simultaneously;

(*c*) Leaving sterile gravels at the site;

(*d*) Hydraulic transportation of the fine concentrate.

The longwall method allows higher efficiency stoping and is suitable for complete exploitation of those parts where the ore is high grade. The hydraulic mining method gives a fair prospect of exploiting economically the low grade parts of the Ningyo-togé ore bodies, which is impossible by conventional methods.

Future prospects of uranium resources in Japan

Most uranium ore reserves in Japan are concentrated in the Ningyo-togé deposits. Economically by, these ores are thought to be rather low grade compared with foreign ores now being exploited, so that Japan finds it difficult to compete in the open world marked. However, with the inevitable future demand for low grade ores, the favourable properties of the domestic ores for simplifying mining and milling, and the successful prospecting in the Ningyo-togé area and other promising regions, strengthen hopes for the future.

PART 2. A NEW PROCESS FOR RECOVERY OF URANIUM FROM LOW GRADE ORE *

Since 1958 the Atomic Fuel Corporation has been developing new processes for treating domestic low grade ore and has completed the fundamental experiments. The corporation is now constructing a pilot plant at the Ningyo-togé Mine.

In this new process three methods are combined: (*a*) washing and classifying to improve the grade of ore, as described earlier, (*b*) acid pug leaching process to extract the uranium content into the leaching solution as easily and fully as possible and (*c*) amine conversion process by which a high purity uranyl chloride solution may be obtained from a pregnant sulphuric acid

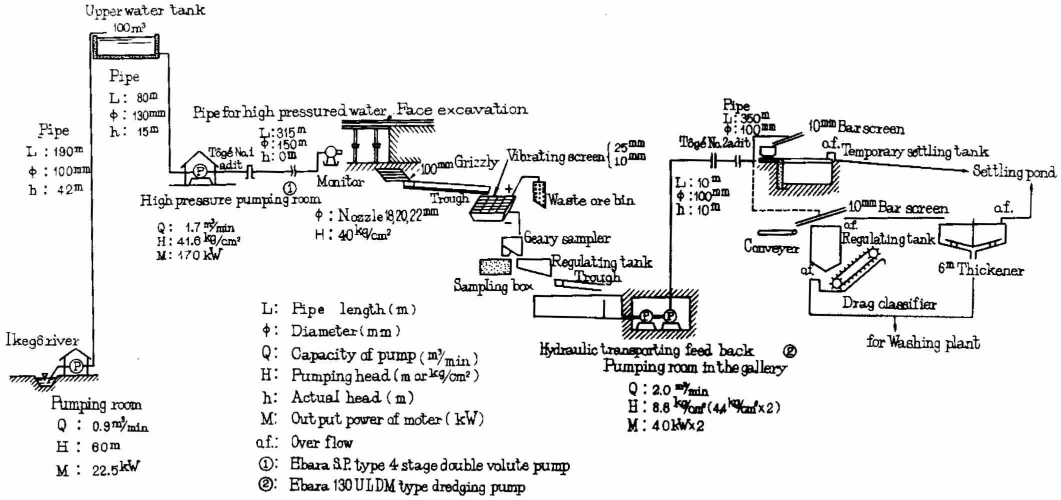

Figure 5. Schematic flowsheet for hydraulic mining test now under way at the Ningyo-togé mine

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* T. Yamashita, T. Murase, T. Amanuma, and K. Hashimoto.

solution. Purified uranyl chloride solution will be converted into uranium tetrafluoride by reduction of the uranyl ion and hydrofluorination in a wet process; it is used as a raw material for producing metallic uranium or uranium hexafluoride.

ACID PUG LEACHING

The wash concentrate contains from 25-50% clay minerals which prevents full contact between the uranium and the sulphuric acid in conventional acid leaching. Consequently, the extraction rate of uranium is comparatively low, and as soluble silica is extracted abundantly and colloids form in dilute acid, solid-fluid separation after leaching is very difficult.

The method developed to overcome these difficulties is a technique which increases uranium recovery and facilitates the solid-fluid separation, by heating and washing the concentrate with the addition of a small amount of concentrated sulphuric acid. By this means the uranium is soluble and silica is insoluble.

Experiments and results

Sulphuric acid pug leaching is comparatively easy and 95% of the uranium can easily be leached out if the water content is reduced to between 20-25% and the amount of sulphuric acid added is greater than 75 kg/t ore and further if the concentration of sulphuric acid is kept above 200 g/l.

When the temperature of the ore is kept between 100°-120 °C to provide this heating after mixing, the result obtained is very good and practicable industrially. Dissolution of iron increases nearly proportionally to uranium, but it has little influence upon refining.

The settling rate of the slimes after leaching is much faster than in the conventional method, and the same applies to filtration rate. This means good scrubbing efficiency when washing the pulp and thus a clean solution of high uranium concentration (2-3 g/l) is obtainable.

A typical analysis of the ore and the pregnant solution is shown in Fig. 10. Compared with the conventional method, dissolution of impurities except iron is not greatly increased and there is a marked decrease of silica. This is one of the characteristics of this method, and occurs because various kinds of colloid particles, which consist mainly of soluble silica contained in the ore, are changed to an insoluble form after being hard dried at 120 °C in the presence of sulphuric acid.

Apparatus for acid pug leaching

The schematic diagram of the equipment used in the experimental acid pug leaching process is shown in Fig. 6. The equipment consists chiefly of filter, mixer and dryer; heating is by means of oil and steam.

The wash concentrate is made into a pulp containing 20% solid in a repulping unit. The water content of the pulp is reduced to 20-25% by filtration at normal temperature and then by filtration under steam conditions and finally by drying by hot air.

Dried ore is carried to the roll mixer on a conveyor and pug leached with concentrated sulphuric acid addition and then carried further to a dryer by a paddle screw conveyor through which the pug leaching is continued.

The dryer has a control device by which the temperature of the ore may be kept at approximately 120 °C by means of hot air at 300 °C supplied from the oil burner. The ore becomes hard dry whilst it is maintained at this temperature for 10 minutes.

The hard dried ore is sent to another repulper, warm water is added to leach out uranium and the pulp is filtered by an Oliver filter.

CONVERSION PROCESS

A new process was developed to convert sulphate pregnant solution into chloride solution in order to link directly with a wet hydrofluorination process.

The uranyl sulphate complex in the pregnant solution is extracted with a kerosene solution of tri-n-octylamine (TNOA) and then, on scrubbing the pregnant solvent with concentrated hydrochloric acid, this complex is converted into the chloro-complex while being retained in the organic phase. The sulphate ion transfers from the organic to the aqueous phase. There is also a difference in the amine extraction behaviour of impurities in sulphuric acid and in hydrochloric acid solutions. Uranium undergoes a double purification process in the organic phase by the treatments described. Purified uranyl chloride solution is obtained when uranium is stripped from the amine solvent with dilute hydrochloric acid. This conversion process can be shown by the following relation:

$$(R_3NH)_4UO_2(SO_4)_3 + 6HCl \longrightarrow R_3NH.UO_2Cl_3 + 3R_3N.HCl + 3H_2SO_4$$

Experiments and results

There is a great deal of literature [8-10] relating to the extraction of uranyl sulphate complexes by alkylamines and it is generally accepted that tertiary amines show comparatively good selectivity.

To apply this method an amine must be selected which will fully extract the sulphate complex and also the chloro complex. In our experiment, 0.2*M* TNOA in kerosene plus 6% 2-ethyl-hexanol satisfactorily achieved this purpose.

In the conversion process, the sulphate ion has to be transferred to the aqueous phase and the uranyl complex kept in the organic phase as completely

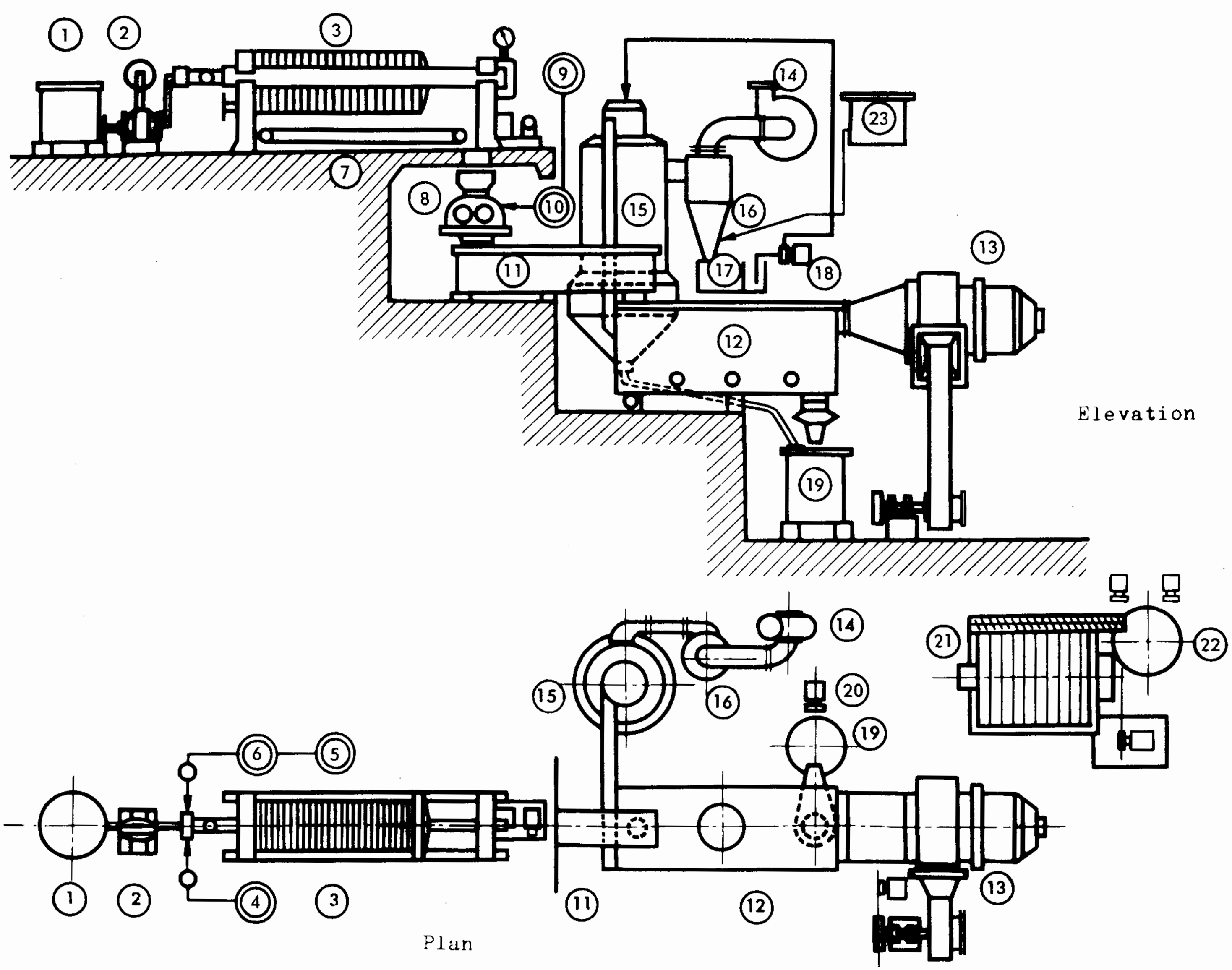


Figure 6. Schematic flow diagram of experimental apparatus for acid pug leaching

1: Repulper; 2: Diaphragm pump; 3: Filter press; 4: Steam line; 5: Compresser; 6: Heater; 7: Conveyor; 8: Roll mixer; 9: Service tank (H_2SO_4); 10: Pump; 11: Paddle screw mixer; 12: Hard drying apparatus; 13: Oil furnace; 14: Draft fan; 15: Cyclone scrubber; 16: Secondary cyclone; 17: Tank; 18: Pump; 19: Repulper; 20: Pump; 21: Oliver filter; 22: Repulper; 23: Service tank (washing solution) as possible. The sulphate is retained in the hydrochloric acid waste solution from the conversion process, and some chloride is retained in the solvent after uranium stripping. Therefore the problem is whether hydrochloric acid can be used again in the conversion process and then as solvent in the extracting process.

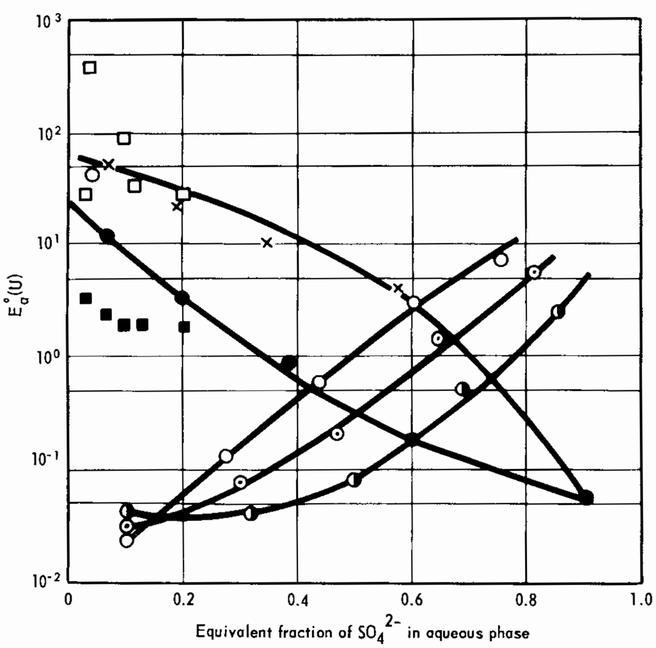
To clarify these points, the following experiments were carried out.

Extraction equilibrium of uranium, sulphate and chloride ions.

The relations between equivalent fractions of sulphate ion in equilibrium and uranium extraction coefficients, $E_a^o(U)$ are shown in (Fig. 7). $E_a^o(U)$ tends to decrease with increasing amounts of complexing substance, chloride or sulphate ions. In practice, the value of $E_a^o(U)$ should be more than 50 at the time of extraction. This value signifies that the equivalent fraction of chloride allowable is 0.1 maximum, which corresponds to a limiting concentration of chloride of approximately 1 g/l. Figure 7 shows also that if the total acid concentration is kept at 8*N* in the conversion process, there is little change in $E_a^o(U)$, even though the concentration of uranium varies between 0.8-7 g/l. Furthermore, for effective conversion, the maximum equivalent fraction of SO_4^{2-} permissible is 0.2, or about 77 g/l.

Conversion

Two methods are considered for the actual conversion operation: (*a*) use, once, of the minimum amount of hydrochloric acid; (*b*) use of large amounts of hydrochloric acid and recycle until the equivalent fraction of sulphate in the converting solution (8*N* HCl) reaches 0.2.



	Total acid concentration	U concentration (mg/ml)	Amine form
-○- -⊙- -◐-	0.3 ~ 1N	0.84	RCl
-●-	5N	0.84	RCl
-■-	5N	7.08	$RUO_2(SO_4)_n$
-×-	8N	0.84	RCl
-□-	8N	7.08	$RUO_2(SO_4)_n$

Figure 7. E_a^o (U) versus equivalent fraction of sulphate ion in aqueous phase

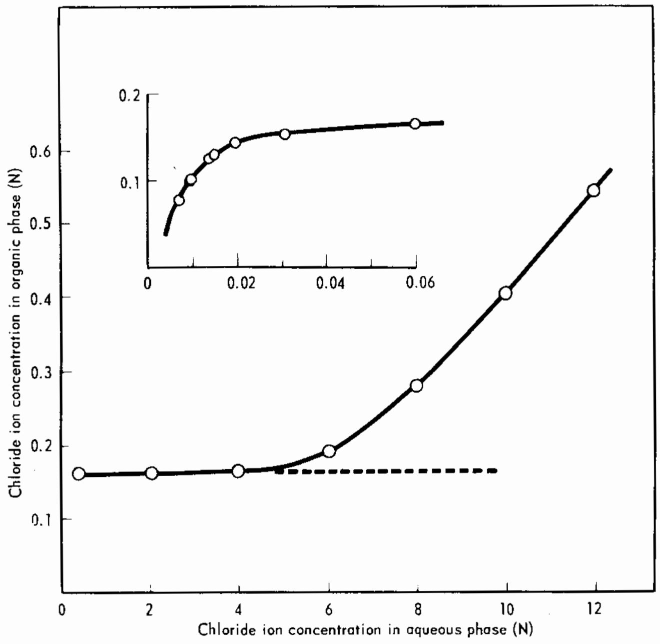


Figure 8. Chloride ion distribution

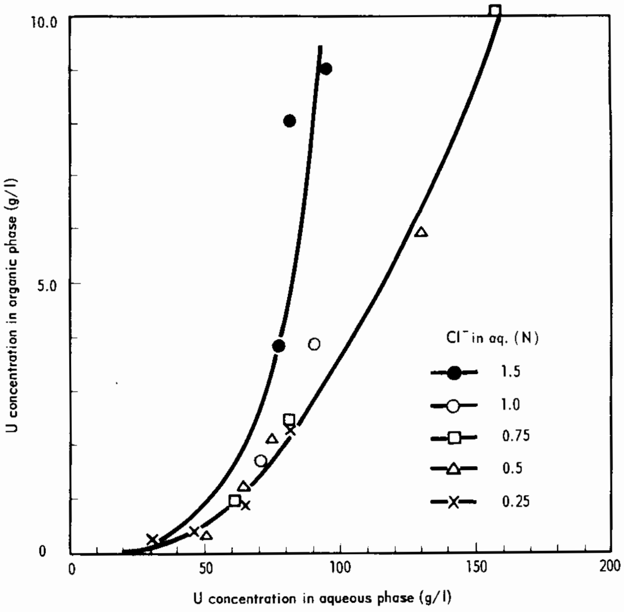


Figure 9. Uranium stripping curve

Conversion can be accomplished by either method, but the former is better because in (*b*) increase of chloride ion in the amine may hamper the stripping process.

Stripping

In the stripping process, the amine salt may be dissolved in the aqueous phase in which it is emulsified when it is contacted with water; therefore dilute hydrochloric acid solution of about 0.05*N* is preferred as stripping reagent.

The distribution curve for chloride ions obtained in amine extraction is shown in Fig. 8. Chloride increases gradually in the organic phase if the chloride ion concentration exceeds 4*N* in the aqueous phase.

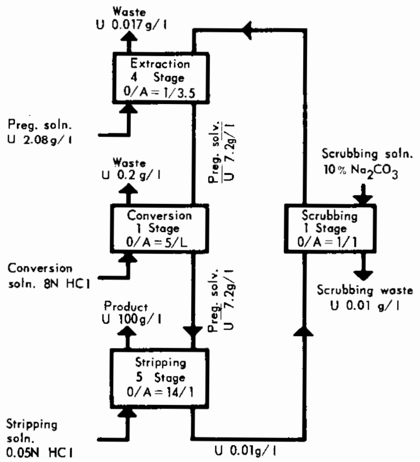
Figure 9 shows the stripping equilibrium curves when the chloride ion concentration in the aqueous phase is kept at a determined level.

Circulation of the solvent

The concentration of uranium in the solvent after stripping is less than 0.6 g/l and the amine is present in the form $R_3N.HCl$, but the extractability of uranium is somewhat lower than if chloride ion were absent. The results of scrubbing tests of the organic phase after stripping showed that one stage scrubbing using 10% sodium carbonate solution is desirable to remove chloride from the organic phase, both as regards smooth operation and cost reduction.

Decontamination effect of the conversion process

Stripping coefficients were determined for some elements in the sulphuric acid and the hydrochloric acid systems, and the decontamination effects were estimated by comparing these coefficients with those of uranium in the respective system.



Element		U	Fe	Al	Si	V	Mo
Ore %		0.236	2.76	7.76	28.9	0.0025	0.0012
Pregnant solution g/l		2.08	18.5	6.81	0.618	0.0039	0.0027
D F	Extraction	-	12 400	111 900	10 160	64	4
	Conversion	-	43	253	6	1	0.4

Figure 10. Results obtained with small scale conversion process

The results of experiments are shown in Table 2. Decontamination from phosphorus, arsenic and boron is remarkably efficient by this method and it can be used for vanadium, molybdenum and other elements which are difficult to eliminate.

Table 2. Separation coefficients

Element	Scrub[a]	S_0^a (M)	S_0^a(M)/S_0^a(U)
U^{VI} 67 mg/11 ml . .	A	0.020	—
	B	0.008	—
V^V 0.276 mg/11 ml .	A	1.473	73.7
	B	0.285	35.6
P^V 0.158 mg/11 ml .	A	14.8	740
	B	38.4	4 800
As^V 0.153 mg/11 ml	A	4.66	233
	B	24.5	3 100
Mo^{VI} 1.35 mg/11 ml	A	0.012	0.60
	B	0.152	19.0
B^{III} 2.02 mg/11 ml .	A	19.2	960
	B	10.9	1 360

[a] A : 0.2*N* H_2SO_4 B : 8*N* HCl

In connection with the acid pug leaching process, a small scale test has been carried out of an over-all process from leaching of ore to conversion to uranyl chloride solution in order to observe the purification achieved. The experimental conditions are outlined and the results are shown in Fig. 10; the same results could be obtained under actual operating conditions at the pilot plant.

CONCLUSION

A new processing technique has been described which would be suitable for the treatment of low grade ore containing large amounts of clay minerals which is difficult to treat by the conventional acid leaching method. Such ores are abundant in Japan. Economic aspects will be clarified by operating the pilot plant now under construction. We believe that this method will prove to be important in the future, in many countries of the world, when it becomes necessary to treat these low grade ores.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/844 Japon

Les ressources en uranium et le traitement des minerais d'uranium au Japon

Atomic Fuel Corporation

La prospection systématique de l'uranium par le Service géologique du Japon et l'Atomic Fuel Corporation a permis de reconnaître des réserves naturelles de plus de trois millions de tonnes de minerais contenant plus de 0,01 % de U_3O_8 (leur teneur moyenne est 0,06 %-0,07 %; la quantité d'uranium contenu et pouvant être extrait est d'environ 2 000 tonnes).

A l'heure actuelle, la majeure partie des réserves est située dans le district de Ningyo-togé, dans le massif Chugoku, dans le sud-ouest du Japon. Les gisements d'uranium se sont formés horizontalement dans les parties de base des roches sédimentaires néogènes tertiaires qui recouvrent les granites.

Au Japon, on connaît beaucoup de régions dont les conditions géologiques ressemblent à celles de Ningyo-togé; dans ces régions, les recherches et la prospection se poursuivent activement et l'on s'attend à un accroissement rapide des réserves à bref délai.

Si l'on juge les minerais du point de vue de la teneur seulement, il est impossible au Japon de concurrencer les prix acceptés sur le marché mondial pour l'uranium obtenu par les méthodes classiques. Malgré leur faible teneur en uranium, les minerais japonais possèdent nombre de propriétés intéressantes : ils sont principalement composés de conglomérats très légèrement liés et d'arkose; les minéraux uranifères qui se trouvent sous forme de petits cristaux dans les parties tendres et poreuses sont très solubles dans les acides; ils ne contiennent pratiquement aucun minéral qui gêne le traitement et ils ne contiennent pas d'éléments à grande section efficace d'absorption des neutrons.

Les caractères décrits ci-dessus permettent non seulement de s'attendre à une réduction des coûts de l'exploitation minière par la méthode hydraulique, mais encore de mettre au point une technique de traitement économique des minerais pauvres nationaux.

Le procédé de traitement des minerais uranifères ainsi mis au point est le suivant : les minerais sont broyés, lavés et classés et on obtient un concentré de particules passant au tamis 100. La teneur du concentré est d'environ 0,3 % en U_3O_8, et 70 % de l'uranium est récupéré. Les particules de minerai sont conditionnées à une humidité d'environ 20 %, malaxées et homogénéisées avec une petite quantité d'acide sulfurique concentré, chauffées à 120 °C pendant quelques minutes, puis lavées à l'eau chaude pour lessiver l'uranium.

La filtrabilité a pu ainsi être grandement améliorée car la silice soluble colloïdale est transformée en une forme insoluble et on obtient une solution-mère ayant une teneur en uranium plus élevée que celle que donnent les méthodes classiques d'attaque à l'acide.

On extrait l'uranium par une amine sous forme de complexe de sulfate d'uranyle, qui est converti ensuite en complexe de chlorure par lavage avec de l'acide chlorhydrique concentré, l'uranium restant toujours dans la phase organique. On obtient une solution de chlorure d'uranium raffinée en épuisant le solvant par l'acide chlorhydrique très dilué.

On prépare finalement le tétrafluorure d'uranium anhydre par réduction électrolytique, hydrofluoration et déshydratation.

A/844 Япония

Урановые ресурсы и извлечение урана в Японии

Фирма „Атомик Фьюэл“

В результате систематических поисковых работ, проводимых геологоразведочной службой Японии и фирмой «Атомик фьюэл», было установлено, что национальные ресурсы урановой руды, содержащей свыше 0,01% U_3O_8, составляют 3 000 000 *т* (среднее содержание 0,06—0,07%; общее количество урана, которое может быть извлечено, составляет приблизительно 2000 *т*).

В настоящее время запасы урановой руды сконцентрированы в районе Нингуо-Тоге, в так называемом массиве Чугоку, расположенном

на юго-западе Японии. Залежи урановой руды располагаются в горизонтальном направлении в основании неогенных третичных осадочных пород, налегающих на гранитные породы.

В Японии имеется много районов с такой же геологической структурой, как в Нингуо-Тоге, и в этих районах ведутся в настоящее время энергичные исследования и поисковые работы, поэтому в будущем можно ожидать резкого увеличения запасов урановой руды.

При существующем содержании урана в рудах Япония не может успешно конкурировать по стоимости с действующими мировыми ценами, используя обычные методы производства. Несмотря на низкое содержание урана в рудах Японии, они обладают многочисленными благоприятными свойствами, а именно: японские урансодержащие руды состоят из слабоцементированных конгломератов и аркозового песчаника; урановые минералы, залегающие в виде тонкозернистых кристаллов в мягких и пористых пластах, легко растворимы в кислоте и почти не содержат никаких минералов, затрудняющих процесс обработки или включающих элементы с высоким эффективным сечением поглощения нейтронов.

Эти характеристики позволяют ожидать снижения стоимости добычи урана за счет использования гидравлического метода, а также разработки экономичного технологического процесса обработки бедных руд Японии.

Приведено описание процесса извлечения урана, разработанного фирмой «Атомик фьюэл». Руда размельчается, промывается и сортируется в рудный концентрат из частиц размером меньше 100 меш. Содержание U_3O_8 в концентрате составляет 0,3%, а извлечение — до 70%.

Мелкие частицы руды доводятся до 20%-ной влажности и равномерно выщелачиваются небольшим количеством концентрированной серной кислоты, нагреваются в течение нескольких минут до температуры 120° C и затем обрабатываются горячей водой для вымывания урана.

Таким образом можно значительно повысить фильтруемость, так как растворимый коллоидальный кремнезем переходит в нерастворимую форму, и получить раствор с более высокой концентрацией урана, чем при помощи обычного кислотного выщелачивания.

Этот раствор подвергается процессу экстракции аминами, после чего комплекс сульфата уранила превращается в хлористый комплекс путем промывки соляной кислотой при сохранении его в органической фазе. В результате обработки растворителя сильно разбавленной соляной кислотой получают очищенный раствор UO_2Cl_2.

И, наконец, путем электролитического восстановления, гидрофторирования и дегидратации получают безводный четырехфтористый уран.

A/844 Japón

Reservas de uranio y procesos de recuperacion en el Japón

Atomic Fuel Corporation

Los resultados de la prospección sistemática efectuada por el Geological Survey del Japón y por la Atomic Fuel Corporation muestran que las reservas nacionales de mena de uranio con leyes mayores de 0,01 % U_3O_8 pasan de los 3 000 000 de t (su ley media está entre 0,06-0,07 %; y el contenido total de uranio recuperable es unas 2 000 t).

En la actualidad, la reserva de mena está concentrada en el distrito de Ningyo-togé, en la llamada región del Macizo Chugoku, al Sudoeste del Japón. Las capas de menas de uranio se presentan horizontalmente en las partes basales de las rocas sedimentarias terciarias neogénicas que hay sobre los granitos.

En el Japón hay muchas zonas con condiciones geológicas similares a la de Ningyo-togé y en esas zonas hay actualmente en curso investigaciones y prospecciones intensas, de modo que se puede esperar en el futuro un brusco incremento de las reservas de mineral.

Basándose solamente en las leyes de esos minerales es imposible que el Japón compita con éxito con el precio mundial del uranio obtenido merced a los métodos de producción convencionales. A pesar de sus leyes tan bajas, los minerales japoneses de uranio tienen muchas propiedades favorables, esto es, constan de conglomerados y arkosa cementados de forma muy suelta; los minerales de uranio que se presentan como cristales de grano fino en las partes blandas y porosas son fácilmente solubles en ácido, y casi no hay minerales que interfieran con el tratamiento ni tampoco hay elementos de sección eficaz alta para la absorción de neutrones.

Estas características nos permiten no sólo esperar una disminución de los costes de minería por método hidráulico, sino también desarrollar una tecnología del tratamiento de las menas de baja ley del país.

El proceso desarrollado por nosotros para la recuperación del uranio es el siguiente. La mena se tritura, se lava y clasifica para concentrar el mineral de la fracción inferior a 100 mallas. La ley del concentrado es de aproximadamente 0,3 % U_3O_8 y la recuperación llega al 70 %.

Las partículas finas de la mena se acondicionan a aproximadamente el 20 % de humedad y se humedecen uniformemente con una pequeña cantidad de ácido sulfúrico concentrado, se calientan a 120 °C durante unos pocos minutos y luego se tratan con agua caliente para lixiviar el uranio.

Así podemos mejorar mucho la filtrabilidad porque la sílice coloidal soluble se transforma en insoluble, y se obtiene una solución fértil más concentrada en uranio que la que se logra por la lixiviación ácida convencional.

La solución fértil se trata por el proceso de extracción con aminas, y el complejo de sulfato de uranilo se conviete, por lavado con HCl concentrado en un complejo de cloruro que se mantiene en la fase orgánica. Se obtiene luego una solución refinada, de UO_2Cl_2 por reextracción del disolvente con HCl muy diluido.

Por último se prepara UF_4 por los pasos de reducción electrolítica, hidrofluoruración y deshidratación.

Application of geologic concepts to future uranium exploration

By R. D. Nininger, J. W. Gabelman and H. H. Adler *

Uranium exploration in the USA was so successful from 1948 to 1958 that, toward the latter part of this period, uranium production threatened to exceed requirements and it was necessary to limit government purchases. This limitation resulted in the virtual cessation of exploration and the restriction of further development of deposits to that needed to provide ore to fulfil existing sales contracts.

Present production rates could be maintained over a number of years beyond termination of the present government purchase program in 1970 from known reserves and ore discovered in the course of mine development in existing uranium mining districts. However, these districts cannot sustain prolonged production at present rates. Rapidly rising world requirements for uranium for nuclear power forecast for the late 1970s and beyond are of such magnitude [1] that they will have to be met by production from uranium mining districts yet to be discovered.

The technology of sub-surface exploration by drilling has steadily advanced and will continue as the only certain means of establishing the presence of uranium ore at depth. "Long-hole" underground drilling to guide mine development and explore ore body extensions has proved to be highly successful and is used extensively. Sample recovery from drill holes has been greatly improved through the addition of latex to drilling mud which coats drill cores and allows 100% recovery of friable rocks. Better information can be obtained from non-core drilling because of improvements in gamma-ray, resistivity, density and other logging techniques and instrumentation and in log interpretation.

Other geophysical as well as geochemical techniques will also continue to be important adjuncts of both regional and local exploration, but the initial selection of the most favorable regions for exploration will have to be based mainly on appraisal of the geologic factors governing uranium deposition. For this purpose it will be necessary to consider the geochemical cycle of uranium, its source, and the environment most suitable for its concentration. Although there is an abundance of empirical data available on the local and regional distribution of uranium, there remains the important task of selecting the criteria which will be most useful in evaluating the many unexplored areas that have some degree of geologic favorability.

Uranium deposits in sandstone are emphasized in this paper because they constitute 95 per cent of the present reserves of the United States. Although the geologic features of these deposits and their environment are well documented, the source of uranium, the course of its migration, and the geochemical evolution of the deposits are problematical. However, they are also critical factors in selecting exploration targets.

Fundamentally, the formation of sandstone-type uranium deposits is dependent on (*a*) a source of uranium and (*b*) a favorable environment for its deposition. Naturally, the probability of successful selection of target areas is increased where the geologic evidence points to the co-existence of favorable source and depositional areas. The concurrent use of such empirical evidence should, therefore, greatly simplify the task of discovering new deposits and reduce the time and cost required. The following concepts may suggest various ways of systematizing this quest.

The concepts discussed here may well be equally applicable to the extensive conglomeratic deposits in other parts of the world.

REGIONAL ZONING OF METALS

The relative geographic and geologic positions of epigenetic metal deposits, including uranium, in parts of North and South America indicate that districts of similar mineralogy, or of similar development of mineral zoning, commonly are grouped in linear regional zones [2-6]. Groups of these regional zones parallel major tectonic features or are concentric around centers of igneous activity. Also, the zones are arranged in paragenetic sequence in response to gradients of decreasing temperature and intensity of mineralization. These gradients radiate outward from sites of strongest deformation. The kinds and relative quantities of metals represented in one entire group of zones characterize a particular metallogenic province.

The consistent spatial relationships suggest mineral-

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ization intensity gradients that control significant concentrations of the various metals and offer evidence of a genetic association which is practically useful. Uranium is present in the mineralization gradients identified with the tectonic cycles of the southern Rocky Mountains and Basin-and-Range provinces of the western USA, the Sierra Madre Occidental of Mexico and the Andes of South America. It occurs in various temperature environments throughout the mineralization cycle, but increases in quantity toward the low temperature end of the gradient. Large uranium deposits in sandstone consistently tend to occupy a geographic position on the outer edges of mineralized areas or regions. No major deposits have been noted in regional zones of other metals, nor do uranium zones trend independently of other metal zones as would be expected if the different zones resulted from entirely different processes.

In view of these associations it may be concluded that the respective mineralization processes of each zone are interrelated in some manner. By the time mineralizing solutions have reached the low temperature and shallow depth typical of the depositional environment of uranium deposits in sandstone, however, they may have acquired the characteristics of ground waters, and their migration may be restricted largely to aquifers.

If uranium is present in a metallogenic province and mineral zoning gradients can be recognized within the province, it may be possible to predict that the largest and most concentrated quantities of uranium will occur at or beyond the known termination of the gradients. These gradients can be complete and associated with major tectonic features such as mobile belts, or they can be short and associated with local and smaller tectonic features within mobile belts.

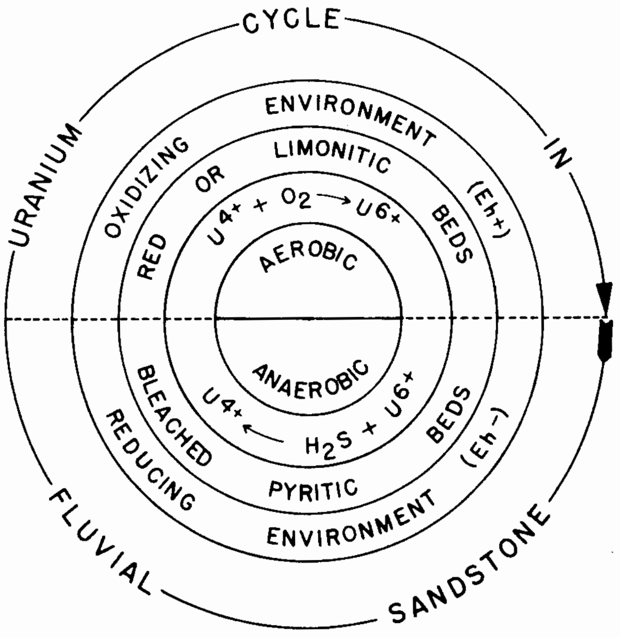

Figure 1. General features of uranium cycle

A correlation is indicated between the temperature and intensity of mineralization and the age, depth, and intensity of tectonic deformation within an uplift or mobile belt, so that the mineralization gradient generally is superimposed on a deformation gradient progressing from early, strong, deep deformation to later, weaker, more shallow deformation.

ENVIRONMENTAL FACTORS OF URANIUM DEPOSITION IN SANDSTONES

Specific localities determined to be favorable for sandstone-type uranium ores on the basis of regional zonal relationships may be evaluated from the standpoint of the effects of geologic environment on uranium deposition. The ore-forming processes are evidently sensitive to pH conditions, Eh potentials, and oxidative and reductive capacities characteristic of natural environments.

Uranium is transported mainly in the form of uranyl carbonate or sulfate complexes. Precipitation is induced by reduction of uranyl to uranous ions that are highly insoluble under normal ground-water conditions and combine to form uraninite or coffinite. These minerals comprise the major black ores in the USA. On re-oxidation to the uranyl state under atmospheric conditions, or by oxygen-charged waters, uranium is complexed with inorganic anionic radicals to form predominantly soluble ions, which are removed by ground-water solutions, or insoluble minerals such as the uranium vanadates, carnotite and tyuyamunite. The latter comprise the oxidized ores prevalent in the Colorado Plateau region of the USA. Less often, uranium combines with silicate, phosphate, arsenate and other anionic radicals to form secondary minerals none of which is ordinarily as common in ores as uraninite, coffinite, or the uranyl vanadates. The general features of this uranium cycle are shown in (Fig. 1).

It is apparent from geochemical considerations that the black sandstone-type ores could not have formed without the development of reducing loci in the sediments. The organic matter that is virtually ubiquitous in sandstone-type ores functions in the dual capacity of absorbing and reducing uranium to form organo-uranium complexes [7] and providing the energy source for anaerobic bacteria which generate hydrogen sulfide, an effective uranium reductant and precipitant [8, 9]. Sulfur-isotope evidence, which evidently permits a distinction between bacteriogenic hydrogen sulfide formed *in situ* and petroliferous and magmatic hydrothermal sulfides [8-10], strongly points to the probability that the uranium ores were formed in a reducing environment created by bacteriogenic hydrogen sulfide.

All the important sandstone-type ores that have been analyzed isotopically, e.g. the Ambrosia Lake and Laguna deposits in New Mexico, the Gas Hills deposits in Wyoming, and the Big Indian Wash deposits in Utah, yield evidence of having been precipitated by bacteriogenic hydrogen sulfide. The ores are generally found in arkosic sediments containing large accumulations of organic matter that is now predominantly sub-bituminous in rank. The host sediments are presumed to have been derived from highlands under conditions favoring accelerated erosion by seasonal rainfall sufficiently intense to wash away periodically the vegetation cover and disintegrate the granitic rock slopes [11]. These conditions accounted for intermittent rapid deposition and burial of large quantities of organic debris as the coarse, feldspathic sediments swiftly accumulated in the intermontane basins. Local heavy growth of vegetation marginal to streams meandering into the savannah basins probably also produced pockets of organic debris in the channel fill. Generally high water tables preserved the organic matter from aerobic conditions that are accompanied by oxidation. In the presence of this readily decomposable organic matter, sulfate-reducing bacteria generated hydrogen sulfide that later reacted with the metallic elements brought in by meteoric or juvenile waters during or subsequent to uplift of the basin flanks.

The interchangeability of the uranyl and uranous ionic states as a function of the reduction-oxidation potential of the environment provides a mechanism for the gradual accretion of uranium in these sediments. Uranyl ions carried into the sediments in oxygen charged waters are reduced to the uranous state, forming uraninite and coffinite as they encroach on the reducing environment. Simultaneously, uranium is solubilized at the oxidized edge of this zone and carried again into the reducing zone where it is redeposited. This cycling action appears to occur along a rather sinuous reduction-oxidation boundary which divides "bleached" pyritiferous sandstone containing black, unoxidized ore from oxidized limonitic or hematitic sandstone [12]. This reduction-oxidation interface constitutes the rather sharply defined edge of the familiar uranium roll structures evident in the black ore deposits of the Shirley Basin [13] and Gas Hills districts, Wyoming, and preserved in carnotite deposits of the Colorado Plateau. Similar boundaries have also been observed at the oxidized edges of the fracture-controlled "stack" ores in the Ambrosia Lake area, New Mexico, which are thought to have resulted from the redistribution of older more or less horizontal tabular or lenticular trend ores along zones of increased permeability [14]. The oxidation of the sediments has been recognized as an effective guide to ore in the Shirley Basin and Ambrosia Lake districts [13, 15] and in other major producing areas.

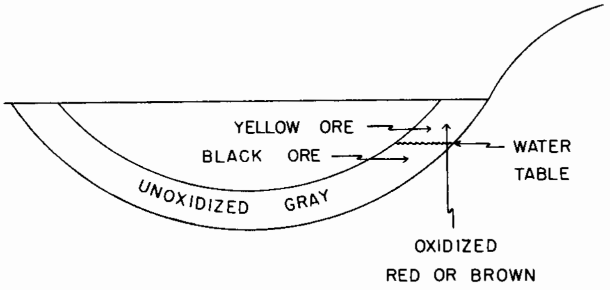

Figure 2. Restricted post-orogenic oxidation

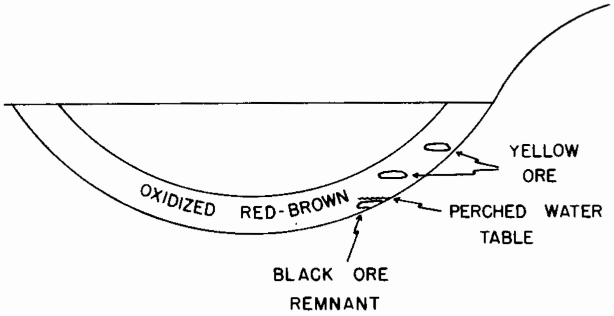

Figure 3. Extensive post-orogenic oxidation

Much of the uranium in the deposits studied has been accumulating in recent times at or near ground water tables (Fig. 2), and in some the major part of uranium deposition occurred less than 130 000 years ago [16-19]. It seems reasonable to conclude, therefore, that whereas uranium may have initially gained access to geochemically favorable environments in the host sandstones in either juvenile or ground waters, the ores have been extensively reworked more recently by meteoric solutions (Fig. 3).

Potentially favorable ground may be recognized on the basis of specific or inferential evidence of (*a*) regional or local paleodrainage channelways related to paleotopographic or structural features and (*b*) the existence of both reduced and oxidized conditions in the sandstone. Although oxidized at their outcrops, all black ore-bearing sandstones are carbonaceous and unoxidized at depth. It is evident, therefore, that the sediments were not formed under extensive aerobic conditions that characteristically destroy the organic matter and result in red-bed formation.

Uranium deposits are known in rocks of Pennsylvanian and Permian age which consist predominantly of reddish continental sediments [20], but the prospects of uranium discovery in such red-bed facies are minimal inasmuch as oxidizing conditions were evidently extensive at the time of deposition of these formations, thus destroying most of the organic matter necessary for ore deposition.

The major ore-bearing formations in the USA are an assemblage of continental sediments consisting of unusually reducing facies and red-bed strata. The ore beds are, or were, in effect, reduced facies, extensive in some areas and limited in distribution in others, with sufficient reducing capability to cause widespread deposition of uranous and sulfide minerals. These sediments were chemically extraordinary in that their reducing capacities could be regenerated by microorganisms as long as the enclosed organic matter could sustain bacterial life. Many of these beds were extensively oxidized after uplift, rather than during deposition, causing basin-ward ingression of redox boundaries. These sandstones are potential sources of uranium wherever they have been only partially oxidized by ground-water solutions.

Although the sandstone-type uranium deposits in the USA have a wide geographical distribution, they are restricted primarily to three major host rocks, the lower part of the Chinle Formation of Triassic age, the Morrison Formation of Jurassic age, and the Wasatch and Wind River formations of Tertiary (Eocene) age. Various Cretaceous and Miocene formations are also ore-bearing, but uranium mineralization was apparently less intense and more local in distribution. While the distribution of ore deposits indicates a relationship to the regional transmissive capacity of the host rocks [21], the adjoining eolian and marine beds, although possessing relatively uniform transmissive properties, seldom provide the geochemical environment suitable for ore deposition generally found in the fluvial carbonaceous sandstones.

The most significant aspect of this concept of uranium deposition is that uranium accumulates in suitable permeable rocks only where it encounters chemical conditions precluding its further migration. Such chemical traps appear to be of no importance if they exist in sedimentary rocks of deep basins to which oxygenated uraniferous waters have had no access. Traps nearest the source of these solutions and in the path of migration will be the first to take up the uranium.

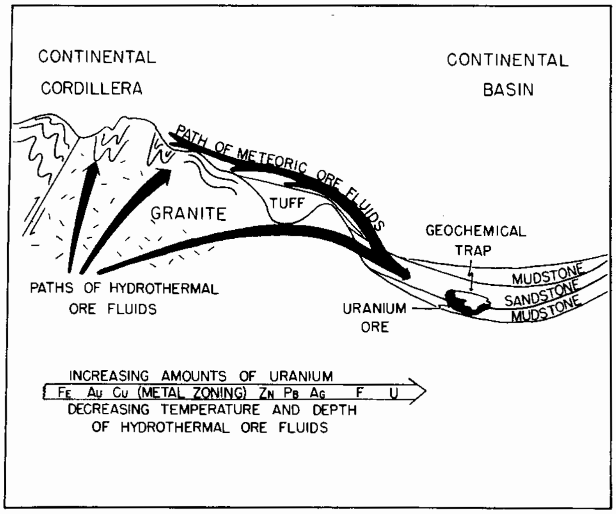

Figure 4. Gravitational gradient for migration of uranium

A logical inference from uranium discoveries to date is that the depositional sites along the flanks of uplifts were generally accessible to uraniferous solutions and that the most recent impact of these uplifts was to create a gravitational gradient for migration of uranium into favorable depositional environments (Fig. 4). In the USA virtually all important ore deposits in sandstones show evidence of such topographic influence.

Obviously, opportunities for migration and accumulation of uranium are especially favorable around structural highs. The deposits may be located near the basin rim if the sediments extend deeply into the basin and oxidation is relatively shallow, e.g. in the Grants area, New Mexico, or they may occur near the basin trough if the host sediments are relatively shallow and ground-water drainage is well developed into the basin interior, e.g. in the Shirley and Powder River basins, Wyoming. Where oxidation and erosion of the sands has been extensive, dip reversal caused by faulting or folding may halt the progressive basinward migration of the uranium and result in the preservation of ore in a subsidiary trough, as in the Gas Hills area, Wyoming.

APPLICATION

According to the concept of mineral zoning, the most favorable locations for major uranium mineralization within tectonic mobile belts are near or along the foreland side. These would lie at the low-temperature ends of mineral zoning gradients of regional proportions commonly oriented across the mobile belt and also at the low temperature ends of more localized zonal gradients generally associated with smaller individual uplifts; more specifically on the gently dipping flank between an uplift and a closed or semiclosed basin of continental sedimentation. The ideal host rocks are permeable fluviatile sandstones rich in carbonaceous debris.

The United States

The most productive uranium districts in the Cordilleran mobile belt of the United States occur toward its eastern or foreland side [22] (Fig. 5). They are in interior regions of uncommonly weak deformation such as the Colorado Plateau and the Wind River and Shirley basins of Wyoming, as well as along the margin of the Great Plains in the Powder River Basin, Wyoming, and the Black Hills of Wyoming and South Dakota. Within these regions are other areas which contain uranium deposits but which have not yet proved to be productive districts of equal significance. Further exploration may well demonstrate their importance.

Similar regions along the Cordilleran foreland contain much ground with zonal and host-rock

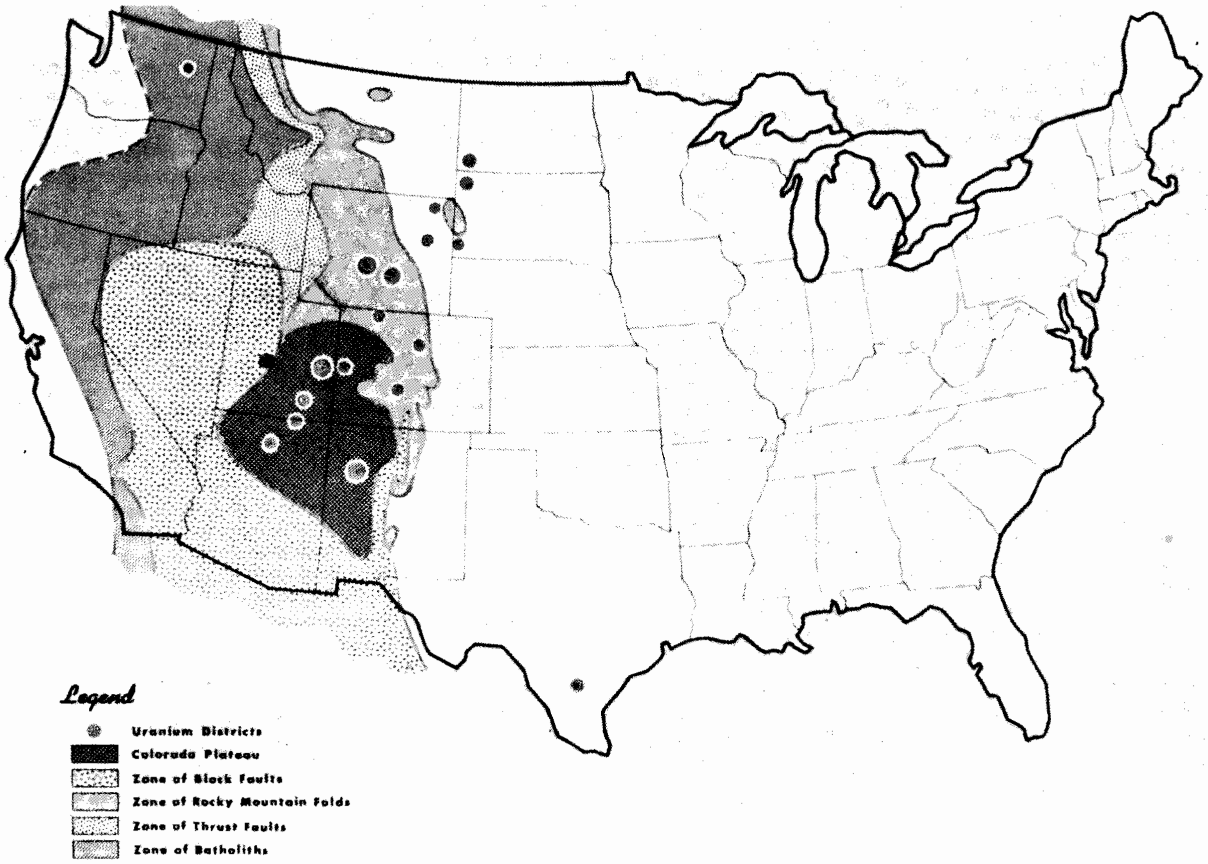

Figure 5. Important uranium districts of the USA in relation to zones of orogenic deformation

favorability in which uranium has not been found. These regions offer fertile prospecting ground. Many intermontane areas lying within and toward the eastern edge of the mobile belt are worthy of study; these include the Crazy Mountain-Reed Point syncline of southern Montana, the Rock Springs uplift and adjacent basins of Wyoming, the North Park Basin of Colorado, and the Rio Grande graben of New Mexico. Each of these is note worthy for one or more favorable criteria including epithermal mineral deposits, associated uplifts, carbonaceous, poorly sorted sandstones, and small uranium occurrences.

Most depositional basins along the margin of the Great Plains are open and offer less possibility for uranium entrapment than closed basins within the mountain belt. Among many local areas offering some exploration possiblities, however, are the Bearpaw and Little Rocky Mountain laccolithic uplifts of southern Montana that are similar to the La Sal, Abajo, Henry, and La Plata laccolithic uplifts of the Colorado Plateau which have central small precious- or base-metal deposits and marginal uranium deposits. The Denver and Raton basins, along the mountain front in Colorado and New Mexico, are terminal to mineralization gradients in the neighboring Front Range and Sangre de Cristo ranges and contain favorable host rocks as well as small uranium occurrences.

The Cordilleran region is the most recently active mobile belt of America and contains the structures of several Cenozoic superimposed or juxtaposed orogenies. The only other prominent mobile belt in the United States is the Appalachian system of Hercynian age. This mobile belt has an associated mineralization gradient of similar age, but important concentrations of uranium are not known. However, this system swings westward through the southern states beneath Mesozoic and Cenozoic rocks and passes down the east coast of Mexico. Intersections of tectonic elements or systems are known preferentially to localize mineralization which accompanied the later system. The existence of Tertiary uranium deposits in Karnes County, Texas, not too far distant from the Llano uplift focuses attention on this feature. The Ouachita and Ozark uplifts of Oklahoma and Arkansas are also worthy of examination.

Worldwide possibilities

The same criteria can be applied throughout the world for the evaluation of mobile belts as potential uranium provinces and the selection of local exploration targets.

Many of the mobile belts throughout the world would be suspect, particularly the Cenozoic Cordilleran belt of South America and the Precambrian and

Hercynian belts on the east margin of the Brazilian and Guianan shields; the active belts around the Australian shield; the Alpine-Himalayan belt and the Atlas Mountains of North Africa. Within or on the foreland sides of those belts the most favorable local areas are the flanks of small uplifts associated with low temperature mineralization gradients. The uplifts should be marginal to depositional basins with fluvial deposits.

For the mobile belts mentioned, local areas of particular favorability include the Tucano and related Cretaceous-Tertiary coastal basins of north-east Brazil, the eastern foreland or intermontane basins of the Peruvian Andes from Colombia to Argentina, the transition shelf between the shield and the Great Dividing Range of eastern Australia, and the southern High Atlas and Saharan mountain chains of North Africa.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/257 États-Unis d'Amérique

Application de concepts géologiques à la prospection future de l'uranium

par R. D. Nininger *et al.*

La plupart des régions d'extraction de l'uranium actuellement importantes aux États-Unis ont apparemment atteint ou passé la période de maturité. Les besoins rapidement croissants des centrales nucléaires prévues pour les années 1970-1979 dépasseront largement l'accroissement des réserves que l'on peut attendre des mines en exploitation et des zones avoisinantes, et ces besoins devront être satisfaits principalement par des gisements non encore découverts. La mise au point et l'utilisation de critères géo-

logiques de la genèse du minerai d'uranium et de sa situation géographique seront les facteurs dominants dans le choix des régions favorables et des objectifs d'une prospection précise; on pense que la plus grande partie des réserves nouvelles d'uranium à bon marché se trouveront dans des gisements de grès. Les méthodes géophysiques et géochimiques joueront un rôle important dans la prospection détaillée de nouvelles régions, mais il est moins certain qu'elles seront le moyen initial de la découverte de telles régions.

Des concepts géologiques fondés sur des données empiriques concernant la présence d'uranium dans des gisements de grès et de conglomérats sont exposés dans le mémoire, et l'on pense qu'ils constituent une base intéressante pour l'évaluation des possibilités de présence d'uranium dans des régions inexplorées des États-Unis et du monde. Ces concepts présupposent une corrélation entre l'origine de l'uranium et certains événements tectoniques (qui sont également associés à la formation de gisements hypogènes de divers métaux) mais n'exigent pas nécessairement que l'uranium soit hypogène.

D'après des études concernant les gisements de minerais métalliques sur les continents américains, il est apparu que dans toute région les ceintures ou centres de minéralisation de plus grande intensité et à plus haute température coïncident généralement avec des unités tectoniques linéaires ou bien apparaissent aux intersections de ces unités ou en des centres volcaniques. La minéralisation apparaît en zones et en séquences paragénétiques le long de gradients d'intensité décroissante rayonnant à partir de ces régions focales. Bien que l'uranium puisse être présent dans toutes les zones, il est le plus abondant dans les zones extérieures peu profondes et à basse température, où il est déposé à partir de solutions à caractéristiques téléthermales ou d'eaux d'infiltration. Les liquides causant la minéralisation en zones peuvent déposer de l'uranium hypogène ou enlever de l'uranium du granite, du tuf ou d'autres roches au cours de modifications et les modifier chimiquement assez pour permettre un lessivage supergène. Le lessivage supergène de roches nouvelles peut également être déclenché par des événements tectoniques, et le dépôt peut se produire dans les mêmes régions marginales favorables à la minéralisation hypogène.

Dans les zones à basse température, le dépôt d'uranium dans les grès est déterminé par des caractéristiques particulières aux milieux de roches sédimentaires. Le caractère et la distribution de dépôts de minerais non oxydés dans des grès carbonés perméables indique l'importance des processus de réduction et d'oxydation dans la formation de minerais. Les dépôts de minerais sont directement liés aux interfaces formés par les incursions d'eaux d'infiltration oxydantes dans des zones de réduction produites par la décomposition bactérienne anaérobie de matières organiques. On peut localiser les terrains qui peuvent être productifs en situant ces limites grâce à leurs particularités minéralogiques évidentes.

Les régions présentant une coïncidence de zones hypogènes à basse température, de canaux de circulation de solutions supergènes et de milieux sédimentaires favorables se trouvent généralement le long des bords communs à des saillies orogéniques et aux bassins continentaux adjacents. Une évaluation montre les possibilités de présence d'uranium en diverses régions des États-Unis et d'ailleurs où de tels lieux favorables semblent exister.

A/257 США

Применение геологических понятий в будущих разведках урана

Р. Д. Найнингем *et al.*

Большинство современных наиболее важных уранодобывающих районов США, по-видимому, достигли или пережили этап наибольшего развития. Растущие потребности в ядерном топливе, предсказываемые на 1970-е годы, намного превзойдут ожидаемые приросты запасов на действующих рудниках. Удовлетворение потребностей будет осуществляться главным образом за счет открытия новых месторождений. Развитие и использование геологических особенностей генезиса и условий образования урановых руд становится решающим фактором при выборе первоочередных перспективных районов и определении конкретных объектов разведки. Ожидается, что большая часть вновь открытых запасов дешевого урана будет находиться в минерализованных песчаниках. Геофизические и геохимические методы будут играть важную роль в детальной разведке новых районов; однако менее вероятно, что именно они будут служить первоначальными средствами поисков.

В настоящем докладе рассматриваются геологические понятия, основанные на эмпирических данных относительно залегания урана в песчаниках и конгломератах. Эти понятия, как полагают, составляют основу для оценки урановых запасов в неразведанных районах США и других стран мира. Эти понятия предполагают связь между отложениями урана и тектоническими явлениями, которые сопровождаются также образованием гипогенных месторождений различных металлов, но не обязательно обусловливают гипогенное происхождение урана.

В результате изучения металлических рудных месторождений на американском континенте стало очевидным, что пояса или центры наиболее интенсивной и высокотемпературной минерализации в любом районе совпадают в общем с линейными тектоническими структурами, с пересечением таких структур или с вулканическими центрами. Минерализация происходит в зональных контурах и в парагенетической последовательности в направлении радиально уменьшающейся интенсивности от этих центральных очагов. Хотя уран может отлагаться во всех зонах, больше всего он концентрируется в наиболее удаленных от центра, неглубокозалегающих низкотемпературных зонах, где он выпадает из растворов с телетермическими или почвенно-водными характеристиками. Растворы, создающие минеральное зонирование, могут отлагать гипогенный уран или выщелачивать уран из гранита, туфа и других пород, или же преобразовывать их химически в достаточной мере для более эффективного гипергенного выщелачивания. Гипергенное выщелачивание свежих пород может быть также вызвано тектоническими явлениями, и отложение урана может произойти в тех же периферийных районах, благоприятствующих гипогенной минерализации.

В низкотемпературных зонах отложение урана в песчаниках контролируется условиями, присущими образованию осадочных пород. Характер и распределение неокисленных рудных тел в проницаемых углистых песчаниках указывают на важную роль при рудообразовании, восстановительных и окислительных процессов. Рудные тела непосредственно связаны с контурами, образованными вторжением окисляющих подземных вод в зоны восстановления, созданные анаэробным бактерийным разложением органических веществ. Потенциально продуктивные участки могут быть установлены путем нахождения этих контуров по их характерным минералогическим свойствам.

Районы, в которых имеется совпадение низкотемпературных гипогенных зон, миграционных каналов для гипергенных растворов и благоприятных осадочных сред встречаются в основном вдоль общих границ орогенических поднятий и смежных континентальных бассейнов. Дается оценка перспективных по урану различных районов в США и других стран мира, где предполагается наличие подобных очагов.

A/257 Estados Unidos de América

Aplicación de conceptos geológicos a la futura exploración del uranio

por R. D. Nininger *et al.*

La mayoría de las regiones mineras de los Estados Unidos que son importantes en la actualidad, aparentemente han alcanzado o pasado el período de mayor producción. Las crecientes demandas de energía nuclear esperadas para los años de 1970 a 1980 excederán grandemente los aumentos que se espera se harán en las reservas actuales con material sacado de las minas actualmente en explotación y de zonas cercanas. Estas demandas tendrán que ser satisfechas en su mayor parte con la producción procedente de nuevas minas aún no descubiertas. El desarrollo y uso de conocimientos geológicos acerca de la formación del mineral de uranio y de las regiones más favorables para su desenvolvimiento serán factores dominantes para determinar las regiones que podrán ser exploradas más favorablemente. Se espera que la mayor parte de las reservas de uranio de bajo precio que serán descubiertas en un futuro próximo se encontrarán en depósitos de piedra arenisca. Los métodos geofísicos y geoquímicos tendrán probablemente un papel importante en la exploración detallada de las nuevas regiones, pero es menos probable que estos métodos sean los medios iniciales que se utilicen para localizar estas nuevas regiones.

Se presentan datos geológicos que concuerdan con los datos empíricos en lo que respecta a la presencia del uranio en piedra arenisca y conglomerados. Se cree que estos datos forman una buena base para la evaluación de la reserva potencial de uranio en regiones no exploradas de los Estados Unidos y de cualquier otro lugar del mundo. Esto presupone una relación entre la derivación del uranio y acontecimientos tectónicos (que también están asociados a la formación de depósitos hipogénicos de varios metales), pero no quiere decir necesariamente que el uranio sea hipogénico.

Como resultado de los estudios hechos en yacimientos minerales en el continente americano, resulta aparente que las bandas o centros de mineralización de mayor intensidad y más alta temperatura de cada región coinciden generalmente con unidades tectónicas lineales y ocurren en las intersecciones de dichas unidades o en centros volcánicos. La mineralización ocurre en zonas y en secuencias paragenéticas cuya intensidad decrece radialmente a medida que se alejan de las áreas de concentración. Aunque el uranio puede formarse en cualquier zona, es más abundante en las zonas más exteriores y de baja temperatura, donde se deposita de soluciones con características teletermales o de aguas subterráneas. Los fluidos que crean las bandas de mineralización pueden depositar uranio hipogénico o pueden separar el uranio del granito, de rocas volcánicas u otras rocas durante su alteración y modificarlas químicamente lo suficiente como para permitir una lixiviación supergénica más efectiva. La lixiviación supergénica de las rocas nuevas puede también ser causado por fenómenos tectónicos y una deposición puede ocurrir en las mismas regiones marginales favorables para la mineralización hipogénica.

En las zonas de baja temperatura, la deposición del uranio en piedra arenisca es controlada por las características peculiares de las rocas sedimentarias que rodean la piedra arenisca. Las características y distribución de masas de mineral que no ha sufrido oxidación en piedra arenisca carbonosa permeable indica la importancia de los procesos de oxidación y reducción en la formación del mineral. Las masas minerales están directamente relacionadas con las interfases formadas por la introducción de aguas subterráneas con características oxidantes en zonas de reducción creadas por la descomposición de bacterias anaerobias en la materia orgánica. Las tierras potencialmente productivas pueden ser delineadas localizando sus contornos por medio de sus salientes características mineralógicas.

Las regiones en donde coinciden las zonas hipogénicas de baja temperatura, los canales de migración de soluciones supergénicas y las rocas sedimentarias favorables a la formación de uranio se hallan generalmente a lo largo de los bordes comunes de los levantamientos orogénicos y de las cuencas continentales adyacentes. Un estudio de estas condiciones muestra las posibilidades de la existencia de uranio en varias regiones de los Estados Unidos y en otras partes del mundo donde se cree que existen estas condiciones favorables.

Р/353 СССР

Гетерогенное окисление UO_2 и процессы выщелачивания урана в кислых растворах

Е. А. Каневский, А. П. Филиппов, Г. М. Несмеянова

Процессы кислотного выщелачивания урана из руд отличаются большой сложностью. Однако основные закономерности этих процессов, как показано в докладе, связаны с кинетикой окисления и растворения окислов урана. Поэтому своеобразные особенности гетерогенных процессов окисления и растворения UO_2 в кислых растворах представляют большой интерес.

В ранее опубликованных работах были рассмотрены гетерогенные процессы взаимодействия UO_2 и MnO_2[1], каталитическое влияние ионов железа[2], влияние ионного состава Fe (III) и концентрации ионов водорода на окисление и растворение UO_2[3]. В настоящем докладе приведены новые экспериментальные данные и сделаны некоторые обобщающие выводы.

1. РАСТВОРЕНИЕ UO_2 В СЕРНОКИСЛОМ РАСТВОРЕ С УЧАСТИЕМ ОКИСЛИТЕЛЕЙ

Из многочисленных окислителей, которые могут быть использованы при растворении UO_2 в сернокислых растворах, ограничимся рассмотрением тех веществ, которые имеют основное значение в урановой промышленности, то есть азотной кислоты, хлорноватой кислоты и двуокиси марганца, а также ионов железа (III).

а) АЗОТНАЯ КИСЛОТА

В случае применения азотной кислоты в сернокислых растворах на холоду ее окислительные свойства заметно проявляются только в области относительно концентрированных растворов H_2SO_4. С возрастанием концентрации азотной кислоты эффективность этого вещества в качестве окислителя также повышается (табл. 1).

Таблица 1. Зависимость степени растворения урана от концентрации серной и азотной кислот

Концентрация H_2SO_4, *M*	Степень растворения при концентрации HNO_3, в молях, (%)			
—	—	0,032	0,094	0,186
0,05	1,0	1,0	1,0	1,0
0,10	1,0	1,1	1,1	1,0
0,26	1,0	1,1	1,0	1,8
0,51	0,9	1,1	1,0	3,1
1,02	0,9	1,1	1,9	7,2
2,04	1,0	18,0	27,0	38,0

Опыты проводились в автоклаве. Условия опыта: навеска UO_2 — 5 *г*, температура 20° С, продолжительность — 3 *ч*, азотную кислоту добавляли в стехиометрическом количестве. В аналогичных условиях проводили исследование влияния температуры, но продолжительность опыта составила 1 *ч*. Экспериментальные данные приведены на рис. 1. Окислительная активность азотной кислоты, так же как и при повышении концентрации HNO_3 и H_2SO_4, растет не постепенно, а скачкообразно. Начало энергичного окислительного действия азотной кислоты в указанных условиях соответствует температуре 70° С, то есть температуре, при которой начинается сильное разложение[4] HNO_3.

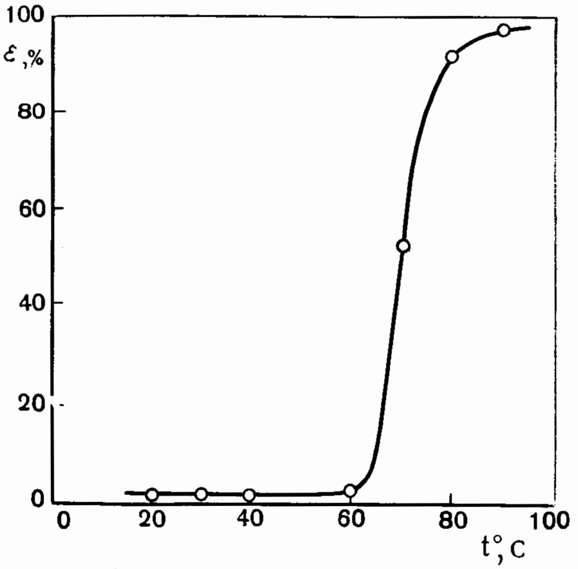

Рис. 1. Зависимость степени взаимодействия UO_2 и азотной кислоты в H_2SO_4 концентрации 10 г/л от температуры

Эти особенности азотной кислоты наиболее естественно объясняются при допущении, что в определенных условиях процесс автокаталитического разложения HNO_3 протекает быстро, причем продукты распада представляют собой сильные окислители.

Феттер [5] при исследовании электрохимического восстановления растворов азотной кислоты средней и высокой концентрации сделал вывод о том, что окислительно-восстановительный потенциал (о.-в. п.) растворов находится в логарифмической зависимости от концентрации азотистой кислоты. Напротив, Монк и Эллингем [6] полагают, что потенциалопределяющей является реакция

$$HNO_3 + 2H^+ + 2\bar{e} \rightarrow HNO_2 + H_2O, \qquad (1)$$

то есть непосредственный окислитель — азотная кислота. В связи с такими противоречивыми мнениями необходимо дальнейшее исследование этого вопроса.

Результаты одновременного исследования кинетики растворения UO_2 и установления потенциала в системе $UO_2 — H_2SO_4 — HNO_3$ при 20° С приведены на рис. 2. При введении в сернокислый раствор азотной кислоты и двуокиси урана о.-в. п. повышается постепенно и даже за два часа не достигает постоянной величины.

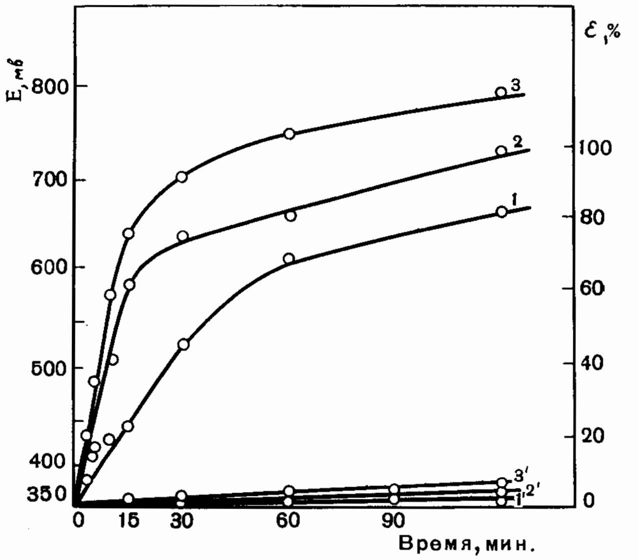

Рис. 2. Зависимость величины о.-в. п. системы H_2SO_4—HNO_3—UO_2 (кривые 1, 2, 3) и степени растворения урана (кривые 1', 2', 3') от концентрации HNO_3 и продолжительности процесса при 20° С. Кривые 1 и 1' соответствуют HNO_3 20 г/л; 2 и 2' — 60 г/л; 3 и 3' — 100 г/л; концентрация H_2SO_4 — 45 г/л

Сопоставление кривых 1 и 1', 2 и 2', 3 и 3' показывает, что между кинетикой установления о.-в. п. и растворением двуокиси урана нет прямой зависимости. В то время как окисление и растворение UO_2 даже в растворе, содержащем 100 *г/л* HNO_3, достигает за два часа лишь нескольких процентов, о.-в. п. за это время повышается на 300 *мв*. Эти экспериментальные факты понятны, если азотная кислота в данных условиях не является непосредственным окислителем, а в процессе окисления принимают участие продукты ее разложения и именно они определяют о.-в. п. системы.

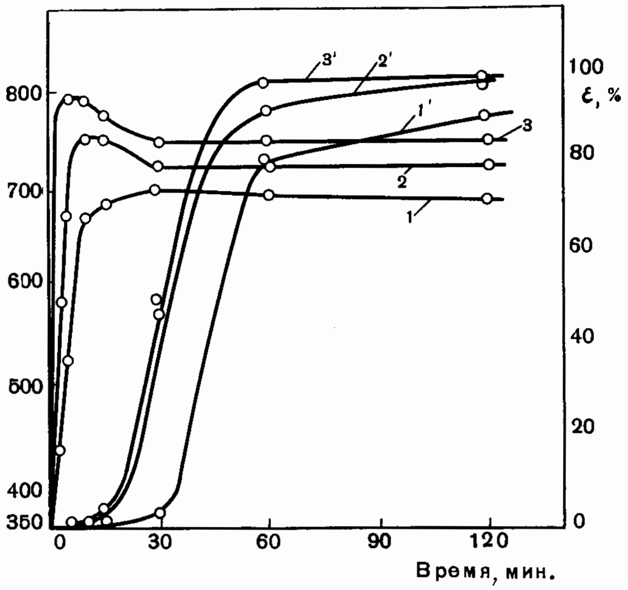

Рис. 3. Зависимость величины о.-в. п. системы H_2SO_4—HNO_3—UO_2, (кривые 1, 2, 3) и степени растворения урана (кривые 1', 2', 3') от концентрации HNO_3 и продолжительности процесса при 70° С. Кривые 1 и 1' соответствуют концентрации HNO_3 10 г/л; 2 и 2' — 25 г/л; 3 и 3' — 60 г/л; концентрация H_2SO_4 — 45 г/л

Кей и Стерн [4] указывают, что ниже 70° С скорость разложения даже 100%-ной азотной кислоты неизмеримо мала. Поэтому наблюдающееся растворение UO_2, вероятно, связано с ускорением разложения HNO_3 под каталитическим влиянием продуктов ее восстановления — окислов азота.

При температуре 70° С в той же системе процессы окисления и растворения UO_2, как следует из рис. 3, протекают значительно быстрее, чем при 20° С. Не менее существенно изменяется и кинетика установления о.-в. п.

Авторы ограничиваются качественной характеристикой кинетики рассматриваемого процесса в виду исключительной сложности исследуемой гетерогенной системы, содержащей твердое тело, раствор и газ, причем количество последнего зависит от целого ряда параметров. Вместе с тем из приведенных выше данных можно сделать существенные выводы о свойствах азотной кислоты при ее взаимодействии с двуокисью урана.

Исследование факторов, определяющих окислительную активность азотной кислоты при ее взаимодействии с двуокисью урана, показывает, что HNO_3 не является непосредственным окислителем. Все факторы, благоприятствующие повышению окислительной активности азотной кислоты, одновременно являются факторами, способствующими ускорению ее разложения. Поэтому очевидно, что при взаимодействии HNO_3 с окислами урана непосредственным окислителем является один из продуктов ее разложения или даже одновременно несколько образующихся при этом веществ, например HNO_2 и NO_2.

б) ХЛОРАТЫ

Окисление двуокиси урана хлоратом при 20° С, как и гомогенное окисление U (IV) [7], протекает медленно. В табл. 2 приведены результаты опытов при концентрации H_2SO_4 100 *г/л*.

Таблица 2. Кинетика растворения UO_2 при 20° С с введением стехиометрических количеств хлората

Продолжительность, ч	Степень растворения, %	
	Эксперимент	По уравнению (9)
1,0	0,020	0,020
2,0	0,023	0,023
3,0	0,026	0,026
4,0	0,030	0,029
5,0	0,031	0,032
6,0	0,034	0,035

Скорость гетерогенного процесса с участием компонентов раствора, обозначенных y и z, может быть выражена по закону действующих масс уравнением

$$w = kS\,[y]^a\,[z]^b, \tag{2}$$

где S — величина поверхности твердой фазы, a и b — показатели степени, соответствующие порядку реакции по данному компоненту. В том случае, когда один из компонентов взят в большом избытке по отношению к растворяемому твердому телу,

$$w = k'S\,[y]^a, \tag{3}$$

где $k' = k[z]^b \approx \text{const}$.

Примем, что закономерности кинетики гомогенного окисления U (IV) хлоратом в сернокислом растворе можно распространить на соответствующий гетерогенный процесс окисления и отождествить $[y]$ с концентрацией хлората, а $[z]$ с концентрацией водородных ионов. Скорость гомогенной реакции выражается уравнением

$$w = k\,[HClO_3]^{1/3}, \tag{4}$$

где $[HClO_3]$ — концентрация недиссоциированной хлорноватой кислоты. На основании уравнений (3) и (4)

$$w = k'S\,[y]^{1/3} = k'S\,[y_0]^{1/3}(1-\varepsilon)^{1/3}, \tag{5}$$

где ε — степень взаимодействия в момент τ.

По Доливо-Добровольскому [8] для растворения монодисперсных веществ

$$S = S_0\,(1-\varepsilon)^{2/3}. \tag{6}$$

Поэтому

$$w = k'S\,[y_0]^{1/3}(1-\varepsilon) = w_0\,(1-\varepsilon). \tag{7}$$

С учетом того, что скорость процесса мала, в первом приближении

$$w = \frac{dx}{d\tau} = w_0\,(1-\varepsilon) \approx w_0 \tag{8}$$

Поэтому $\varepsilon = {}^x/_{x_0}$ определяется уравнением

$$\varepsilon = w_0\tau + \text{const}. \tag{9}$$

Величина const связана с содержанием U(VI) в двуокиси. Экспериментальные данные подтверждают уравнение (9).

Степень растворения UO_2 в H_2SO_4 концентрации 100 *г/л* при 80° С и стехиометрическом количестве хлората приведена в табл. 3. В этом случае уравнение (8) приобретает вид

$$\frac{d\left(\frac{x}{x_0}\right)}{d\tau} = \frac{d\varepsilon}{d\tau} = w_0'\,(1-\varepsilon)$$

или

$$-\frac{d\,(1-\varepsilon)}{d\tau} = w_0'\,(1-\varepsilon),$$

откуда следует, что

$$-\lg\,(1-\varepsilon)/\tau = w_0'' = \text{const}. \tag{10}$$

В табл. 3 эта зависимость сопоставлена с экспериментальными данными. Средняя величина $w_0'' = w_0' \cdot 2{,}303 = 0{,}345$ (по данным табл. 3), откуда следует, что $\varepsilon = 1 - 10^{-0{,}345\tau}$. Значения ε, вычисленные по уравнению (11), находятся в согласии с экспериментальными данными.

Таблица 3. Проверка уравнений (10) и (11) на основании экспериментальных данных (при 80° С)

τ, ч	ε	$-\frac{\lg\,(1-\varepsilon)}{\tau}$	$\varepsilon_{вычисл.}$
0,5	0,332	0,35	0,328
1,0	0,590	0,39	0,548
2,0	0,790	0,34	0,795
3,0	0,875	0,30	0,908
4,0	0,960	0,35	0,958

в) ДВУОКИСЬ МАРГАНЦА

В ранее опубликованной работе [1] было показано, что при большом избытке MnO_2 скорость реакции остается неизменной во времени, но зависит от соотношения UO_2 и MnO_2. При стехиометрическом количестве MnO_2 реакция замедляется (табл. 4), влияние температуры незначительно.

Сопоставление результатов седиментометрического анализа полидисперсной двуокиси марганца с геометрической поверхностью этого порошка свидетельствует о существовании конгломератов частиц в сернокислом растворе. Такие же конгломераты образуются в системе, содержащей UO_2 и MnO_2. По-видимому, в этих условиях скорость процесса не определяется скоростью химического взаимодействия; процесс про-

Таблица 4. Влияние продолжительности процесса и температуры на степень растворения UO_2 при ее взаимодействии с MnO_2

τ, мин	Значения ε, %		
	20° С	30° С	40° С
5	12,0	12,4	14,6
15	15,8	17,5	17,9
30	20,2	20,3	24,4
45	23,0	22,9	25,8
60	25,8	25,6	30,4
120	29,6	29,6	35,2
180	30,8	30,7	38,2
240	35,3	35,4	41,4
300	39,1	41,0	46,6
360	44,3	46,5	48,4

текает в поверхностных гидратированных слоях частиц UO_2 и MnO_2, которые находятся в тесном контакте друг с другом. Поскольку условия этого контакта связаны с соотношением числа частиц UO_2 и MnO_2 в конгломератах и относительными размерами частиц, то наблюдаются различные кинетические закономерности при стехиометрическом количестве и избытке MnO_2. Вследствие решающей роли контакта частиц взаимодействие UO_2 и MnO_2 в сернокислом растворе, если нет большого избытка двуокиси марганца, протекает сравнительно медленно.

г) ИОНЫ ТРЕХВАЛЕНТНОГО ЖЕЛЕЗА

Большая роль ионов Fe(III) при кислотном выщелачивании урана из руд отмечена в ряде работ[2, 9–12]. Однако некоторые закономерности взаимодействия UO_2 с Fe (III) исследованы недостаточно. В недавно опубликованных работах[3] отмечена зависимость степени взаимодействия при определенной продолжительности процесса от величины pH. Обычно принимают, что это процесс протекает по уравнению

$$UO_2 + 2Fe^{3+} \rightarrow UO_2^{2+} + 2Fe^{2+}, \qquad (12)$$

но если в нем принимает участие только негидролизованный ион Fe^{3+}, то влияние pH не должно наблюдаться.

В работе Беттса[13] было показано, что скорость окисления урана (IV) железом (III) в хлорнокислом растворе при возрастании концентрации кислоты с 0,105 до 1,02 1 *M* уменьшается. Аналогичное явление еще раньше было отмечено[14] при окислении железом (III) нептуния (IV) и повышении концентрации водородных ионов с 0,5 до 1,0 *M*. Авторы объясняют такое влияние концентрации водородных ионов тем, что в процессе окисления принимают участие гидролизованные ионы Fe (III), а именно $FeOH^{2+}$ и $Fe(OH)_2^+$.

По-видимому, Fe (III) в качестве окислителя в кислых растворах сохраняет те же свойства и в случае гетерогенных процессов. При таком предположении процесс, выражаемый суммарным уравнением (12) состоит из двух последовательных реакций, как это показано в приведенной ниже схеме для окисления с участием $FeOH^{2+}$:

$$2Fe^{3+} + 2H_2O \rightleftarrows 2FeOH^{2+} + 2H^+, \qquad (13а)$$

$$\frac{UO_2 + 2FeOH^{2+} + 2H^+ \rightarrow UO_2^{2+} + 2Fe^{2+} + 2H_2O}{2Fe^{3+} + UO_2 \rightarrow 2Fe^{2+} + UO_2^{2+}}. \qquad (13б)$$

Специальными опытами, в которых исследовалось влияние скорости потока растворителя на взаимодействие UO_2 (в виде закрепленных прессованных таблеток) с сернокислым раствором, содержащим Fe (III), показано, что в определенных условиях процесс находится в кинетической области. Этот вывод справедлив для рассмотренных далее экспериментальных данных.

Реакция (13 *а*), представляющая собой обратимый процесс, протекает быстро, поэтому вероятно, что скорость суммарного процесса определяет одну из стадий гетерогенного окисления (13 *б*). Отсюда вытекает, что скорость растворения двуокиси урана должна быть пропорциональна концентрациям ионов $FeOH^{2+}$ или других ионов Fe (III). Иначе говоря, кинетика взаимодействия UO_2 с ионами Fe (III) определяется скоростью процессов:

$$UO_2 + Fe^{3+} \rightarrow UO_2^+ + Fe^{2+}, \qquad (14а)$$

$$UO_2 + FeOH^{2+} \rightarrow UO_2^+ + Fe^{2+} + OH^-, \qquad (14б)$$

$$UO_2 + Fe(OH)_2^+ \rightarrow UO_2^+ + Fe^{2+} + 2OH^-, \qquad (14в)$$

$$UO_2 + \frac{1}{2} Fe_2(OH)_2^{4+} \rightarrow UO_2^+ + Fe^{2+} + OH^-, \qquad (14г)$$

если рассматриваемая реакция имеет первый порядок в отношении Fe (III).

При таком предположении скорости реакций (14 *а* — 14 *г*) выражаются уравнениями:

$$\begin{aligned} w_1 &= k_1 S\,[Fe^{3+}], \\ w_2 &= k_2 S\,[FeOH^{2+}], \\ w_3 &= k_3 S\,[Fe(OH)_2^+], \qquad (15) \\ w_4 &= k_4 S\,[Fe_2(OH)_2^{4+}]^{1/2}. \end{aligned}$$

Если с помощью уравнений (15) выразить концентрации всех ионов Fe (III) через $[Fe^{3+}]$ и учесть, что

$$w = w_1 + w_2 + w_3 + w_4, \qquad (16)$$

то

$$w = \left(k_1 + \frac{k_2K_1}{[H^+]} + \frac{k_3K_1K_2}{[H^+]^2} + \frac{k_4K_d^{1/2}K_1}{[H^+]}\right) S\,[Fe^{3+}], \qquad (17)$$

где K_1 и K_2 — соответственно первая и вторая константы гидролиза Fe^{3+}, а K_d — константа димеризации $FeOH^{2+}$. При постоянной концентрации водородных ионов уравнению (17) можно придать вид

$$w = k'S\,[Fe^{3+}]. \qquad (18)$$

При допущении, что рассматриваемый процесс является реакцией второго порядка в отношении Fe (III), как легко убедиться,

$$w = \left(k_1 + \frac{k_2 K_1^2}{[\mathrm{H}^+]^2} + \frac{k_3 K_1^2 K_2^2}{[\mathrm{H}^+]^4} + \frac{k_4 K_d K_1^2}{[\mathrm{H}^+]^2}\right) S\,[\mathrm{Fe}^{3+}]^2, \quad (19)$$

а при постоянной концентрации водородных ионов

$$w = k'' S\,[\mathrm{Fe}^{3+}]^2. \quad (20)$$

Ионный состав растворов Fe (III) существенно зависит от концентрации водородных ионов, поэтому непосредственное применение уравнений (17) и (19) оказывается невозможным. Можно, однако показать[3], что в той области pH, где еще нет выпадения осадка гидроокиси железа,

$$[\mathrm{Fe}^{3+}] = -\frac{[\mathrm{H}^+]}{4K_d K_1}\left[\left(\frac{[\mathrm{H}^+]}{K_1} + \frac{K_2}{[\mathrm{H}^+]} + 1\right) - \right.$$

$$\left. - \sqrt{\left(\frac{[\mathrm{H}^+]}{K_1} + \frac{K_2}{[\mathrm{H}^+]} + 1\right)^2 + 8K_d\,\mathrm{Fe(III)}}\,\right] \quad (21)$$

Из этого уравнения следует, что при повышении концентрации водородных ионов величина $[\mathrm{Fe}^{3+}]$ увеличивается.

Вследствие этого, как следует из уравнений (17 — 20), скорость реакции при определенном значении pH должна пройти через максимум, так как величины K' и K'' при возрастании концентрации водородных ионов уменьшаются.

Интегрирование уравнений (18) и (20) затруднено вследствие того, что не только $[\mathrm{Fe}^{3+}]$, но и величина S являются функцией продолжительности процесса. Скорость любого процесса растворения твердого тела, если процесс находится в кинетической области, может быть выражена уравнением

$$w = kSf(c), \quad (22)$$

где $f(c)$ — функция концентрации реагирующих веществ. Кроме того, величина поверхности S — функция массы растворяющегося твердого тела. Поэтому

$$w = -\frac{dm}{d\tau} = kf(c)\,f(m), \quad (23)$$

или

$$-\frac{dm}{f(m)} = kf(c)\,d\tau.$$

Если мы обозначим

$$c = \Phi(\tau) \text{ и } f(c) = f[\Phi(\tau)] = F(\tau), \quad (24)$$

то

$$-\frac{dm}{f(m)} = kF(\tau)\,d\tau,$$

или

$$k = \frac{\int_m^{m_0} \frac{dm}{f(m)}}{\int_0^{\tau} F(\tau)\,d\tau}. \quad (25)$$

Для витающих тел шарообразной формы уравнение

$$\int_m^{m_0} \frac{dm}{f(m)} = \frac{3\rho_S^{2/3}}{(36\pi)^{1/3}}\left(m_0^{1/3} - m^{1/3}\right), \quad (26)$$

а так как $m = m_0(1 - \varepsilon)$, то

$$\int_m^{m_0} \frac{dm}{f(m)} =$$

$$= \frac{3\rho_S^{2/3} m_0^{1/3}}{(36\pi)^{1/3}}\left[1 - (1 - \varepsilon)^{1/3}\right] = A\left[1 - (1 - \varepsilon)^{1/3}\right] \quad (27)$$

Величина $\int_0^{\tau} F(\tau) \equiv \int_0^{\tau} f(c)\,d\tau$ может быть найдена графически интегрированием при правильном выборе функции $f(c)$, что проверяется независимостью величины k от начальной концентрации. Количественная обработка экспериментальных данных для взаимодействия монодисперсной двуокиси урана с Fe (III) может быть произведена по уравнению *

$$k' = \frac{A\left[1 - (1 - \varepsilon)^{1/3}\right]}{\int_0^{\tau} F(\tau)\,d\tau}, \quad (28)$$

$F(\tau) \equiv f(c) \equiv [\mathrm{Fe}^{3+}]$, если реакция имеет первый порядок в отношении Fe (III), и $F(\tau) = f(c) \equiv c^2$, если порядок реакции равен двум. При $F(\tau) = [\mathrm{Fe}^{3+}]$ константа k' не зависит от исходной концентрации Fe (III). Таким путем удалось показать, что реакция имеет первый порядок в отношении ионов железа. Очевидно, U (VI) образуется путем диспропорционирования U (V). В работе[15] было показано, что диспропорционирование U (V) в сернокислых растворах — быстрый процесс.

Поскольку k_1 является функцией концентрации водородных ионов, то по уравнению (17) можно оценить значения констант скорости процессов (14 *а* — 14 *г*). Оказалось, что $k_1 \approx 1$, $k_2 \approx 10$, $k_3 \approx 10\,000$, а $k_4 \approx k_2$. Эти результаты вычисления констант скорости отдельных реакций полностью подтверждают предположение о весьма большой роли гидролизованных ионов Fe (III) при окислении и растворении $\mathrm{UO_2}$.

2. ЗАКОНОМЕРНОСТИ РАСТВОРЕНИЯ $\mathrm{UO_2}$ В СЕРНОКИСЛОМ РАСТВОРЕ С УЧАСТИЕМ РАЗЛИЧНЫХ ОКИСЛИТЕЛЕЙ И ИОНОВ ЖЕЛЕЗА

В реальных условиях выщелачивания урана из руд, как уже отмечалось, практически всегда в растворах содержатся ионы железа, что оказывает существенное влияние на процессы окисления и растворения первичных минералов урана. Рассмотрим в связи с этим некоторые закономерности растворения при широком варьирова-

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* Вывод уравнения опускается, так как он является громоздким.

нии величины pH с использованием в качестве окислителей азотной кислоты, двуокиси марганца, хлората калия и добавки Fe (II).

Окислители вводили в стехиометрическом количестве по отношению к двуокиси урана, а концентрация Fe (II) (0,5 *г/л*) при данном объеме раствора соответствовала примерно 12% необходимого количества Fe (III) для окисления UO_2. Величина pH в течение всего опыта поддерживалась постоянной. Опыты[3] проводились при температуре 25° C и продолжительности 1 *ч*.

На рис. 4 сопоставлена зависимость извлечения урана в раствор при использовании в качестве окислителя Fe (III), MnO_2, HNO_3 и $KClO_3$. Аналогичный характер кривых *1* и *2* связан с тем, что в обоих случаях растворение урана определяется одним и тем же процессом. Взаимодействие ионов Fe (III) и UO_2 нецелесообразно выражать уравнением (12); точнее, такая схема в известной мере справедлива только при величинах $pH < 1$. При других величинах pH преобладающее значение приобретают гидролизованные ионы Fe (III) и реакция протекает, например, по схеме

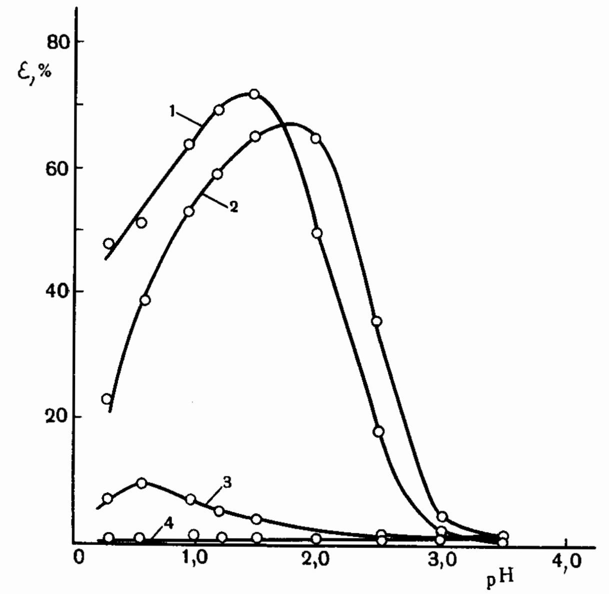

Рис. 4. Зависимость степени растворения UO_2 от величины pH при участии окислителей и добавки Fe (II)
1 — Fe(III); *2* — MnO_2 + Fe(II); *3* — $KClO_3$ + Fe(II); *4* — HNO_3 + Fe(II)

$$UO_2 + 2FeOH^{2+} \rightarrow UO_2^{2+} + 2FeOH^{+}, \qquad (29а)$$

$$2FeOH^{+} + MnO_2 + 4H^{+} \rightarrow 2FeOH^{2+} + Mn^{2+} + 2H_2O. \qquad (29б)$$

Реакция (29 *б*) протекает быстро, и скорость растворения UO_2, а следовательно, при определенной продолжительности процесса, и степень растворения UO_2 определяются ее взаимодействием с гидролизованными ионами Fe (III). Иначе говоря, ионы железа в этом процессе играют роль индуктора в свете представлений Шилова[16].

На рис. 4 наблюдается некоторое несовпадение максимумов кривых *1* и *2*. Они соответствуют pH 1,5 и 1,8. По-видимому, это объясняется различной величиной концентрации Fe (III), участвующего в рассматриваемом процессе и при введении стехиометрического количества Fe (III).

Слабо выраженный максимум на кривой *3* расположен при значительно меньшей величине pH в сравнении с кривой *1*. Если бы растворение UO_2 с использованием хлората в качестве окислителя и добавлением Fe (II) протекало аналогично растворению с участием MnO_2 и Fe (II), то и положение максимума на кривой и наибольшая величина ε были бы в обоих случаях одинаковыми. Наблюдаемое различие становится понятным, если допустить, что скорость процесса по уравнению (30 *б*) меньше скорости взаимодействия UO_2 и Fe (III):

$$UO_2 + 2FeOH^{2+} + 2H^{+} \rightarrow UO_2^{2+} + 2H_2O + 2Fe^{2+}, \qquad (30а)$$

$$2Fe^{2+} + \frac{1}{3}HClO_3 + H_2O \rightarrow 2FeOH^{2+} + \frac{1}{3}Cl^{-} + \frac{1}{3}H^{+}. \qquad (30б)$$

При использовании HNO_3 и HNO_3 + Fe (II) в качестве окислителя (кривая *4*) очевидно, что процессы, подобные (29 *б*) или (30 *б*), в рассматриваемых условиях не протекают.

Эти особенности растворения UO_2 в кислых растворах с участием окислителей и ионов железа объясняют закономерности выщелачивания урана из руд с использованием тех же окислителей.

Как известно, попытки использования азотной кислоты в качестве окислителя при выщелачивании без подогревания дали отрицательный результат[17]. Это полностью согласуется с рассмотренными выше поведением азотной кислоты при гетерогенном процессе окисления и растворением UO_2 в кислых растворах. Большая эффективность азотной кислоты при выщелачивании урана из руд с подогреванием до 80—90° C также хорошо объясняется автокаталитическим разложением HNO_3 под влиянием продуктов ее восстановления, отличающихся очень большой окислительной активностью.

Хлораты нашли применение при кислотном выщелачивании в основном без подогревания, но при этом процесс отличается сравнительно большой продолжительностью. Так же протекает окисление и растворение UO_2 с участием этого окислителя и ионов железа в сернокислом растворе.

Сравнительно быстрое растворение UO_2 с участием MnO_2 и ионов железа объясняет основное значение, которое приобрел этот окислитель в гидрометаллургии урана. Вместе с тем при выщелачивании урана из руд в условиях эффективного окисления его первичных минералов существенное значение приобретает другой фактор — скорость диффузии по капиллярам, порам руды. В тех случаях, когда доступ реагента к минералам урана не затруднен, оптимальная область pH (см. рис. 4) и условия выщелачивания руд практически совпадают. Однако в большинстве случаев выщелачивание проводится при более низком значении pH. Это объясняется тем, что снижение скорости растворения первичных минералов урана при таких значениях pH, возможно, компенсируется растворением вмещающих пород и связанным с этим ускорением процесса.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/353 USSR

Heterogeneous oxidation of UO_2 and uranium leaching processes in acid solutions

By E. A. Kanevsky *et al.*

Comparison of the standard potentials of oxidation-reduction processes with the rate at which uranium(IV) is oxidized by different oxidizing agents in acid solution shows that the dominant part is played by kinetic factors. In the absence of oxidizing agents, the dissolution of UO_2 is practically undetectable, but when an agent is present the rate of solution coincides with that of oxidation.

The kinetics of the oxidation of uranium dioxide by manganous dioxide in sulphuric acid solution are mainly conditioned by contact between the solid phases. When iron(III) ions are added, they function as direct oxidizing agents despite the lower oxidation-reduction potential of this system.

Study of the process of oxidation of UO_2 by Fe^{III} ions shows the high efficacy of the hydrolysed ions $FeOH^{2+}$ and $Fe(OH)_2^+$. It was established that the reaction is of the first order with respect to Fe^{III} and that the disproportioning rate of U^V in the sulphuric acid solution is higher than that of oxidation of UO_2 by hydrolysed ions Fe^{III}. Of these ions, $Fe(OH)_2^+$ is the most active.

In the presence of HNO_3, the kinetics of the oxidation and solution of UO_2 are determined by the rate of decomposition of the HNO_3; in this case, the presence of Fe^{III} ions is not so important as it is in the system UO_2-MnO_2-Fe^{III}. At low temperatures, Fe^{III} ions do not accelerate the process. The causes of this effect are discussed in the paper.

Study of the kinetics of the oxidation of U^{IV} in solution by chlorates shows that in this reaction the active part of oxidizing agent is played by the decomposition products of the chlorates. The rate of interaction of UO_2 with chlorates in acid solution is similarly determined by the concentration of undissociated chloric acid.

The slow speed of the reaction at low temperatures is explained. The catalytic influence of Fe and Va ions on the process is studied.

The significance of these conclusions for an understanding of the kinetics of the acid leaching of uranium from its ores is discussed.

A/353 URSS

Oxydation hétérogène de UO_2 et procédés de lixiviation de l'uranium en solution acide

par E. A. Kanevsky *et al.*

La comparaison des potentiels standard d'oxydo-réduction et de vitesse d'oxydation d'uranium(IV) en solution acide par différents oxydants montre que les facteurs cinétiques jouent un rôle décisif. En l'absence d'un oxydant, on n'observe pratiquement pas de dissolution de UO_2 mais, lorsqu'on introduit un oxydant, la vitesse de dissolution correspond à la vitesse d'oxydation.

La cinétique de l'oxydation du dioxyde d'uranium en solution sulfurique par le dioxyde de manganèse est en général définie par les conditions de contact des phases solides. Si l'on introduit dans la solution des ions de fer^{III} ceux-ci jouent le rôle d'un oxydant direct malgré le potentiel d'oxydo-réduction plus bas de ce système.

L'étude de l'oxydation de UO_2 par les ions Fe^{III} montre la grande efficacité des ions hydrolysés $FeOH^{2+}$ et $Fe(OH)_2{}^+$. La réaction est de premier ordre par rapport à Fe^{III}, et la dismutation de U^V en solution sulfurique se produit plus rapidement que l'oxydation de UO_2 par les ions hydrolysés Fe^{III}. Parmi ces ions, $Fe(OH)_{2+}$ est le plus actif.

En présence de HNO_3, la cinétique de l'oxydation et de la dissolution de UO_2 est déterminée par la vitesse de décomposition de l'acide nitrique. La présence d'ions fer ne joue pas dans ce cas le même rôle que dans le système UO_2-MnO_2-Fe^{III}. A basse température, les ions fer ne provoquent pas l'accélération du processus. Les causes de ce phénomène sont étudiées.

L'étude de la cinétique de l'oxydation de U^{IV} en solution par des chlorates montre que les produits de décomposition des chlorates jouent le rôle actif dans cette réaction d'oxydation. La vitesse de la réaction entre UO_2 et les chlorates en solution acide est également déterminée par la concentration d'acide chlorique non dissocié.

On explique la vitesse lente de la réaction à basse température. On étudie l'influence catalytique des ions fer et vanadium sur le processus.

On discute de la valeur de ces conclusions pour la cinétique de la lixiviation acide de l'uranium à partir des minerais.

A/353 URSS

Oxidación heterogénea del UO_2 y procesos de la lixiviación del uranio en soluciones ácidas

por E. A. Kanevsky *et al.*

La comparación de los potenciales tipo de los procesos de oxidación-reducción y de la velocidad de oxidación del uranio (IV) en solución ácida por diferentes oxidantes, prueba que los factores cinéticos representan un papel decisivo. En ausencia de oxidantes, no se observa prácticamente la disolución de UO_2, pero si se introduce un oxidante, la velocidad de disolución coincide con la de oxidación.

La cinética de la oxidación del dióxido de uranio, en una solución de sulfato, por el dióxido de manganeso viene determinada, en esencia, por las condiciones de contacto de las fases sólidas. Si se introducen en la solución iones de hierro, los iones hierro (III) representan el papel de un oxidante directo, a pesar del muy bajo potencial de oxidación-reducción de este sistema.

El estudio del proceso de oxidación del UO_2 por iones Fe^{III} pone de manifiesto la muy elevada eficacia de los iones hidrolizados $FeOH^{2+}$ y $Fe(OH)_2{}^+$. Quedó fijado que la reacción es de primer orden respecto del Fe^{III} y que el desproporcionamiento del U^V en la solución de sulfato tiene lugar más rápidamente que la oxidación del UO_2 por los iones hidrolizados del Fe^{III}. De éstos, el más activo es el $Fe(OH)_2{}^+$.

La cinética de la oxidación y de la disolución del UO_2 con participación del HNO_3 viene determinada por la velocidad de descomposición del ácido nítrico. La presencia de iones Fe^{III} no representa, en este caso, el mismo papel que en el sistema UO_2-MnO_2-Fe^{III}. A baja temperatura, los iones Fe^{III} no ejercen una acción aceleradora sobre el proceso. Se examinan las causas de este fenómeno.

El estudio de la cinética de la oxidación del U^{IV} en solución por los cloratos pone de manifiesto que los productos de la descomposición de los cloratos son, en esta reacción, los que inician la oxidación. La velocidad de reacción del UO_2 con los cloratos en solución ácida tembién viene determinada por la concentración del ácido clórico.

Se presenta una explicación del hecho de que la velocidad de reacción sea tan pequeña a baja temperatura. Se investiga la influencia catalítica de los iones hierro y vanadio sobre este proceso.

Se examina el valor de estas conclusiones para fundamentar la cinética de la lixiviación ácida del uranio contenido en los minerales.

Industrial application of catalytic precipitation of uranium

By B. Bunji, B. Zogović, R. Crnojević, N. Pacović and M. Šecerov *

The present paper describes the results of an investigation into the hydrogen reduction of hexavalent to tetravalent uranium from an alkaline solution using uranium dioxide as catalyst, on the basis of which a treatment plant has been built. The process is described and the results critically reviewed. These results and their application present a contribution not only to the separation of metals in the form of their oxides from aqueous solutions using large-scale hydrogen reduction techniques generally, but more particularly to the hydrometallurgy of uranium.

INTRODUCTION

A plant has been built at Kalna, in south-eastern Yugoslavia, for treating uranium ores and for the technical scale production of uranium dioxide. The alkaline process chosen is based on the chemical and mineralogical composition of the ore.

Hydrogen reduction techniques were used for the separation and concentration of uranium from carbonate leach solutions containing 0.5 to 0.7 g U/l of solution. It is not possible to achieve complete separation of uranium or economic recycling of the reagents by precipitating the uranium from such solutions with hydroxides, or by concentration using ion exchangers.

The reduction procedure adopted permits the quantitative separation and concentration of uranium, but as the reaction is catalytic the choice of the catalyst and its form greatly influence the applicability of the process. For the reduction of U^{VI} to U^{IV} from carbonate leach solutions, the most suitable catalyst is uranium dioxide, itself a product of the reaction.

The reaction by which hydrogen reduction of metals in solution proceeds may be explained by the difference of potential between the metal and the hydrogen in much the same way as the well known cementation reactions [1].

The precipitation of metallic nickel or cobalt by hydrogen reduction of an ammonium sulphate solution resulting from ammonia pressure leaching is being practised commercially in Canada [5].

Forward and Halpern [6] have described the reduction of U^{VI} to U^{IV} using a hydrogenation catalyst such as finely divided nickel powder. Bunji and Zogović [7] used uranium dioxide as catalyst since complete separation of nickel powder from the product is not feasible commercially.

The reduction of hexavalent uranium can be represented as follows :

$$Na_4[UO_2(CO_3)_3] + H_2 \longrightarrow UO_2 + Na_2CO_3 + 2NaHCO_3$$

The final object of the study was the use of uranium dioxide as a catalyst on the commercial scale. The process was first developed in the laboratory, then tried out in a pilot plant and finally put into practice at the Kalna plant. Briefly, it comprises carbonate-air leaching of the uranium bearing ores under pressure, clarification of the leach, and recovery of the uranium from the clarified solution by hydrogen reduction, the sodium carbonate recovered being returned to the leaching circuit.

The technological development of the process to the industrial stage is described below and the technical and economic features of the reduction process are examined.

RESULTS OF INVESTIGATIONS

The rate at which the reduction reaction $U^{VI} \rightarrow U^{IV}$ proceeds, and its completeness, depend on many factors, the most important of which are, as described elsewhere [6,7]: the partial pressure of the hydrogen, the temperature, the catalyst, the concentration of UO_2^{2+} and the concentrations of carbonate and bicarbonate.

When uranium dioxide is used as catalyst, the reaction rate is proportional to the square root of the partial pressure of the hydrogen for the intervals studied up to 30 atmospheres, as shown in Fig. 1.

From the effect of the temperature on the reaction rate, and in accordance with Arrhenius' diagram (Fig. 2), it follows that the activation energy is 10.2 kcal/mole, which, over a temperature range from 100 to 150 °C, produces an increase in the reaction rate of about 35% for each 10 deg C rise in temperature. Most of the experiments were performed to investigate the action of the catalyst on the reaction rate. The investigations bore on the type of catalyst and the method of preparing it.

In the first laboratory experiments, carried out in an autoclave with a mechanical mixer, uranium dioxide powder was used as catalyst. These investigations showed that the reaction rate depends on the

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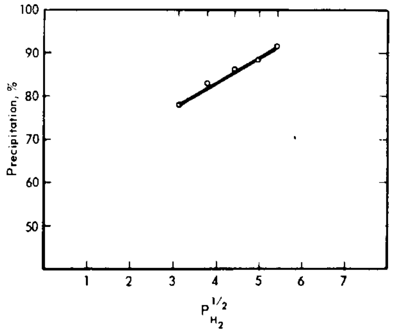

Figure 1. Effect of hydrogen pressure on the rate of uranium reduction

$T = 150$ °C; $UO_2^{2+} = 1$ g/l;
UO_2 catalyst surface area = 150 cm²/l;
$Na_2CO_3 = 10$ g/l; Time = 40 min

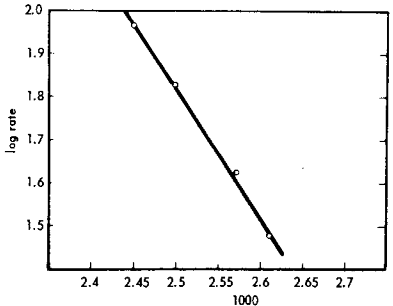

Figure 2. Effect of temperature on the rate of reduction of U^{VI} to U^{IV}

$UO_2^{2+} = 1$g/l; H_2 pressure = 15 atm;
UO_2, catalyst surface area = 150 cm²/l;
$Na_2CO_3 = 30$ g/l; $NaHCO_3 = 10$ g/l

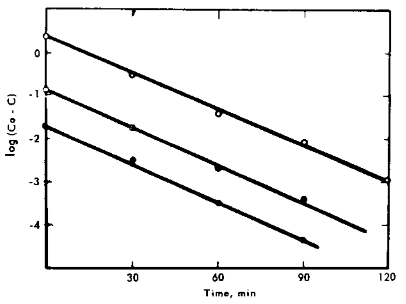

Figure 3. Effect of uranium concentration in the solution on rate of reduction reaction

Ca = initial U concentration;
C = U concentration at time t;
$T = 150$ °C; H_2 pressure = 15 atm;
UO_2 catalyst surface area = 150 cm²/l;
$Na_2CO_3 = 30$ g/l; $NaHCO_3 = 10$ g/l

surface area of the catalyst, in the sense that the reaction proceeds more quickly as the total area of the catalyst increases The oustanding feature of the experiments was that the surface of the catalyst was continually being increased by the formation, as a product of the process, of new particles of the oxide, which themselves act catalytically. Under these conditions, the particle size of the UO_2 also increases, although this was not measured. Experiments on the use of UO_2 powder in a continuous process in the pilot plant or on the commercial scale failed to give satisfactory results. This was due in part to the difficulty of keeping the powdered catalyst in contact with the solution during reduction, and in part to that of recovering the UO_2 from the spent solution so that it could be used again as the catalyst.

Accordingly, experiments were carried out using uranium dioxide as a fixed catalyst instead of a catalyst in suspension for precipitating uranium from a carbonate solution.

Preliminary tests, carried out with nickel wire as catalyst, showed that the layer of UO_2 deposited on the wire grew continuously, without any adverse effect on the reaction rate, which remained constant. The thickness of the layer was more than 5 mm, and the density of the UO_2 recovered varied from 4-5 g/cm³. In view of this encouraging result, experiments were begun using partly sintered uranium dioxide, pre-pressed into the desired shape, as a fixed catalyst.

The results obtained on the reduction of the uranyl ion to UO_2 using partly sintered oxide with a density of about 5 g/cm³ proved that in this case too rate of reduction is high; the reaction follows the same rules as when using UO_2 powder. In preparing the sintered catalyst, the aim was to achieve the maximum surface to weight ratio.

From the point of view of the applicability of a process, it is necessary to know how long the reduction must be continued to give quantitative recovery, in the present case of uranium dioxide from uranyl carbonate solution.

It was established that the reduction reaction half-time is 15 minutes, at 150 °C, using sintered UO_2 as catalyst with a total geometrical surface of 125 cm² for each litre of solution, and hydrogen at a pressure of 15 atmospheres. Under the same conditions, the reaction half-time in the pilot plant was 12 minutes. By reaction half-time is meant the time taken for the concentration to fall to one half its initial value. This value is constant for first-order reactions.

From Fig. 3 it will be seen that the reduction of hexalent to tetravalent uranium, using uranium dioxide as catalyst, is a first-order reaction, so that the time taken to reach one-half of the initial concentration is independent both of the initial concentration of UO_2^{2+} in the solution and of the moment from which the reaction is being observed.

Since, after reduction is complete, the concentration of carbonates is almost the same as in the initial solution, the spent liquor can be used again for leaching. It is therefore necessary that the concentration of uranyl ion in the spent solution be as low as possible; 3-5 g/m³ is quite satisfactory, however.

For a plant throughput of 200 m³ per day the following operating constants were adopted: hydrogen pressure, 15 atm; temperature, 150 °C; and relative initial geometrical surface of the catalyst (sintered UO_2), *ca* 150 cm² per litre of solution treated. It was anticipated that with these constants the reaction half-time would be 15 minutes. This period was chosen to enable a larger amount of solution, and to some extent solutions richer in uranium, to be treated. The foregoing conditions having been taken on the basis of the results obtained in the laboratory and pilot plant, it became possible to determine the size of the reaction vessels and to work out the technological flowsheet for the industrial plant.

DESCRIPTION OF REDUCTION PLANT

A clear solution, produced by alkaline leaching of the ore, and containing about 600 g U/m^3 and 20 g $Na\ CO_3$ and about 10 g $NaHCO_3$ per litre, is fed by a centrifugal pump with a capacity of 200 l/minute to the reaction vessel system The pump delivery pressure is the same as the working pressure in the vessels—namely, 20 atm. Before reaching the reaction vessels the solution passes through heat exchangers where it is preheated to about 100 °C by the solution leaving the reaction plant. The temperature of the spent solution is about 150 °C at the inlet to and about 70 °C at the outlet from the heat exchangers.

The preheated solution then passes to vessels in which it is saturated with hydrogen. The saturated solution passes to three reaction vessels, each having a volume of 6 m^3. The vessels are interconnected so that they can be operated either in series or individually, in parallel. The solution enters at the bottom of the vessel and after passing over the catalyst overflows at the top; this provides the only agitation used in the reduction process. The initial catalyst is sintered uranium dioxide, in cylindrical lengths arranged in such a way that a geometrical surface of 150 cm^2 is available for each litre of solution, which is brought up to 150 °C by injecting steam into the vessels. The spent liquor, after passing through the heat exchangers, is either filtered or returned direct to the ore-milling circuit. In the conditions described, spent solutions have been obtained containing up to 3 g U/m^3, the concentrations of carbonate and bicarbonate remaining almost unchanged. The UO_2 is deposited on the surface of the initial catalyst, thus increasing the surface of the latter. For this reason, the solution leaving the reduction plant is clear, and contains no particles of UO_2; this makes the use of a fixed catalyst preferable to that of powder in suspension.

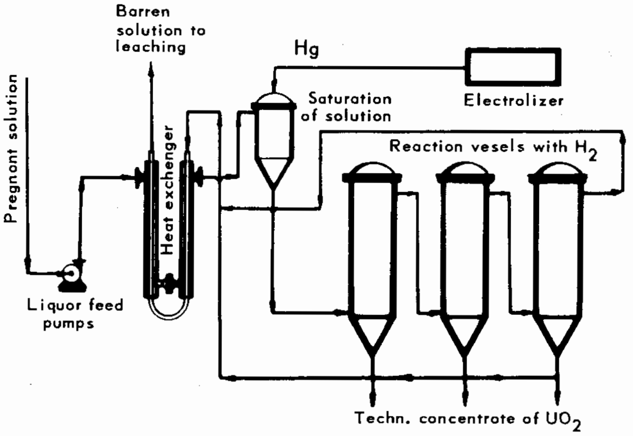

Figure 4. Flowsheet of the hydrogen reduction process for the production of technical UO_2 from alkaline solutions at Kalna

Figure 4 gives the flowsheet for the reduction process used at Kalna. Figures 5 and 6 are views respectively of the Kalna plant as a whole and the reaction-vessel installation.

The UO_2 product contains 72-75% U (calculated on the basis of 85-88% U_3O_8). The UO_2 is removed batchwise from the individual reaction vessels. Each vessel is operated continuously until upwards of 10 tons of U_3O_8 have accumulated in it.

ECONOMIC AND TECHNICAL ASPECTS OF THE PROCESS

It should be pointed out that rich ore deposits are becoming increasingly rarer, with the consequence that pyrometallurgical methods of treatment are giving way to hydrometallurgical processes. The

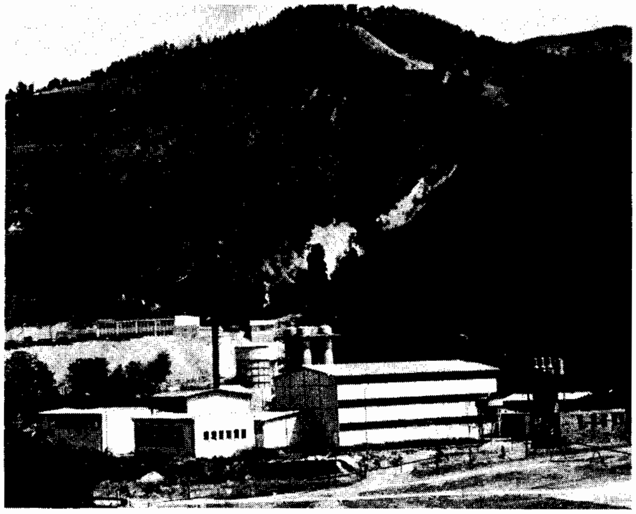

Figure 5. Aerial view of industrial plant for alkaline treatment of uranium ores at Kalna

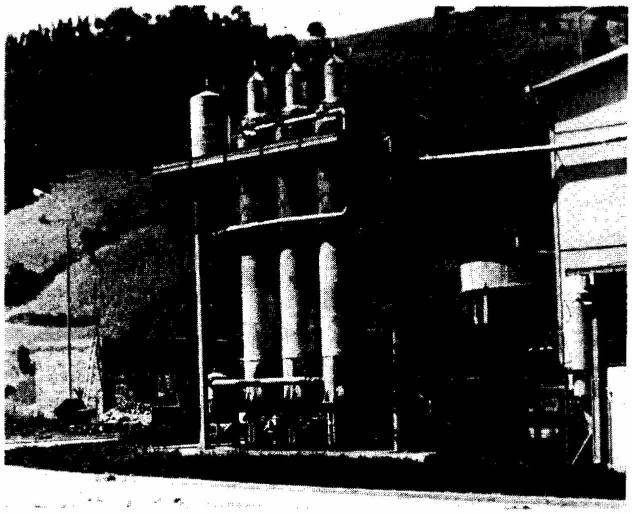

Figure 6. Reaction vessels for reduction of uranium from alkaline leach solution at Kalna

recovery and concentration of metals from solutions is daily becoming a more and more important factor in choosing between hydrometallurgical processes themselves so far as their technical and economic aspects are concerned.

In the hydrometallurgy of uranium, alkaline leaching under pressure followed by separation of the uranium from the leach solution is becoming more and more significant. This makes it necessary to gain insight into the economic and technical factors favouring one or other of the methods of separating and concentrating uranium from alkaline solutions. These mainly relate to the methods of precipitation, ion exchange and reduction under pressure.

First of all, it should be emphasized that the precipitation of uranium from aqueous solutions of sodium carbonate is of rather restricted application, inasmuch as it can be practised only where the concentration of uranium in the solution exceeds 2 g/l, which presupposes a uranium content in the ore of more than 0.2%. For this reason, we shall limit ourselves here to some comparisons of the processes of ion exchange and reduction under pressure which enable uranium to be separated from solutions at low concentrations.

The use of the ion exchange method is based on the following reaction:

$$4RCl + Na_4[UO_2(CO_3)_3] \rightleftharpoons R_4[UO_2(CO_3)_3] + 4NaCl$$

It follows that during the adsorption of uranium a chloride ion is extracted from the resin, which leads to a steady increase in the concentration of chloride in the inlet solutions and hence to a constant decrease in the capacity of the exchanger. It should be added that in most cases the concentration of sodium carbonate in the leach is about 30 g/l, and that of sodium bicarbonate about 15 g/l, and that such concentrations greatly diminish the capacity of the exchanger (which generally does not exceed 10 g U/l of resin). In order to avoid the accumulation of chloride in the initial solution, and to reduce the carbonate and bicarbonate contents, three-stage filtration is essential. This means a 50% increase in the capital cost of the filtration plant as compared with two-stage filtration. On the other hand, the introduction of three-stage filtration results in high sodium carbonate utilization, while at the same time the capacity of the ion exchanger is increased.

The ratio of the reagent and energy consumptions in the reduction and in the ion exchange processes respectively, when treating ore with a content of about 600 g U/t, is 1 : 1.5. Here it must be remembered that these data have been obtained when using three-stage filtration in conjunction with ion exchange. Accordingly, the additional cost of providing the third filtration stage has not been taken into account, though this is a prerequisite for the process.

These data on the application of reduction and ion exchange are based on the operation of a pilot plant with a throughput of 50 tons of ore a day. The product contained 72-75% U, i.e., calculated on 85-88% U_3O_8, and the sodium diuranate about 76% U_3O_8.

From these data it may be inferred that though the ion exchange process can be used for concentrating uranium from carbonate solutions, it is not the best method. As already mentioned, it was for this reason that our experiments were directed to establishing the technical and economic applicability of the process of reduction under pressure to the extraction of uranium dioxide from carbonate solutions.

It should again be pointed out that the reduction process can be used as soon as a two-stage filtration plant has been installed; this cuts capital costs and also operating costs for the ore processing as a whole. The spent liquors, after reduction is complete, contain not more than 4 g U/m^3, with almost unaltered concentrations of carbonate and bicarbonate, and can therefore be used again in the process.

The hydrogen used as the reducing agent is produced *in situ* by electrolysis; total consumption amounts to about 350 Nl/m^3 of solution. These data have been obtained from pilot plant operations. The UO_2 produced contained the following impurities: SiO_2, 2.3%; Zr, 1.1%; Na_2O, 2%; CaO 1.5%; and traces of iron, alumina copper, thorium, strontium, rubidium, antimony and other elements.

Thus it has been proved that the reduction process for extracting uranium from carbonate solutions is technically and economically feasible on the industrial scale.

It should be noted that there are further possibilities of improving this particular process; while at the same time real prospects are opened up of extending the use of pressure reduction techniques to other hydrometallurgical processes.

CONCLUSIONS

This study of the reduction process for uranium (VI) to uranium(IV) and its industrial scale application justify the following deductions:

(*a*) Catalytic reduction of U^{VI} to U^{IV} is a first-order reaction with an activation energy of 10.2 kcal/mole. A reaction half-time of 10-15 minutes is possible, depending on conditions and the system in which the reaction is carried out.

(*b*) The application of the process of hydrogen reduction to the separation and concentration of uranium from alkaline solutions is technically and economically feasible. The use of UO_2 as a fixed catalyst makes it possible on the industrial scale to separate uranium simply and quantitatively from solutions, with a high degree of recycling of the carbonate solution.

(*c*) Parallel technical and economic analyses show that for solutions containing about 600 g of uranium per cubic metre, hydrogen reduction is cheaper than ion exchange, the ratio being 1:1.5 in favour of reduction.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/414 Yougoslavie

Application industrielle de la précipitation catalytique de l'uranium

par B. Bunji *et al.*

Les recherches effectuées récemment ont confirmé que le processus de réduction de U^{VI} en U^{IV} est de nature catalytique; le choix du catalyseur et sa forme ont une grande influence sur l'applicabilité du procédé.

On a démontré que pour réduire U^{VI} en U^{IV} à partir de solutions aqueuses de carbonate de sodium, il est préférable d'utiliser comme catalyseur UO_2, qui est, en même temps, un produit de la réaction elle-même.

Les essais de laboratoire ainsi que les essais semi-industriels utilisant un fil de nickel comme catalyseur ont montré que l'oxyde d'uranium se dépose sur le fil de nickel. L'épaisseur de la couche d'oxyde déposé atteignait jusqu'à 5 mm et sa masse spécifique était de 4-5 g/cm^3. Le processus de réduction de U^{VI} a été mis au point avec un catalyseur déposé de cette manière. En vue de déterminer les qualités catalytiques de l'oxyde d'uranium en l'absence du fil de nickel, on a étudié le processus de réduction et examiné la possibilité d'utiliser UO_2 en poudre et UO_2 fritté et précomprimé pour obtenir les formes voulues.

L'accroissement de l'énergie d'activation du catalyseur à des températures plus élevées dans un courant d'hydrogène est signalé. Le processus de réduction est une réaction du premier ordre et on peut obtenir des demi-temps de réaction de 10 à 15 minutes.

Sur la base des résultats à l'échelle du laboratoire et à l'échelle semi-industrielle, on a construit une installation industrielle pour la précipitation continue de l'uranium à partir des solutions carboniques de lixiviation.

On décrit l'usine et les avantages qui ont conduit au choix du procédé ainsi que les résultats obtenus, et on fait une comparaison analytique avec d'autres méthodes.

L'effet de la précipitation de l'uranium est discuté d'après les caractéristiques du catalyseur et du système, notamment la surface de contact du catalyseur, le demi-temps de réaction, la concentration de l'uranium et des réactifs, la méthode d'agitation, la température et la pression.

A/414 Югославия

Промышленное применение каталитического осаждения урана

Б. Бунчи ***et al.***

Исследования последнего времени подтвердили, что процесс восстановления урана (VI) до урана (IV) носит каталитический характер. Выбор и форма катализатора оказывают большое влияние на осуществимость этого процесса.

В настоящем докладе показано, что при восстановлении урана (VI) до урана (IV) из водных растворов карбоната натрия лучшим катализатором служит UO_2, которая одновременно является продуктом самой реакции.

Лабораторные и полупромышленные опыты с никелевой проволокой показали, что окись урана осаждается на поверхности проволоки. Толщина слоя осажденной окиси доходит до 5 *мм* и более при плотности 4—5 *г/см*^{3}. Процесс восстановления урана (VI) был проведен с катализатором, осаждаемым таким же способом. В целях проверки каталитических свойств двуокиси урана при отсутствии никелевой проволоки было исследовано восстановление с применением порошкообразной и спеченной двуокиси урана.

Показано увеличение энергии активации катализатора при высокой температуре в потоке водорода. Процесс восстановления является реакцией первого порядка продолжительностью 10—15 *мин*.

На основании лабораторных и полупромышленных опытов была сделана промышленная

установка для непрерывного осаждения урана из выщелачивающих содовых растворов.

Дается описание этой установки, приводятся основания для выбора процесса, а также полученные результаты и аналитическое сравнение с другими методами.

Рассмотрены эффективность осаждения урана в зависимости от катализатора и условий в системе, например продолжительности реакции, концентрации реагентов и урана, способа перемешивания, температуры и давления.

A/414 Yugoslavia

Aplicación industrial de la precipitación catalítica del uranio

por B. Bunji *et al.*

Investigaciones recientes han confirmado que el proceso de reducción de U^{VI} a U^{IV} es catalítico y que en él la selección y la forma del catalizador tienen gran influencia sobre la posibilidad de llevar a cabo dicho proceso.

Se ha comprobado que el proceso de reducción de U^{VI} a U^{IV} en soluciones acuosas de carbonato sódico se realiza mejor con UO_2 como catalizador, el cual se produce al mismo tiempo en la reacción.

Los ensayos realizados en el laboratorio y en planta piloto, con alambre de níquel, han hecho ver que el óxido de uranio se deposita en la superficie del alambre. El espesor del óxido depositado alcanzó 5 mm o más, oscilando la densidad entre 4 y 5 g/cm^3. El proceso de reducción se realizó con el catalizador depositado de esta forma. Para comprobar las propiedades catalíticas del dióxido de uranio, sin la presencia del hilo de níquel, se ha estuiado el proceso de reducción así como los resultados de la aplicación del dióxido de uranio en forma de polvo y de anillos pretensados.

Se ilustra la energía de activación del catalizador a temperatura elevada en corriente de hidrógeno. El proceso de reducción es una reacción de primer orden y la reacción pue de efectuarse en un tiempo comprendido entre 10 y 15 minutos.

Tomando como base los resultados de los ensayos en el laboratorio y en planta piloto, se ha emprendido la construcción de una fábrica, en escala de producción, para la precipitación continua de uranio a partir de soluciones de lixiviación con carbonato.

Se hace una descripción de la instalación y se explican los motivos de la elección del proceso, los resultados obtenidos una comparación analítica.

Se discute el efecto de la precipitación del uranio en relación con las condiciones del catalizador y del sistema como el área del catalizador, el tiempo de la reacción, la concentración del uranio y de los reactivos, el método de agitación, la temperatura y la presión.

Co-extraction of thorium and cerium by neutral phosphorus organic compounds

By A. Alian *

The study of co-extraction of the rare earth elements with thorium is of great importance due to their occurrence in thorium concentrates obtained in the processing of monazite. Tri-n-butylphosphate (TBP) is the usual extractant in the purification of thorium and uranium compounds [1-4]. Other neutral phosphorus organic compounds were studied as extractants, mainly for uranium [5]. The extraction of thorium and the rare earths by these compounds or their solutions in inert diluents was studied only recently [6-8].

The aim of the present study is mainly to find the best conditions for the separation of thorium and lanthanides when these elements are extracted by neutral phosphorus organic solvents. As a first step, the structure of extractable species was investigated. The values of the separation coefficient (factor) were calculated on the basis of the confirmed extraction mechanism.

In the trivalent state, the rare earths are extracted almost at the same rate. Consequently, one rare earth can be used to represent the whole group and since cerium is more abundant than any other lanthanide in thorium concentrates, it has been selected for the present work.

EXPERIMENTAL

The solvents used, TBP and di-isoamylmethyl phosphonate (DAMPK), were purified by distillation under vacuum. Extraction was carried out by shaking equal volumes of organic and aqueous phases in graduated tubes or in separating funnels till equilibrium is attained. Experiments were at room temperature or in an air thermostat at 25 °C±1.

Pure salts were used in experiments with macro-amounts of metal nitrates, while for micro-amounts the isotopes ^{234}Th and ^{141}Ce were used (UXl). ^{234}Th was separated from pure uranyl solution by adsorption, from 7*M* hydrochloric acid solution, on a cation exchange resin followed by elution with 2*M* oxalic acid solution. Oxalic acid was then decomposed by addition of hydrogen peroxide and evaporation. ^{234}Th was also prepared by batch extraction with 30% TBP solution in xylene from a uranyl salt solution in 6*M* HCl; ^{234}Th remained in the aqueous phase. ^{141}Ce was prepared by irradiating CeO_2 in the reactor.

For the evaluation of the partition coefficient, thorium was determined either colorimetrically or radiometrically by counting the β-radiations of ^{234}Th. Cerium was determined radiometrically by counting the β-radiations of ^{141}Ce. Two series of experiments were carried out to evaluate the separation coefficient. In the first, thorium was determined colorimetrically, whereas cerium, in the same sample, was determined radiometrically; in the second, both thorium and cerium were determined radiometrically. In the latter case, equal parts from both organic and aqueous phases were evaporated to dryness and the total activity in these samples was measured using an end window G-M counter. This activity corresponds to the sum of ^{234}Th and ^{141}Ce radiations. The same samples were then counted using an aluminium absorber of 236 mg/cm² thickness. All the radiations from ^{141}Ce were thus cut off together with 79.20% of the radiations from ^{234}Th. By simple calculation, the activity from ^{141}Ce and ^{234}Th in both phases could be estimated and the separation coefficient evaluated.

Extraction mechanism

It was shown in a previous study [8] that thorium and cerium are extracted by DAMPK from nitric acid solutions, at low acidities, according to the following mechanism:

$$Th^{4+} + 4NO_3^- + 2\ DAMPK \longrightarrow Th(NO_3^-)_4.2\ DAMPK \qquad (1)$$

$$Ce^{3+} + 3NO_3^- + 3\ DAMPK \longrightarrow Ce(NO_3^-)_3.3\ DAMPK \qquad (2)$$

It is clear that thorium and cerium are extrated by DAMPK forming in the organic phase thorium nitrate disolvate and cerium nitrate trisolvate, respectively. This means that the extraction of thorium and cerium by TBP and DAMPK takes place according to one and the same mechanism. Moreover, it was found that the values of the partition coefficients of the two elements for DAMPK are much higher than the corresponding values for TBP.

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The comparison of the results of this work, on the extraction of thorium by TBP and DAMPK with those for its extraction by tri-n-octylphosphine oxide (TOPO) [6], from different acidic media, shows that the extraction efficiencies of phosphorus organic compounds regularly increase when passing from alkyl phosphates to phosphine oxides (Table 1) This is explained, as in uranium extraction, by an increase in the electronegative properties of these solvents in the same order.

Table 1. Extraction of thorium from different acidic media by TNP, DAMPK and TOPO

Concentration of the solvent = $0.1M$
Concentration of thorium = $0.008M$

Acid	Molar concentration M	Partition coefficient (D)		
		TBP	DAMPK	TOPO
HNO_3	1	0.01	0.18	2 100
	2	0.02	0.32	420
	4	0.04	0.55	78
	6	0.04	0.34	27
HCl	1	< 0.001	0.001	0.26
	3	< 0.001	0.003	11
	5	< 0.001	0.019	145
	7	< 0.001	0.085	208
	8	0.001	0.38	64
	9	0.003	1.90	28
	10	0.008	3.08	32
H_2SO_4	1	< 0.001	< 0.001	0.3
	2	< 0.001	< 0.001	0.3
	3	< 0.001	0.001	0.3
$HClO_4$	1	< 0.001	0.002	26
	2	< 0.001	0.006	9.9
	4	< 0.001	0.019	8.3
	5	< 0.001	0.070	16
	6	0.001	0.40	56

In the present work, the structure of extractable species was confirmed cryoscopically: the molecular weights of the compounds formed when DAMPK was saturated with thorium and cerium nitrates were determined by measuring the depression in the freezing point of benzene The experimental values of the molecular weights were estimated at different concentrations of these solvates in benzene (Tables 2 and 3).

The results indicate the formation of solvates with two molecules of DAMPK in the case of thorium nitrate and with three molecules of DAMPK in the case of cerium nitrate, which is in accordance with the extraction mechanism described.

The constancy of the values of the molecular weights, at different concentrations in benzene, shows that these compounds are not ionizing or polymerizing in the organic phase.

Table 2. Molecular weight of thorium nitrate-DAMPK solvate at different concentrations in benzene

Volume of the solvate solution ml	Weight of pure solvate g	Weight of pure benzene g	Δt	Molecular weight
1	0.893	22.3075	0.195	945
3	2.680	23.0095	0.582	970
5	4.465	23.7115	0.932	970
8	7.150	24.7645	1.430	965
12	10.716	26.1685	2.057	946

Table 3. Molecular weight of cerium nitrate-DAMPK solvate at different concentrations in benzene

Volume of the solvate solution ml	Weight of pure solvate g	Weight of pure benzene g	Δt	Molecular weight
0.5	0.366	22.1300	0.074	1 099
1.5	1.097	22.4800	0.227	1 030
3	2.193	23.0095	0.440	1 062
6	4.386	24.0625	0.838	1 051
10	7.310	25.4665	1.365	1 009
15	10.965	27.2215	1.874	1 023

The formation of neutral solvates was also confirmed by measuring the infra-red spectra of pure solvents and of solvents saturated with the metal nitrates. The characteristic absorption bands of inorganic nitrates were observed only in the spectra of the solvates in the region 810 cm^{-1} for thorium and 820 cm^{-1} for trivalent cerium.

Evaluation of the stability of extractable compounds of thorium and cerium by TBP and DAMPK

It is easy to show that, for the extraction of thorium or cerium by TBP and DAMPK from an aqueous solution of the same composition, the following relation is true :

$$\frac{K}{K'} = \frac{D}{D'} \cdot \frac{[\mathrm{DAMPK}]^n}{[\mathrm{TBP}]^n} \tag{3}$$

where K and K' are the equilibrium constants of the extraction reaction for TBP and DAMPK, respectively, D and D' are the corresponding values of the partition coefficient If TBP = DAMPK, then

$$\frac{K}{K'} = \frac{D}{D'} \tag{4}$$

The ratio K/K' gives a comparative evaluation of the stability of extractable species by the two solvents. For the determination of this ratio, experiments were carried out on the extraction of the two elements by TBP and DAMPK at constant ionic strength of the aqueous phase. Sodium and calcium nitrates were used as salting out agents since nitric acid is

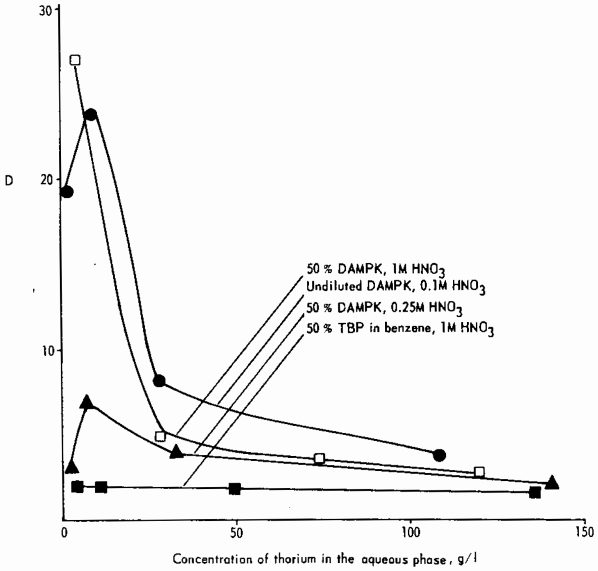

Figure 1. The effect of thorium concentration on partition coefficient for thorium

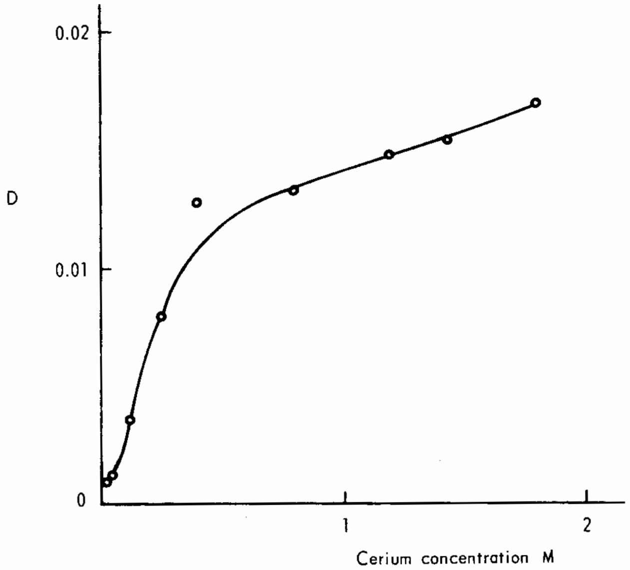

Figure 2. The effect of cerium concentration on partition coefficient for cerium

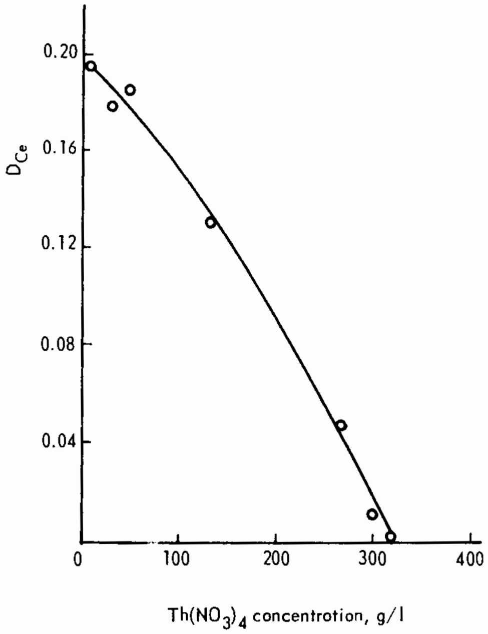

Figure 3. The effect of thorium concentration on partition coefficient for cerium

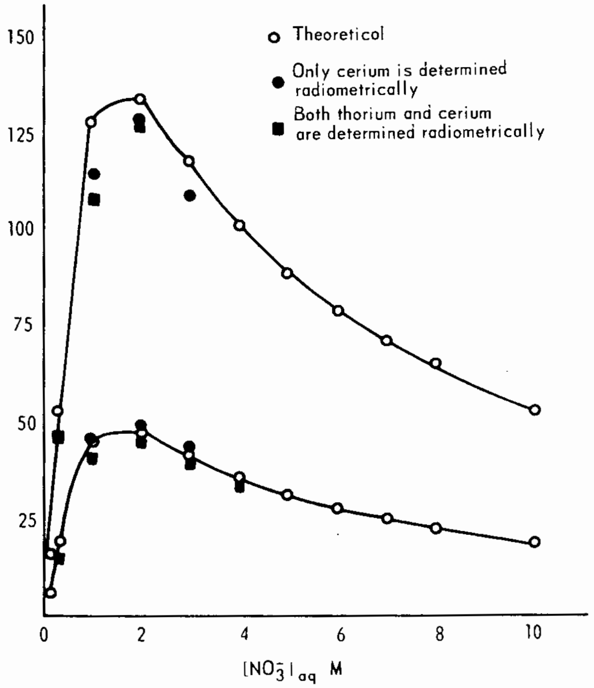

Figure 4. The effect of $[NO_3^-]_{aq}$ on separation coefficient of thorium and cerium

not extracted by the two solvents at the same rate. The experimental values of D for thorium are presented in Table 4.

The value of K was taken as 36 [9].

From Table 4 it is clear that the value of the stability constant of the thorium complex with DAMPK (K') is equal to 835 ± 72, which is about 23 times greater than the corresponding value for TBP. By the help of the calculated K' value, it is easy to calculate the D values for thorium at different nitrate ion concentrations in the aqueous phase, and at different DAMPK concentrations in the diluent using the following equation:

$$D = \frac{K'[\mathrm{NO_3^-}]^4_{\mathrm{aq}}[\mathrm{DAMPK}]^2_0}{1 + \Sigma \beta_i [\mathrm{NO_3^-}]_i} \qquad (5)$$

where β_i is the stability constant of the thorium complex with the nitrate ions (Table 5). It is clear from Table 5 that the calculated and the experimental D values are satisfactorily the same, which is an indication of correctness of the extraction mechanism and of the calculated K' value.

The values of D for cerium extraction from nitric acid solutions of the same composition are presented in Table 6.

When K is taken as 1 ± 0.1 [10], the calculated value of K' is 8 ± 0.7.

Co-extraction of cerium with thorium

The above mentioned work deals with the extraction of the individual elements. It is of greater importance, however, to study the extraction of the two elements when they are present together in solution. The values of the separation coefficient ξ of the two elements could be estimated on the basis of partition data:

$$\xi = D_{\mathrm{Th}}/D_{\mathrm{Ce}} \qquad (6)$$

The values of D are affected, however, by the metal concentration in the aqueous phase; consequently the value of ξ is changed. The effect of the metal concentration, in the aqueous phase, on the extraction coefficient by DAMPK is shown in Figs. 1 and 2. In addition, it was found that the cerium partition coefficient sharply decreases with the increase of the thorium concentration in the aqueous phase (Fig. 3). This is explained by the competition between cerium and thorium for the free solvent; thorium forms a more stable complex with the solvent molecules.

The separation coefficient of thorium and cerium (ξ) can be calculated, in general, on the basis of the confirmed extraction mechanism of the two elements. From the relation expressing the value of D it can be shown that ξ can be given by:

$$\xi = \left(\frac{K_{\mathrm{Th}}}{K_{\mathrm{Ce}}}\right)\left(\frac{[\mathrm{NO_3^-}](1 + \Sigma \beta_i [\mathrm{NO_3^-}]_i)}{[\mathrm{S}](1 + \Sigma \beta_{i'} [\mathrm{NO_3^-}]_{i'})}\right) \qquad (7)$$

where K_{Th} and K_{Ce} are the equilibrium constants of the extraction reaction of the two elements; β_i and $\beta_{i'}$ are the stability constants of thorium and cerium complexes with the nitrate ions, and [S] is the solvent concentration. β_i and $\beta_{i'}$ and also K_{Th} and K_{Ce} for TBP were determined by Fomin and co-workers [9, 10], K_{Th} and K_{Ce} for DAMPK were determined in this work

The value of ξ thus depends on the total nitrate ion concentration in the aqueous phase and on the free solvent concentration in the organic phase. Eq. (7) may be written in the following form:

$$\xi = \left(\frac{K_{\mathrm{Th}}}{K_{\mathrm{Ce}}}\right)\left(\frac{1}{[\mathrm{S}]}\right) f([\mathrm{NO_3^-}]) \qquad (8)$$

In Table 7 are given the values of $f([\mathrm{NO_3^-}])$ and the calculated ξ values at different nitrate ion concentrations in the aqueous phase for 1M TBP and 1M DAMPK. In the same table are also given the experimental ξ values. It is clear that the calculated and experimental ξ values satisfactorily agree with each other.

Table 4. Thorium partition coefficient at different nitrate ion concentrations in the aqueous phase

Nitrate ion concentration M	Solvent (D)		K'/K	K'
	0.4M TBP	0.4M DAMPK		
0.62	0.08	1.8	23	828
1.0	0.13	3.2	25	900
1.3	0.16	4.6	28	1 008
1.5	0.24	6.0	23	828
2.00	0.37	7.8	21	756
2.20	0.41	9.0	22	792
2.50	0.40	9.6	24	864
3.00	0.52	10.5	20	720

Table 5. Thorium partition coefficient for the extraction by DAMPK solutions in xylene

HNO_3 0.1M

Nitrate ion concentration n the aq. phase, M	Equilibrium DAMPK concentration, M	D	
		Calculated	Experimental
0.1	0.80	0.26	0.31
0.2	0.80	0.32	0.31
1.0	0.50	5.1	5.9
2.0	0.20	1.9	2.3

Table 6. Cerium partition coefficient at different nitrate ion concentrations in the aqueous phase

HNO_3 0.01M, $Ce(NO_3)_3$ $10^{-6}M$

Concn. of $Ce(NO_3)_3$ in the aq. phase, M	Solvent (D)		K'/K	K'
	0.4M TBP	0.4M DAMPK		
1.26	0.0065	0.06	9.2	9.2
1.68	0.017	0.138	8.3	8.3
2.52	0.095	0.69	7.3	7.3
3.50	0.193	1.39	7.2	7.2

Table 7. Separation coefficient of thorium and cerium at different nitrate ion concentrations

$[NO_3^-]$, M	f (N_3^-O)	Separation coefficient					
		TBP			DAMPK		
		Calculated	Experimental		Calculated	Experimental	
0.1	0.14	5.0	—	—	14.5	—	—
0.3	0.50	18.0	17.5	14.8[a]	52	46	46.4[a]
1	1.24	44.5	45	39.5[a]	129	115	109[a]
2	1.29	46.5	47	44.7[a]	134	131	128[a]
3	1.13	40.5	43	39.1[a]	118	110	119[a]
4	0.97	35.0	—	32.6[a]	101	—	—
5	0.85	30.6	—	—	88.5	—	—
6	0.75	27.0	—	—	78	—	—
7	0.67	24.0	—	—	70	—	—
8	0.60	21.6	—	—	64.5	—	—
10	0.50	18.0	—	—	52	—	—

[a] Both thorium and cerium are determined radiometrically.

Table 8. Effect of the hydrogen ion concentration on extraction of thorium and cerium(III)

Ionic strength of the equilibrium aqueous phase = 4.8

DAMPK concentration, M		Nitric acid concentration, M		$LiNO_3$ concentration, M	D	
Original	Equilibrium	Aqueous	Organic		Th	Ce
4		4.8	3.05	0	155	2.85
1.6	0.18	3.2	1.07	1.6	74	0.25
0.8		2.8	0.59	2.0	57	0.12
0.4		2.3	0.21	2.5	40	0.03

The effect of the equilibrium nitrate ion concentration on ξ is shown in Fig. 4. It is evident that the separation coefficient of thorium and cerium has a maximum value at an equilibrium nitrate ion concentration of 1.6*M*. This value for 1*M* TBP is equal to 48, and for 1*M* DAMPK is 136.

In technology, thorium is usually extracted from solutions with high metal concentrations, and the solvent is, therefore, almost completely saturated with thorium. This brings about an increase in the value of ξ as indicated by Eq. (7).

An important point is that DAMPK is not only more efficient for the extraction of the individual metals but also for their separation.

It is also noteworthy that (7) holds for the extraction of thorium and cerium from solutions of low acidities only; i.e., when a neutral nitrate (as $NaNO_3$ or $Al(NO_3)_3$) is used as salting-out agent. From data on the effect of nitric acid concentration on the value of *D*, for the extraction of thorium by TBP or DAMPK [8], it was clear that the two metals are extracted at high acidities through another mechanism. This was confirmed by studying the effect of hydrogen ion concentration on the extraction of thorium and cerium at constant ionic strength and constant free solvent concentration (Table 8).

The sharp increase in the value of *D* with increasing hydrogen ion concentration cannot be explained by a decrease in the hydrolysis rate of the two metal nitrates; hydrolysis is negligible under the given conditions. Moreover, it was found that the logarithmic relation between *D* and $[H^+]$ aq is expressed by a straight line the slope of which is equal to 1.8 and to 6 for thorium and cerium respectively. This can be interpreted by the formation of double salts or mixed solvates in which the solvent is a compound of nitric acid with DAMPK ($DAMPK.HNO_3$) or a mixture of the latter and DAMPK.

Separation of macro-amounts of thorium nitrate from cerium nitrate

For these experiments a solution was prepared of the following composition:

ThO_2	160 g
CeO_3	5 g
P_2O_5	1.5 g
$NaNO_3$	1.5*M*
Free nitric acid	0.4*M*

This solution is supposed to be similar in composition to the aqueous feed solution for thorium extraction in technology. Solvents used in this study were 40% solution TBP and 40% solution DAMPK in xylene. A batch counter-current extraction, similar to that described by Fareeduddin *et al.* [4], was used to compare the efficiencies of TBP and DAMPK. The solvent feed ratio was 2 to 1. In some series of experiments, the radioactive isotope ^{234}Th was added to the aqueous solution after the second batch extraction. The process was then continued till all radioactivity in the aqueous phase had disappeared. In other series, the radioactive isotope ^{141}Ce was added to the original solution, in order to study the scrubbing process. Cerium extracted in the organic phase was scrubbed many times with 0.1 volume of a solution containing $0.5M$ $NaNO_3$ and $0.1M$ HNO_3.

It was found that whereas 7 stages were necessary for the complete extraction of thorium by the TBP solution, 4 stages were sufficient using DAMPK. Cerium was completely removed from the organic phase after 3 scrubbing stages in case of TBP and after 4 stages in case of DAMPK.

The subsequent stripping of thorium from the organic phase was carried out with $0.01M$ HNO_3 solution. All the thorium could be recovered in 3 stages with TBP and in 4 stages with DAMPK. This means that the total number of stages could be decreased by using DAMPK instead of TBP

However, when nitric acid was used as a salting-out agent, thorium could be back-washed into the aqueous phase only with difficulty. In the latter case, the total number of stages for DAMPK could be decreased by using other stripping solutions, carbonate or hydroxide for example.

These studies are still in the laboratory stage of development. The above results indicate, however, that it will be quite possible to use DAMPK and other neutral phosphorus organic compounds in the technology of thorium and to realize savings in costs.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/455 République arabe unie

Coextraction du thorium et du cérium par des composés organophosphoriques neutres

par A. Alian

L'étude de la coextraction du thorium et du cérium est très importante en raison de la présence de ce dernier dans les concentrés de thorium obtenus au cours du traitement de la monazite.

Les valeurs du coefficient de séparation des deux éléments pourraient être calculées sur la base des mesures de partage. Mais les valeurs du coefficient de partage sont elles-mêmes influencées par la concentration du métal dans la phase aqueuse; par conséquent, les valeurs du coefficient de séparation sont changées. De plus, on a trouvé que le coefficient de partage du cérium diminuait rapidement avec l'augmentation de la concentration de thorium dans la phase aqueuse. Ceci est dû à la compétition entre le cérium et le thorium pour le solvant libre; le thorium forme des complexes plus stables avec les molécules du solvant. Le coefficient de séparation des deux éléments (ξ) peut être calculé sur la base du mécanisme confirmé d'extraction. ξ est exprimé par l'équation

$$\xi = D_{\mathrm{Th}}/D_{\mathrm{Ce}}. \qquad (1)$$

Sur la base du mécanisme d'extraction des deux éléments, il est facile de démontrer que ξ peut être exprimé par l'équation

$$\xi = \left(\frac{K_{\mathrm{Th}}}{K_{\mathrm{Ce}}}\right)\left(\frac{[NO_3^-]\,(1 + \Sigma\beta_{\mathrm{i}}\,[NO_3^-]_{\mathrm{i}})}{[S]\,(1 + \Sigma\beta_{\mathrm{i'}}\,[NO_3^-]_{\mathrm{i'}})}\right) \qquad (2)$$

K_{Th} et K_{Ce} sont les constantes d'équilibre de la réaction d'extraction des deux éléments; β_{i} et $\beta_{\mathrm{i'}}$ sont les constantes de stabilité des complexes de thorium et de cérium avec les ions NO_3^-.

β_i et $\beta_{i'}$ et aussi K_{Th} et K_{Ce} pour TBP et DAMP (qui est un phosphonate d'alkyle) sont déterminés expérimentalement.

La valeur de ξ dépend ainsi de la concentration totale de l'ion nitrate dans la phase aqueuse et de la concentration du solvant libre dans la phase organique. Il est à noter que l'équation ci-dessus s'applique seulement à l'extraction aux basses acidités. L'équation (2) peut être écrite de la manière suivante :

$$\xi = \left(\frac{K_{\mathrm{Th}}}{K_{\mathrm{Ce}}}\right)\left(\frac{1}{[\mathrm{S}]}\right) f([\mathrm{NO}_3^-]). \qquad (3)$$

Les valeurs de f ($[\mathrm{NO}_3^-]$) et les valeurs correspondantes de ξ sont calculées aux différentes concentrations de l'ion nitrate dans la phase aqueuse pour la concentration $1M$ du solvant. On a trouvé que les valeurs de ξ calculées et expérimentales sont en accord ce qui est une indication de l'exactitude du mécanisme donné. On a aussi trouvé que le coefficient de séparation du thorium et du cérium atteint une valeur maximale à une concentration d'équilibre du nitrate de $1{,}6M$. La valeur maximum de ξ pour $1M$ TBP est égale à $\approx$ 48.

En technologie, le thorium est habituellement extrait des solutions à forte concentration de métal et le solvant sera ainsi presque complètement saturé de thorium. Ceci entraîne une augmentation dans la valeur de ξ comme indiqué par l'équation (3).

A/455 OAP

Совместная экстракция тория и церия нейтральными фосфорорганическими соединениями

А. Алиан

В связи с тем что в получаемых при переработке монацита ториевых концентратах находится также и церий, исследование их совместной экстракции является весьма важной задачей.

Величины коэффициентов разделения этих элементов можно вычислить на основе данных о распределении. Однако значения коэффициентов распределения меняются в зависимости от концентрации металла в водной фазе и соответственно изменяются значения коэффициента разделения. Кроме того, было найдено, что коэффициент распределения церия резко падает с увеличением концентрации тория в водной фазе. Это происходит благодаря своего рода соревнованию между торием и церием за свободный растворитель, причем торий образует более прочные комплексы с молекулами растворителя. На основе установленного механизма экстракции можно вычислить коэффициент разделения двух элементов (ξ). Этот коэффициент выражается соотношением

$$\xi = D_{\mathrm{Th}}/D_{\mathrm{Ce}}.$$

На основе механизма экстракции этих двух элементов легко показать, что ξ может быть выражен следующим уравнением

$$\xi = \frac{K_{\mathrm{Th}}}{K_{\mathrm{Ce}}}\,\frac{[\mathrm{NO}_3^-]\,(1+\Sigma\beta_i\,[\mathrm{NO}_3^-]_i)}{S\,(1+\Sigma\beta_{i'}\,[\mathrm{NO}_3^-]_{i'})}\,, \qquad (2)$$

где K_{Th} и K_{Ce} — константы равновесия реакции при экстракции этих двух элементов; β_i и $\beta_{i'}$ —константы стабильности комплексов тория и церия с NO_3^- -ионами.

β_i и β_i', а также K_{Th} и K_{Ce} для ТБФ и ДАМФК (которое относится к алкилфосфонатам) определяют экспериментально.

Таким образом, коэффициент разделения зависит от общей концентрации нитрат-иона в водной фазе и от концентрации свободного растворителя в органической фазе. Следует отметить, что приведенное выше уравнение справедливо лишь для экстракции при низких кислотностях. Уравнение (2) может быть написано в виде

$$\xi = \frac{K_{\mathrm{Th}}}{K_{\mathrm{Ce}}}\,\frac{1}{S}\,f\,([\mathrm{NO}_3^-]) \qquad (3)$$

Величины $f([\mathrm{NO}_3^-])$ и соответствующие величины ξ рассчитывались при различных концентрациях нитрат-иона в водной фазе для 1 M концентрации растворителя. Оказалось, что расчетные и экспериментальные величины ξ согласуются друг с другом, что указывает на правильность данного механизма экстракции. Найдено, что коэффициент разделения тория и церия имеет максимальную величину при равновесной концентрации нитрат-иона 1,6 M. Для 1 M ТБФ максимальный коэффициент разделения составляет около 48.

В промышленной технологии торий обычно экстрагируется из растворов с высокой концентрацией металла и поэтому растворитель будет почти полностью насыщен торием. Это обстоятельство приводит к повышению величины ξ, как показывает уравнение (3).

A/455 República Arabe Unida

Coextracción de torio y cerio con compuestos neutros orgánicos de fósforo

por A. Alian

Es muy importante el estudio de la extracción conjunta del torio y del cerio debido a la existencia del cerio en los concentrados de torio obtenidos en el tratamiento de la monacita.

Los valores de los coeficientes de separación de los dos elementos podrían calcularse en función de los datos de partición. Como los valores de estos coeficientes están afectados por la concentración de dichos metales en la fase acuosa, varían por lo tanto los valores de los coeficientes de separación. Además se ha encontrado que el coeficiente de reparto del cerio disminuye considerablemente al aumentar la concentración de torio en la fase acuosa, fenómeno debido a la competición entre el cerio y el torio frente al disolvente libre; el torio forma complejos más estables con las moléculas de disolvente. El coeficiente de separación de los dos elementos (ξ) puede calcularse basándose en el mecanismo de extracción confirmado. ξ se expresa por la relación siguiente:

$$\xi = D_{\mathrm{Th}}/D_{\mathrm{Ce}}. \qquad (1)$$

Basándose en el mecanismo de extracción de los dos elementos es fácil demostrar que ξ puede expresarse por la ecuación siguiente:

$$\xi = \left(\frac{K_{\mathrm{Th}}}{K_{\mathrm{Ce}}}\right)\left(\frac{[\mathrm{NO}_3^-]\,(1 + \Sigma\beta_i\,[\mathrm{NO}_3^-]_i)}{[\mathrm{S}]\,(1 + \Sigma\beta_{i'}\,[\mathrm{NO}_3^-]_{i'})}\right) \qquad (2)$$

en la que K_{Th} y K_{Ce} son las constantes de equilibrio de la reacción de extracción de los dos elementos; β_i y $\beta_{i'}$ son las constantes de establidad de los complejos de torio y cerio con los iones NO_3^-.

β_i, $\beta_{i'}$ y K_{Th} y K_{Ce} para el TBP y DAMPK (que es un miembro de los alkilofosfonatos) se determinaron experimentalmente.

Los valores de ξ dependen de la concentración total del ion nitrato en la fase acuosa y de la concentración de disolvente libre en la fase orgánicia. Hay que hacer notar que la ecuación anterior solamente se cumule en la extracción a baja acidez. La ecuación (2) puede escribirse en la forma siguiente:

$$\xi = \left(\frac{K_{\mathrm{Th}}}{K_{\mathrm{Ce}}}\right)\left(\frac{1}{[\mathrm{S}]}\right) f([\mathrm{NO}_3^-]) \qquad (3)$$

Los valores de $f([\mathrm{NO}_3^-])$ y los correspondientes de ξ se han calculado a diferentes concentraciones del ion nitrato en la fase acuosa para la concentración $1M$ de disolvente. Se ha encontrado que los valores calculados y experimentales de ξ concuerdan, lo que indica que el mecanismo propuesto es correcto. También se ha visto que el coeficiente de separación entre el torio y el cerio tiene un valor máximo a una concentración de equilibrio de nitrato de $1{,}6M$. El valor máximo para el TBP $1\,M$ es aproximadamente igual a 48.

En el proceso de fabricación, el torio se extrae corrientemente de disoluciones que lo contienen en concentración elevada por lo que el disolvente está casi completamente saturado con torio, lo cual da lugar a un aumento del valor de ξ como se deduce de la ecuación (3).

The production of uranium tetrafluoride by thermal decomposition of ammonium uranous fluoride in a fluidized bed

By R. E. Robinson,* J. C. Geertsma * and J. C. Paynter **

In 1958, Brodsky and Pagny [1] reported a process for the conversion of uranyl nitrate solution to sodium uranous fluoride ($UF_4.NaF$) which could be used for calciothermic reduction to uranium metal in the standard bomb reduction process. Investigation of this process was commenced at the Government Metallurgical Laboratory, but work on the production of sodium salt was abandoned because only disodium salt ($UF_4.2NaF$) could be made, which is unsuitable for calciothermic reduction. Since then, the production of ammonium salt has been investigated and a pilot plant is in operation.

In this process, uranyl nitrate is reacted batchwise with ammonium fluoride, formic acid and sulphur dioxide in solution to give a green crystalline precipitate of ammonium uranous fluoride ($UF_4.NH_4F$). The precipitate is filtered and dried to give a free-flowing powder of tap density about 2.8 g/cm³. When heated, the double fluoride salt decomposes according to the following reaction:

$$UF_4 . NH_4F \longrightarrow UF_4 + NH_4F$$

The UF_4 can be used for calciothermic reduction or for the production of uranium hexafluoride. For the former purpose, it should contain only the minimum amount of NH_4F as any residual NH_4F is vaporised in the metal reduction bomb thus causing an undesirable pressure build-up. Calculations based on the increase in pressure indicate that a nitrogen content (assumed to be present as NH_4F) below 20 parts per million UF_4 basis, should not give rise to unacceptable pressure increases; and this figure has been provisionally accepted as the maximum permissible level for nitrogen content.

Preliminary batch tests in a horizontal 5 in diam. stainless steel tube furnace heated to 450 °C showed that $UF_4.NH_4F$ could be decomposed to give a product containing 5 ppm nitrogen. Further pilot plant experiments were therefore justified to develop a process for the decomposition of the $UF_4.NH_4F$ and to investigate the possibility of recovering NH_4F economically.

Van Impe [2] has investigated the decomposition of a static bed of $UF_4.NH_4F$. At 500 °C in a vacuum furnace, the nitrogen content was reduced to 500 ppm. Further heating at 500 °C in a hydrogen atmosphere reduced the nitrogen content to 5 ppm.

Galkin *et al.* [3] also studied the decomposition reaction and found that it occurs in two stages. The loss in weight in the temperature range 320-360 °C was 5.9% and in the range 420-450 °C it was 4.2%.

THERMAL DECOMPOSITION OF $UF_4.NH_4F$ IN A FLUIDIZED BED

Reasons for choice of a fluidized bed

(*a*) A fairly narrow temperature range is desirable for the final stages of the decomposition. If the temperature is too high, the material shows a tendency to sinter and form hard agglomerates; if too low, the decomposition is slow and incomplete. The uniform temperature characteristic of a fluidized bed is an advantage over other types of furnace.

(*b*) Substantial quantities of heat are required to decompose the powder. The high heat transfer rates possible in a fluidized bed are an obvious advantage.

(*c*) The fluidized bed contains no moving mechanical parts as for example in a stirred bed reactor. This is an important advantage at these high temperatures in the presence of very corrosive fluoride vapours.

(*d*) Preliminary tests indicated that agitation of the powder and the rapid removal of NH_4F gas increased the rate of decomposition. The use of a fluidizing gas (nitrogen was chosen because of its low cost and inertness) would achieve these conditions.

Small-scale experimental work

A 6 in diameter stainless steel fluidized bed reactor was constructed with a view to assessing the feasibility of using a fluidized bed, and obtaining design data for a larger pilot plant unit. The reactor was designed to process up to 40 lb $UF_4.NH_4F$ per batch.

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Table 1. Corrosion rates in ammonium fluoride atmosphere at 450 °C

Specimen size : 0.5 dm²
Exposure time : 28 hours

Sample	Composition (%)	Weight loss (g/dm²)	Corrosion rate mg/ft²/h	Relative cost of sheet
Nickel	99Ni	—0.0167[a]	— 5.6[a]	2.25
Monel	67Ni/30Cu/1.5Fe	—0.0217[a]	— 7.3[a]	2.08
Ni-o-nel	40Ni/35Fe/20Cr/3Mo/2Cu	—0.0318[a]	—10.7[a]	2.00
Inconel	80Ni/13Cr/7Fe	—0.0336[a]	—11.4[a]	2.16
Stainless steel	18Cr/8Ni/3.75Mo/2.5Cu	0.2216	74.9	1.17
Stainless steel (type 316)	18Cr/8Ni/3Mo	0.3142	106.3	1.00
Stainless steel (type 310)	28Cr/18Ni	0.4782	161.6	1.25
Corronel 230	55Ni/36Cr/5Fe/1Cu/1Mn	0.5373	181.6	3.16

[a] The negative sign represents an increase in the weight of the test piece.

Materials of construction

Stainless steel proved to be unsatisfactory as a material of construction, due to the formation of a non-adherent scale of iron and chromium fluorides.

The contamination caused by the scale resulted in a product with an impurity content above nuclear grade specifications. Corrosion test pieces were placed in the upper section of the reactor and the results are given in Table 1 which shows that the high nickel alloys all underwent a gain in weight which is due to the formation of an adherent nickel fluoride film. Of all the materials, Monel probably gives the best balance between cost and corrosion rate and is also the most readily available of the nickel alloys. Although its tensile strength decreases rapidly at temperatures above 460 °C, it is nevertheless adequate to withstand the operating conditions.

Fluidization characteristics

The bed fluidized satisfactorily in most runs at a nitrogen flow of approximately 1 ft³/min. A conical gas distributor was experimented with in the initial runs but this gave poor fluidization due to severe channelling in the bed. A porous metal distributor was then fitted and proved to be very satisfactory in all subsequent runs. It also had the advantage over other types of distributors of preventing powder leaking into the inlet gas line. Although some of the batches of $UF_4.NH_4F$ would not fluidize at all, the work on this unit demonstrated that in most cases $UF_4.NH_4F$ could be decomposed to UF_4 containing less than 20 ppm nitrogen in approximately 7 hours at a maximum temperature of about 450 °C. The design of a larger pilot plant reactor was therefore justified.

Pilot plant design and operation

Equipment

The pilot plant as originally constructed is shown in Fig. 1. Additional details of the fluidized bed reactor are shown in Fig. 2. The plant was designed to operate batch-wise to decompose approximately 1 200 lb $UF_4.NH_4F$ per batch, equivalent to a production rate of 100 t/yr.

The fluidized bed unit was constructed of Monel. The heat required in the fluidized bed section was supplied by 36 sheathed resistance heating elements (Calrod elements) each of 900 watt capacity. These were arranged circumferentially around the outside wall of the unit at ½ inch spacing. Additional heating elements were also fixed to the conical section and the top coverplate, for heating up the entire unit to operating temperature to prevent condensation of NH_4F. The heating elements were surrounded by a stainless steel reflector which was lagged externally.

The bed heating elements were controlled by an on-off temperature controller actuated by a thermocouple in the fluidized bed. The additional heating elements were controlled by Simmerstat bi-metal regulators. Four thermocouples indicated the temperature at various points in the bed.

The bed of powder was supported by a porous metal plate distributor held between the two flanges as shown in Fig. 2. Grids above and below the distributor plate helped to support it. A porous Monel metal plate was used initially but it corroded and was replaced by a distributor made of Rigimesh Monel metal having a 10 micron pore opening. This latter material, which has a woven structure, has a much higher tensile strength than the porous Monel metal, which was made by sintering metal particles to form a coherent sheet. The Rigimesh metal distributor has been in use for over 150 hours without any signs of deterioration. The good distribution of fluidizing gas given by the Rigimesh resulted in very even fluidization over the entire bed area.

A filter for the exit gases was necessary to remove the particles carried up by the fluidizing gas, and a sintered porous metal filter was used for the first few runs. This corroded to such an extent that the filter disintegrated. It appeared that the point of

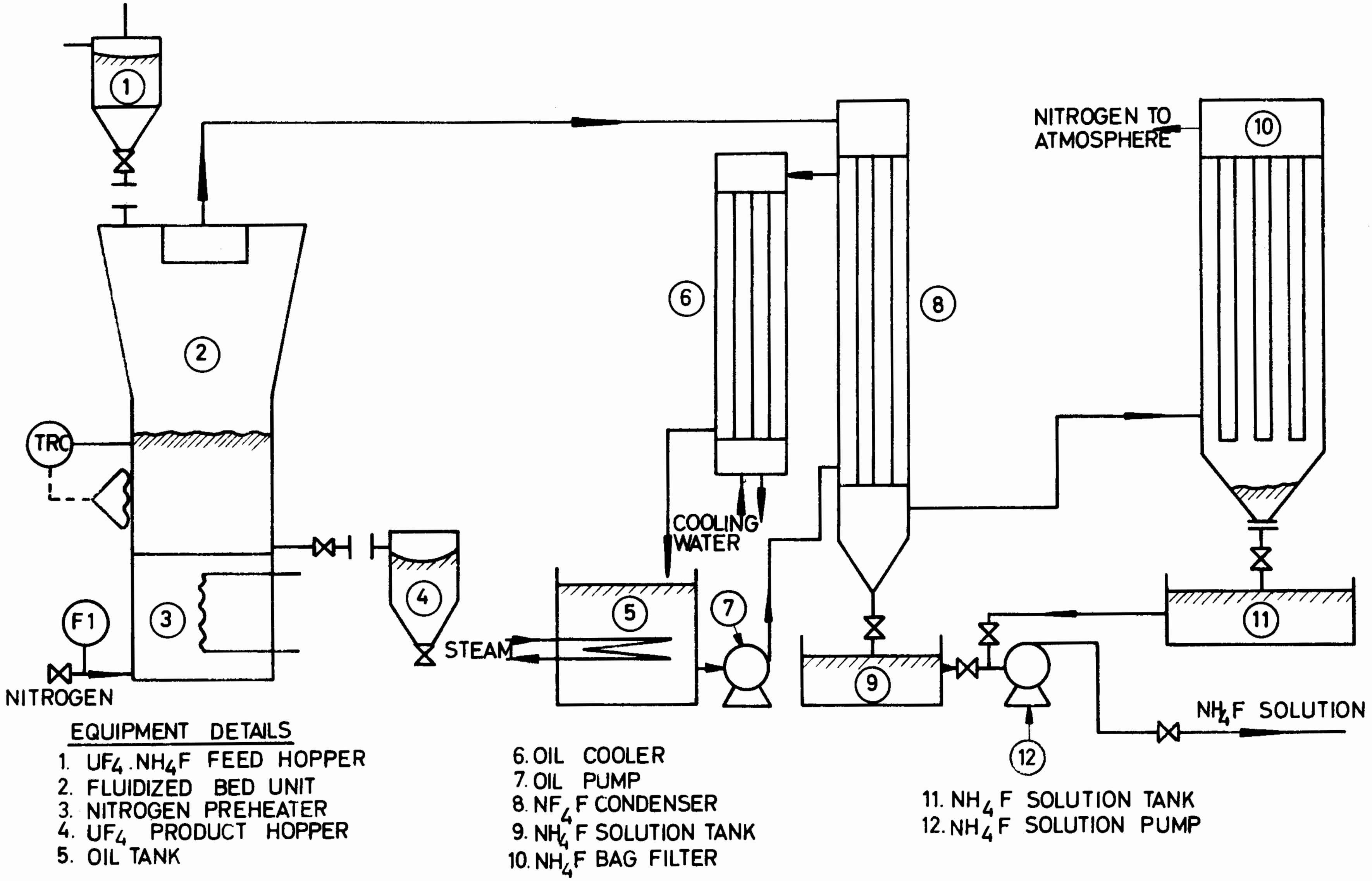
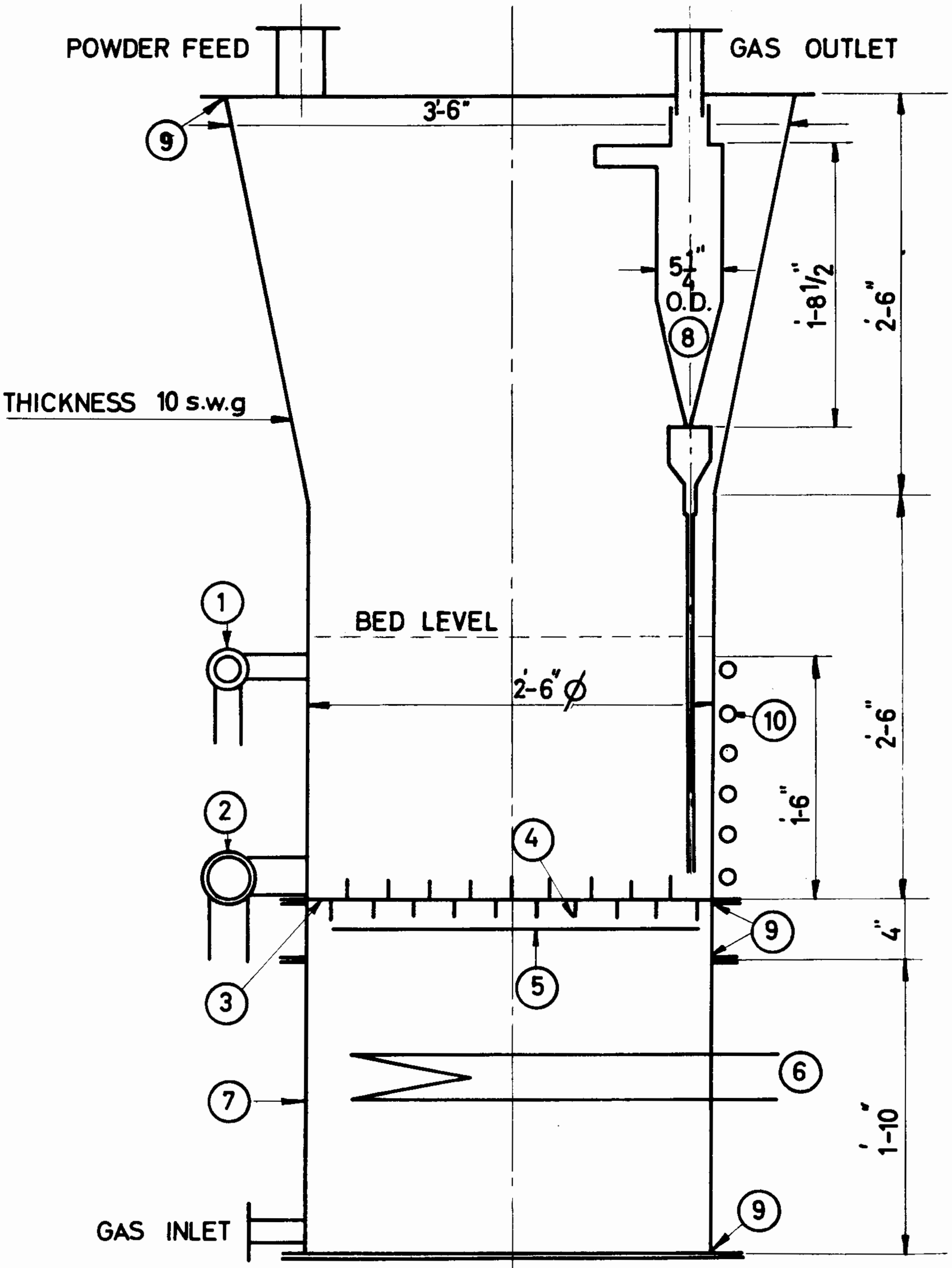


Figure 1. Flowsheet of $UF_4.NH_4F$ decomposition pilot plant (original process)



EQUIPMENT DETAILS.

1. POWDER SAMPLE VALVE
2. UF_4 DISCHARGE: 2 IN PLUG VALVE
3. DISTRIBUTOR PLATE: POROUS METAL.
4. SUPPORT GRIDS FOR DISTRIBUTOR PLATE
5. RADIATION SHIELD (INCONEL)
6. PREHEATER HEATING ELEMENTS.
7. GAS PREHEATER SECTION (STAINLESS STEEL TYPE 321)
8. CYCLONE (½ IN N.B. DIPLEG)
9. MILD STEEL BACKING FLANGES ON 10 s.w.g MONEL.
10. BED HEATING ELEMENTS

MATERIALS: MONEL EXCEPT WHERE OTHERWISE INDICATED

Figure 2. Fluidized bed reactor

contact between the individual metal particles in the sintered metal is attacked by the corrosive NH_4F with the result that the material as a whole loses its strength. A cyclone was then installed and this operated satisfactorily with a powder loss of approximately 2½% per batch at a gas rate of 20 ft³/min.

The nitrogen preheater was an integral part of the fluidized bed unit as shown in Fig. 2. Experience on the small-scale unit had shown that unless the preheater was situated close to the fluidized bed the hot gas was cooled considerably by heat losses to the metal of the interconnecting pipes. Nine 1 000 watt Calrod heating elements at 2 in spacing provided the heat to raise the gas temperature to 450 °C. The radiation shield shown in Fig. 2. prevented direct radiant heating of the distributor plate.

The asbestos gaskets used were slowly attacked by the NH_4F vapour and where possible a solid Monel ring was placed just inside the inner perimeter of the gaskets to prevent the decomposition products contaminating the product.

Operating procedure

About 1 200 lb $UF_4.NH_4F$ was charged into the fluidized bed reactor (see Fig. 2). The flow of fluidizing gas (nitrogen) was adjusted to about 20 ft³/min. The bed temperature was raised to about 315 °C when decomposition commenced, and the bed temperature was thereafter increased slowly over a period of approximately 9 hours until 460 °C was reached. Up to the present time the rate of heating has been limited by the rate of cooling of the NH_4F gas stream so that at the most only 22 of the available Calrod heating elements have been in use. With this number of heating elements a heat transfer rate of 6 000 Btu/hft² has been achieved without overheating the Monel metal wall. The upper section of the unit was maintained throughout at a temperature slightly above that of the bed to prevent condensation of the NH_4F from the exit gas stream.

When decomposition was complete, the nitrogen flow and the heating elements were switched off and the bed allowed to cool for 18 hours. In order to discharge the UF_4, the bed was fluidized and the fluidized powder flowed out through the open powder outlet valve into the UF_4 hopper.

Care was taken throughout to maintain a positive pressure of nitrogen in the system in order to prevent moisture or oxygen entering the unit. If the equipment had to be opened up for maintenance it was thoroughly purged with nitrogen before the next run. The UF_4 was very hygroscopic and was stored in a dry nitrogen atmosphere.

Operating characteristics

A typical decomposition curve showing the variation of the bed temperature with time is given in Fig. 3.

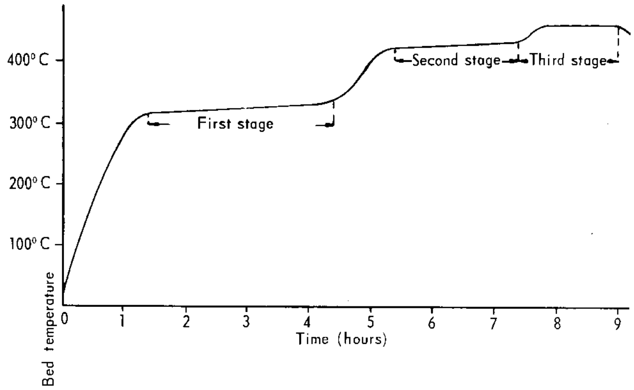


Figure 3. Thermal decomposition of $UF_4.NH_4F$ (temperature changes)

The decomposition proceeded in three stages. During the first stage, which was of approximately 3 hours duration, the temperature rose from 315 to 330 °C and about 60% of the NH_4F was removed. Thereafter, the rate of NH_4F evolution decreased markedly resulting in a rapid temperature rise from 330 to 420 °C. The second stage of the decomposition commenced at 420 °C and was of about 2 hours duration. The temperature was approximately constant (420-430 °C) during this period when virtually all the remaining 40% of the NH_4F was removed. The rate of evolution of NH_4F decreased to almost zero when the temperature reached 430 °C. The third stage was of about 1½ hours duration at a bed temperature of 460 °C. This ensured that a product containing less than 20 ppm nitrogen was obtained.

The heat of sublimation of NH_4F is reported by Luft [4] as being 36 kcal/mole at 25 °C. This value agreed closely with the heat of decomposition of $UF_4.NH_4F$ as estimated from the heat input to the bed, and is considered to be sufficiently accurate for future design purposes.

Using the operating sequence described above, a UF_4 product containing not more than 20 ppm nitrogen could be produced consistently. No UO_2F_2 (uranyl fluoride) could be detected, but the product usually contained less than 0.5% U_3O_8, which was probably formed by reaction of UF_4 with the small quantity of oxygen and moisture introduced with the $UF_4.NH_4F$. Only trace quantities of other impurities were introduced by the operation, and a product conforming to nuclear grade specifications was obtained. In the early runs, a great deal of difficulty was experienced in obtaining satisfactory fluidization of the bed. This was found to be due to the poor low properties of the $UF_4.NH_4F$ powder. Modifications were made in the precipitation process so as to produce a compound of larger average particle size, after which no further difficulty was encountered [6]. It is known that fine materials (e.g. copper or zinc filings) of particle size less than 60 micron have a pronounced tendency to adhere to each other [7]. It may be of significance that the unsatisfactory powder was predominantly in the 10-20 micron particle size range, whereas the fluidizable powder was predominantly in the 40-50 micron size range. The unsatisfactory powder, when examined under a microscope, exhibited a definite tendency to form long chains of adherent particles. This phenomenon may partly explain the poor flow properties, but it is probable that the particle shape was also a contributing factor [6].

The surface area of the UF_4 product, as determined by nitrogen adsorption at the temperature of liquid nitrogen, was approximately 1.5 m^2/g. The tap densities of both the $UF_4.NH_4F$ and UF_4 were approximately 2.8 g/cm^3.

The average dust losses from the reactor were approximately $2\frac{1}{2}\%$ of the charge. 84% by weight of the powder was in the range 28-53 micron; about 2% was less than 10 micron. The cyclone was designed to recover approximately 97% of 10 micron material and the loss of $2\frac{1}{2}\%$ of the charge is therefore to be expected.

AMMONIUM FLUORIDE RECOVERY AND NITROGEN RECYCLE

At ordinary temperatures NH_4F is a solid, but at higher temperatures the solid sublimes and dissociates so that it is present in the vapour phase as NH_3 and HF[4]. It was economically desirable to recover the NH_4F from the hot nitrogen stream in such a way that it could be reused and the nitrogen recycled to the fluidized bed. The following methods of recovering NH_4F were investigated.

Scrubbing with water

Water scrubbing of the gases containing NH_4F in a packed tower was investigated on the small scale unit. This method had the advantage of being a very efficient means of cooling the hot gases. The scrubbing was not complete (efficiencies were about 95%) and a wet dense fume was evident in the exit gas from the scrubber. In addition, the use of water requires that the nitrogen would have to be thoroughly dried before recycling in order to prevent excessive reaction of water with the UF_4. Various alternative methods of removal not involving the introduction of water were therefore investigated.

Dry condensation

Small scale tests

An attempt was made to recover the NH_4F as a solid sublimate by rapidly cooling the hot gases from the small scale fluidized bed unit. In every case, however, a liquid phase was first formed. This liquid solidified at approximately 110 °C to form a hard adherent substance which had a composition intermediate between that of NH_4F and NH_4HF_2.

Euler and Westrum [5] have investigated the system NH_4F-HF, and found that NH_4F and NH_4HF form a solid solution with an equimolar eutectic point at 109 °C. From these results, it would appear that on cooling a vapour containing equal mole ratios of NH_3 and HF a liquid phase would always form before a solid sublimate.

A two-stage recovery system was then investigated in which a liquid was condensed at about 115 °C in the first stage. In the second stage, the residual gases were cooled by dilution with cold air, and the sublimate that formed was removed from the nitrogen stream by a bag filter. The presence of ammonia (NH_3) in the gases leaving the bag filter confirmed that a substance was being formed which was deficient in NH_3 as compared with NH_4F.

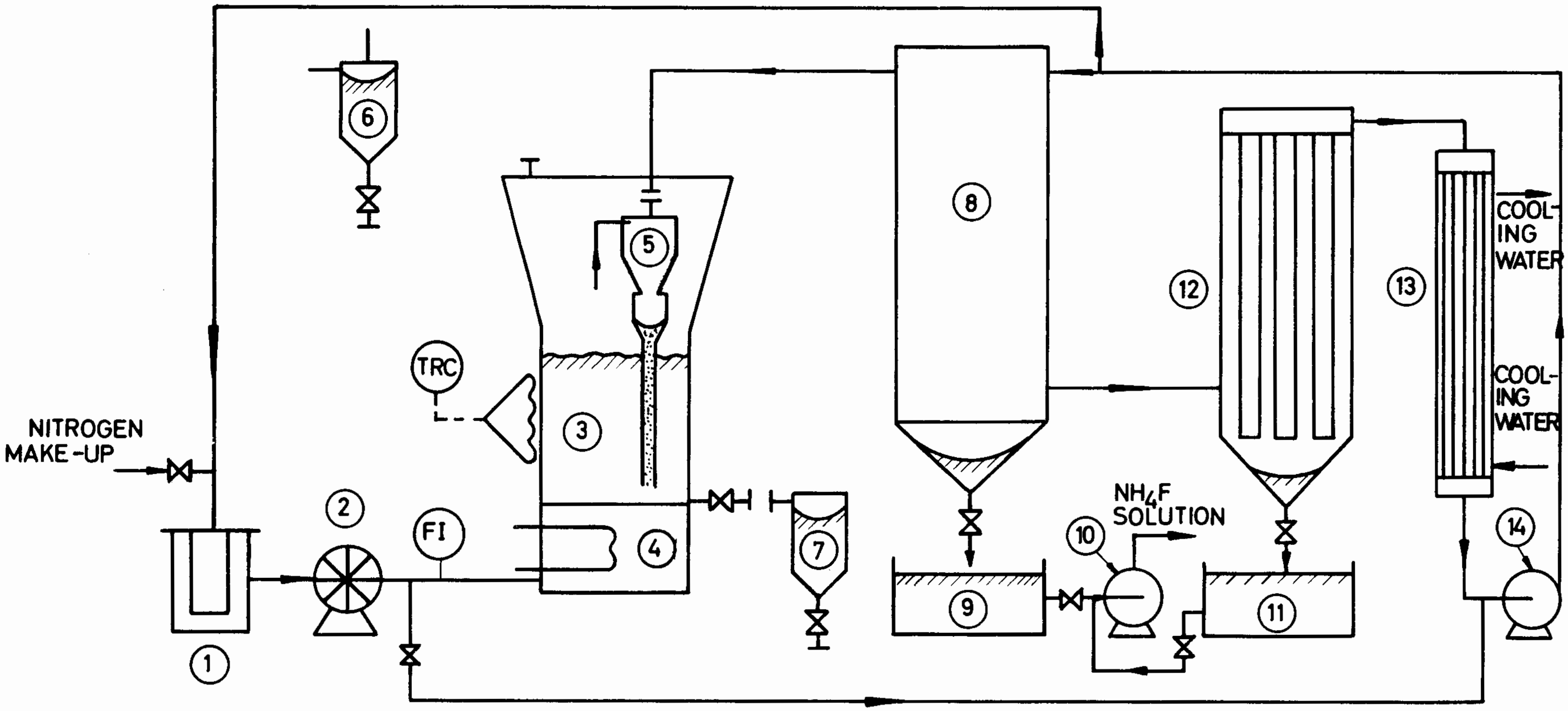
Pilot plant for liquid condensation

In view of the above, it was decided to design the NH_4F recovery section of the pilot plant as a two-stage system. The flowsheet is shown in Fig. 1. The hot gases from the fluidized bed passed to the tube-side of an oil-cooled condenser. The oil entered at about 115 °C and the heat gained from the condensing NH_4F-NH_4HF_2 liquid was removed in an oil cooler. The hot liquid phase drained from the base of the condenser into the NH_4F solution tank. The gases in equilibrium with the NH_4F-NH_4HF_2 liquid phase passed from the condenser along an oil-heated pipe to a bag filter unit. Heat losses from the bag filter unit caused the gases to be cooled. The NH_4F sublimate which formed was removed by the filter bags but at this stage of the investigations the nitrogen containing some NH_3 was not recycled. The NH_4F sublimate was dissolved in water in the tank below the filter unit and the solution was returned to the $UF_4.NH_4F$ precipitation plant (see Fig. 1). This circuit was only used for the first two runs.

Disadvantages of the liquid condensation method

It was not possible to remove completely all the UF_4 particles from the gases leaving the fluidized bed, and these collected in the condenser tubes and the drainage pot at the base of the condenser. During periods of rapid NH_4F evolution, most of the particles passed out at the base of the condenser, but towards the end of the decomposition, the powder built up and blocked the condenser tubes. This problem could possibly have been overcome by avoiding the carry over of dust from the fluidized bed unit, but in the light of difficulties with the design of suitable filters the use of the condenser was considered impracticable.

Further, the presence of NH_3 in the nitrogen leaving the bag filter unit required that, before the nitrogen could be recycled, it would have to be treated to remove the NH_3. This treatment would probably have involved a water scrubbing stage which would



EQUIPMENT DETAILS

1. NITROGEN BLOWER FILTER
2. NITROGEN BLOWER
3. FLUIDIZED BED UNIT
4. NITROGEN PREHEATER
5. FLUIDIZED BED CYCLONE
6. $UF_4.NH_4F$ FEED HOPPER
7. UF_4 PRODUCT HOPPER
8. COOLING CHAMBER
9. NH_4F SOLUTION TANK
10. NH_4F SOLUTION PUMP
11. NH_4F SOLUTION TANK
12. NH_4F BAG FILTER
13. CIRCULATING GAS COOLER
14. CIRCULATING GAS FAN

Figure 4. Flowsheet of $UF_4.NH_4F$ decomposition pilot plant (modified process)

have necessitated an additional costly drying operation.

At about this time it was noted, during an emergency release of hot gases from the fluidized bed through the relief valve, that on meeting the cold atmosphere only a solid sublimate of NH_4F was formed. It was concluded that if the hot NH_4F-bearing gases could be rapidly cooled to less than 110 °C, the liquid phase would not be formed. It was decided to modify the NH_4F recovery section in accordance with this finding and include equipment for recycling nitrogen to the fluidized bed.

Pilot plant for recovery of sublimate

The modified pilot plant flowsheet is shown in Fig. 4. The hot gases from the fluidized bed reactor were rapidly cooled by mixing with a large volume (approximately 1 200 ft^3/min) of cool nitrogen in the polythene cooling chamber. Great care was taken in the design to ensure that the gases did not cool significantly before reaching the cold atmosphere of the cooling chamber. The mixed gases left at a temperature not exceeding 80 °C and the solid sublimate which formed on cooling was removed in the bag filter unit. The nitrogen was then cooled to approximately 35 °C in the watercooled shell-and-tube cooler, before being recycled to the cooling chamber. Nitrogen for fluidization was filtered and then circulated by means of a Roots gas blower to the fluidized bed preheater. The gas flow rate to the bed was controlled by means of a by-pass valve as shown in Fig. 4. The solid NH_4F passed down a chute into the NH_4F solution tank where it dissolved rapidly. A valve in the chute prevented moisture entering the bag filter unit when the plant was shut down. The UF_4 and NH_4F which settled in the base of the cooling chamber were removed periodically.

This method of recovery has proved very satisfactory and there has been no evidence of the formation of a liquid phase. Clearly, the technique for obtaining only NH_4F solid is to cool the vapour rapidly to less than 110 °C. An almost pure stream of nitrogen was returned to the fluidized bed. The recycling of fluidizing gas reduced the average nitrogen usage from about 12 000 ft^3/batch to less than 600. A certain wastage was inevitable due to the need for purging the system at start-up, and the use of nitrogen in discharging the product. In addition, the temperature of the various items of equipment varied a great deal during a run, and it was necessary to purge and make-up with fresh nitrogen to compensate for the thermal expansion and contraction of the gas in the system.

The temperature of the gas leaving the cooling chamber was kept below 80 °C to ensure a good recovery of NH_4F. At higher temperatures, the increasing NH_4F vapour pressure would have resulted in an undesirable release of NH_4F vapour to the cooler, where it would condense and in the course of time cause a blockage of the tubes.

The woollen bags of the bag filter unit stood up well to the combined effects of temperature and NH_4F corrosion. The filtration efficiency was completely satisfactory. The solid built up to form a mat of about ½ inch thick on the filter bags, which resulted in a pressure drop of 3-6 in water gauge. The bags were satisfactorily cleaned by an intermittent nitrogen blowback, but it is expected that a filter unit with a mechanical cleaning action would give a lower pressure drop.

RECOMMENDATIONS FOR LARGE SCALE PLANT DESIGN

The batch method of operation is unsatisfactory owing to the wastage of nitrogen as discussed above in heat energy losses as a result of the intermittent cooling and heating cycles, and the inefficient use of the equipment.

Consideration has been given to a design for a continuous plant to produce 500 tons of UF_4 per annum. The fluidized bed reactor will have three countercurrent sections, controlled at temperatures of 340, 430 and 460 °C to correspond with the three stages of the reaction. The NH_4F recovery circuit will be almost identical in size and nature to the modified circuit described in this paper.

The estimated use of nitrogen is 0.4 ft^3/lb uranium which represents a cost in South Africa of 0.34 SA cents/lb uranium. The estimated power consumption for heating and pumping is 0.3 kWh/lb uranium which represents a cost of 0.12 SA cents/lb uranium. The total cost of power and reagents will therefore be in the region of 0.5 SA cents/lb. uranium.

CONCLUSIONS

(*a*) A process has been developed, on a batch pilot plant scale, for thermally decomposing $UF_4.NH_4F$ in a fluidized bed at a maximum temperature of 460 °C to produce UF_4 containing less than 20 ppm nitrogen (present as NH_4F).

(*b*) A technique has also been developed on a pilot plant scale for recovering the NH_4F formed in the decomposition reaction. Rapid cooling of the hot exit gases to less than 80 °C results in the formation of NH_4F solid sublimate which is easily removed by bag filtration.

(*c*) The high nickel alloys, in particular Monel, are suitable materials of construction for the fluidized bed reactor.

(*d*) The UF_4 produced in the process has very desirable properties. It is free-flowing, has a high surface area of 1.5m^2/g and a tap density of approximately 2.8 g/cm^3. It contains less than 0.5% U_3O_8.

(*e*) A continuous plant could readily be developed from the present batch plant. The cost in South Africa of power and reagents would be approximately 0.5 SA cents/lb uranium.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/464 Afrique du Sud

Production de tétrafluorure d'uranium par la décomposition thermique de fluorure uraneux d'ammonium en lit fluidisé

par R. E. Robinson *et al.*

Le mémoire décrit une installation pilote destinée à produire environ 100 tonnes de tétrafluorure d'uranium par an. L'installation comprend un réacteur à lit fluidisé, où le fluorure uraneux d'ammonium est calciné dans un courant d'azote, un système pour l'extraction du fluorure d'ammonium des gaz sortants et un système de recyclage de l'azote gazeux.

On donne les détails du plan et de la construction du réacteur à lit fluidisé, des matériaux de construction ainsi que des caractéristiques de fluidisation du fluorure uraneux d'ammonium. On décrit deux systèmes d'extraction du fluorure d'ammonium.

Le premier comprend la condensation de difluorure d'ammonium sous forme de liquide à une température soigneusement contrôlée, et le second fait usage d'une chambre de refroidissement pour condenser le gaz en une poudre solide.

A/464 ЮАР

Производство четырехфтористого урана термическим расположением четырехфтористогоураната аммония в псевдокипящем слое

Р. Э. Робинсон *et al.*

Дается описание опытной установки, предназначенной для производства примерно 100 *т* четырехфтористого урана в год. Установка состоит из реактора с псевдокипящим слоем, в котором четырехфтористый уранат аммония обжигается в потоке азота, системы для регенерации фтористого аммония из газообразных отходов и системы для повторного использования газообразного азота.

Приводятся подробные данные о конструкции и строительстве реактора с псевдокипящим слоем, конструкционных материалах и особенностях флюидизации четырехфтористогоураната аммония. Описываются две системы для регенерации фтористого аммония.

В первой происходит конденсация кислого фтористого аммония в жидкость при тщательно контролируемой температуре, а во второй с помощью камеры охлаждения газ конденсируется до образования твердого порошка.

A/464 Sudáfrica

Producción de tetrafluoruro de uranio por calcinación de fluoruro doble de uranilo y de amonio en lecho fluidificado

por R. E. Robinson *et al.*

Se describe una planta piloto concebida para producir unas 100 t anuales de tetrafluoruro de uranio. La instalación consiste en un recipiente de reacción de lecho fluidificado en el que el fluoruro doble de uranilo y amonio se calcina en corriente de nitrógeno, en un sistema de recuperación del fluoruro de amonio a partir de los gases efluentes y en un sistema de circulación del nitrógeno gaseoso.

Se facilitan detalles acerca del diseño y construcción del reactor de lecho fluidificado, de los materiales de construcción y de las características de fluidificación del fluoruro doble de uranilo y amonio. Se describen dos procedimientos para la recuperación del fluoruro de amonio.

El primero consiste en condensar el difluoruro de amonio en forma de líquido a una temperatura cuidadosamente regulada, mientras que el segundo utiliza una cámara de enfriamiento para condensar el gas en forma de sólido pulverulento.

La chloruration, procédé de concentration le plus universel des minerais d'uranium

par J. Zienkiewicz et T. Adamski *

La chimie et la technologie de l'uranium ont fait, depuis un peu plus de vingt ans, un tel pas en avant que l'étude de cet élément est aujourd'hui bien plus avancée que celle des éléments les plus répandus et dont l'humanité connaît l'usage depuis des millénaires. Il reste cependant à faire la lumière sur certaines de ses propriétés, qui ont une importance aussi bien théorique que pratique. De nouvelles recherches sur l'uranium s'imposent non seulement en raison de leur intérêt scientifique, mais aussi parce que les ressources en minerais aisément accessibles et riches en uranium sont déjà largement entamées. D'autre part, les difficultés croissantes que présente dans de nombreux pays l'extraction des matières premières énergétiques du type classique obligent à avoir recours à l'extraction de l'uranium en tant que combustible nucléaire, qu'il s'agit d'obtenir non pas à n'importe quel prix, mais à un prix de revient économiquement justifié, comparable à celui du pétrole ou de la houille.

Il n'est donc pas étonnant que des minerais contenant 10^{-4} à 10^{-3} % d'uranium soient soigneusement analysés et que l'on étudie la possibilité de les utiliser comme matière première complexe. On peut, par exemple, obtenir ainsi, sur une grande échelle, du vanadium en plus de l'uranium, à partir de minerais appropriés.

Les méthodes chimiques courantes de la technologie de l'uranium ne permettent qu'une utilisation insignifiante, par rapport à la masse totale du minerai traité, des minéraux autres que l'uranium contenus dans celui-ci. C'est ce qui a amené à entreprendre une analyse théorique de la possibilité d'appliquer un procédé de dissociation plus poussé du minerai, à savoir la chloruration à température élevée et l'extraction, en plus des composés volatils d'uranium, de composés volatils d'autres éléments dispersés, ainsi que des chlorures d'aluminium, de fer et de silicium, qui ont une grande importance économique. Les résultats

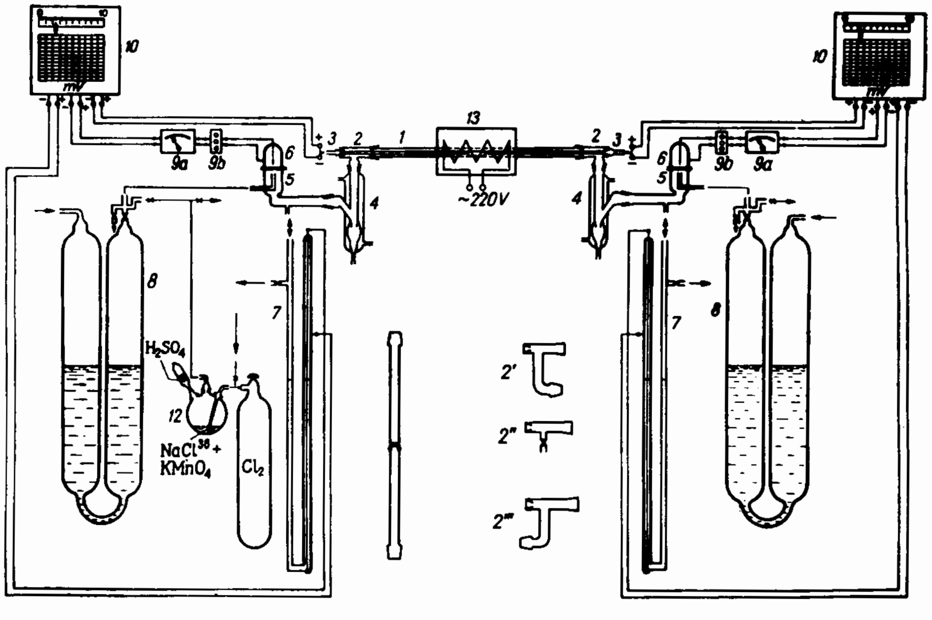

Figure 1. Appareillage universel

1 : Réacteur; 2 : Raccords; 3 : Manchons de thermocouples; 4 : Condenseurs; 5 : Cloches à fenêtre; 6 : Détecteurs; 7 : Manomètres à liquide; 8 : Récipients de gaz; 9*a* : Intégrateurs; 9*b* : Dispositifs de coupure; 10 : Potentiomètres enregistreurs; 11 : Bouteilles avec le gaz; 12 : Ballon pour le radioisotope; 1' : réacteur vertical; 2', 2'', 2''' : Raccords auxiliaires

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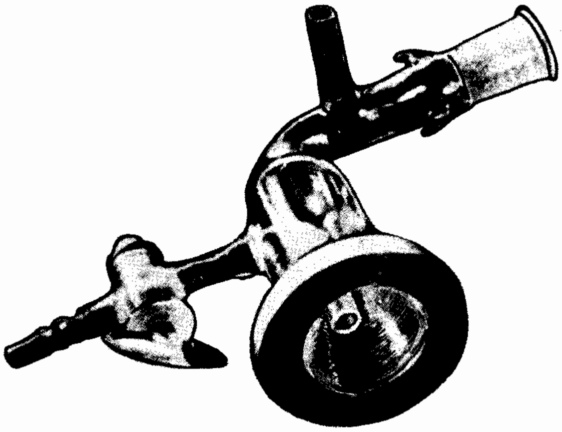

Figure 2. Cloche à fenêtre

des recherches préliminaires ont confirmé les conclusions positives de l'analyse [1].

ÉTUDES A L'AIDE D'OXYDES D'URANIUM SYNTHÉTIQUES [2, 3, 4]

Principes généraux

Pour mieux connaître les processus chimiques qui interviennent pendant la chloruration des composés d'uranium présents dans les minerais, on s'est basé sur le fait que les constituants qui décident de la valeur économique d'un minerai sont les oxydes minéraux d'uranium. C'est pourquoi les recherches ont porté sur les oxydes principaux d'uranium — UO_2, UO_3, U_3O_8 — dans les systèmes

$$[UO_x, Cl_2]$$

$$[(UO_x, C), Cl_2].$$

Pour étudier la cinétique et, en partie, le mécanisme de la chloruration, le chlore utilisé pour cette réaction était marqué au chlore — 36 (isotope à longue vie d'activité β) et on enregistrait l'évolution de la radioactivité, de la pression et de la température de la phase gazeuse du stysème examiné.

Méthode expérimentale

Sur la base des principes ci-dessus, on a élaboré une méthode de recherche et construit l'appareillage indispensable. Une des variantes de celui-ci, à savoir « l'appareillage universel », est représentée sur la figure 1.

A l'aide de cet appareillage, on peut faire des expériences aussi bien à volume constant qu'à pression constante. Il convient pour l'étude d'éléments dont les chlorures sont volatils ou non, à la température de la réaction. Dans le cas des oxydes d'uranium, l'appareillage peut être simplifié, les condenseurs étant superflus. De nouvelles simplifications sont possibles dans le cas d'études à volume constant : on peut alors supprimer la moitié des appareils de mesure et d'enregistrement.

L'élément essentiel et original de l'appareillage est la cloche à fenêtre, représentée sur la figure 2, qui sert en même temps de support à un compteur à fenêtre en bout.

Résultats de l'étude du système $[UO_x, Cl_2]$

Il convient de traiter à part la réaction du chlore avec UO_2. Dès la température de 225 °C, le chlore se combine violemment au bioxyde d'uranium en donnant, UO_2Cl_2 comme l'a montré l'analyse. Ce dernier se décompose avec violence au-dessus de 700 °C, avec sublimation partielle et condensation dans les parties plus froides de l'appareillage. Par suite de réactions secondaires, le produit final solide n'est pas UO_2, mais U_3O_8 sous la forme dite « substance noire », dont les cristaux ont des composantes de dimensions linéaires cent fois plus grandes que celles de la substance initiale. Dans la suite de la réaction, lorsque la température augmente, le chlore agit comme dans sa réaction avec U_3O_8, décrite plus loin.

La marche de la réaction $[UO_2, Cl_2]$ à volume constant et à gradient de température positif est illustré par le diagramme de la figure 3, où τ est le temps en minutes, p, $t°$ la température en °C, la pression en atmosphères et I la radioactivité relative en % de la radioactivité initiale.

La réaction de synthèse, qui se produit à des températures plus basses, peut être représentée de la façon suivante :

$$UO_2 + Cl_2 \longrightarrow UO_2Cl_2,$$

et celle de la décomposition, caractéristique pour des températures plus élevées :

$$4\ UO_2Cl_2 \longrightarrow U_3O_8 + UCl_6 + Cl_2$$

La réaction du chlore avec d'autres oxydes d'uranium se passe tout autrement. Le chlore ne commence à se combiner aux oxydes solides qu'à 900-1 000 °C et la réaction se poursuit lentement, donnant finalement un produit dont la composition correspond à la formule UO_2Cl_2. Étant donné que UO_2Cl_2 se décompose vers 700 °C, on est en droit de supposer que ce produit est le résultat de réactions secondaires. La réaction de U_3O_8 avec le chlore peut être représentée de la façon suivante :

$$\begin{cases} U_3O_8 + Cl_2 \longrightarrow 3\ UCl_4 + 4O_2 \\ UCl_4 + O_2 \longrightarrow UO_2Cl_2 + Cl_2 \end{cases}$$

Comme on le sait, UO_3 se décompose à des températures beaucoup moins élevées que celles où commence la chloruration des oxydes supérieurs d'uranium avec formation de U_3O_8 et O_2, et par conséquent sa réaction avec le chlore ne s'écarte pas du schéma ci-dessus.

Résultats de l'étude du système $[(UO_x, C), Cl_2]$

Ce système est le plus important du point de vue pratique, car l'introduction d'un réducteur baisse

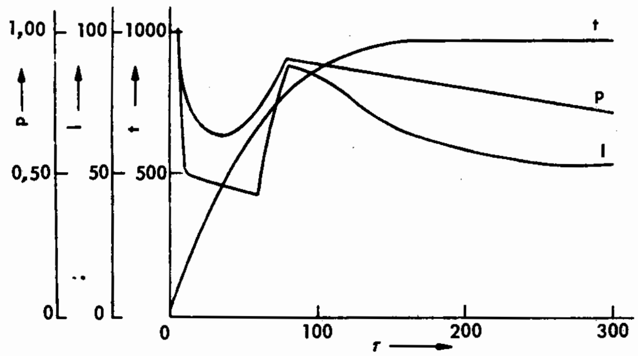

Figure 3. Système [UO_2, Cl_2]

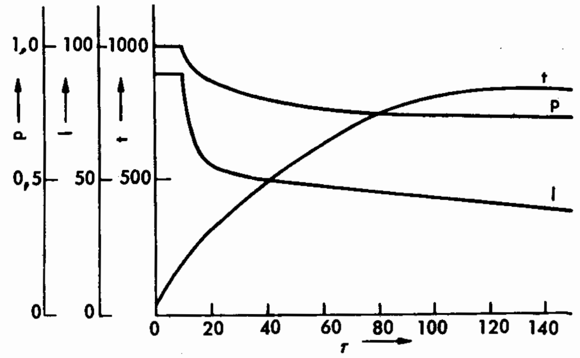

Figure 4. Système [(UO_2, C), Cl_2]

la température de la réaction et accélère celle-ci. Les recherches sur ce système pourront servir de base à des études technologiques.

Les graphiques obtenus en étudiant l'évolution des réactions de UO_2, U_3O_8 et UO_3 avec le chlore sont représentés sur les figures 4, 5, 6. La signification des symboles, ainsi que les unités adoptées, sont les mêmes que pour la figure 3.

Comme le montre la figure 4, la réaction de UO_2 avec le chlore commence à 225 °C et se poursuit comme dans le système sans réducteur, décrit plus haut. Cependant, l'introduction du carbone dans le système empêche UO_2Cl_2 formé au début de la réaction de se décomposer jusqu'à la formation d'oxyde d'uranium, en le réduisant jusqu'à UCl_4, qui de son côté, présente une grande stabilité thermique. Le ralentissement considérable de la réaction que l'on observe est causé par le colmatage de la surface de la substance initiale par les produits de la réaction à une température inférieure à celle de leur passage à l'état gazeux.

L'introduction du carbone dans le système [UO_x, Cl_2], où $x = 8/3$ ou 3, provoque des changements importants, comme on le voit sur les figures 5 et 6. Le chlore commence à réagir à moins de 300 °C. L'allure de la courbe de radioactivité indique ensuite un ralentissement notable de la réaction, causé par le colmatage de la surface de la substance initiale par des produits peu volatils.

Les résultats de l'analyse des produits de la réaction du système [U_3O_8, C, Cl_2] en fonction de la température de réaction sont indiqués dans le tableau 1 qui donne en même temps les schémas proposés des réactions.

ÉTUDES A L'AIDE D'OXYDES D'URANIUM NATURELS

Indépendamment des études systématiques sur les oxydes synthétiques, on a effectué des expériences de contrôle avec des oxydes minéraux naturels à 66 % de U. La réaction dans le système [(UO_x naturel, C), Cl_2] a été réalisée à différentes températures en déterminant le degré de saturation des valences de U par le chlore, ainsi que le rapport U^{IV}/U^{VI}, dans les produits de la réaction. Les résultats de ces expériences présentent une grande analogie avec ceux décrits au paragraphe précédent.

ÉTUDES SUR LA CHLORURATION D'OXYDES DE CERTAINS ÉLÉMENTS PRÉSENTS DANS LES MINERAIS D'URANIUM

La méthode radiométrique, décrite plus haut, a été appliquée à l'étude de la marche de la chloruration des oxydes de thorium, zirconium, tungstène, fer et vanadium. On a constaté que ZrO_2 et ThO_2 réagissent avec le chlore à peu près comme U_3O_8 ou UO_3, la

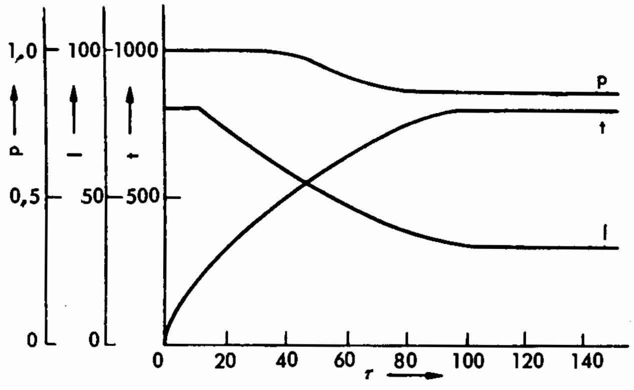

Figure 5. Système [(UO_3O_8, C), Cl_2]

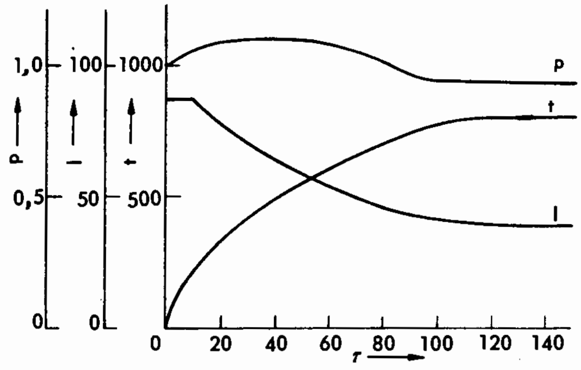

Figure 6. Système [(UO_3, C), Cl_2]

Tableau 1. Produits et schémas des réactions [(U_3O_8, C), Cl_2]

Température de réaction (°C)	Rendement de la réaction	U^{IV}/U^{VI}	Cl/U	Schéma proposé [a]
300	100	0:1	2:1	$\frac{1}{3}U_3O_8 + \frac{2}{3}C + Cl_2 \longrightarrow UO_2Cl_2 + \frac{2}{3}CO$
400	100	0:1	4:1	$\frac{2}{3}U_3O_8 + \frac{16}{3}C + 4Cl_2 \longrightarrow UO_2Cl_2 + UCl_6 + \frac{16}{3}CO$
675	100	0:1	4:1	$\frac{2}{3}U_3O_8 + \frac{16}{3}C + 4Cl_2 \longrightarrow UO_2Cl_2 + UCl_6 + \frac{16}{3}CO$
800	100	1:1	5:1	$\frac{2}{3}U_3O_8 + \frac{16}{3}C + 5Cl_2 \longrightarrow UCl_4 + UCl_6 + \frac{16}{3}CO$
1 000	100	1.25:1	4,5:1	$\frac{3}{4}U_3O_8 + 6C + \frac{11}{2}Cl_2 \longrightarrow \frac{5}{4}UCl_4 + UCl_6 + 6CO$

[a] Pour simplifier le schéma, on n'a pas introduit CO_2 qui se forme en même temps que CO. A une température de 450 °C environ, on a obtenu 50 % de CO_2, et à 300 °C, 54 % de CO_2.

réaction dans le système [MeO_x, Cl_2] ne commençant que vers 900 °C. L'introduction de carbone dans le système abaisse la température du début de la réaction au-dessous de 300 °C.

WO_2 réagit déjà à 200 °C, et la réaction est aussi violente que celle avec UO_2 L'analogie entre ces deux réactions est toutefois limitée à la partie synthèse; à cause de sa grande volatilité, $WOCl_4$ formé sort de la zone de réaction et ne se décompose pas.

Fe_2O_3 réagit avec le chlore à partir de 450 °C. A côté du composé volatil $FeCl_3$, il se forme $FeCl_2$, qui ralentit la réaction en colmatant la surface de l'oxyde initial. Au-delà de 800 °C, $FeCl_2$, se transforme violemment en $FeCl_3$.

L'application de la méthode radiométrique à l'étude de la chloruration de V_2O_5 permet d'obtenir un tableau fort intéressant. La réaction commence à 200 °C, en donnant $VOCl_3$; à 500 °C, on obtient VOCl; à 850 °C, les oxychlorures du vanadium de valence inférieure à 5, qui n'ont pas quitté la zone de réaction, se combinent avec le chlore pour former dans une réaction énergique des composés de vanadium pentavalent.

Les études ci-dessus ont un caractère préliminaire. Tout comme pour les oxydes d'uranium, qui sont un constituant naturel des minerais d'uranium, il convient de soumettre les minéraux accompagnant l'uranium à une analyse minéralogique et d'appliquer la méthode radiométrique après avoir déterminé leur composition chimique. Ces études sont en cours.

L'uranium est toujours accompagné de composés de silicium. L'application de la méthode radiométrique à l'étude de ceux-ci rencontre de grandes difficultés à cause de la grande volatilité de $SiCl_4$. On a pu obtenir certains renseignements sur l'évolution de la réaction en appliquant la méthode décrite dans la partie précédente. Il a été constaté que le quartz et les autres variétés cristallines de SiO_2, soigneusement broyés et mélangés avec du charbon, ne réagissent pas même à la température de 1 000 °C, tandis que certains silicates, que l'on trouve également dans les minerais d'uranium, réagissent avec le chlore à des températures moins élevées pour former $SiCl_4$.

ÉTUDES SUR LA CHLORURATION DES MATIÈRES PREMIÈRES D'URANIUM [5]

Principes généraux

Ainsi qu'on l'a vu dans la première partie, les résultats des études préliminaires sur la chloruration des minerais d'uranium sont positifs. Dans le système [(matière première, C) Cl_2] à 800 °C, presque tout l'uranium contenu dans le minerai quitte la zone de réaction sous forme de chlorures volatils et se condense dans les systèmes collecteurs. Les études décrites dans la deuxième partie ont prouvé que UO_2, en l'absence de réducteur, et les autres oxydes d'uranium, en présence de carbone, se combinent avec le chlore à une température inférieure à 300 °C. Il était souhaitable de vérifier expérimentalement sur le minerai : si la méthode de chloruration est universelle; dans quelles conditions il est possible d'obtenir un concentré d'uranium; si CO peut être utilisé au lieu de C.

Méthode expérimentale

Le schéma de l'appareillage représenté à la figure 7 restait en principe inchangé dans toutes les expériences sur la chloruration des matières premières d'uranium. Seules ses dimensions étaient modifiées selon la quantité de la substance étudiée. Pour les études sur le domaine d'application de la méthode, on a utilisé 1 000 à 2 000 g de minerai, pour les études systématiques en vue de déterminer les paramètres technologiques, 40 à 50 g, et pour les études sur la possibilité d'utiliser CO comme réducteur 2 500 g environ.

Études sur le domaine d'application de la méthode

Les recherches ont porté sur les minerais granitiques, gréseux, sulfureux, les cendres de charbons uranifères et les charbons uranifères contenant 0,083-0,127 % U. La matière réduite à moins de 0,20 mm, mélangée à de la poudre de charbon de bois et à un liant organique, était cokéfiée pour obtenir un aggloméré poreux qui était ensuite concassé en grains de grosseur convenant aux dimensions du four. La houille uranifère était concassée en grains de la dimension voulue et cokéfiée. La substance initiale ainsi obtenue était chargée dans le four en une couche de 600 à 800 mm d'épaisseur, l'air était chassé par un courant d'azote, la température de la substance était amenée à 800 °C pour assurer l'évacuation des produits de la chloruration d'uranium, et on connectait le courant de chlore. La quantité de chlore ainsi introduite était de 50 à 100 % de la quantité nécessaire en théorie pour la chloruration complète des constituants de la matière première. Le rendement d'extraction d'uranium était évalué d'après la teneur en uranium de la masse solide avant et après la réaction. Les résultats obtenus atteignaient 96 %. Il convient de noter que certaines des matières premières étudiées (minerais sulfureux, cendres) traitées par voie humide classique donnaient des rendements d'extraction extrêmement bas.

Études systématiques sur l'extraction d'uranium

Ayant démontré par les expériences ci-dessus l'universalité du procédé, on a choisi une des matières premières, à savoir le minerai granitique contenant 0,083 % U, que l'on a transformée en aggloméré et soumise à cinq séries d'essais différents par l'un des facteurs, les autres restant « normaux ».

Les facteurs, leurs symboles et leurs valeurs « normales » étaient les suivants :

Quantité de chlore introduite, q : 100 %;

Débit de chlore v : 0,08 g par cm^2 de section de la couche de substance initiale;

Température de la zone de réaction, θ : 800 °C;

Teneur en carbone de l'aggloméré, [C] : 33 %;

Concentration du chlore dans le gaz introduit [Cl]: 1.

Le rendement d'extraction était évalué en pourcentage d'après la teneur en uranium avant et après la réaction. Pour illustrer la marche de l'expérience, on examinera plus en détail les effets de la variation des deux facteurs q et θ. R désigne le rendement d'extraction. La figure 8 représente l'influence de la variation de q, et la figure 9 celle de la variation de θ sur R.

L'étude de l'influence des autres facteurs montre qu'on peut faire varier v considérablement, c'est-à-dire de 0,032 à 1,25 g/cm^2, sans modifier le résultat, que [C] peut être abaissé jusqu'à 17 % et qu'au lieu du chlore pur on peut utiliser du chlore de concentration. [Cl$_2$] = 0,4.

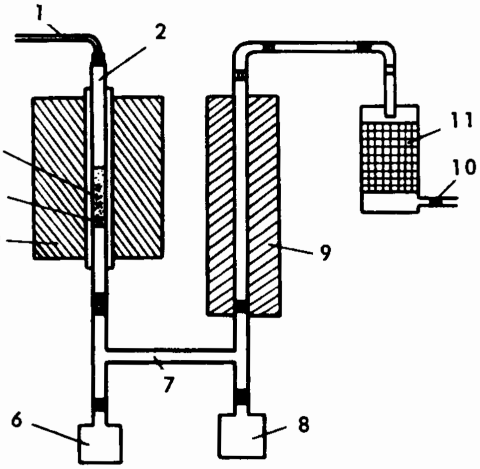

Figure 7. Schéma de l'appareillage pour l'étude de la chloruration des matières premières d'uranium

1 : Entrée des gaz; 2 : Réacteur; 3 : Matière initiale solide; 4 : Disque perforé en graphite; 5 : Four électrique; 6 : Condenseur des produits solides; 7 : Tube de jonction; 8 : Condenseur des produits liquides; 9 : Condenseur à CO$_2$ sec; 10 : Sortie des gaz; 11 : Adsorbeur

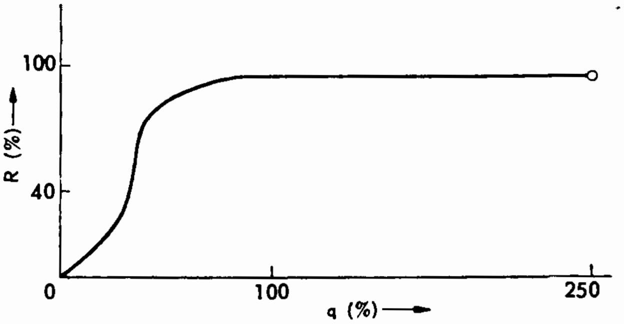

Figure 8. $R = f(q)$

ÉTUDES SUR L'UTILISATION D'UN RÉDUCTEUR GAZEUX (CO)

Les difficultés que présente la préparation des minerais ne contenant pas de carbone en vue d'obtenir le système [matière première, (C, Cl$_2$)] ont été à l'origine des recherches sur le système [matière première, (CO, Cl$_2$)] entreprises pour étudier, d'une part, la chloruration du produit broyé en lit fluidisé et d'autre part, la chloruration de la matière première non broyée, en lit fixe. On a utilisé du minerai granitique contenant 0,083 % U.

La chloruration en lit fluidisé présentait des difficultés techniques par suite de l'agglutination de la couche et de la formation de canaux verticaux par où passait la plus grande partie du chlore. L'agglutination était due à la formation de chlorures liquides non volatils, entre autres de calcium et de magnésium, éléments qui accompagnent presque toujours l'uranium. Il a fallu renoncer à cette méthode.

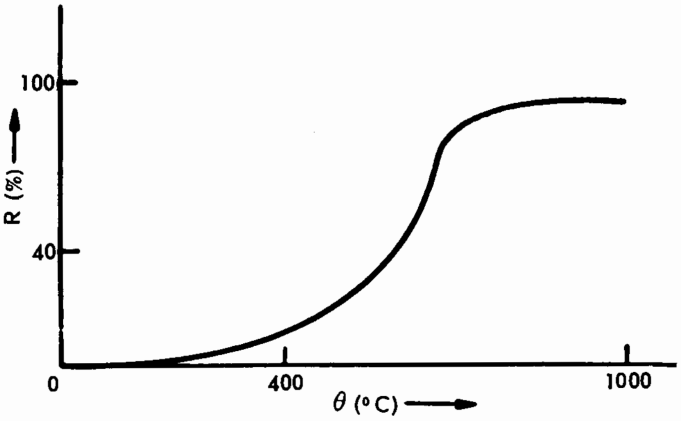

Figure 9. $R = f(\theta)$

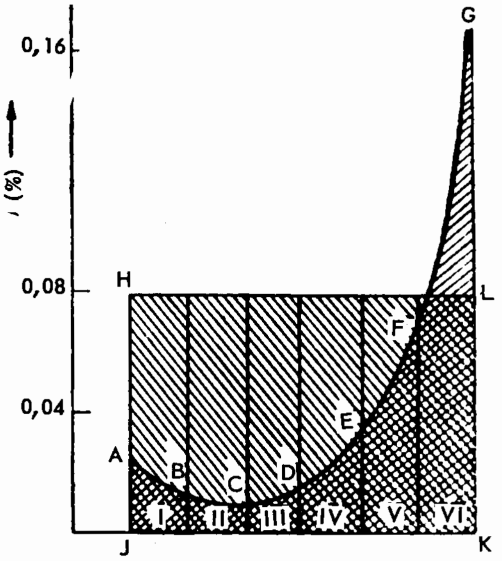

Figure 10. Bilan uranium

La chloruration en lit fixe était effectuée d'une façon analogue à ce qui est indiqué dans le paragraphe traitant de la méthode expérimentale, mais en raison d'écarts du bilan d'uranium, le produit obtenu était déchargé par le haut, en couches successives de volume égal I à VI, pour chacune desquelles on déterminait la teneur moyenne en uranium. De cette façon, on a obtenu le diagramme de la figure 10.

La surface HIKL représente la quantité initiale d'uranium et la surface ABCDEFGKJ la quantité retrouvée dans la masse restant après la réaction. Ainsi qu'il ressort du diagramme, les couches II et III contiennent le moins d'uranium, le rendement d'extraction y étant de 86 %, tandis que dans les couches suivantes, la teneur en uranium augmente, dépassant dans la dernière couche la teneur initiale. Si l'on fait abstraction de la couche I, où le rendement est plus bas du fait qu'en arrivant les gaz abaissent sa température, l'augmentation de la teneur en uranium dans les couches III et IV peut s'expliquer par des réactions secondaires des composés de chlore et d'uranium, formés dans les couches inférieures, réagissent avec l'excès d'oxydes d'éléments accompagnant l'uranium. Ce phénomène n'avait pas lieu dans les expériences précédentes, où l'excès de carbone empêchait les réactions secondaires. On peut également éliminer les réactions secondaires en diminuant le temps de contact des gaz de sortie avec la phase solide.

TENDANCES NOUVELLES DES RECHERCHES

L'Institut de recherches nucléaires de Varsovie a mis au point une nouvelle technique pour les réactions gaz-solide, par contact entre le solide broyé et le gaz, circulant dans le même sens ou à contre-courant dans la zone de réaction. Compte tenu des résultats des recherches décrites dans ce qui précède, cette technique peut être appliquée aux procédés de concentration d'uranium dans les minerais. Actuellement, les expériences se poursuivent dans deux directions :

a) La réaction se fait à haute température, aux environs de 800 °C, les produits de la réaction étant dirigés avec les gaz de sortie vers les installations de condensation, alors que le résidu appauvri tombe au fond du réacteur, d'où il est évacué périodiquement, ou de façon continue;

b) La réaction se fait à basse température, aux environs de 300 °C; les composés chlorés d'uranium et d'autres éléments importants (thorium, zirconium, etc.), formés dans ces conditions, restent dans le résidu solide, d'où ils sont retirés par lixiviation pour être ensuite concentrés par un procédé d'extraction par solvant.

EFFET ÉCONOMIQUE DE L'APPLICATION DU PROCÉDÉ PAR CHLORURATION

Pour montrer qu'un traitement complexe des minerais uranifères se justifie du point de vue économique, on s'est servi de données expérimentales relatives à un charbon uranifère, en considérant uniquement le bilan — matière uranium, aluminium, fer et silicium, ainsi que le bilan énergétique. Le coût des substances initiales et la valeur des produits étaient, respectivement, d'environ 40 et 180 dollars par tonne de charbon, le bilan énergétique étant positif. Cette marge suffit amplement pour couvrir les frais d'exploitation et d'amortissement et garantit des bénéfices substantiels.

CONCLUSIONS

Les minerais uranifères doivent être traités comme une matière première complexe. Le fait de considérer les minerais uranifères comme une source complexe de différents éléments dispersés ainsi que de divers produits secondaires rend nécessaires de nouvelles recherches et ouvre des perspectives d'une amélioration considérable de l'économie de la production d'uranium.

La chloruration est un procédé universel. Un procédé universel de traitement complexe des matières premières uranifères peut être basé sur la réaction avec le chlore.

L'emploi du radiochlore permet d'étudier le processus de chloruration. L'emploi de l'isotope radioactif ^{36}Cl dans les études de la chloruration des composés chimiques crée de nouvelles possibilités d'étudier la cinétique et le mécanisme de cette réaction. L'appareillage universel proposé permet des recherches sur les composés à différents états de concentration, dans un large intervalle de températures. Il a permis notamment de mieux connaître le processus de chloruration des oxydes d'uranium.

Bases pour la technologie. La concentration de l'uranium présent dans la matière première à l'aide de la réaction avec le chlore peut être réalisée à l'échelle industrielle par différents procédés, suivant le type de matière première : sa composition chimique et l'utilité de l'extraction de divers composés. Des recherches ont permis de préciser les conditions du traitement technologique en couche fixe (ou bien se déplaçant lentement) pour une matière première non préparée ou préparée. Des recherches sont en cours sur l'application de nouveaux procédés technologiques rapides gaz-phase solide.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/805 Poland

Chlorination as the most flexible method of concentrating uranium ores

By J. Zienkiewicz and T. Adamski

In the course of studies undertaken with the object of finding new and less costly methods of concentrating ores of uranium, attention was drawn to the possibility of treating them with chlorine at high temperatures. A fresh start was made on detailed research into the reactions between chlorine and uranium oxides and other uranium minerals at different temperatures, using pure chlorine, both alone and in the presence of reducing agents, namely: graphite and carbon monoxide. The mechanism and kinetics of the reactions was studied using ^{36}Cl as a tracer. The work resulted in the important discovery that uranium dioxide reacts with chlorine at a temperature as low as 225 °C, with formation of uranyl chloride (UO_2Cl_2), while in the presence of carbon the chlorination of both U_3O_8 and UO_3 proceeds at 300 °C.

The results thus obtained may be taken as a basis for developing different technological processes for the treatment of different types of ore. The decisive part is played by the other valuable elements present in the ores, capable of forming volatile or recoverable chlorides during the process (e.g., titanium, vanadium, molybdenum, niobium and tantalum). It is also possible to produce anhydrous aluminium chloride and silicon chloride in the same process, both of which are valuable by-products.

A new, high-efficiency apparatus for bringing granular solids into reaction with gases at high temperatures has been developed.

Chlorination is considered to be a promising and important method of processing uranium ores that can be readily adapted to a number of specific needs.

A/805 Польша

Хлорирование как универсальный метод обогащения урановых руд

Я. Зенкевич, Т. Адамски

С целью найти наиболее экономичный метод обогащения урановых руд обращено внимание на возможность воздействия хлором при высоких температурах. Проведены новые детальные исследования реакции хлора с окислами и минералами урана в широком диапазоне температур как с чистым хлором, так и в присутствии восстановителей: угля и окиси углерода. Механизм и кинетика реакций подвергались изучению с применением изотопа Cl^{36} в качестве индикатора. Опыты обнаружили важный с технологической точки зрения факт, что реакция двуокиси урана с хлором протекает уже при температуре 225° С с образованием уранилхлорида UO_2Cl_2, в то время как хлорирование U_3O_8 и UO_3 в присутствии угля протекает при температуре 300° С.

Полученные результаты могут служить основой для разработки различных технологических схем, которые подбираются для различных типов руды. Решающее значение имеет

содержание других ценных элементов, находящихся в рудах, если они образуют в этих условиях летучие или извлекаемые хлориды, например титан, ванадий, молибден, ниобий, тантал. Имеются возможности тем же методом получать безводный хлористый алюминий и хлористый кремний, которые являются ценными побочными продуктами.

Сконструирована новая, высокоэффективная аппаратура для осуществления реакций между гранулированными твердыми веществами и газами при высоких температурах.

Хлорирование следует считать очень универсальным, интенсивным и гибким методом переработки урановых руд.

A/805 Polonia

La cloruración como método general de concentración de minerales de uranio

por J. Zienkiewicz y T. Adamski

Con objeto de encontrar métodos más económicos para la concentración de minerales de uranio, se ha estudiado la posibilidad de usar la cloruración a temperaturas elevadas. Se ha hecho una investigación detallada de la reacción del cloro con los óxidos y los minerales de uranio a diferentes temperaturas, tanto con cloro puro como en presencia de agentes reductores : grafito y monóxido de carbono. Se ha estudiado el mecanismo y la cinética de las reacciones utilizando cloro-36 como trazador, y se ha observado un hecho importante : la reacción del dióxido de uranio con el cloro se produce ya a 225 °C, formándose cloruro de uranilo UO_2Cl_2, mientras que la cloruración del U_3O_8 y la del UO_3 en presencia del carbono se realiza a 300 °C.

Los resultados obtenidos pueden servir de base para desarrollar distintos esquemas tecnólogicos que pueden adaptarse a diferentes tipos de minerales. Tienen importancia decisiva las concentraciones de otros elementos valiosos que a veces contienen los minerales y que forman cloruros volátiles o que se pueden extraer en el mismo proceso (p.ej., titanio, vanadio, molibdeno, niobio y tántalo). También existe la posibilidad de obtener tetracloruro de silicio y cloruro de aluminio anhidro, que son subproductos valiosos, en el mismo proceso.

Se ha desarrollado una nueva instalación de gran eficacia para realizar las reacciones de sólidos granulares con gases a temperaturas elevadas.

Se considera que la cloruración es un método general, eficaz y flexible de tratamiento de minerales de uranio de todos los tipos.

P/836 South Africa

Laboratory and pilot plant tests on the production of ammonium uranous fluoride in refining operations

By R. E. Robinson, * J. C. Geertsma, * C. W. A. Muir ** and G. Peratides **

The conventional "dry way" process for the production of uranium tetrafluoride requires the use of anhydrous hydrogen fluoride which is not produced in South Africa on a commercial scale. Accordingly investigations were made on the precipitation of uranium fluorides from aqueous solutions.

The majority of wet precipitation processes which have been reported in the literature produce a uranium tetrafluoride hydrate. The disadvantages associated with such hydrates are usually poor bulk density, poor filtering qualities and difficulties in obtaining an anhydrous product without degrading the UF_4 in the drying process. However, the successful use of the Winlo process [1] in the USA and the Excer process [2] in Japan shows that the problems can be overcome.

The production of anhydrous uranous double salts of uranium of the type UF_4xMF_4 where M is either calcium, sodium, potassium or ammonium, has been studied by several investigators as an alternative. Of these processes, the double fluoride cycle described by Brodsky and Pagny [3] was chosen for further study. This process involves the introduction of SO_2 gas into a solution containing an alkali fluoride, $UO_2(NO_3)_2$, and HCOOH in suitable concentrations at a temperature above 80 °C. Brodsky and Pagny stated that nascent hyposulphurous acid is formed which reduces hexavalent uranium ions to the tetravalent state. The uranous ions then combine immediately with the alkali fluoride to precipitate the unhydrated uranous double salt.

The reaction with sodium fluoride was represented as follows:

$$UO_2(NO_3)_2 + 5NaF + HCOOH + 2SO_2 \longrightarrow UF_4.NaF + 2NaNO_3 + 2NaHSO_3 + CO_2$$

After preliminary testwork [4] in which sodium uranous fluoride was prepared and found to be unsuitable for metallothermic reduction to uranium metal, attention was turned to the production of ammonium uranous fluoride, $UF_4.NH_4F$. This material has the advantage over the sodium salt that it can be decomposed by heating to form UF_4, which could be used for either the production of uranium metal or uranium hexafluoride.

During further testwork, it became apparent that the reactions involved were far more complex than had been supposed and that the design of a production plant would involve many more difficulties than at first indicated. Accordingly it was decided that further investigations should be in two main directions:

(*a*) A fundamental study of the nature of the reactions occurring;

(*b*) A practical pilot plant study of the engineering problems involved in the use of the process.

The results of these two approaches are described in the sections that follow.

FUNDAMENTAL STUDIES ON THE NATURE OF THE REACTIONS INVOLVED IN THE PROCESS

Experimental

Apparatus. A diagram of the apparatus used appears in Fig. 1. The vessel was located in a thermostatically-controlled oil bath. The stirrer was designed to create a vortex in the solution for efficient gas absorption, and ran at 2 000 rpm.

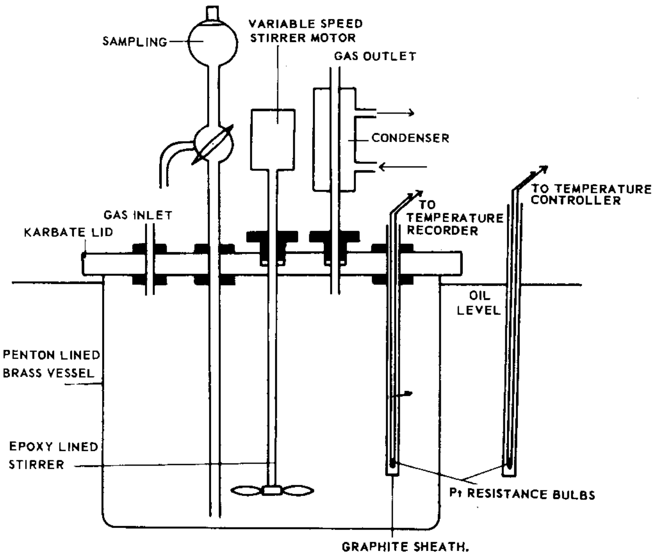

Figure 1. Sketch of reaction vessel

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Sampling. 10-15 ml portions of the slurry were withdrawn at regular intervals and filtered immediately. The sudden cooling during these operations served to decrease the reaction rate sufficiently so that uranium analyses on aliquot samples taken immediately from the filtrates gave a satisfactory indication of the progress of the reaction.

Test procedure. $UO_2(NO_3)_2$, NH_4F and HCOOH solutions were mixed in appropriate proportions to provide a total of 2 000 ml which was heated in the reactor to the required temperature. Sulphur dioxide gas was then introduced through a rotameter to start the reaction.

Results and discussion

Effect of temperature. Figure 2 shows the effect of temperature variation on the reaction rate using a head solution containing 50 g/l U (as $UO_2(NO_3)_2$), and an NH_4F addition 5% in excess of the stoichiometric requirement based on the reaction:

$$U^{4+} + 5NH_4F \longrightarrow UF_4.NH_4F + 4NF_4^+$$

The formic acid addition was 25 g/l. These concentrations were used in the same proportions in all other experiments, except where any one of them was the variable being studied.

The curve in Fig. 2, which was obtained from the slopes of a family of curves showing the depletion of uranium in solution with time at different temperatures, shows that the rate of reaction increases markedly with temperature, reaching a maximum of 88 °C at a barometric pressure of 625 mm Hg in Johannesburg. At temperatures higher than this, it is thought that the decrease in solubility of SO_2 at temperatures close to boiling point probably accounts for the slight decrease in rate of reaction.

Effect of reagent concentrations at constant temperature. Figure 3 shows the results of increasing the uranium content of the head solution to 100 and 150 g/l, with the other reagents increased in the same proportion.

The initial portion of curve 1 appears to be anomalous, but the samples taken in the time interval 0-25 minutes show low values due to the precipitation of ammonium uranyl fluoride ($UO_2F_2.3NH_4F$), which is formed when concentrated $UO_2(NO_3)_2$ and NH_4F solutions are first mixed. After a relatively short period this compound redissolves and thereafter the curve is also in the form of a straight line. The dotted portion projects back to the original uranium concentration of 150 g/l uranium.

The most striking features of the curves in Fig. 3 are that they are linear (following a short induction period probably caused by the time required for SO_2 to build up to a required concentration in the solution) and also that the slopes of the curves are proportional to an initial reagent concentration.

If a first or higher order reaction were rate determining, a non-linear relationship would be expected, since the decrease in driving force, as one or more of the reactants was consumed would cause a corresponding decrease in reaction rate.

The linearity, which is apparent until nearly all the uranium is precipitated, implies that the driving force is constant during the reaction, and as noted above, is a function of the initial concentration of one or more of the reactants.

In a true zero order reaction, where the rate of reaction is independent of the concentration of the reactants, the rate curves would be in the form of a series of parallel lines. Such a situation might obtain if the diffusion of SO_2 into the solution was the rate-controlling step, as the diffusion rate in each instance would be very similar, being only slightly affected by solute concentration differences.

In the case under consideration, where linearity is associated with the proportionality of reaction rate to an initial reagent concentration, it was concluded that a particular reagent, or a compound derived from it, must be continuously regenerated. Such regeneration would mean that the concentration of active reducing agent would be constant. The constant

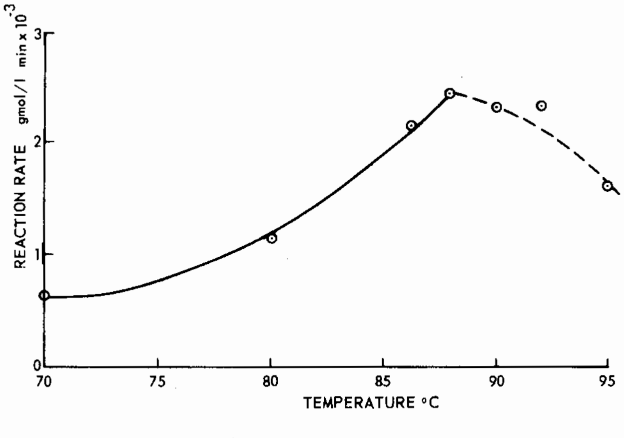


Figure 2. Effect of temperature on reaction rate

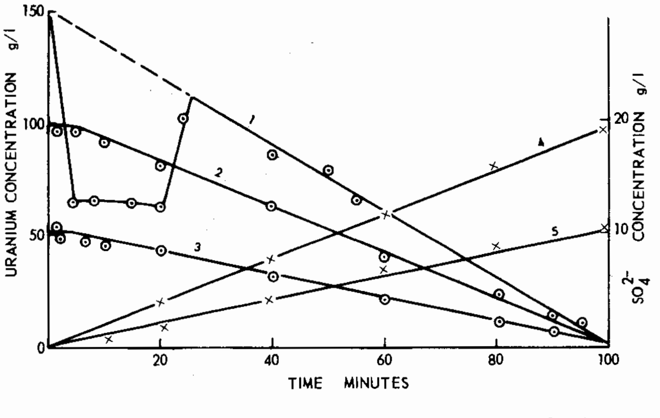


Figure 3. Effect of reagent concentration at 86 °C

driving force would then be explained assuming the regeneration-reduction reaction to be the slowest step in a series of intermediate chain reactions.

In these tests, samples were also analysed for sulphate content, and curves 4 and 5 show its rate of appearance. The straight line form confirms that the reaction is not of the first or a higher order. The molecular ratios of U : SO_4 derived from curves 4 and 5 indicate that one SO_4 molecule is produced for every two UO_2 ions that react.

Effect of formic acid concentration at constant temperature. Figure 4 shows the effect of varying the HCOOH concentration at 50 g/l uranium and a 5% excess of NH_4F over the stoichiometric requirement.

Figure 4 was obtained from a family of curves which showed the effect of varying initial HCOOH additions. The slopes from the straight line portions of the curves were used.

The rate increases to a limiting value as the concentration is increased. It is considered that this limit is imposed by the diffusion rate of sulphur dioxide into the solution. At lower rates it is probable that one step in a chain of consecutive reactions limits the reaction velocity.

Analyses of the effluent gas from the reactor for CO and CO_2 content indicate that only a small proportion of the formic acid is completely oxidized according to reactions of the type:

$$HCOOH + O \longrightarrow H_2O + CO_2$$
$$HCOOH \longrightarrow H_2O + CO$$

CO_2 was not evolved preferentially at the beginning of the reaction. In an earlier paper [5] a reaction mechanism was proposed which allowed for the regeneration of HSO_2 ions and also satisfied the requirement that one SO_4 ion be produced for every two reacting UO_2 ions. This mechanism, however, required that all the HCOOH react with CO_2 evolution in an initial reaction to produce HSO_2 ions, as indicated by Brodsky and Pagny.

If CO_2 is not quantitatively evolved, the alternative is that the active reducing agent is based on a formaldehyde complex, since formaldehyde is the intermediate in the breakdown of HCOOH according to the sequence:

$$HCOOH \longrightarrow HCHO \longrightarrow CO_2$$

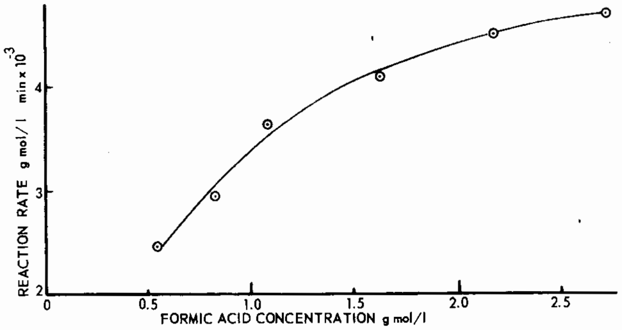


Figure 4. Effect of formic acid concentration at 86 °C

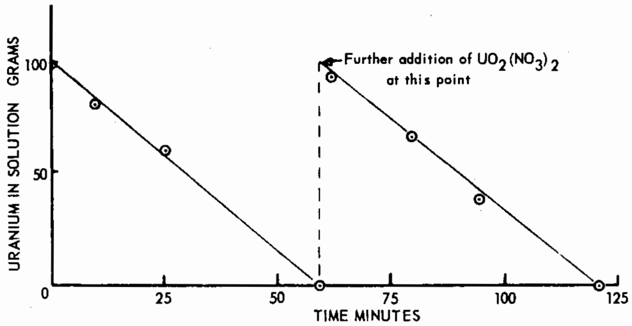


Figure 5. Re-use of depleted solution

On this basis in the system under consideration, the small amount of CO_2 evolved would be formed by a side reaction in which HCOOH is completely oxidized.

Effect of variation in concentration of other reactants. Further tests where the concentration of $UO_2(NO_3)_2$ and NH_4F were varied in turn, with other concentrations constant, indicated that such variations had little effect on reaction rate.

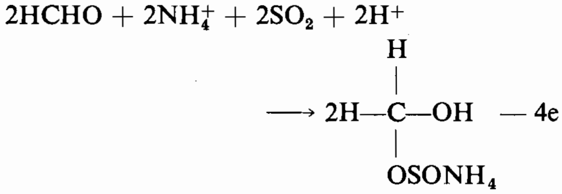
Re-use of solution remaining after complete uranium precipitation (depleted solution). Figure 5 shows the effect of re-using the solution remaining after complete uranium precipitation to initiate further reduction in a subsequent test. 1 000 ml head solution, containing 100 g/l U, 81.6 g/l NH_4F (including 5% excess), and 100 g/l HCOOH were allowed to react. At the completion of the reaction 1 000 ml of solution containing 100 g uranium and 81.6 g NH_4F were then added without any further formic acid addition. Samples during the course of the ensuing reaction were taken and were analysed for uranium content, the results being used to plot the reaction rate curve shown in Fig. 5.

This figure clearly illustrates that the active reducing agent has not been used up during the first precipitation reaction, and that further quantities of uranium can be precipitated by the addition of uranyl nitrate and NH_4F to the depleted solution at the end of the first stage.

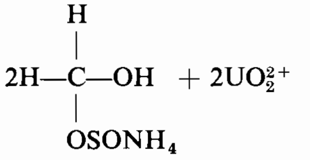
From a practical viewpoint, these effects are of considerable importance, since formic acid is one of the most expensive reagents in the process. These experiments have indicated that after the initial addition of formic acid, the active reducing agent formed from the formic acid, and present in the depleted solution, can be re-used.

Reaction mechanism. From the results obtained the following reaction mechanism is proposed:

$$2SO_2 + 2H_2O \longrightarrow 2HSO_3^- + 2H^+ \qquad (1)$$
$$2HCOOH + 2HSO_3^- \longrightarrow 2HCHO + 2HSO_4 \qquad (2)$$



$$2HCHO + 2NH_4^+ + 2SO_2 + 2H^+ \longrightarrow 2H{-}\overset{\displaystyle H}{\underset{\displaystyle OSONH_4}{C}}{-}OH \quad -4e \qquad (3)$$



$$2H{-}\overset{\displaystyle H}{\underset{\displaystyle OSONH_4}{C}}{-}OH + 2UO_2^{2+} \qquad (4)$$

$$\longrightarrow 2U^{4+} + 2HCOOH + 2NH_4^+ + H_2O + S_2O_5^{2-} + 4e$$

$$2HSO_4^- + S_2O_5^{2-} \longrightarrow SO_2 + S_2O_6^{2-} + SO_4^{2-} + H_2O \quad (5)$$

$$2U^{2+} + 10NH_4F \longrightarrow 2UF_4.NH_4F + 8NH_4^+ \quad (6)$$

The summation of these steps leads to the following over-all equation:

$$2UO_2^{2+} + 3SO_2 + 10NH_4F \xrightarrow{HCOOH} 2UF_4.NH_4F + 8NH_4^+ + S_2O_6^{2-} + SO_4^{2-}$$

Decontamination factors. Decontamination factors were determined by adding a known amount of the contaminant to the head solution at the beginning of a test. In each case a solution containing 100 g/l U, 81.6 g/l NH_4F and 50 g/l HCOOH was allowed to react at a temperature of 88 °C. The resulting precipitates were then analysed to determine the amount of the particular contaminant present in the precipitate after a standardized washing procedure. Table 1 shows the results that were obtained.

Table 1. Decontamination factors

Element	Ni	Fe	Cr	Mo	Mn	V	B	Si	Pb
Quantity in solution ppm [a] . . .	1 000	1 358	1 000	1 000	5 000	1 000	1 000	5 000	200
Quantity found in ppt. ppm. . . .	6	210	175	86	508	< 10	< 3	< 20	200
Decontamination factor	167	6	6	12	10	> 100	> 330	> 29	1

[a] ppm = parts contaminant per million parts uranium.

It should be emphasized that these values are not absolute and would probably be affected by different precipitation conditions. It is obvious though that a reasonably pure feed solution must be used, and the precipitation reaction is not sufficiently selective to consider the discontinuation of the preliminary solvent extraction step to produce a uranyl nitrate solution of nuclear grade specification.

PILOT PLANT TESTWORK

Pilot plant design

Because of uncertainties relating to the materials of construction for handling the extremely corrosive liquids, difficulties associated with the removal of the precipitate and an incomplete understanding of the critical factors influencing the particle size of the precipitate, it was decided that the pilot plant would be based on batchwise operation where a careful control could be maintained over the operating conditions.

A reactor was designed to treat half a metric ton of uranium per day (Fig. 6), and incorporated with other ancilliary apparatus as indicated in Fig. 7.

Materials of construction

Metals and alloys. Corrosion testing [6, 7] has indicated that only the alloys Coronel grades 230 and 240 could be considered. On a large scale, however, their cost would be prohibitive. It was therefore decided to use plastic materials wherever possible.

Plastic and allied materials. Extensive use was made of the following types of plastics in the construction of the plant:

(*a*) Penton, a chlorinated polyether, was used mainly in the form of a homogeneous lining on mild steel. This type of fabrication was used in the construction of the reactor and the fluoride solutions preheater (Fig. 7). After 250 hours of operation, no signs of ageing have been detected. The material suffers from the disadvantage of a low resistance to mechanical shock.

(*b*) Polyethylene was used for storage tanks for ammonium fluoride, formic acid and certain pipelines where the temperatures are below 50 °C.

(*c*) Polypropylene was used for the construction of the impeller and the lining on the stirrer shaft in the reactor where temperatures of up to 95 °C occur. The reactant solution has been stirred at speeds of up to 1 700 rpm and no signs of deformation of the impellers have been observed after over 100 hours of operation. The mechanical strength of polypropylene is such that it can be used for fairly large self-supporting structures and its use is being extended wherever possible.

(*d*) Other materials such as polytetrafluoroethylene (PTFE) have found application in the gas seal to the stirrer shaft and in valve diaphragms, and polyvinyl

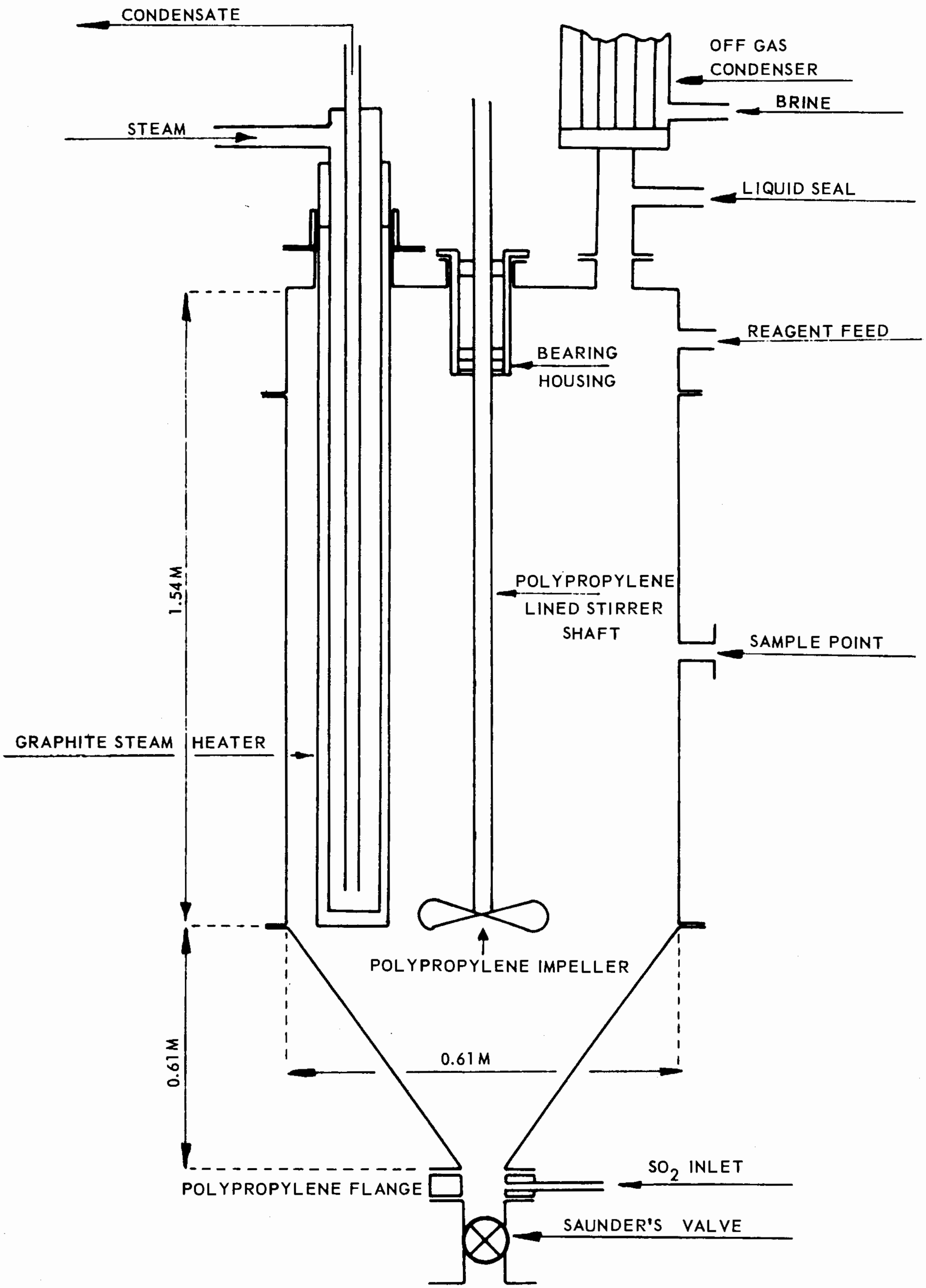


Figure 6. Main details of reactor

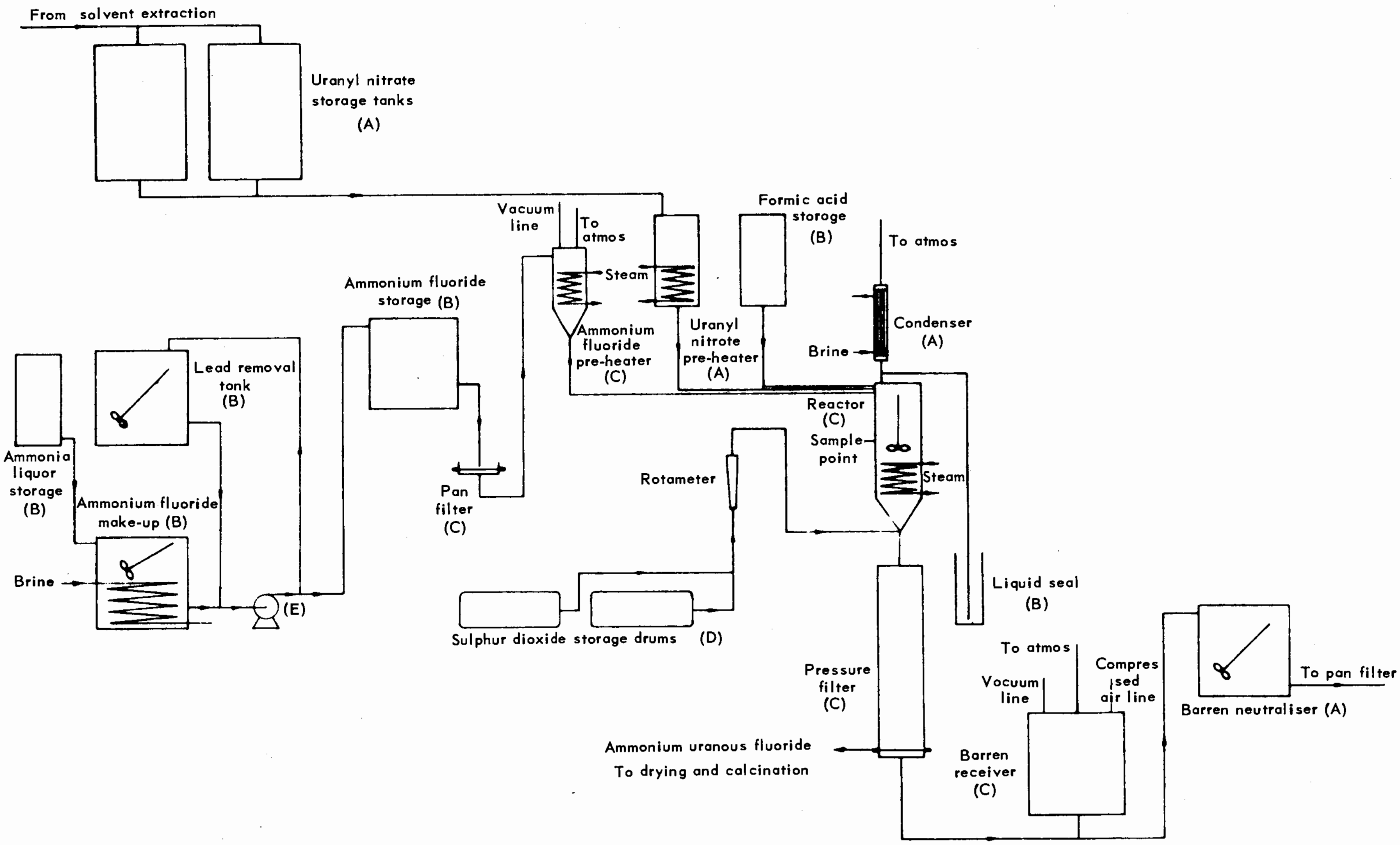


Figure 7. Flowsheet of French process. Ammonium uranous fluoride precipitation

Materials of construction: (A) Stainless steel Aisi grade 316; (B) Polyethylene; (C) Penton-lined mild steel; (D) Mild steel; (E) Kardate

Table 2. Production data

Series	Total No. batches treated	Stirring efficiency	Wt uranium in feed (kg)	Wt uranium in product (kg)	Production efficiency %
1	12	Poor	210.8	174.7	82.87
2	75	Moderate	3 395.2	3 316.9	97.69
3	14	Good	648.0	640.0	98.77
Total	101	—	4 254.0	4 131.6	97.12

chloride was used extensively for solution lines at ambient temperatures. Karbate, a resin-impregnated graphite, has given very satisfactory service as a material of construction for pumps and has shown no sign of deterioration in 18 months' service. Neoprene has been used in lines carrying hot fluoride solution, showing a slight tendency to deform after prolonged use.

Plant operation

Reactor solution heating. Initially the heating of the reactor solution was achieved by using two 3 kW hairpin resistance heating elements (Calrod elements) in a graphite sheath packed with silicon carbide. The arrangement failed after 5 hours' operation due to the high temperature gradient across the sheath. A system of heating using controlled injection of steam into the solution was then employed. This system was used for 20 hours' operation but proved unsatisfactory as contaminants in the form of scale and rust from the steam pipes were introduced. Furthermore, the resulting condensation caused operating difficulties by increasing the solution volume. This system was replaced by a graphite steam heater, as shown in Fig. 6, which was found to be highly satisfactory.

Stirring. It was initially considered that the higher the bulk density of the precipitate, the better would be the fluidization characteristics. Preliminary bench scale tests [8] indicated that the bulk density increases significantly with increase in the degree of agitation, and that this was the most important factor.

After a large number of trial stirring assemblies, a 20 cm diameter impeller on a 1.5 m stirrer shaft running at 800 rpm and coupled to a 3 hp motor was found to be satisfactory. A material with a bulk density as high as 2.88 and with excellent fluidization characteristics was obtained.

Reagent concentrations. The laboratory scale tests described in the first main section, indicated that the concentration of the formic acid was the most important rate determining factor. In practice, however, it was found that the precipitation of ammonium uranyl fluoride $UO_2NH_4F_5$ at the beginning of the reaction imposed a limitation on the reagent concentrations that could be used. The following concentrations in the reactor solution were found to be the most convenient for plant operation:

Uranium as $UO_2(NO_3)_2$: 130-140 g/l
Fluoride as NH_4F: 50-60 g/l
Formic acid: 65-70 g/l

Using reagent feed ratios of uranium 100 parts, NH_4F 82 parts (5% excess) and HCOOH 50 parts, the uranium was completely precipitated after 2 hours.

Filtration of the $NH_4F.UF_4$ precipitate. The precipitate obtained at the maximum degree of agitation filtered very readily. The area of the pressure filter was 0.25 m^2, and this could handle a complete batch of 400 kg of slurry in 40 minutes, which included three washings of the precipitate and unloading the filter. The advantage of the pressure filter is that a product containing not more than 4% moisture was obtained and this could be readily removed by drying to form an anhydrous material.

Results and discussion

Production and material balance. Table 2 shows the production balance at various periods in the pilot plant operation.

The high uranium losses from the system in the initial series occurred because at high reagent concentrations a precipitate of $UO_2NH_4F_5$ is formed during the first few minutes. Because stirring was inadequate, the precipitate settled at the bottom of the reactor and was subsequently lost in the filtration stage as it was soluble in the wash water. As indicated by Table 2, the uranium loss decreased with increasing stirring efficiency. The average time required to charge, complete the reaction, and discharge the reactor is 2 hours 15 minutes, which is equivalent to a production rate of approximately half a metric ton of uranium per 24 hours.

Purity of product. Initially very few of the batches prepared conformed to nuclear grade specifications due to iron and lead contamination. The main source of iron and the entire source of the lead was traced to the ammonium fluoride reagent. To overcome this contamination difficulty, the ammonium fluoride solution was treated using a 10% excess of phosphoric acid to precipitate the iron, and after filtration the lead in the filtrate was precipitated using an ammonium sulphide solution. During the preheating stage, compressed air was blown through the fluoride solution to remove the dissolved hydrogen sulphide gas.

Table 3. Reagent consumption

Reagent	Quantity used (kg)	Cost per kg reagent ($)	Total cost ($)
Sulphur dioxide	1 450	17.29	553
Ammonia liquor	2 690	5.32	315
Formic acid	1 850	19.18	781
Ammonium bifluoride	2 260	23.70	1 166
Lime	1 090	1.19	28
Total cost for treatment of	3 395 kg	uranium . . .	2 843

These simple precautions have now reduced the iron and lead content of the product to 30 ppm and < 10 ppm respectively.

Reagent consumption and costs. Table 3 gives an indication of the average reagent cost for 75 of the batches treated (Series 2, Table 2).

The cost of treatment was therefore 83.7 cents per kg uranium.

The ammonium bifluoride used in the pilot plant studies was imported into South Africa at a relatively high cost. For large scale production, it is almost certain that ammonium fluoride produced as a by-product by the local fertilizer industry could be used. The price of this material would be very much lower than that indicated in Table 3 even allowing for the necessity for further purification. This figure would be reduced further by recycling the ammonium fluoride recovered in the calcination step. It is estimated that these factors would effect a saving of $0.32 per kg.

The small scale laboratory tests indicated that a considerable saving in the formic acid reagent could be effected by re-using the depleted solution. It is estimated that a saving of up to 40% of the formic acid could be achieved in this way, that is $0.09 per kg uranium.

Sulphur dioxide, when produced on a large scale, would be significantly cheaper than as purchased in such quantities at the price shown in Table 2. A further saving of $0.11 per kg could thus be effected on a large scale plant.

Taking these factors into account it is suggested that the reagent costs for the process would in all probability be less than $0.31 per kg uranium.

This figure compares very favourably with reported data of other processes, particularly if the non-availability of certain chemicals in South Africa is considered. For example the total reagent costs quoted by the Atomic Fuel Corporation of Japan for the Excer process [2] are $1.37 per kg uranium.

CONCLUSIONS AND RECOMMENDATIONS

(*a*) For a given feed solution, the rate of precipitation of ammonium uranous fluoride is constant after an initial induction period.

(*b*) The main factor influencing the rate of precipitation in a batch process is the initial concentration of formic acid in the feed solution.

(*c*) These results indicate that there exists a constant driving force during the course of precipitation and it is suggested that this is maintained by the continuous regeneration of an active reducing agent.

(*d*) It is also suggested that the active reducing agent is a complex derived from formic acid, which is regenerated by SO_2. This complex could be one of a group of compounds of the formaldehyde sulphoxylate type.

(*e*) These suggestions indicated that the depleted solution obtained after complete precipitation could be used to initiate further precipitation, without the necessity of adding further quantities of formic acid. This indication has been confirmed in batchwise experiments, and suggests that a continuous process in which the depleted solution is recycled would result in a significant saving in formic acid requirements.

(*f*) Decontamination factors for the precipitation reaction were measured for a variety of elements. The results indicate that some preliminary purification of the feed solution (e.g. by solvent extraction) is necessary to obtain a product conforming to nuclear grade specifications.

(*g*) In spite of severe corrosion problems, it has been possible to operate a pilot plant for the production of ammonium uranous fluoride of nuclear grade quality.

(*h*) Reagent costs on the pilot plant have amounted to $0.84 per kg of uranium. It is considered that on a large scale these costs could be reduced to $0.31 per kg, which compares favourably with other processes.

(*i*) Further work to investigate a continuous process in which the depleted solution is recycled is recommended.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/836 Afrique du Sud

Essais de production au laboratoire et en pilote de fluorure uraneux d'ammonium dans les opérations de raffinage

par R. E. Robinson *et al.*

Le fluorure uraneux d'ammonium ($UF_4 \cdot NH_4F$) est précipité à partir d'une solution de nitrate d'uranyle ($UO_2(NO_3)_2$), de fluorure d'ammonium (NH_4F) et d'acide formique (HCOOH) par introduction d'anhydride sulfureux (SO_2). Les essais de laboratoire ont montré qu'à haute température la vitesse de précipitation de $UF_4 \cdot NH_4F$ est constante et dépend essentiellement de la concentration initiale en HCOOH. La réaction se propage de façon constante, ce qui est attribué à la régénération continue d'un agent de réduction actif; on propose un mécanisme de réaction fondé sur l'existence d'un système acide formique-sulfoxylate de formaldéhyde. On a pu montré l'intérêt pratique que l'utilisation d'un agent de réduction régénéré présente pour réduire le coût des réactifs.

Les essais en pilote ont montré qu'on pouvait préparer un produit de pureté nucléaire, une fois résolus les gros problèmes de corrosion. On pense que le coût relativement élevé du réactif (0,84 dollar par kilogramme de U) pourrait être abaissé à 0,31 dollar par kilogramme de U en opérant à plus grande échelle.

A/836 ЮАР

Лабораторные и полузаводские испытания получения фторида аммония и урана в качестве промежуточного продукта при операциях очистки

Р. Э. Робинсон *et al.*

Фторид аммония и урана ($UF_4 \cdot NH_4F$) осаждали из раствора, содержащего нитрат уранила, фторид аммония и муравьиную кислоту, путем введения двуокиси серы. Лабораторные испытания показали, что при повышенной температуре скорость осаждения фторида аммония и урана была постоянной и сильно зависела от начальной концентрации муравьиной кислоты. Постоянная движущая сила в ходе реакции обусловлена непрерывной регенерацией активного восстанавливающего агента, и был предложен механизм реакции, основанный на образовании системы муравьиная кислота — сульфоксилат формальдегида. Показаны практические преимущества метода с точки зрения стоимости восстанавливающего агента за счет повторного использования регенерированного агента.

Полузаводские испытания показали, что можно получать продукт ядерной чистоты после преодоления серьезных проблем, связанных с коррозией. Считается, что современная сравнительно высокая стоимость реагентов 0,84 долл. за 1 *кг* урана при увеличении масштабов производства может быть снижена до 0,31 долл. за 1 *кг* урана.

A/836 Sudáfrica

Ensayos de laboratorio y planta piloto sobre la producción de fluoruro uranoso amónico como producto intermedio en las operaciones de purificación

por R. E. Robinson *et al.*

El fluoruro uranoso amónico, $UF_4.NH_4F$, se precipitó a partir de soluciones que contenían nitrato de uranilo, $UO_2(NO_3)_2$, fluoruro amónico, NH_4F, y ácido fórmico, HCOOH, mediante la introducción de dióxido de azufre, SO_2. Los ensayos de laboratorio mostraron que a temperaturas elevadas la velocidad de precipitación del $UF_4.NH_4F$ era constante y en gran parte dependía de la concentración inicial de HCOOH. La constancia de la fuerza impulsora durante la reacción se atribuyó a la regeneración continua de un agente reductor activo y se propuso

un mecanismo de reacción basado en la formación de un sistema ácido fórmico-formaldehido sulfoxilato. Se demostraron las ventajas prácticas de los costes de reactivo reductor por reutilización del agente reductor regenerado.

Los ensayos en planta piloto pusieron de manifiesto que se puede producir un producto con pureza de calidad nuclear después de haber resuelto problemas importantes de corrosión. Se considera que el coste actual, relativamente alto, del reactivo de 0,84 dólares por kg de uranio podría reducirse a mayor escala, a 0,31 dólares por kg de uranio.

Nuevas orientaciones hidrometalúrgicas en la industria del uranio

por R. J. Cadirola, J. M. García Bourg, J. E. López Pardo, E. G. Macchiaverna y C. A. Wiedmer *

Uno de los objetivos actuales en la industria del uranio es la reducción de costos de producción: dos métodos para lograrlo pueden ser: *a*) afinar las técnicas existentes; *b*) reemplazar los productos intermedios. Los sectores de hidrometalurgia de la Comisión Nacional de Energía Atómica (CNEA) están llevando a cabo un programa de ensayos aplicando ambos métodos a las técnicas de intercambio iónico y extracción por solventes.

En la primera parte se hace un estudio comparativo del comportamiento de distintos solventes aminados, resumiendo los resultados de los ensayos previos correspondientes a cualquier operación de este tipo. De esta manera se facilita la elección del solvente aminado más conveniente, y se logra el ajuste de las condiciones de operación, según los requerimientos de cada caso.

En la segunda se estudian las posibilidades del uraniltricarbonato de amonio, como producto intermedio, en relación con la torta amarilla (*yellow cake*), indicándose sus formas de obtención tanto con intercambiadores sólidos como extractantes líquidos.

ESTUDIO COMPARATIVO DEL COMPORTAMIENTO DE ALGUNAS AMINAS COMO EXTRACTANTES DEL URANIO A PARTIR DE LÍQUIDOS DE LIXIVIACIÓN SULÚFRICA **

En el presente capítulo se describen, en forma resumida, los ensayos previos que se realizan en los laboratorios de investigación aplicada, con la finalidad de dar apoyo técnico a esta rama industrial de la hidrometalurgia. Con el objeto de que estos ensayos puedan cumplir con la finalidad de proveer una orientación rápida al sector industrial, para el que están dirigidos, se presentan sus resultados en forma de estudio comparativo de algunas de las variables de mayor influencia en el comportamiento de los solventes aminados, que aquí se tratan.

La actual orientación de la industria hidrometalúrgica del uranio, lleva a nuevas y crecientes exigencias con respecto al comportamiento físico-químico de los solventes aminados. Así los diseños de plantas de extracción líquido-líquido en contracorriente de tipo « compacto », bajan los costos de producción gracias a la eliminación de su sistema de bombeo, pero esta ventaja trae aparejada la dificultad de tener un tope mínimo para la velocidad de sus agitadores, por debajo del cual no se logra el necesario flujo de líquidos en contracorriente. En tales circunstancias, los solventes aminados que se elijan para trabajar en dichas plantas, deberán poseer muy buenas características con respecto a su poder resolutivo de separación de fases.

Con relación al mecanismo físico-químico de los solventes aminados, se sigue en este capítulo la vieja similitud [1-4] con las resinas intercambiadoras de iones (bases débiles), conforme al criterio de Coleman [4]: « La incertidumbre en el comportamiento del mecanismo y la falta de determinación de los coeficientes de actividad en la fase orgánica, no impide el empleo efectivo de la extracción con aminas... »

Sobre estas bases se expone a continuación el pertinente comentario sobre los datos obtenidos y su manera de presentación.

Isotermas de equilibrio

En la figura 1 se presentan las isotermas de equilibrio en extracción de las aminas: Adogen 368 (Archer-Daniels-Midland C°), Alamine 336 (General Mills), LA-2 (Rohm and Haas) y Trilaurilamina (Rhône-Poulenc).

La representación gráfica tiene como fundamento metodológico el estudio comparativo de tales isotermas, mediante coordenadas relativas [5] referidas, respectivamente, a la concentración inicial de la fase acuosa y al valor de saturación de la fase orgánica. Por medio de este arbitrio se logra la visualización inmediata del distinto comportamiento de los solventes estudiados, permitiendo además realizar el cálculo aproximado del número de etapas teóricas (método de Mc Cabe-Thiele) sobre un gráfico único para todas las isotermas de equilibrio comparadas, con el empleo de una sola recta de operación.

En cuanto a estas isotermas de equilibrio y a partir

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* Comisión Nacional de Energía Atómica.

** Por J. M. García Bourg, J. E. López Pardo y C. A. Wiedmer.

de la figura 1, puede inferirse las ventajas de las aminas terciarias, sin perjuicio de atender a que, para la elección de una amina, debe tomarse en cuenta no sólo el coeficiente de extracción, sino otros factores como: selectividad, carga máxima (saturación de la amina en uranio), poder resolutivo de separación de fases, pérdida por solubilidad, etc.

En la figura 2 se muestra la influencia del pH (acidez sulfúrica) sobre las isotermas de equilibrio en extracción para el caso particular de la amina Alamine 336. Con ello se pretende dar al operador de una planta de extracción, que trabaje dentro de estas condiciones, los elementos de juicio suficientes como para poder controlar o ajustar el proceso de acuerdo a sus necesidades.

Es de remarcar, por otro lado, que en este campo de la hidrometalurgia se presentan habitualmente relaciones de compromiso, que necesariamente deben ser tenidas en cuenta.

Separación de fases

Es condición esencial para un sistema de extracción líquido-líquido en contracorriente, lograr una efectiva separación de fases. De lo contrario, es imposible mantener los flujos en sentido inverso. Los fenómenos que se oponen a la condición enunciada son los cortocircuitos, las pérdidas por arrastre mecánico y el grado de solubilidad del solvente [6]. A excepción de las pérdidas por solubilidad, las demás se suelen producir por fenómenos de emulsión. Si bien el control de la emulsión se verá afectado por el tipo de solvente, también se debe tomar en cuenta el diluyente, los aditivos y las condiciones de operación. Dentro de estas últimas se debe distinguir las de carácter físico-químico (relación de fases, temperatura, pH, etc.) y las de orden mecánico (diseño del mezclador, agitador, sistema de circulación de fluidos, velocidad de agitación, etc.), siendo estas últimas las variables restrictivas en el diseño de plantas tipo compacto que se han mencionado en el comienzo. Para condiciones normales de operación, se mantiene el criterio de trabajar en fase orgánica continua [2, 5 y 7].

En el estudio de la separación de fases, se muestra el comportamiento de distintos solventes por medio de las figuras 3, 4, 9 y 10 tanto en extracción, como en desextracción con cloruro de sodio. Si bien en las isotermas de equilibrio en extracción la Trilaurilamina aventajaba al resto, de estos últimos resultados se ve claramente la conveniencia del empleo de Adogen 368 y Alamine 336.

En las figuras 5 y 6 se puede ver la influencia de los distintos diluyentes, como son los kerosenos de Shell y Yacimientos Petrolíferos Fiscales (República Argentina) y aguarrás de esta última empresa.

Las figuras 7 y 8 señalan la influencia del pH en la fase acuosa, mejorando visiblemente con su aumento.

Efecto análogo se observó con respecto a las isotermas de extracción, pero aquí es necesario recordar que la selectividad de la amina decrece sensiblemente con el aumento del pH [8]. Este es uno de los tantos ejemplos de relaciones de compromiso, que se presentan en este tema. Finalmente, en las figuras 11 y 12, se muestra la influencia de la temperatura sobre el poder resolutivo de separación de fases en extracción con Adogen 368.

Por otro lado, al comparar estos dos grupos de curvas, se ve la influencia de la concentración de amina con respecto a la separación de fases. Tanto en un caso como en el otro, se ven las mejoras que produce el aumento de temperatura. Los datos graficados obrantes en este capítulo, aunque parciales, proveen sin embargo de elementos de juicio imprescindibles para resolver, por medio de balances económicos, cuál debe ser el camino a seguir, de acuerdo a las exigencias, para cada caso particular de aplicación.

Nota concerniente las figuras 1 a 12

CONDICIONES DE OPERACIÓN

Figuras 1 y 2

Líquido de lixiviación « Malargüe » [a]	1,1 g U/l
Relación de fases, orgánica a acuosa	O/A : 1/1
Tiempo de contacto	1 minuto
Temperatura	20 °C
pH	1,3

Figuras 3 y 4

Relación de fases	O/A : 2/1
Superficie de interfase	10,9 cm^2
Tiempo de agitacíon	1 minuto
Temperatura	20 °C

Figuras 5, 6, 7 y 8

Relación de fases	O/A : 2/1
Superficie de interfase	10,9 cm^2
Tiempo de agitación	1 minuto
Temperatura	22 °C

Figuras 9, 10 11 y 12

Relación de fases	O/A : 1,5/1
Superficie de interfase	10,9 cm^2
Tiempo de agitación	1 minuto
Temperatura	20 °C

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[a] *Malargüe :* Líquidos de lixiviación de los yacimientos « Cerro Huemul » y « Agua Botada », Dpto. Malargüe, Provincia de Mendoza, República Argentina.

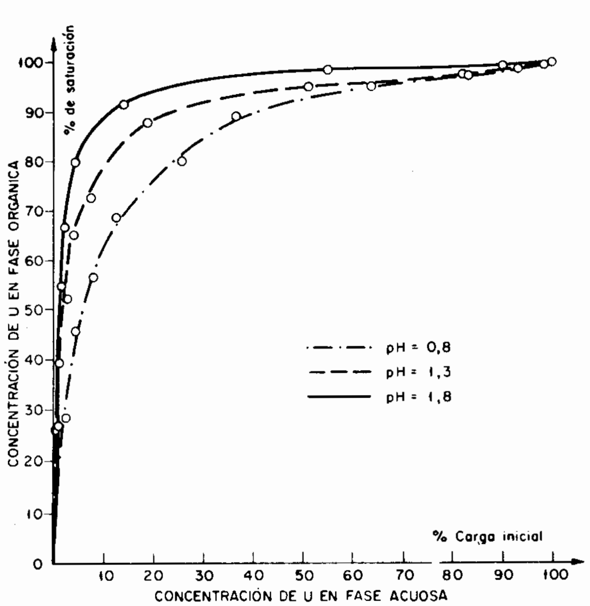

Figura 1. Isotermas de equilibrio en extracción con distintas aminas
(Amina 0,15*M* en kerosene Shell desodorizado, con alcohol iso-octílico, 3 % en volumen)

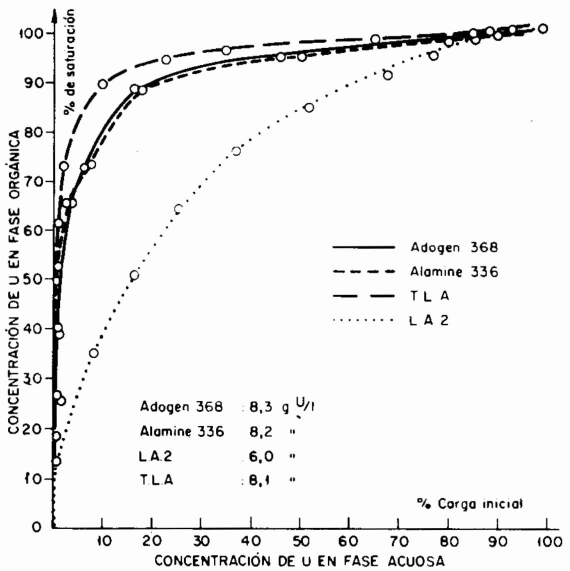

Figura 2. Isotermas de equilibrio en extracción con Alamine 336 a distintos pH
(Alamine 336 0,15*M* en kerosene Shell desodorizado, con alcohol iso-octílico, 3 % en volumen)

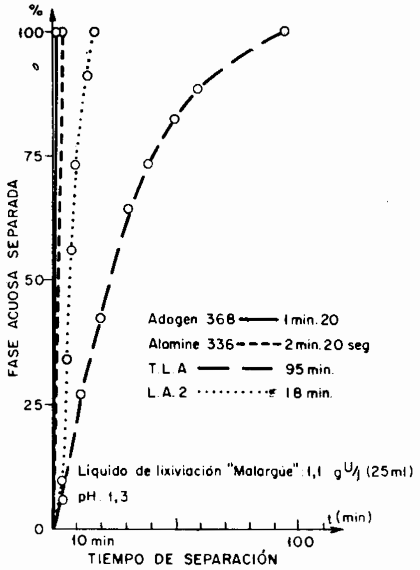

Figura 3. Separación de fases en extracción
(Amina 0,15*M* en kerosene Shell desodorizado, con alcohol iso-octílico, 3 % en volumen)

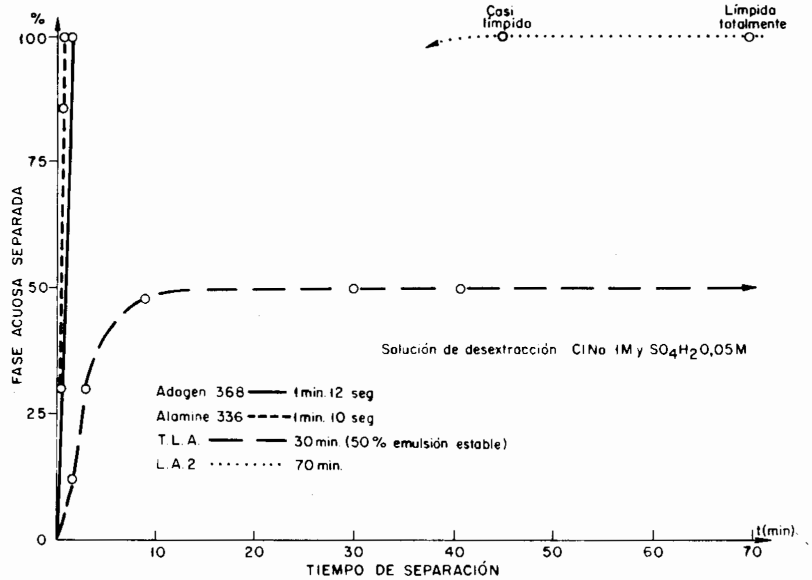

Figura 4. Separación de fases en desextracción
(Amina 0,15*M* en kerosene Shell desodorizado, con alcohol iso-octílico, 3 % en volumen)

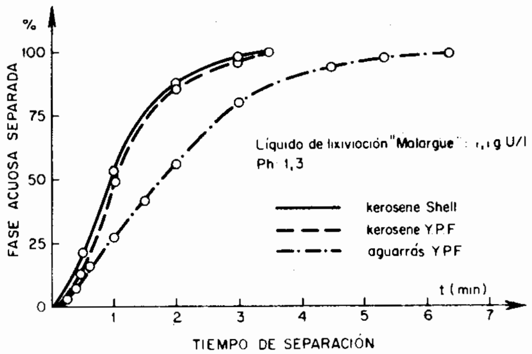

Figura 5. Separación de fases en extracción Influencia del diluyente
(Adogen 368 0,15*M*, con alcohol iso-octílico, 3 % en volumen)

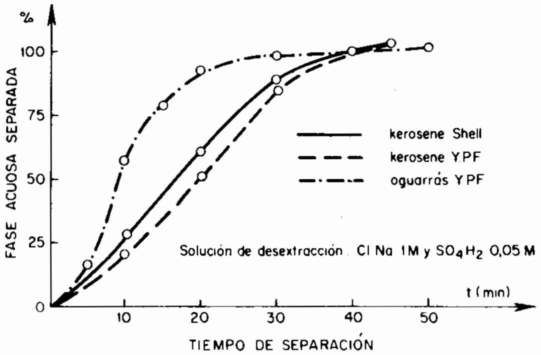

Figura 6. Separación de fases en desextracción Influencia del diluyente
(Adogen 368 0,15*M*, saturada, con alcohol iso-octílico, 3 % en volumen)

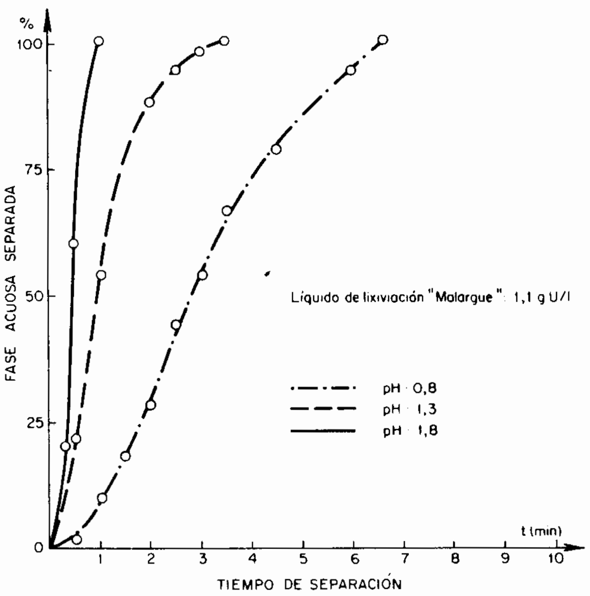

Figura 7. Separación de fases en extracción Influencia del pH (SO_4H_2)
(Adogen 368 0,15*M* en kerosene Shell desodorizado, con alcohol iso-octílico, 3 % en volumen)

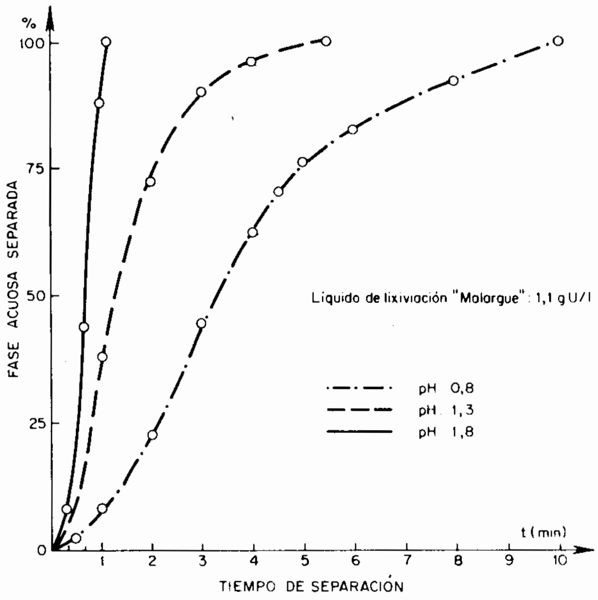

Figura 8. Separación de fases en extracción Influencia del pH (SO_4H_2)
(Alamine 0,15*M* en kerosene Shell desodorizado, con alcohol iso-octílico, 3 % en volumen)

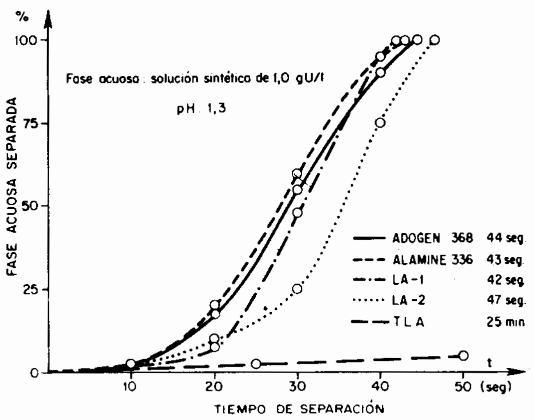

Figura 9. Separación de fases en extracción
(Amina 0,10*M* en kerosene Shell desodorizado, con iso-decanol, 3 % en volumen)

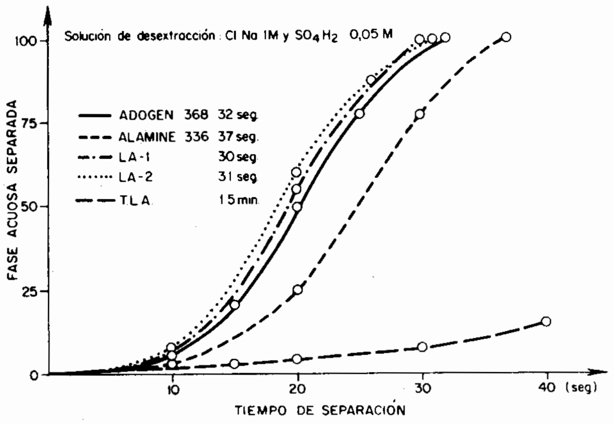

Figura 10. Separación de fases en desextracción
(Amina 0,10*M*, saturada, en kerosene Shell desodorizado, con iso-decanol, 3 % en volumen)

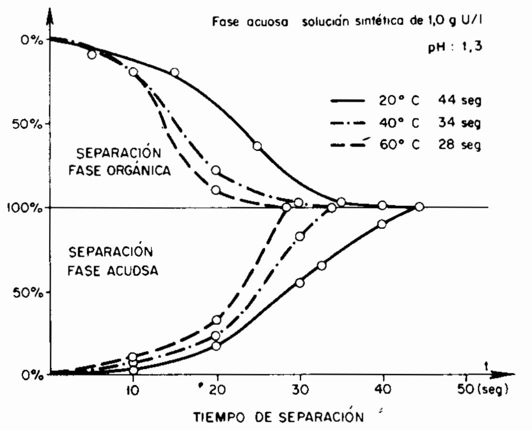

Figura 11. Separación de fases en extracción Influencia de la temperatura
(Adogen 368 0,10*M* en kerosene Shell desodorizado, con iso-decanol, 3 % en volumen)

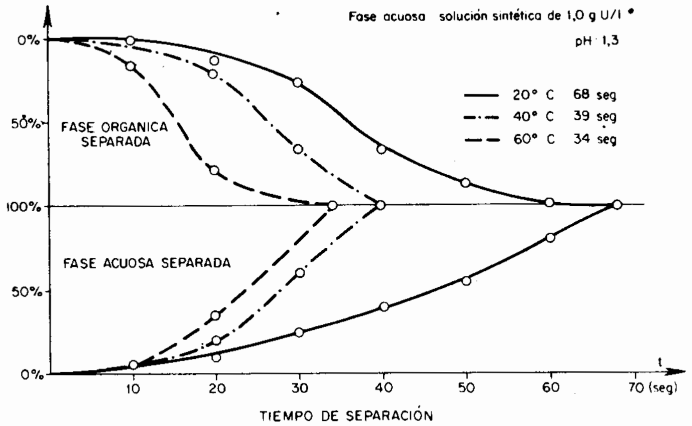

Figura 12. Separación de fases en extracción. Influencia de la temperatura
(Adogen 368 0,15*M* en kerosene Shell desodorizado, con iso-decanol, 3 % en volumen)

EL URANIL TRICARBONATO DE AMONIO, COMO CONCENTRADO URANÍFERO DE INTERÉS HIDROMETALÚRGICO *

En esta segunda parte se consideran especialmente las posibilidades de disminución de costos por obtención de un concentrado uranífero que pueda competir con la ya clásica torta amarilla, considerando como tal, específicamente, al uranil tricarbonato de amonio (que denominaremos AUTC).

Este complejo, ampliamente estudiado, puede ser obtenido por cualquiera de las dos técnicas de concentración usualmente utilizadas, como lo son las de intercambio iónico sólido o líquido. Posee además versatilidad como para ser sustancia base para toda una serie de compuestos de interés en la industria nuclear.

Solubilidad de los uranil tricarbonatos alcalinos

El uranio (VI) forma en sus soluciones una serie de complejos con número de coordinación 6, dando con carbonatos, oxalatos, sulfatos, acetatos y otros aniones, sales dobles de uranilo y otros cationes [9-11]. Entre estos, los uraniltricarbonatos $[UO_2(CO_3)_3]^{4-}$ son importantes en la hidrometalurgia, siendo sus sales alcalinas, y particularmente las de amonio y sodio, las que por sus características de solubilidad tienen interés para el presente trabajo.

Tanto la sal de amonio como la de sodio, tienen una solubilidad en solución acuosa, que es inversamente proporcional a la concentración del co-soluto. En la figura 13 se resumen los resultados obtenidos para la sal de sodio por Bunce *et al.* [12] y para las sales de amonio por Hurst y Crouse [13, 14] y por Macchiaverna [15].

Otro aspecto fundamental ha sido estudiado por Elovskikh y Starbovsky [16], quienes determinan que la presencia simultánea de sodio y amonio produce complejos mixtos, donde la solubilidad del uranio se encuentra exaltada en relación a las solubilidades individuales. Así el complejo $Na_2(NH_4)_2[UO_2(CO_3)_3]$ tiene solubilidad del orden de 170 g U/litro. En la figura 14 indicamos los resultados que hemos obtenido para la variación de la solubilidad en soluciones con relación variable Na/NH_4 en las concentraciones que utilizamos en el presente trabajo, informandose además la influencia de la temperatura.

Por otra parte, como lo han indicado Mc Claine *et al.* [9], los uranil tricarbonatos tienen tendencia a dar soluciones sobresaturadas, en las cuales se produce una cristalización retardada. Hemos constatado además que ese retardo en llegar al equilibrio, está en cierto modo relacionado con el cociente $(NH_4)_2CO_3/NaHCO_3$ (tabla 2).

Resumiendo podemos decir que, dado el hecho que la solubilidad del AUTC es baja en soluciones relativamente concentradas de sales de amonio (carbonatos y sulfatos, nitratos o cloruros), se puede prever el uso de las mismas para obtener una separación espontánea y en una sola etapa del uranio, tanto por elución precipitante directa de solventes orgánicos cargados, como para igual operación con intercambiadores iónicos sólidos. Se aprovecha en este caso la propiedad de dar soluciones sobresaturadas con cristalización retardada, favorecida por la presencia de sodio (que impide así el grave problema tecnológico de precipitación en el lecho de resina).

Obtención del AUTC en los procesos con resinas de intercambio iónico

El estudio de la obtención del AUTC con resinas sólidas va dirigido fundamentalmente a la recuperación del uranio de los líquidos de lixiviación alcalina de las menas uraníferas, si bien es posible realizar un proceso análogo con lixiviados ácidos previa neutralización de la acidez libre de la resina. Para eluir el uranio sorbido en los intercambiadores, se ha recurrido clásicamente a la elución con cloruros o nitratos. La obtención de concentrados exije entonces una precipitación del uranio, como diuranato, en las fracciones concentradas (corazón) de la elución. Este proceso obliga además a una regeneración de la resina, dado que, en los procesos alcalinos, es de fundamental importancia para la economía de los mismos, el reciclado de los reactivos de lixiviación; éstos no deben estar contaminados con cloruros o nitratos, iones altamente interferentes en la sorción del U [15, 17]. Por otro lado el eluente es sólo parcialmente reciclado.

Como consecuencia de estos problemas, hemos estudiado la posibilidad de elución utilizando los mismos aniones lixiviantes. Las condiciones particulares de los parámetros que afectan este proceso han sido ya informadas en trabajos previos [18, 19] y retenemos para el presente las conclusiones fundamentales.

1. El uranio sorbido en resinas aniónicas, particularmente el proveniente de lixiviados alcalinos, puede ser eluído con soluciones de carbonato de amonio y bicarbonato de sodio.
2. Dicha capacidad de elución es función de la fuerza iónica del eluente (tabla 1).
3. Que la elución resulta algo mejorada trabajando a 40-50 °C (tabla 1).
4. El problema de la separación del uranio en los eluídos, puede ser resuelto utilizando la propiedad del AUTC de dar soluciones sobresaturadas, que cristalizan en forma retardada, espontánea y cuantitativamente. La concentración del uranio en la sobresaturación y el retardo en la cristalización están relacionados con el cociente $(NH_4)_2CO_3/NaHCO_3$.

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* Por E. G. Macchiaverna y R. J. Cadirola.

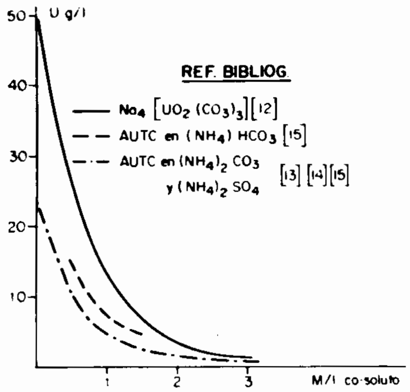

Figura 13. Solubilidad del AUTC y NaUTC (Los números entre corchetes remiten a la bibliografía que figura al final de este documento)

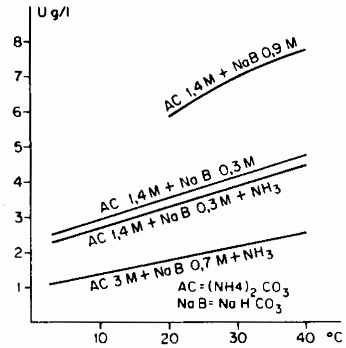

Figura 14. Solubilidad AUTC

CURVAS DE ELUCION DEL URANIO

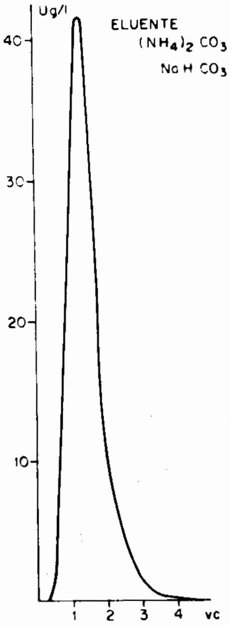

Figura 15

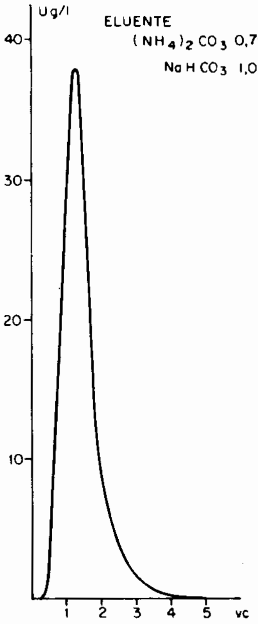

Figura 16

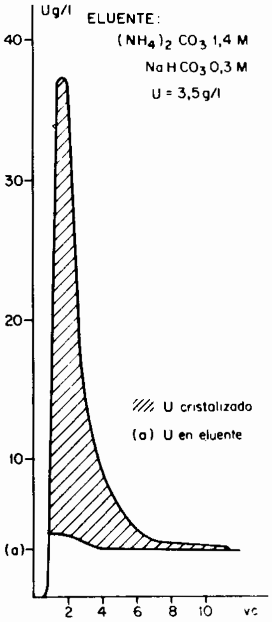

Figura 17

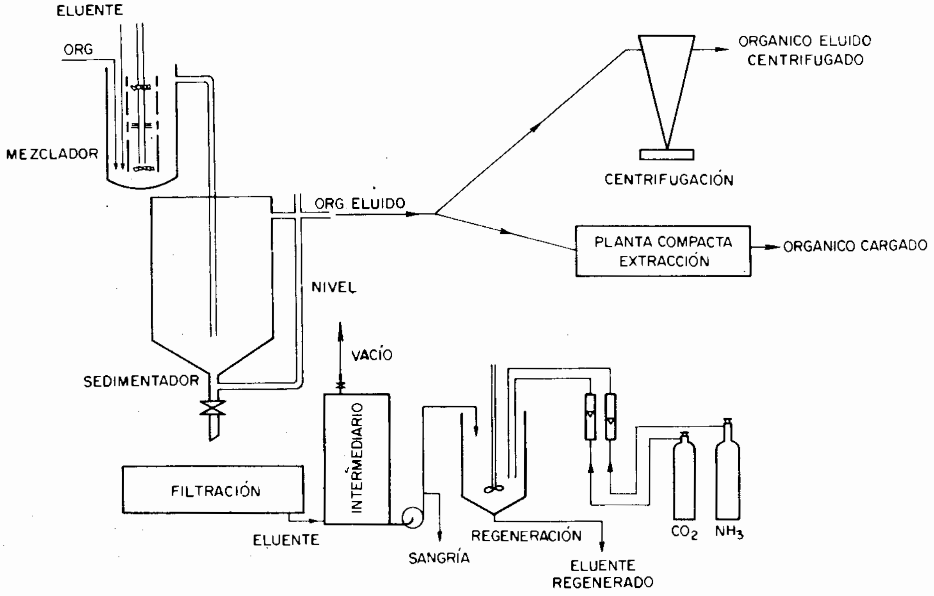

Figura 18. Elución precipitante AUTC

Este parámetro controla el proceso de separación, evitando el problema de precipitación en el lecho de resina. En la tabla 2 indicamos los tiempos promedios de cristalización para las fracciones más concentradas, y en la tabla 3 la variación de la concentración de U, con el tiempo.

Tabla 1. Elución de resinas de intercambio iónico. Capacidad de elución en función de la concentración

Eluente Concentración molar		Elución[a]	
$(NH_4)_2CO_3$	$NaHCO_3$	20-25 °C	50 °C
1,4	0,9	5	3,5
1,4	0,3	6	4
1,4	0,1	6,5	6
1,1	0,7	5,5	—
1,1	0,3	7,5	—
0,75	1,0	7,0	4,5
0,3	1,0	7	—
0,70	0,45	9	—

[a] Se expresa en volúmenes de columna necesarios para obtener efluentes con 20 ppm de uranio.

Tabla 2. Elución de resinas de intercambio iónico. Retardo de cristalización del AUTC en el segundo volumen de columna

Concentración molar		Retardo m
$(NH)_2CO_3$	$NaHCO_3$	
1,4	0,9	25
1,4	0,3	10
1,4	0,1	3
1,1	0,3	15
1,1	0,1	4

Tabla 3. Elución de resinas de intercambio iónico. Variación de la concentración de U con el tiempo

Eluente : $(NH_4)_2CO_3$ 1,4M + $NaHCO_3$ 0,3M

Tiempos	2.° volumen de columna	3.° volumen de columna
0	38,1	6,75
1 h	12,6	5,36
24 h	5,40	4,60
48 h	5,30	4,40
72 h	5,20	4,30
7 d	5,15	4,28
14 d	5,15	4,26

5. De acuerdo con la relación Na/NH_4 en el eluente se pueden obtener tres tipos de eluciones fundamentales (figuras 15, 16, 17):

a) $(NH_4)_2CO_3$ 1,4M + $NaHCO_3$ 0,9M, que permite una elución completa del uranio en 5-6 volúmenes de columna con separación parcial del uranio como AUTC;

b) $(NH_4)_2CO_3$ 0,75M + $NaHCO_3$ 1M, que permite una elución total, evitando la separación del AUTC, pero haciendo necesaria la recuperación del uranio de la solución carbonatada por alguna otra vía (problema semejante con el de la fracción que no precipita en la elución *a*);

c) $(NH_4)_2CO_3$ 1,4M + $NaHCO_3$ 0,3M, saturada en AUTC y previo agregado de NH_3 para llevar a la estequiometría del carbonato de amonio. Se produce la separación total del uranio eluído por cristalización retardada. Queda en la resina 15 % del uranio sorbido, que puede: i) ser eluído con un eluente más concentrado o con alguno del tipo 1 o 2; ii) considerarlo como uranio « en giro » y dejarlo en la columna (en un nuevo ciclo de sorción no se produce ninguna pérdida de uranio en los efluentes iniciales).

La elución precipitante retardada

Podemos decir entonces que el uso de un eluente con carbonato de amonio y bicarbonato de sodio, previamente saturado en AUTC, nos permite aprovechar al máximo las propiedades de sobresaturación y cristalización retardada del sistema, obteniéndose un concentrado de uranio, como AUTC, sin requerimientos adicionales de reactivos y energía.

La cristalización puede considerarse realizada en un período de 24 a 72 horas (tabla 3), de acuerdo con las necesidades de operación. Una vez producida la misma, el eluente es reciclado previa regeneración con CO_2 y NH_3.

Por otra parte, el proceso admite aún el juego del factor temperatura, dado que (figura 14) es posible realizar la elución a 40 °C y enfriar el eluído a 5 °C, lo que facilita la cristalización, obteniéndose una solución no saturada a 40 °C con lo cual mejoramos su capacidad eluente para el siguiente ciclo.

Elución precipitante directa

Las propiedades de las soluciones de carbonato de amonio saturadas con AUTC y conteniendo bicarbonato de sodio, como eluentes del uranio sorbido en intercambiadores sólidos puede ser utilizada como tal en la elución de solventes orgánicos selectivos, cargados con uranio, pero en estos casos será evidentemente innecesario el agregado de sal de sodio para producir el efecto retardante en la cristalización del AUTC, dada la naturaleza física del sistema.

Las propiedades eluentes del carbonato de amonio para los extractantes líquidos han sido ya establecidas anteriormente [2, 20], si bien se utilizaron soluciones de baja concentración para evitar la cristalización del AUTC. El aprovechamiento de la precipitación espontánea ha sido realizado por Hurst y Crouse [13, 14]. Además, ha sido estudiada la elución precipitante directa del U con NaOH, NH_4OH, $CaCO_3$,

Tabla 4. Características de diversos eluentes en la elución precipitante directa

Eluente, molar		Concentraciones									Decantación cristales
		Uranio (mg/l)									
		no eluido					en « finos »				
$(NH_4)_2CO_3$	$(NH_4)_2SO_4$	Tiempos de contacto (m)									
		1	2	5	10	30	2	5	10	30	
2,5	1	3,7	0,7	0,5	0,4	0,4	450	< 5	< 5	< 5	rápida
2,5	2	6,5	1,0	0,4	0,4	0,4	450	< 5	< 5	< 5	lenta
1	2	1,9	1,0	0,8	0,4	0,4	385	20	< 5	< 5	rápida
0,5	2	2,5		0,5	0,4	0,4	550	225	10	< 5	rápida

$Ca(OH)_2$ y MgO [2, 20], aunque los primeros dan precipitados de difícil filtración.

Para la correcta realización de la elución del U bajo forma de AUTC, es necesario considerar diversos factores, que ya hemos indicado en otros trabajos [21] (además de los trabajos realizados por Hurst y Crouse [13, 14]). Reteniendo para el presente las conclusiones fundamentales y aplicándolas como ejemplo para el caso de los solventes aminados, podemos decir:

1. Las soluciones de carbonato de amonio acompañadas por otras sales de amonio y fundamentalmente sulfato (que se produce durante la elución de aminas previamente cargadas con uranio proveniente de lixiviados ácidos), saturadas en AUTC, son eluentes del U, en intercambiadores líquidos, produciendo en una sola operación la elución y separación del uranio, como una tercera fase sólida cristalina, de AUTC, permitiendo el reciclado del eluente.

2. Es posible utilizar a este fin soluciones de variada concentración en las sales eluentes (tabla 4). Aquéllas que dan los mejores resultados varían en los siguientes límites: carbonato de amonio 0,5 a 2,5*M*; sulfato de amonio 0,5 a 2*M*.

3. No se debe sobrepasar una concentración salina total de 3,5 a 4*M*, pues las soluciones de alta densidad impiden la decantación de los cristales formados. Las concentraciones correctas varían entre 2 y 3*M* (tabla 4).

4. Dichas soluciones deben ser neutralizadas con amoníaco para llegar a los valores estequiométricos correspondientes al carbonato de amonio, debiendo el pH variar entre 8,5 y 9,4. Un pH mayor puede dar precipitados de tipo poliuranatos y uno bajo impedir la cristalización cuantitativa.

5. Para que la cristalización se realice es necesario alcanzar en el eluente una sobresaturación del U, que puede llegar a ser 30 % o 70 % superior a la solubilidad normal. En ensayos continuos en mezcladores decantadores, se obtiene rápidamente la sobresaturación. El comienzo de la precipitación es facilitado por la presencia de cristales de AUTC.

6. El sistema debe operar en fase orgánica continua y las mejores relaciones de fases O/A son : 3 a 5/1, debiendo cuidarse la provisión suficiente de agente eluente en relación al uranio a eluir.

7. En las condiciones anteriores y en ensayos en tandeo (*batch*) se establece que:

a) El uranio es eluído en 99,9% en tiempos de contacto (TC) de 2 minutos;

b) Las separaciones de fases con TC de 2 o más minutos, son de 30-60 s;

c) Que la separación y decantación de cristales es rápida y función de la densidad del eluente (densidad aparente AUTC: 1,5 g/ml);

d) Si bien el uranio es eluído cuantitativamente, quedan en suspensión en la fase orgánica, decantando lentamente, una cierta cantidad de finos cristales flotados. La naturaleza de los mismos parece apartarse del AUTC [14, 21]. Separados por decantación y centrifugados, resultan ser cristales « mojados » en fase acuosa, ya que les sobrenada una capa acuosa y una orgánica en relación 2/1. La concentración de estos « finos » disminuye con el tiempo de contacto (tabla 4), el grado de agitación y la relación de fases (tabla 5). En dos minutos de TC puede estimarse en unas 500 ppm U y en 10 minutos de menos de 5 ppm.

Tabla 5. Uranio residual en finos

Eluente : $(NH_4)_2CO_3$ 2,5*M* + $(NH_4)_2SO_4$ 1*M*

Relación de fase organica a acuosa	Tiempos de contacto	
	5 m	10 m
	Uranio (ppm)	
4	< 5	< 5
3	< 5	< 5
2,5	300	< 5
1,5	750	570
1,25	870	700
1	1 700	700
0,72	1 100	900

8. La realización de ensayos continuos en mezcladores-decantadores confirma lo expuesto antes, excepto en la formación de finos, que aumentan en su concentración. Se confirma con todo que éstos disminuyen con el TC y la agitación. Para un TC de 15 a 30 minutos pueden estimarse de 100 a 500 ppm U/org.

9. Las condiciones de operación física de esta elución exije el trabajo con mezcladores-decantadores de diseño especial (figura 18):

a) *Mezclador:* dadas las condiciones ya expuestas, para minimizar la concentración de finos, se utiliza un mezclador con relaciones altura/diámetro 1,5 a 2/1, con desborde superior. Para aumentar el contacto se usa un tipo de superagitador (1/3 de diámetro del tanque);

b) *Decantador:* es un tanque de fondo cónico para favorecer el drenado de cristales que van a filtración;

c) Puede utilizarse un mezclador-decantador interno.

10. El eluente que filtra con los cristales es reciclado previa regeneración a las condiciones iniciales y a la realización de una sangría. Esta última es necesaria por el incremento constante de concentración de sulfatos y otros iones. La misma es de 10 a 20 % del volumen de eluente, según la concentración de éste.

11. El orgánico sobrenadante del decantador y que contiene finos puede ser sometido a las siguientes operaciones:

a) Lavado en un segundo mezclador-decantador con solución de carbonato de amonio 0,5 a 1*M* (quedando con TC de 10 minutos una concentración de 50 a 100 ppm de U), o bien lavando con sulfúrico 0,2 a 0,5*M* (U residual de 20 a 50 ppm);

b) Filtración del orgánico (U residual 20 a 50 ppm);

c) Centrifugación por supercentrífuga (U residual menor que 5 ppm);

d) Pasaje directo del orgánico a extracción, considerando el U, como uranio en giro. No se observa en este caso ninguna dificultad en la etapa de extracción.

Como ejemplo de este tipo de elución resumimos los resultados de un ensayo piloto realizado en las instalaciones de Planta Córdoba, de la CNEA:

El eluente es: $(NH_4)_2CO_3$ 1,5*M* + $(NH_4)_2SO_4$ 1,5*M*, pH 9,2. Se utiliza un mezclador de 70 litros y un decantador de 180 litros (figura 18). Los cristales se filtran por Nutcha de 0,5 m². El volumen total de eluente en giro es de 125 litros. Los caudales usados son: orgánico 100 l/hora y acuoso 25 l/hora, siendo los tiempos de retención en el mezclador: 30 minutos, y decantador: 90 minutos. Se agita con superagitador (figura 18) a 800 rpm. Los finos se separan por supercentrífuga en una parte del ensayo y en otra se envían con el orgánico directamente a extracción. Se obtienen los siguientes valores promedios:

Concentración orgánico	4,65 g U/litro
Concentración de finos en orgánico	140 ppm U
Concentración en el org. centrifugado	menos de 5 ppm U
Concentración promedio en el eluente de entrada	1,40 g U/litro
Concentración promedio en el eluente de salida	1,75 g U/litro

Balance de uranio

U entrado	7,90 kg
U precipitado	7,45 kg (94 %)
U en finos	0,24 kg (3 %)
U en eluente por sobresaturación	0,15 kg (2 %)

Consumo de reactivos

Consumo	kg CO_2/kg U_3O_8	kg NH_3/kg U_3O_8
Elución	0,65	0,35
Elución y sangría (13 %)	1,1	0,95
Consumo final[a]	0,15	0,15

---

[a] Con recuperación parcial CO_2 y NH_3 por descomposición del AUTC y sangría.

Ventajas de la obtención del AUTC

Las ventajas fundamentales de la obtención de AUTC, en relación a la torta amarilla, pueden ser resumidas en las siguientes consideraciones:

1. Su obtención como compuesto de pureza relativamente alta.

2. Economía de operación y reactivos al obtenerse en una sola etapa la elución y separación del uranio como compuesto sólido.

3. Economía de reactivos al permitir el reciclado de las soluciones eluentes.

4. Para los intercambiadores sólidos evitar la regeneración y el correspondiente consumo de reactivos, eliminando al mismo tiempo la grave interferencia de los iones nitrato y cloruro, para el procesado de lixiviados alcalinos de menas uraníferas.

5. Su extrema versatilidad química, dado su carácter de carbonato de base volátil, para ser transformado en otros compuestos, con una recuperación adicional de reactivos (CO_2 y NH_3). Así por ebullición de la solución acuosa puede obtenerse el diuranato de amonio. Por calentamiento a 230-250 °C, UO_3 y a 500 °C, U_3O_8. Por disolución ácida pueden obtenerse soluciones concentradas de otras sales de uranilo. Puede ser sometido a reducción a U^{VI}.

6. Desde el punto de vista operacional es un sólido de fácil manipulación, que decanta rápidamente y es fácilmente filtrado y lavado.

7. Las características del producto obtenido están indicadas a continuación:

a) *Para el obtenido con resinas de intercambio iónico con lixiviados alcalinos de esquistos de Teufelsloch* [22]*:*

Cristales AUTC secos al aire: U, 45 %; CO$_3$, 34,1 %; NH$_3$, 12,7 %.

AUTC calcinado 250 °C (2 horas): U, 73,9 %.

Espectrográfico: Ca, de 100 a 200 ppm; Al, Mg, Cr, 10 a 20 ppm; Si, B, 5 a 10 ppm; Mn, Cu, 2 a 5 ppm; Li, menos de 1 ppm.

b) *Para el AUTC obtenido con solventes aminados* (*lixiviado mineral Malargüe*)*:*

Cristales secos al aire: U, 43-45 %.

Espectrográfico: Fe, 100 a 1 000 ppm; Ag, Mo, 10-50 ppm; Cu, 5 a 20 ppm; V, Mg, 10 a 20 ppm; As, menos de 20 ppm; Cd, Ni, Cr, Pb, menos de 10 ppm; Mn, 1 a 5 ppm; B, 0,5 a 1 ppm.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/839 Argentina

New hydrometallurgical trends in the uranium industry

By R. J. Cadirola *et al.*

The uranium industry is at present going through a period when reduction of costs is regarded as one of the principal objectives. Two methods of achieving this purpose are (*a*) by improving existing techniques to obtain the maximum yield and (*b*) by replacement of the present intermediate products by others offering better economic and technical prospects.

The Hydrometallurgical Groups of the National Atomic Energy Commission (NAEC) are carrying out a programme in which both methods are applied to ion exchange techniques, and to solvent extraction.

In the case of liquid ion exchangers, a comparative study has been carried out so that maximum advantage is taken of their specific properties.

The first part of the paper contains a summary of the results of preliminary tests associated with any operation of this type, with the object of facilitating the selection of the most suitable amine solvent for use under the desired conditions.

A comparative study was therefore carried out of the behaviour of certain amines with acid leaching, the results being expressed in the form of equilibrium curves, effect of pH, phase separation resolving power, effect of diluent, etc.

The results obtained show the undeniable advantages, under normal operating conditions, of certain tertiary amines over the others tested.

The second part of the paper, dealing with the search for new intermediate products, shows the results of studies on the potential of ammonium uranyl

tricarbonate (AUTC) as a substitute for yellow cake.

AUTC is highly versatile from the chemical and technological points of view, and its preparation is studied in connection with the technology of both solid and liquid ion exchange materials.

In each case, the conditions of preparation the elimination of interfering factors, operating conditions, etc. were studied.

For solid ion exchange substances, the paper gives the results obtained with the delayed spontaneous crystallization technique, while for liquid ion exchangers the results of direct precipitation elution are quoted.

A/839 Argentine

Nouvelles orientations hydrométallurgiques dans l'industrie de l'uranium

par R. J. Cadirola *et al.*

Actuellement, l'industrie de l'uranium traverse une période dans laquelle l'un de ses buts principaux est la réduction des prix de revient. On dispose de deux méthodes pour l'obtenir : *a*) perfectionnement des techniques actuelles afin de les utiliser pleinement, et *b*) remplacement des produits intermédiaires existants par d'autres, offrant de meilleures perspectives du point de vue technique et économique. Les groupes d'hydrométallurgie de la Commission nationale de l'énergie atomique (CNEA), mettent en œuvre un programme d'essais sur ces deux méthodes, en les appliquant à la technique de l'échange d'ions et de l'extraction par solvants.

Pour les échangeurs liquides, on a réalisé une étude comparative pour l'utilisation intégrale de leurs propriétés.

Dans la première partie de ce mémoire, nous indiquons les résultats obtenus dans les essais préalables à toute opération de ce type, dont le but est de faciliter le choix du solvant aminé le plus convenable dans les conditions requises.

A cet effet, on fait une étude comparée du comportement de quelques amines avec des produits de l'attaque acide et on en donne les résultats sous forme de courbes d'équilibre, d'influence du pH, du pouvoir de séparation des phases, de l'effet du diluant, etc.

Les résultats obtenus révèlent les avantages certains de plusieurs amines tertiaires sur d'autres dans des conditions normales d'exploitation.

Dans la seconde partie du mémoire, qui a trait à la recherche de nouveaux produits intermédiaires, on présente les résultats obtenus dans l'étude des possibilités offertes par l'uranyl-tricarbonate d'ammonium (AUTC) remplaçant le classique « gâteau jaune ».

Ce composé, AUTC, a une grande souplesse d'utilisation du point de vue chimique et technologique, et on présente une étude visant à son obtention au moyen d'échangeurs solides ou liquides.

Pour chacune de ces techniques on étudie les conditions d'obtention, d'exploitation d'opération, d'élimination des facteurs perturbateurs, etc.

Pour les échangeurs solides on fournit les résultats obtenus avec la technique de cristallisation spontanée retardée et, pour les échangeurs liquides, on donne les résultats relatifs à l'élution avec précipitation directe.

A/839 Аргентина

Новые гидрометаллургические исследования в урановой промышленности

Р. Х. Кадирола *et al.*

На современной стадии развития урановой промышленности одной из основных задач является снижение себестоимости продукции. Решение этой задачи возможно двумя путями: *а*) усовершенствование существующих технологических схем и достижение максимального выхода; *b*) замена существующих промежуточных продуктов другими, обладающими лучшими экономическими и техническими характеристиками.

Гидрометаллургический отдел Национальной комиссии по атомной энергии Аргентины выполняет программу исследований, включающих использование как ионообменных процессов, так и экстракции растворителем.

В отношении жидких экстрагентов было проведено сравнительное изучение с точки зрения максимального использования их специфических свойств.

В первой части доклада содержится обобщение результатов предварительных опытов, связанных с любой операцией подобного типа, чтобы облегчить выбор аминового экстрагента, наиболее подходящего для требуемых условий.

В связи с этим проводилось сравнительное изучение свойств некоторых аминов по отношению к выщелачивающим кислотам; приводятся результаты в виде кривых равновесия, влияния pH, скорости фазового разделения, влияния растворителя и пр.

Полученные результаты показали явные преимущества при нормальных условиях процесса некоторых третичных аминов по сравнению с другими веществами.

Во второй части доклада, относящейся к исследованию новых промежуточных продуктов, показаны потенциальные возможности карбонатов урана, в частности уранилтрикарбоната аммония (УТКА), как заменителей обычного химического концентрата (желтого кека).

УТКА является крайне неустойчивым в химическом и технологическом отношении продуктом; его получение исследуется в связи с технологией твердых и жидких ионообменных веществ.

В каждом случае изучаются условия получения, методы устранения посторонних факторов, режим процесса и т. д.

В отношении твердых ионообменных веществ в докладе приводятся результаты, полученные по методу самопроизвольной кристаллизации, а в отношении жидких экстрагентов приводятся результаты непосредственного осаждения из них металла при регенерации.

Record of session 2.12

Prospecting techniques and recovery from ores

Chairman: J. Neumann (Czechoslovakia)

Paper P/521 (presented by A. W. Wylie)

DISCUSSION

S. ALPAN (Turkey): Is it advisable to prospect for thorium, having regard to the demand and the present concentration process?

A. W. WYLIE (Australia): Expensive prospecting for thorium is probably not justified at this stage. But in Australia we have a thorium mineral, monazite, as a by-product of the beach-sand mining industry, which produces rutile, zircon, etc. We are also interested in a thorium fuel cycle and hence in developing a means of utilizing our own thorium at some stage.

J. GABELMAN (United States of America): Have you any estimates of the unit cost of producing nuclear-pure thorium as a major product rather than a by-product?

A. W. WYLIE (Australia): The costs given in the paper are reagent costs only and do not include the chemical plant conversion costs. They represent the cost of producing thorium as a major product, and not as a by-product.

Paper P/844 (presented by Y. Imai)

DISCUSSION

P. MAGET (France): I should like to ask Dr. Imai two questions. First, why was TNOA chosen as the solvent and, second, what are the physical and chemical properties of the UF_4 obtained?

Y. IMAI (Japan): We made a thorough study of several kinds of amines and found that TNOA was suitable for our purpose in so far as the stability, selectivity and velocity of phase separation were concerned; moreover, it is more readily available in our country.

As to your second question, the chemical properties of the UF_4 are the same as, or better than, those in the standard specification of UF_4. With regard to the physical properties, we found no difficulty in reducing by means of magnesium. The average recovery of uranium metal was over 95%.

R. L. FAULKNER (United States of America): In hydraulic mining, does the dissolution of uranium minerals give rise to any problem and does the method tend to produce excessive amounts of fine material with a consequent low recovery of uranium?

Y. IMAI (Japan): In hydraulic mining the water is recycled through two stages in thickening tanks to prevent the loss of uranium dissolved and to recover fine materials.

A. FAURE (South Africa): What treatment is given to the aqueous effluent from the conversion section, in which the uranium sulphate complex is converted to the uranium chloro-complex? I should also like to ask if the recovery of uranium and hydrochloric acid from this solution has been investigated.

Y. IMAI (Japan): The aqueous effluent from the conversion section is neutralized with caustic solution to recover uranium. With regard to the recovery and re-use of hydrochloric acid, we believe it is more economical to use it as little as possible and to discard it after neutralization.

F. BAZILE (France): What economies are effected by your method as compared with conventional methods?

Y. IMAI (Japan): We roughly estimate that the cost involved in using our process is 25% less than that by the conventional process.

A. M. SEDOV (USSR): Is the regular method or the hydraulic method used to obtain the ores referred to in the paper? If it is the latter, is hydrocyclonic ore separation used?

Y. IMAI (Japan): The hydrocyclonic method has been investigated, but the main flowsheet for our pilot plant is based on the ordinary settling out system.

M. PERARNAU PERRAMON (Spain): I should like to ask if the ore contains pyrites and whether any dissolution of uranium has been observed during hydraulic washing.

Y. IMAI (Japan): The ore contains pyrites. Dissolution of uranium into water is not very significant; however, the water is re-cycled to prevent loss of the uranium.

M. PERARNAU PERRAMON (Spain): Do the filtering of the hydraulic concentrate and the drying on the filter give rise to any difficulties?

Y. IMAI (Japan): The filtering operation is not easy. Steam can be used effectively for reducing the water content of the cakes in the filter.

M. PERARNAU PERRAMON (Spain): Does it take long to achieve adequate mixing of mineral and acid in the mixer?

Y. IMAI (Japan): It takes less than ten minutes.

M. PERARNAU PERRAMON (Spain): What is the dryer made of?

Y. IMAI (Japan): The dryer is made of mild steel lined with nickel-alloy.

M. PERARNAU PERRAMON (Spain): How many extraction stages with water and filtrate are considered necessary? I should also like to ask what is the total liquid to mineral ratio.

Y. IMAI (Japan): Repulping and filtering must be carried out twice. The liquid to mineral ratio is almost 1 : 1.

Paper P/414 (presented by B. Bunji)

DISCUSSION

J. LECOQ (France): I gather from the paper you presented that the pilot plant studies indicate that your process is cheaper than that using ion exchange resins. Have you sufficient data to say whether your process would also be more advantageous for a high-capacity plant, producing, for example, 1 000 tons per day, and what the difference in cost-price per ton of the ore treated would be?

B. BUNJI (Yugoslavia): The plant at Kalna has a capacity of 200 tons per day and the data obtained indicate that the reduction process is at least 10% cheaper per ton of the ore treated than the cost by the ion exchange process. Moreover, it should be noted that the higher purity of the product offers possibilities of further cost reduction in the purification step (solvent extraction). We know by now that the precipitation-reduction process offers a sound and economical solution. When the capacity is increased to 1 000 tons per day, a further cost reduction will be possible.

F. BAZILE (France): Is the purity of the product obtained with your process comparable with that obtained using conventional processes?

B. BUNJI (Yugoslavia): The product obtained was of technical grade purity; it was, however, of a higher grade and better quality than that usually obtained by ion exchange techniques. The principal impurities are carbonates and very fine ore particles. All other impurities are in trace quantities.

J. SCHMETS (Belgium): With regard to the catalytic precipitation of uranium, the text which refers to Figure 4 in the section describing the reduction plant indicates that the solution is saturated with hydrogen in the first vessel; the solution is then passed into other vessels under pressure and heated to 150 °C. Does this mean that precipitation is effected at the speeds mentioned solely by diffusion and dissolution of the hydrogen in the solution? If this is not the case, how is good contact effected?

B. BUNJI (Yugoslavia): As indicated in Figure 4, only the saturation from pregnant solution takes place in the first pressure vessel. Precipitation occurs in subsequent vessels, which are filled up with a UO_2 catalyst in roll form. In the saturation vessel no precipitation was observed. At present hydrogen is used only up to the saturation stage. However, when hydrogen gas was used as the agitation agent in the vessels with the catalyst, an increase in the reaction rate was observed. Several technical difficulties render this technique slightly more expensive.

H. HUET (France): Have you studied the UO_2 obtained by your process from the point of view of sintering? It seems that its purity is not sufficient. In that case could you give us some details of the sequence of treatments used later with a view to converting it either into sinterable oxide or into uranium metal of nuclear purity?

B. BUNJI (Yugoslavia): It was found that the impure UO_2 obtained by the method described can be converted into nuclear-grade UO_2 suitable for sintering after purification. At the moment I am not able to give more details. We are, however, studying the possibility of purification by dissolving the impure UO_2 and reprecipitating. We know that the impure UO_2 can be dissolved and that both the dissolution and reduction processes are selective for UO_2. By replacing the hydrogen by oxygen, and the barren solution by water, we have obtained a nuclear-grade UO_2, but at present we have only a very rough idea of the production cost.

Paper P/478 (presented by I. Wendt)

DISCUSSION

P. MAGET (France): With regard to the paper presented by Dr. Wendt, I am particularly interested in the description of the Ellweiler pilot plant. The paper shows how the liquor resulting from sulphuric acid treatment, i.e., the so-called pregnant liquor, is treated in ion exchange columns and then by solvents in order to obtain nuclear-pure uranate. I should like to ask three questions. First, what consumption of reagents, expressed for example in kilograms per kilogram of treated uranium, is necessary for ion exchange, treatment by solvents and precipitation? Secondly, what is the result of the analysis of the nuclear-pure uranate obtained? Thirdly, has the uranate obtained been used to prepare uranium metal and, if so, how and with what results?

I. Wendt (Federal Republic of Germany): I have not at hand all the data asked for but I can give some figures. Detailed information regarding the pilot plant at Ellweiler can be found in Reference [39] in the bibliography.

With regard to your first question, the consumption of $NaNO_3$ in the circulation process is about 1.2-2 kg per kg U_3O_8. As regards your second question, a chemical and spectrographical analysis of the final product was carried out and it was found that the purity is well within the limits of the requirements for nuclear-pure material. As to your third question, the refining and production of uranium metal is carried out by the Nuklear-Chemie und-Metallurgie GmbH (NUKEM) in Wolfgang, near Hanau. I have no information on the results obtained by the company.

V. Ziegler (France): In connection with the air-borne radiometric survey referred to in the paper, mention is made of an accessory unit which permits the registration of aero-magnetic data, etc. I should like to ask, first, whether the registration of aero-magnetic data is made systematically or if it is infrequent. Secondly, when the aero-magnetic survey is carried out, what is the resultant percentage increase in cost? Thirdly, is the registration of position by the Doppler system still used for radiometric survey or only for aero-magnetic surveys?

I. Wendt (Federal Republic of Germany): With reference to your first question, only an air-borne scintillation-counter survey is, in most cases, required for uranium prospecting. As to your second question, when a general aero-magnetic survey is made a scintillation-counter survey is, as a rule, carried out simultaneously, as the increase in cost due to this additional measurement is almost negligible in comparison with the cost of a purely magnetic survey. With regard to your third question, the flight altitude is usually much lower (about 50 to 100 m above the ground) for a narrow-grid uranium survey than for a magnetic survey. Up to now we have used electronic navigation equipment and altimeters only in magnetic or combined air-borne surveys.

A. Faure (South Africa): Has consideration been given to the use of D2EHPA (di-2-ethyl hexilphosphoric acid) as a solvent for the purification of the nitrate solution from the ion exchange process? It is believed this solvent might work more satisfactorily in the dilute nitrate solution, and be more specific for uranium.

I. Wendt (Federal Republic of Germany): Preliminary experiments with D2EHPA have been carried out, but up to now we have not sufficient data to present final results.

A. Faure (South Africa): In order to obtain satisfactory extraction of uranium into TBP solvents, a nitrate concentration of the order of 150 grammes per litre had to be used in South Africa. It was found that these solutions caused rapid degradation of the ion exchange resins. Have similar effects been observed in your pilot plant?

I. Wendt (Federal Republic of Germany): The nitrate concentration used was 80-100 grammes per litre and the purity obtained in the elution was equal to that obtained using higher concentrations. With this concentration we did not observe a degradation of the resins.

J. Gabelman (United States of America): In areas containing radioactive sedimentary rocks where exploration has been unsuccessful, is there any evidence that large quantities of uranium were never derived from eroding source rocks or that large quantities were deposited syngenetically with the sediments but have simply not been reconcentrated.

I. Wendt (Federal Republic of Germany): We have found indications in the so-called Hardegsen clay that large quantities of uranium have been derived from the source rocks, but reconcentration is not adequate. The maximum concentrations only amount to about some 100 ppm.

Paper P/503 (presented by H. Carreira Pich)

DISCUSSION

J. Lecoq (France) : Up to what capacity is a semi-mobile processing plant of the type you described more economical than a conventional plant as regards the cost-price of the uranium concentrate produced?

H. Carreira Pich (Portugal): I have some difficulty in giving a direct reply to your question because different parameters must be taken into consideration and special conditions are involved in each case. Thus, for a conventional plant or a semi-mobile plant, on the one hand there is the cost of transporting the ore from the deposits to the conventional plant and the higher cost of the conventional plant to consider; on the other hand the higher output obtained in conventional plants and the cost of fixed assets lost when plants are moved must be taken into account. Thus, the capacity of the plant is dependent on the fact that equipment must be easily transportable from one mine to the other. I believe that a semi-mobile plant should be used when it is necessary to process small, scattered deposits and, broadly speaking, I think these plants would be suitable for capacities not exceeding about 50 tons of ore per day.

T. Batuecas Rodriguez (Spain): I should like to point out that since 1960 research has been carried out in Spain on static leaching (natural, by percolation and by capillarity) on the laboratoy, pilot-plant and semi-industrial scale, both as regards the dissolution phase in uranium and its recovery in the leaching liquids. For this purpose there is a laboratory and pilot-plant with a capacity of up to 60 tons in Madrid. There are also semi-industrial leaching plants in Ciudad Rodrigo, i.e., the Valdemascano and Caridad plants with a capacity of 3 000 tons and 5 000 tons respectively, and another plant, La Carretona, with a capacity of 750 tons, in Cáceres. In addition there is a mobile extraction plant, using amines, with a capacity of 50 m^3 per day, in Andújar. The latter plant is now being run-in and will be incorporated in a uranium leaching and recovery system, as mentioned in paper P/494.*

Paper P/353 (presented by A. M. Sedov)

DISCUSSION

R. E. ROBINSON (South Africa): There appears to be a discrepancy between the abstract of the paper and the paper itself as regards the relationship between the concentration of ferric ions and the rate of reaction. Can one assume that the paper is correct in stating that the reaction is of the second order with respect to ferric ions? This statement indicates that if one were to double the ferric-ion concentration, keeping all other factors constant, the rate of reaction would increase by a factor of 4. This implies that at very high ferric-ion concentrations extremely short reaction times should be possible. That is not borne out by the results obtained in work carried out at the Government Metallurgical Laboratories in Johannesburg which showed that the relationship between the rate of reaction and ferrio-ion concentration was of the form

$R = ax/(1 + bx)$, where a and b are constants, and x the Fe^{3+} concentrations.

This relationship is of the same form as the Langmuir adsorption isotherm, and the conclusion is reached that the rate-controlling reaction is between ferric complexes adsorbed on the surface of the uranium oxide and the oxide itself. This theory explains why the rate of reaction between ferric ions and UO_2 in perchloric acid medium is extremely small, since no complexes exist between perchlorate anions and ferric cations.

This matter is discussed in detail by P. A. Laxen in a paper presented at an international symposium on hydrometallurgy held at Dallas, Texas, in 1963.

A. M. SEDOV (USSR): Unfortunately the authors of the paper are not attending the present Conference, and Dr. Robinson's question requires theoretical discussion. I shall therefore transmit his comments to the authors. However, the theoretical calculations which appear in the paper are in good agreement with the practical results.

Paper P/257 (presented by J. W. Gabelman)

DISCUSSION

H. ROSATZIN (Switzerland): I understand that organo-uranium compounds play an important role during the deposition of uranium ore. Have any specific organo-uranium compounds been identified?

J. GABELMAN (United States of America): Yes. Asphaltite or thucholite contains uranium. There is also a substance we call *humate* at Grants, New Mexico, which we believe is derived from plant matter.

S. H. U. BOWIE (United Kingdom): If the original mineralization is epigenetic, as the paper suggests, were the complexes necessarily transported in an oxidized state? Secondly, what evidence is there that organic matter functioned in the dual capacity of an absorbing and reducing agent in the formation of organo-uranium complexes?

J. GABELMAN (United States of America): With regard to your first question, the solutions were not necessarily transported in an oxidized state. They could have been transported in an oxidized state in ground waters approaching neutrality, or in the reduced state in highly acid waters, e.g., at a pH of less than 3. As to your second question, the evidence indicates that rich uranium is closely associated with organic matter, and organic material seems to have attracted some uranium. However, this may indicate only that the uranium passing outside of, or away from, the environment has left no trace of its passage. Some organic matter that might be expected to contain uranium does not contain any, which indicates no passage of uranium.

G. BIGOTTE (France): The paper suggests that uranium found in stratiform deposits might always derive, more or less, from uranium in hydrothermal or magnetic deposits. Would it not be advisable, from the point of view of future prospecting, to consider a contrary theory, i.e., that uranium found in lodes may, in certain cases, derive from uranium in stratiform deposits?

J. GABELMAN (United States of America): Yes, we are aware of the fact that uranium from any deposit can move downward as a form of secondary enrichment and be deposited in lower fractures after leaching from above. However, it is possible to distinguish between this uranium and uranium deposited from rising hydrothermal solutions by the sulphur isotope ratios.

A. GANGLOFF (France): Can you explain the term "mobile belts" used in the paper? Does it refer to the recent, large orogenic zones?

J. GABELMAN (United States of America): The term relates to the great and small mobile belts of any age. Large mobile belts were usually active for several

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* This volume, session 2.11.

geological periods, perhaps for more than one era. The accompanying zoned metallogenic cycle could have taken nearly as long, it being understood that mineralization always suitably follows deformation and intrusion.

S. ALPAN (Turkey): In Turkey we have carried out extensive radio-active mineral prospecting and exploration since 1957. 494 000 km^2 were prospected by air-borne survey, 407 000 km^2 by car-borne survey, 73 000 km^2 in a general ground survey and 9 000 km^2 by detailed and systematic survey.

Our early work was confined to checking the anomalies occurring along the crack fillings and veins in granite. Autunite and torbernite mineralization was found, but there was no significant result. Later, prospecting and exploration were carried out in fluorite veins in cyanite with similar results. Also, results from prospecting in metamorphic formations such as gneiss and schists of the Menderes massif were hopeful and work carried out on the neocene and recent sediments yielded very promising results. As a result of investigations in recent sedimentary formations during the last few years we discovered 750 tons of U_3O_8 after extensive exploration work involving drilling, making trenches and sinking shafts. We found 1.5 million tons of uranium ore with an average U_3O_8 content of 0.1-0.2%. Thus we came to the conclusion that primary deposits in the massif might have been leached and the uranium redeposited in the surrounding neocene and recent sediments. Therefore our radiometric survey policy now is to devote our attention to such sediments in and around massifs.

It should be pointed out here that we recorded about 1 000 anomalies during the air-borne survey and, up to now, have checked only a small percentage of them. After we have checked all the important anomalies we may reach further conclusions.

With regard to recovery of ore I should like to make the following comment. Secondary uranium minerals, which are finely dispersed in loosely consolidated gravels, siltstones, sands and clays, occur in the Kasar deposit. The results of the ore recovery tests were very satisfactory because of the free occurrence of secondary uranium minerals in the loosely consolidated sand-gravel gangue. In washing and screening the ore, a coarse, nearly barren fraction is rejected, leaving only finer fractions for leaching treatment; thus the crushing and grinding stages are eliminated. 65% of the ore sample was between 1/32 in to 200 mesh in grain size. This portion of the sample had a U_3O_8 content of 17%. Subsequent treatment in an agitation-leaching plant yielded an ore recovery of 93%. 16% of the sample was between 1/4-1/32 in grain size, with a U_3O_8 content of 12%. This portion was treated by the cheap method of static immersion leaching in H_2SO_4 and yielded an ore recovery of 93%. The remaining portion of the sample (19% by weight and 11% U_3O_8 content) was discarded as waste. By using this simple and cheap treatment the over-all ore recovery was 82.5%.

It is considered that the combined liquor produced by the static and agitation-leaching process may be treated in an ion exchange concentration plant in order to give a high-grade, clean liquor for precipitating a high-grade U_3O_8 yellow cake.

M. ROUBAULT (France): I wish to emphasize the great importance that should be attached to research such as that described in the paper presented by Dr. Gabelman. Present prospecting practice is mainly by the direct method, using counters. This method has made it possible to evaluate the order of magnitude of the tonnages that can reasonably be anticipated in the world, even bearing in mind the areas in which prospecting has not yet been carried out. Now, if one considers the figures given, these tonnages, although large, may one day prove insufficient. This proves that efforts should be made to reach deeper deposits of which there is no surface indication. Only by taking into account general geological and chemical considerations, based on fundamental scientific research, can we reach such deposits. Such research is therefore indispensable if, in the near future, the sites for borings are to be determined, as in the case of oil, by structures and not solely by the presence of traces of mineral deposits.

As Dr. Mabile rightly indicated in paper P/72,* one of the main achievements of the present Conference should be to draw attention to the magnitude of the problem to be solved as a result of the enormously increasing demand for uranium. I think it should also make us realize the need for a considerable improvement in determining the methods to adopt in prospecting and research work.

Paper P/450 (presented by E. Szabó)

DISCUSSION

P. MAGET (France): I should like to know whether the radiometric sorting apparatus described in the paper has been used in industry.

E. SZABÓ (Hungary): The radiometric ore concentration apparatus has not yet been used for industrial purposes and thus we have no precise technical data or its industrial application.

S. TĂTARU (Romania): In conducting experiments similar to those you described involving the separation of ores by flotation, with subsequent leaching of flotation products on an acid or sodium line, we found that flotation reagents have a negative effect on later phases of processing** mainly because they are

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* This volume, session 2.11.

** Plaksin, I. N. and Tătaru, S., *Revista Minelor*, *6* (1962); Tătaru, S., *Revista Minelor*, *6* (1963).

themselves sorbed by the ion exchangers.* I should like to ask whether the residual amount of the flotation reagent does not hinder the sorption and leaching of uranium on a sodium line.

E. SZABÓ (Hungary): We too have observed similar phenomena, but the reduction in the capacity of ion-exchange resin was not great enough to have any significant effect on the applicability of the method.

Paper P/464 (presented by R. E. Robinson)

DISCUSSION

A. M. SEDOV (USSR): What is the percentage of carry-over of uranium from the fluidized bed and what is the decontamination coefficient in the cyclone?

I should also like to ask whether there is any deposition of NH_4F on the surfaces of the piping system and what is the length of piping from the apparatus to the condenser in the experimental plant.

R. E. ROBINSON (South Africa): The amount of carry-over from the fluidized bed depends to a large extent on the particle size of the material. It can vary between approximately 10% and 40%. Of this quantity approximately 90% is returned to the bed by the cyclone.

As to your second question, there is little or no deposition of material in the pipes, because they are maintained at a temperature above the condensation point of ammonium fluoride. The pipes are no more than a few feet (half a metre) in length.

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* Tătaru, S., *Revue roumaine des sciences techniques*, Série métallurgie, *1* (1964).

Compte rendu de la séance 2.12

Méthodes de prospection et de traitement des minerais

Président : J. Neumann (Tchécoslovaquie)

Mémoire P/521 (présenté par A. W. Wylie)

DISCUSSION

S. ALPAN (Turquie) : Peut-on conseiller en ce moment de prospecter en vue de trouver du thorium, compte tenu de la demande et du procédé de concentration actuel?

A. W. WYLIE (Australie) : Des prospections coûteuses en vue de trouver le thorium ne sont probablement pas justifiées en ce moment. Mais nous avons en Australie un minerai de thorium, la monazite, qui est un sous-produit de l'industrie d'exploitation du sable côtier, industrie qui produit du rutile, du zircon, etc. Nous sommes aussi intéressés par un cycle de combustible au thorium, et par conséquent au développement de moyens d'utilisation de notre thorium en temps voulu.

J. GABELMAN (États-Unis d'Amérique) : Avez-vous une idée du coût unitaire de production du thorium de pureté nucléaire comme produit principal et non comme sous-produit?

A. W. WYLIE (Australie) : Les valeurs données dans le mémoire sont les coûts des réactifs seulement et ne comprennent pas les coûts de conversion dans l'usine chimique. Ils représentent le coût de production du thorium comme produit principal, et non comme sous-produit.

Mémoire P/844 (présenté par Y. Imai)

DISCUSSION

P. MAGET (France) : Je voudrais poser deux questions au Dr Imai. D'abord, pourquoi a-t-on choisi la TNOA comme solvant, et ensuite quelles sont les propriétés physiques et chimiques du UF_4 obtenu?

Y. IMAI (Japon) : Nous avons étudié différentes amines, et trouvé que la TNOA convenait dans notre cas en ce qui concerne la stabilité, la sélectivité et la rapidité de séparation des phases; de plus, on pouvait l'obtenir facilement dans notre pays.

En réponse à votre seconde question, je dirai que les propriétés chimiques de UF_4 sont égales ou supérieures à celles des spécifications types. Pour les propriétés physiques, nous n'avons pas eu de difficultés à faire la réduction par le magnésium. La récupération moyenne de l'uranium métallique était supérieure à 95 %.

R. L. FAULKNER (États-Unis d'Amérique) : Dans l'exploitation hydraulique, est-ce que la dissolution des minerais d'uranium pose des problèmes, et la méthode tend-elle à produire des quantités excessives de matières fines avec pour conséquence une mauvaise récupération de l'uranium?

Y. IMAI (Japon) : Dans l'exploitation hydraulique, l'eau est recyclée dans deux étages d'épaississeurs pour éviter les pertes d'uranium dissous et récupérer les particules fines.

A. FAURE (Afrique du Sud) : Comment traitez-vous les effluents aqueux de la section de conversion, dans laquelle le complexe sulfurique d'uranium est transformé en complexe chlorhydrique? Je voudrais aussi savoir si vous avez étudié la récupération de l'uranium et de l'acide chlorhydrique de cette solution.

Y. IMAI (Japon) : Les effluents aqueux de la section de conversion sont neutralisés par une solution caustique pour récupérer l'uranium. En ce qui concerne la récupération et la réutilisation de l'acide chlorhydrique, nous pensons qu'il est plus économique d'en utiliser aussi peu que possible et de le rejeter après neutralisation.

F. BAZILE (France) : Quelles sont les économies que donne cette méthode par rapport aux méthodes classiques?

Y. IMAI (Japon) : Nous estimons que le coût de notre procédé est d'environ 25 % inférieur à celui des procédés classiques.

A. M. SEDOV (URSS) : Pour obtenir les minerais mentionnés dans votre communication, utilisez-vous la méthode habituelle ou la méthode hydraulique? Dans le second cas, utilisez-vous l'hydrocyclone pour la séparation du minerai?

Y. IMAI (Japon) : Nous avons étudié la méthode à l'hydrocyclone, mais le schéma de notre atelier pilote est basé sur le système habituel de décantation.

M. PERARNAU PERRAMÓN (Espagne) : Je voudrais demander si le minerai contient des pyrites et si vous avez observé une certaine dissolution de l'uranium pendant le lavage hydraulique.

Y. IMAI (Japon) : Le minerai contient des pyrites. La dissolution de l'uranium dans l'eau n'est pas importante; cependant l'eau est recyclée pour éviter de perdre de l'uranium.

M. PERARNAU PERRAMÓN (Espagne) : La filtration du concentré hydraulique et le séchage sur filtre donnent-ils lieu à des difficultés?

Y. IMAI (Japon) : L'opération de filtration n'est pas facile. On peut utiliser avec efficacité de la vapeur pour réduire la teneur en eau des gâteaux sur le filtre.

M. PERARNAU PERRAMÓN (Espagne) : Faut-il beaucoup de temps pour obtenir dans le mélangeur un mélange correct du minerai et de l'acide?

Y. IMAI (Japon) : Le mélange prend très peu de temps, moins de dix minutes.

M. PERARNAU PERRAMÓN (Espagne) : En quel matériau est construit l'appareil de séchage?

Y. IMAI (Japon) : L'appareil de séchage est fait en acier doux avec un revêtement en alliage de nickel.

M. PERARNAU PERRAMÓN (Espagne) : Combien faut-il d'étages d'extraction avec l'eau et le filtrat? Je voudrais aussi demander quel est le rapport total liquide/minerai.

Y. IMAI (Japon) : Il faut deux opérations de remise en pulpe et de filtration. Le rapport liquide/minerai est voisin de 1/1.

Mémoire P/414 (présenté par B. Bunji)

DISCUSSION

J. LECOQ (France) : Il semble, d'après le mémoire que vous avez présenté, que les études sur l'installation pilote indiquent que votre procédé est meilleur marché que celui qui utilise des résines échangeuses d'ions. Avez-vous des données suffisantes pour dire si votre procédé serait aussi plus avantageux dans le cas d'une usine de grande capacité, traitant par exemple 1 000 t/j, et quelle serait la différence de prix de revient par tonne de minerai traité?

B. BUNJI (Yougoslavie) : L'usine de Kalna a une capacité de 200 t/j, et les résultats obtenus indiquent que le procédé de réduction est au moins 10 % moins cher par tonne de minerai traité que le procédé par échange d'ions. De plus, il faut remarquer que la pureté plus grande du produit donne la possibilité de faire d'autres économies dans la purification (extraction par solvants). Nous savons maintenant que le procédé de précipitation par réduction nous donne une solution sûre et économique. Quand la capacité sera portée à 1 000 t/j, une nouvelle réduction du prix de traitement sera possible.

F. BAZILE (France) : La pureté des produits obtenus avec votre procédé est-elle comparable à celle des produits obtenus par les procédés classiques?

B. BUNJI (Yougoslavie) : Le produit obtenu est de pureté technique; il est cependant de pureté plus grande et de meilleure qualité que celui qu'on obtient habituellement par les méthodes d'échange d'ions. Les principales impuretés sont des carbonates et de fines particules de minerai. Toutes autres impuretés sont à l'état de traces.

J. SCHMETS (Belgique) : En ce qui concerne la précipitation catalytique de l'uranium, le texte qui se réfère à la figure 4 dans la section décrivant l'usine de réduction indique que la solution est saturée d'hydrogène dans la première cuve; la solution est ensuite transférée dans d'autres cuves sous pression et chauffée à 150 °C. Ceci veut-il dire que la précipitation a lieu à la vitesse mentionnée uniquement par diffusion et dissolution de l'hydrogène dans la solution? Sinon, comment assurez-vous un bon contact?

B. BUNJI (Yougoslavie) : Comme l'indique la figure 4, seule la saturation a lieu dans la première cuve sous pression. La précipitation a lieu dans les cuves suivantes, qui sont remplies de catalyseurs en UO_2 de forme cylindrique. On n'a pas observé de précipitation dans la cuve de saturation. Nous n'utilisons à présent l'hydrogène que jusqu'à l'étape de saturation. Cependant, quand on utilisait de l'hydrogène gazeux comme agent d'agitation dans les cuves contenant le catalyseur, on observait une augmentation de la vitesse de réaction. Diverses difficultés techniques rendent ce procédé un peu plus coûteux.

H. HUET (France) : Avez-vous étudié UO_2 obtenu par votre procédé du point de vue du frittage? Il semble que sa pureté n'est pas suffisante. Dans ce cas, pourriez-vous nous donner quelques indications sur les traitements ultérieurs pour le transformer soit en oxyde frittable, soit en uranium métal de pureté nucléaire?

B. BUNJI (Yougoslavie) : On a trouvé que UO_2 impur obtenu par la méthode décrite peut être transformé en UO_2 de pureté nucléaire, frittable après purification. Pour le moment, je ne peux pas vous donner plus de détails. Nous étudions cependant la possibilité de purifier le produit par dissolution de UO_2 impur et reprécipitation. Nous savons que l'on peut dissoudre UO_2 impur, et que les processus de dissolution et de réduction sont sélectifs pour UO_2. En remplaçant l'hydrogène par de l'oxygène, et la solution épuisée par de l'eau, nous avons obtenu du UO_2 de pureté nucléaire, mais nous n'avons encore qu'une idée assez vague du coût de production.

Mémoire P/478 (présenté par I. Wendt)

DISCUSSION

P. MAGET (France) : Au sujet du mémoire présenté par le Dr Wendt, j'ai été particulièrement intéressé par la description de l'usine pilote d'Ellweiler. Le mémoire montre comment la solution résultant de l'attaque sulfurique est traitée dans des colonnes échangeuses d'ions, et ensuite par des solvants pour obtenir de l'uranate de pureté nucléaire. Je voudrais poser trois questions. D'abord, quelle est la consommation de réactifs, exprimée par exemple en kilogrammes par kilogramme d'uranium traité, nécessaire pour l'échange d'ions, le traitement aux solvants et la précipitation? Deuxièmement, quels sont les résultats de l'analyse de l'uranate de pureté nucléaire obtenu? Troisièmement, l'uranate obtenu a-t-il été utilisé pour préparer de l'uranium métal, et si oui, par quel procédé et avec quels résultats?

I. WENDT (République fédérale d'Allemagne) : Je n'ai pas sous la main toutes les données pour répondre à ces questions mais je peux donner quelques chiffres. Des renseignements détaillés sur l'usine pilote d'Ellweiler peuvent être trouvés dans la référence 39 de la bibliographie.

Pour répondre à votre première question, je dirai que la consommation de $NaNO_3$ dans le procédé de circulation est de l'ordre de 1,2 à 2 kg par kilogramme de U_3O_8. Ma réponse à votre seconde question est la suivante : on a fait l'analyse chimique et spectrographique du produit final, et on a trouvé que la pureté était bien dans la limite exigée pour un matériau de pureté nucléaire. En ce qui concerne votre troisième question, le raffinage et la production de l'uranium métal sont exécutés par la Nuklear-Chemie und -Metallurgie GmbH (NUKEM) à Wolfgang, près de Hanau. Je n'ai pas de renseignements sur les résultats obtenus par cette compagnie.

V. ZIEGLER (France) : A propos des prospections radiométriques aériennes mentionnées dans le mémoire, il est fait mention d'une installation accessoire permettant l'enregistrement des données aéromagnétiques. Je voudrais demander d'abord si l'enregistrement des données aéromagnétiques est fait systématiquement ou s'il est peu fréquent. Deuxièmement, quand le levé aéromagnétique est exécuté, de quel pourcentage élève-t-il le prix de revient de la prospection? Troisièmement, l'enregistrement de position par le système Doppler est-il toujours utilisé pour les prospections radiométriques, ou seulement pour les levés aéronautiques?

I. WENDT (République fédérale d'Allemagne) : En réponse à votre première question, je dirai qu'une prospection aéroportée avec un compteur à scintillations suffit, dans la plupart des cas, pour la prospection de l'uranium. Ma réponse à votre seconde question est la suivante : quand on fait un levé général aéromagnétique, on fait simultanément, en règle générale, un levé par compteur à scintillations, car l'augmentation du prix de revient due à cette mesure supplémentaire est pratiquement négligeable par rapport au coût du levé magnétique seul. En réponse à votre troisième question, il convient de dire que l'altitude de vol est généralement beaucoup plus basse (50 à 100 m au-dessus du sol) pour un levé d'uranium à maille serrée que pour un levé magnétique. Nous n'avons utilisé jusqu'à présent les appareils électroniques de navigation et les altimètres que pour les levés magnétiques et les levés aéroportés combinés.

A. FAURE (Afrique du Sud) : Avez-vous envisagé l'utilisation de D2EHPA (acide 2-di-éthylhexylphosphorique) comme solvant pour la purification de la solution de nitrate issue du processus d'échange d'ions? On pense que ce solvant pourrait être plus efficace en solution nitrique diluée, et être plus spécifique pour l'uranium.

I. WENDT (République fédérale d'Allemagne) : Nous avons fait des expériences préliminaires avec D2EHPA, mais les résultats obtenus jusqu'à maintenant sont insuffisants pour en tirer des conclusions.

A. FAURE (Afrique du Sud) : Pour obtenir une extraction satisfaisante de l'uranium dans les solvants TBP, nous avons dû utiliser en Afrique du Sud une concentration en nitrate de l'ordre de 150 g/l. On a observé que ces solutions provoquaient une dégradation rapide des résines échangeuses d'ions. Avez-vous observé des effets analogues dans votre usine pilote?

I. WENDT (République fédérale d'Allemagne) : La concentration en nitrate est de 80-100 g/l et la pureté obtenue à l'élution est identique à celle que l'on obtient en utilisant des concentrations plus fortes. Nous n'avons pas observé de dégradation des résines, avec ces concentrations.

J. GABELMAN (États-Unis d'Amérique) : Dans les zones de roches sédimentaires radioactives où la prospection n'a rien donné, y a-t-il des indices prouvant que des quantités importantes d'uranium n'ont jamais été extraites des roches initiales érodées, ou que de grandes quantités ont été déposées avec les sédiments syngénétiquement, mais n'ont simplement pas été reconcentrées?

I. WENDT (République fédérale d'Allemagne) : Nous avons trouvé des indications dans l'argile appelée Hardegsen montrant que des quantités importantes d'uranium ont été fournies par les roches initiales, mais la reconcentration n'est pas suffisante. Les concentrations maximales ne s'élèvent qu'à quelque 100 ppm.

Mémoire P/503 (présenté par H. Carreira Pich)

DISCUSSION

J. LECOQ (France) : Jusqu'à quelle capacité une installation de traitement semi-mobile comme celle que vous avez décrite est-elle plus économique qu'une usine classique en ce qui concerne le prix de revient du concentré d'uranium produit?

H. CARREIRA PICH (Portugal) : J'éprouve quelque difficulté à répondre directement à votre question parce qu'il faut considérer divers paramètres et parce que chaque cas correspond à des conditions particulières. Ainsi, pour une usine classique ou une usine semi-mobile, il faut considérer, d'une part, le prix du transport du minerai depuis le gisement jusqu'à l'usine classique, et le coût plus élevé de l'usine classique; d'autre part, il faut tenir compte du rendement plus élevé que donnent les usines classiques, et de la perte d'installations fixes quand on déplace une usine. Il en résulte que la capacité de l'usine est limitée par le fait que le matériel doit être facilement transportable d'une mine à l'autre. Je pense qu'il faut utiliser une usine semi-mobile quand il faut exploiter de petits dépôts dispersés, et je crois que ces installations sont indiquées pour des capacités ne dépassant pas environ 50 t de minerai par jour.

T. BATUECAS RODRIGUEZ (Espagne) : Je voudrais signaler que nous étudions en Espagne depuis 1960 l'attaque statique (naturelle, par percolation et par capillarité) à l'échelle du laboratoire, de l'usine pilote et à l'échelle semi-industrielle, en ce qui concerne la phase de dissolution et la récupération de l'uranium dans les solutions d'attaque. Il y a dans ce but à Madrid un laboratoire et une usine pilote dont la capacité va jusqu'à 60 t. Nous avons aussi des usines d'extraction semi-industrielles à Ciudad Rodrigo, par exemple les usines Valdemancano et Caridad de capacités respectives de 3 000 et 5 000 t, et une autre usine. La Carretona, de 750 t de capacité, à Cáceres. Nous avons de plus à Andujar une usine d'extraction mobile, utilisant des amines d'une capacité de 50 m^3 par jour. Cette dernière installation est au début de son fonctionnement, et elle sera incorporée à un système d'extraction et de récupération de l'uranium, comme l'indique le mémoire P/494 *.

Mémoire P/353 (présenté par A. M. Sedov)

DISCUSSION

R. E. ROBINSON (Afrique du Sud) : Il semble y avoir une certaine divergence entre le résumé du mémoire et le mémoire lui-même en ce qui concerne la relation entre la concentration en ions ferriques et la vitesse de réaction. Peut-on admettre que c'est le mémoire qui est exact lorsqu'il affirme que la réaction est de deuxième ordre par rapport aux ions ferriques? Cette affirmation signifie que, si l'on doublait la concentration des ions ferriques, tous les autres facteurs demeurant constants, la vitesse de réaction serait multipliée par le facteur 4. Pour de très fortes concentrations d'ions ferriques on pourrait donc obtenir des temps de réaction extrêmements courts. Ceci n'est pas confirmé par les résultats obtenus aux laboratoires métallurgiques gouvernementaux de Johannesburg, selon lesquels la relation entre vitesse de réaction et la concentration en ions ferriques est de la forme $R = a\,x/(1 + b\,x)$, où a et b sont les constantes et x la concentration de Fe^{3+}.

Cette relation est de la même forme que l'isotherme d'adsorption de Langmuir, et l'on en tire la conclusion que la réaction qui détermine la vitesse est la réaction entre les complexes ferriques adsorbés à la surface de l'oxyde d'uranium et l'oxyde lui-même. Cette théorie explique pourquoi la vitesse de réaction entre les ions ferriques et UO_2 en milieu d'acide perchlorique est très faible, car il n'existe pas de complexes entre les anions perchlorate et les cations ferriques.

Ce sujet est discuté en détail dans un mémoire présenté par P. A. Laxen à un colloque international d'hydrométallurgie qui s'est tenu à Dallas, Texas, en 1963.

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* Voir, dans le présent volume, la séance 2.11.

A. M. SEDOV (URSS) : Les auteurs du mémoire que j'ai présenté n'assistent malheureusement pas à la Conférence, et la question du D^r Robinson nécessite une discussion théorique. Je transmettrai donc ses observations aux auteurs. Cependant, les calculs théoriques qui figurent dans la communication sont en bon accord avec les résultats pratiques.

Mémoire P/257 (présenté par J. Gabelman)

DISCUSSION

H. ROSATZIN (Suisse) : Il semble que les composés organo-uraniens jouent un rôle important pendant le dépôt des minerais d'uranium. A-t-on identifié des composés organo-uraniens spécifiques?

J. GABELMAN (États-Unis d'Amérique) : Oui. L'asphaltite ou la thucolite contiennent de l'uranium. Il y a aussi une substance que nous appelons « humate » à Grants (New Mexico), que nous pensons dérivée de matières végétales.

S. H. U. BOWIE (Royaume-Uni) : Si la minéralisation initiale est épigénétique, comme le mémoire le suggère, les complexes ont-ils nécessairement été transportés à l'état oxydé? Deuxièmement, quelle preuve y a-t-il que la matière organique a joué un rôle à la fois d'absorbeur et d'agent réducteur dans la formation des complexes organo-uraniens?

J. GABELMAN (États-Unis d'Amérique) : Pour répondre à votre première question, les solutions n'ont pas nécessairement été transportées à l'état oxydé. Elles peuvent avoir été transportées à l'état oxydé dans des eaux souterraines voisines de la neutralité, ou à l'état réduit dans des eaux très acides, c'est-à-dire des pH inférieurs à 3. Quant à votre seconde question, les preuves expérimentales montrent que l'uranium riche est étroitement associé aux matières organiques, et les matières organiques semblent avoir attiré de l'uranium. Cependant, ceci peut vouloir dire seulement que l'uranium qui sort, ou s'éloigne, de l'environnement, n'a pas laissé de traces de son passage. Des matières organiques que l'on s'attend à voir contenir de l'uranium n'en contiennent pas, ce qui indique qu'il n'y a pas eu passage d'uranium.

G. BIGOTTE (France) : Le mémoire suggère que l'uranium que l'on trouve dans des dépôts stratiformes peut toujours venir, généralement parlant, de l'uranium des dépôts hydrothermaux ou magnétiques. Ne faudrait-il pas, du point de vue des prospections futures, considérer une théorie contraire, c'est-à-dire que l'uranium que l'on trouve dans des filons peut, dans certains cas, venir de l'uranium contenu dans des dépôts stratiformes?

J. GABELMAN (États-Unis d'Amérique) : Oui, nous savons que l'uranium d'un dépôt quelconque peut se déplacer vers le bas, et c'est une forme d'enrichissement secondaire, et qu'il peut se déposer dans des failles plus profondes après extraction de la zone supérieure. Cependant, on peut distinguer, d'après les rapports des isotopes du soufre, entre cet uranium et l'uranium déposé à partir de solutions hydrothermales qui s'élèvent.

A. GANGLOFF (France) : Pouvez-vous expliquer le terme *mobile belts* utilisé dans votre mémoire? Ce terme désigne-t-il les grandes zones orogéniques récentes?

J. GABELMAN (États-Unis d'Amérique) : Ce terme désigne les grandes et les petites zones de tous âges. Les grandes zones mobiles ont généralement été actives pendant plusieurs périodes géologiques, peut-être pendant plus d'une ère. Le cycle métallogénique zoné correspondant peut avoir pris presque aussi longtemps, étant entendu que la minéralisation suit toujours les déformations et les intrusions.

S. ALPAN (Turquie) : En Turquie, nous faisons depuis 1957 une exploration et une prospection poussées des minerais radioactifs. 494 000 km^2 ont été prospectés par levés aéroportés, 407 000 km^2 par levés autoportés, 73 000 km^2 par prospection générale au sol et 9 000 km^2 par prospection détaillée et systématique.

Les travaux initiaux ont été limités à la vérification des anomalies dans les fissures et les veines du granite. On a trouvé des minéralisations d'autunite et de torbérnite, mais sans résultat notable. Par la suite, on a prospecté et exploré des veines de fluorite dans la cyanite, avec des résultats analogues. Les résultats des prospections ultérieures des formations métamorphiques, comme le gneiss et les schistes du massif de Mendoren, ont été assez encourageants, et on a exploré les sédiments néocéniens et récents avec des résultats très encourageants. Les résultats des recherches dans les formations sédimentaires récentes entreprises au cours des dernières années ont permis de découvrir 750 t de U_3O_8 après un important travail de prospection comprenant des sondages, des tranchées et des puits. Nous avons trouvé 1,5 million de tonnes de minerai d'uranium avec une teneur moyenne en U_3O_8 de 0,1-0,2 %. Nous sommes ainsi arrivés à la conclusion que les dépôts primaires du massif ont sans doute été dissous et que l'uranium s'est déposé à nouveau dans les sédiments néocènes et récents voisins. Notre politique de prospection radiométrique consiste donc maintenant à porter notre attention sur ces sédiments dans les massifs et aux environs des massifs.

Il faut souligner que nous avons enregistré environ 1 000 anomalies au cours des relevés aériens, et que nous n'en avons encore vérifié qu'un faible pourcentage. Après avoir étudié toutes les anomalies importantes, nous pourrons être conduits à d'autres conclusions.

En ce qui concerne la récupération du minerai, je voudrais faire les remarques suivantes. Des minerais d'uranium secondaires, qui sont finement dispersés dans des graviers mal consolidés, des alluvions, des sables et des argiles, se présentent dans le gisement de Kasar. Les résultats des essais de récupération du minerai ont été très satisfaisants en raison de l'existence de minerais secondaires d'uranium dans la gangue mal consolidée de sable et de gravier. En lavant et en tamisant le minerai, on rejette une partie grossière, pratiquement sans uranium, en laissant seulement les fractions plus fines pour l'attaque; on peut ainsi éliminer les étapes de concassage et de broyage. 65 % de l'échantillon de minerai passaient au tamis 200, et cette portion avait une teneur en U_3O_8 de 17 %. Le traitement ultérieur dans une usine d'attaque avec agitation a permis de récupérer 93 % du minerai. 16 % de l'échantillon avait une taille de grain 1/4-1/32 avec une teneur en U_3O_8 de 12 %. Cette portion a été traitée par la méthode plus économique d'attaque par immersion statique dans H_2SO_4 et a donné une récupération de minerai de 93 %. Le reste de l'échantillon (19 % en poids et 11 % du U_3O_8 contenu) a été rejeté comme stérile. Avec ce traitement simple et économique, le rendement global de récupération du minerai a été de 82,5 %.

On envisage de traiter les solutions combinées, produites par les procédés d'attaque statique et d'attaque avec agitation, dans une usine de concentration par échanges d'ions, de façon à obtenir une solution claire, à haute teneur, pour la précipitation de U_3O_8 de haute pureté.

M. ROUBAULT (France) : Je voudrais souligner l'extrême importance que l'on doit attacher à des recherches telles que celles qui sont décrites dans le mémoire présenté par le D^r^ Gabelman. A l'heure actuelle, l'exploration se fait presque toujours par les méthodes directes avec emploi de compteurs. Cette méthode a permis d'évaluer les ordres de grandeur des tonnages que l'on peut espérer atteindre dans le monde, même si l'on tient compte des régions non encore explorées. Or, si l'on réfléchit aux chiffres qui ont été donnés hier, ces tonnages, bien qu'importants, risquent d'être un jour insuffisants. La preuve est ainsi donnée qu'il faut s'efforcer d'atteindre des gisements qu'aucun indice ne révèle en surface. Seules les considérations géologiques et géochimiques générales issues de recherches fondamentales permettront d'atteindre ce résultat. De telles recherches sont donc indispensables si l'on veut dans un proche avenir déterminer les emplacements de sondage, comme dans le cas du pétrole, en fonction de structures et non seulement d'indices minéralisés.

Comme M. Mabile l'a indiqué avec raison dans le mémoire P/72 *, l'un des résultats essentiels de la présente Conférence pourrait être de nous rendre conscients de l'ampleur du problème à résoudre en face d'une demande d'uranium très rapidement croissante. Je pense que nous devrions aussi comprendre qu'il faut faire un grand pas en avant dans la conception même des méthodes de prospection et de recherche.

Mémoire P/450 (présenté par E. Szabó)

DISCUSSION

P. MAGET (France) : Je voudrais savoir si l'installation de triage radiométrique décrite dans le mémoire a fait l'objet d'une application industrielle.

E. SZABÓ (Hongrie) : L'équipement de concentration radiométrique du minerai n'a pas encore été utilisé industriellement et nous n'avons donc pas de données techniques précises sur son utilisation industrielle.

S. TĂTARU (Roumanie) : Au cours d'expériences voisines de celles que vous avez décrites comprenant la séparation des minerais par flottation, avec attaque ultérieure des produits flottés en milieu acide ou alcalin, nous avons observé que les produits de flottation avaient un effet négatif sur les phases suivantes du traitement, surtout parce qu'ils sont eux-mêmes sorbés sur les échangeurs d'ions **. Je voudrais demander si les qualités résiduelles d'agents de flottation ne gênant pas la sorption et la dissolution de l'uranium en milieu sodique.

E. SZABÓ (Hongrie) : Nous avons aussi observé des phénomènes de ce genre, mais la réduction de la capacité des résines échangeuses d'ions n'était pas suffisante pour avoir un effet marqué sur les possibilités d'utilisation de cette méthode.

Mémoire P/464 (présenté par R. E. Robinson)

DISCUSSION

A. M. SEDOV (URSS) : Quel est le pourcentage d'entraînement de l'uranium à partir du lit fluide, et quel est le coefficient de décontamination dans le cyclone?

Je voudrais aussi demander s'il y a dépôt de NH_4F dans le système de canalisations, et quelle est la longueur de la canalisation entre l'appareil et le condenseur dans l'usine expérimentale.

R. E. ROBINSON (Afrique du Sud) : L'entraînement à partir du lit fluide dépend en grande partie de la taille des particules du matériau. Il peut varier entre

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* Voir, dans le présent volume, la séance 2.11.

* Plaksin, I. N., et Tătaru, S., Revista Minelor, *6*, 1962; Tătaru, S., *Ibid.* (1963).

** Tătaru, S., Revue roumaine des sciences techniques, Série métallurgie, *1* (1964).

10 % et 40 % approximativement. Environ 90 % de cette quantité sont renvoyés au lit fluide par le cyclone.

En ce qui concerne votre seconde question, il n'y a pratiquement pas de dépôt dans les canalisations, parce qu'on les maintient à une température supérieure au point de condensation du fluorure d'ammonium. Les canalisations n'ont pas plus de quelques pieds de long.

Протокол заседания 2. 12

Методы поисков и переработки радиоактивных руд

Председатель: Я. Нейман (Чехословакия)

Доклад Р/521 (представил А. У. Уайли)

ДИСКУССИЯ

С. АЛПАН (Турция): Рекомендуется ли вести поиски тория, если учесть спрос на него и современную технологию обогащения ториевых руд?

А. У. УАЙЛИ (Австралия): Дорогостоящие поиски тория, вероятно, не оправданы на современной стадии. Но в Австралии ториевый минерал монацит является побочным продуктом при разработке прибрежных россыпей для добычи рутила, циркона и т. п. Мы также заинтересованы в ториевом топливном цикле, а следовательно, и в развитии средств использования нашего собственного тория на какой-то стадии.

Дж. ГЭЙБЛМЕН (США): Производились ли какие-нибудь расчеты стоимости производства ядерночистого тория как основного, а не побочного продукта?

А. У. УАЙЛИ (Австралия): Расходы, приведенные в докладе, характеризуют лишь стоимость реагентов и не включают других эксплуатационных затрат химического завода, однако относятся к стоимости получения тория как основного, а не побочного продукта.

Доклад Р/844 (представил Й. Имаи)

ДИСКУССИЯ

П. МАЖЕ (Франция): Мне хотелось бы задать д-ру Имаи два вопроса: во-первых, почему в качестве растворителя был выбран TNOA и, во-вторых, каковы физические и химические свойства получаемого UF_4?

Й. ИМАИ (Япония): Мы провели тщательное изучение нескольких видов аминов и установили, что TNOA пригоден для нашей цели с точки зрения устойчивости, избирательной способности и скорости разделения фаз; кроме того, его легче достать в Японии.

По поводу Вашего второго вопроса могу сказать, что химические свойства UF_4 такие же или даже лучше, чем указано в стандартных технических условиях на UF_4. В отношении физических свойств мы не встретили никаких трудностей при восстановлении магнием. Среднее извлечение металлического урана составляло свыше 95%.

Р. Л. ФОЛКНЕР (США): При гидравлической разработке не создает ли каких-либо трудностей растворение урановых минералов и не дает ли этот способ чрезмерно большие количества шламов с последующим низким извлечением урана?

Й. ИМАИ (Япония): При гидравлической разработке вода рециркулирует через две группы сгустителей для предотвращения потери растворенного урана и для улавливания шламов.

А. ФАУР (ЮАР): Какой обработке подвергается водный элюент после конверсии для перевода урановосульфатного комплекса в урановый хлорокомплекс? Мне хотелось бы также узнать, исследовалось ли извлечение урана и соляной кислоты из этого раствора?

Й. ИМАИ (Япония): Водный раствор после конверсии нейтрализуется раствором каустика для извлечения урана. В отношении извлечения и повторного использования соляной кислоты нам представляется более экономичным расходовать как можно меньше соляной кислоты и сбрасывать ее после нейтрализации.

Б. БЛЮМ (Франция): Какая экономия достигается при использовании Вашего метода по сравнению с обычными методами?

Й. ИМАИ (Япония): Мы приблизительно рассчитали, что расходы при применении нашего метода на 25% меньше, чем при применении обычного процесса.

А. М. СЕДОВ (СССР): Руда, о которой Вы говорили в докладе, добывалась обычным или гидравлическим способом? Если последним, то применяется ли классификация руды в гидроциклонах?

Й. ИМАИ (Япония): Гидроциклонный способ изучался, но основная технологическая схема нашей опытной установки основана на обычной системе осаждения.

М. ПЕРАРНАУ ПЕРРАМОН (Испания): Мне хотелось бы спросить, содержит ли Ваша руда пириты и наблюдается ли растворение урана во время мокрого обогащения?

Й. ИМАИ (Япония): Руда содержит пириты. Растворение урана в воде не очень значительно, однако промывная вода для предотвращения потери урана направляется в оборот.

М. ПЕРАРНАУ ПЕРРАМОН (Испания): Создает ли какие-либо трудности фильтрация и сушка на фильтре концентрата мокрого обогащения?

Й. ИМАИ (Япония): Операция фильтрации нелегкая. Для уменьшения влажности кеков при фильтрации можно с успехом использовать пар.

М. ПЕРАРНАУ ПЕРРАМОН (Испания): Сколько времени требуется для хорошего замеса руды с кислотой?

Й. ИМАИ (Япония): Это не занимает много времени — менее 10 *мин.*

М. ПЕРАРНАУ ПЕРРАМОН (Испания): Из чего выполнена сушилка?

Й. ИМАИ (Япония): Сушилка сделана из мягкой стали, покрытой никелевым сплавом.

М. ПЕРАРНАУ ПЕРРАМОН (Испания): Сколько стадий фильтрации считается необходимым? Мне также хотелось бы знать, каково общее отношение т : ж?

Й. ИМАИ (Япония): Репульпацию и фильтрацию нужно производить дважды. Отношение т : ж почти равно 1 : 1.

Доклад Р/414 (представил Б. Буньи)

ДИСКУССИЯ

Ж. ЛЕКОК (Франция): Я понял из представленного Вами доклада, что работа, проведенная на опытной установке, показывает, что Ваш процесс дешевле сорбционного процесса. Располагаете ли Вы достаточным количеством данных, позволяющих сказать что этот процесс будет также более выгодным в случае завода с большой производительностью, например 1000 *т* руды в сутки, и каково будет при этом отличие себестоимости тонны перерабатываемой руды?

Б. БУНЬИ (Югославия): Установка в Калне имеет производительность 200 *т/сутки,* и полученные данные показывают, что затраты при процессе восстановления на тонну перерабатываемой руды по крайней мере на 10% ниже, чем при сорбционном процессе. Кроме того, следует отметить, что повышенная чистота продукта дает возможность дополнительно сократить расходы на последующей стадии (экстракции). Теперь мы знаем, что осаждение с помощью восстановительного процесса обеспечивает надежное и экономное решение. При увеличении производительности до 1000 *т/сутки* возможно и дальнейшее снижение себестоимости переработки.

Ф. БАЗИЛЬ (Франция): Сравнима ли чистота продукта, получаемого при Вашем процессе, с чистотой продуктов, получаемых при обычных технологических процессах?

Б. БУНЬИ (Югославия): Получаемый продукт является технически чистым, однако он имеет более высокое содержание металла и лучшее качество, чем продукт, обычно получаемый при сорбционном процессе. Основными примесями являются карбонаты и весьма мелкие зерна руды. Все другие примеси присутствуют в индикаторных количествах.

Ж. ШМЕТС (Бельгия): В отношении каталитического осаждения урана текст, который относится к рис. 4 в разделе доклада, посвященном описанию восстановительной установки, показывает, что раствор насыщается водородом в первом аппарате, затем раствор переводится в другие аппараты под давлением и нагревается до 150° С. Означает ли это, что осаждение осуществляется с упомянутыми скоростями лишь путем диффузии и растворения водорода в растворе. Если это не так, то как достигается хороший контакт?

Б. БУНЬИ (Югославия): Как показано на рис. 4, в первом аппарате под давлением происходит лишь поглощение из насыщенного раствора. Осаждение происходит в последующих аппаратах, которые заполняются катализатором UO_2 в форме пластинок. В первом аппарате осаждения не наблюдалось. В настоящее время водород используется только на стадии поглощения. Однако, если газообразный водород используется в качестве барботирующего агента, в аппаратах с катализатором наблюдается увеличение скорости реакции. Ряд технических трудностей несколько удорожает данный способ.

Х. ГЮЕ (Франция): Изучали ли Вы UO_2, получающуюся в Вашем процессе, с точки зрения спекания? Представляется, что она имеет недостаточную чистоту. В таком случае, нельзя ли сообщить нам некоторые подробности, связанные с последовательностью последующих операций, применяемых в целях превращения продукта в спекаемую окись или металлический уран ядерной чистоты?

Б. БУНЬИ (Югославия): Было установлено, что неочищенную UO_2, полученную описанным способом, можно превратить в UO_2 ядерной чистоты, пригодную после очистки для спекания. В настоящий момент я не могу сообщить никаких других подробностей. Но сейчас мы изучаем возможности очистки растворением загрязненной UO_2 и переосаждением. Мы знаем, что загрязненная UO_2 может растворяться и что процессы растворения и восстановления избирательны для UO_2. Заменяя водород кислородом и маточный раствор водой, мы получили UO_2 ядерной чистоты, но в настоящее время мы имеем еще очень приближенное представление о стоимости производства.

Доклад P/478 (представил И. Вендт)

ДИСКУССИЯ

П. МАЖЕ (Франция): В отношении доклада, представленного д-ром Вендтом, меня особенно заинтересовало описание эльвейлерской опытной установки. В докладе показано, как раствор, образующийся в результате сернокислотной переработки, так называемый «насыщенный раствор», обрабатывается в сорбционной колонне и затем растворителями для полученияураната ядерной чистоты. Мне хотелось бы задать три вопроса.

Во-первых, какой расход реагентов, выраженный, например, в килограммах на килограмм получаемого урана, необходим для сорбции, обработки растворителями и осаждения? Во-вторых, каков результат анализа получаемого ядерночистого ураната? В-третьих, использовался ли полученный уранат для получения металлического урана и если так, то как и с какими результатами?

И. ВЕНДТ (ФРГ): У меня нет под рукой всех данных, о которых спрашивают, но я могу привести некоторые цифры. Подробные сведения об опытной установке в Эльвейлере можно найти в работе, указанной в ссылке [39] в библиографии к нашему докладу.

На первый вопрос я могу сказать, что расход $NaNO_3$ в процессе циркуляции составляет около 1,2—2 *кг/кг* U_3O_8. Что касается второго вопроса, проведенный химический и спектрографический анализ конечного продукта установил полное соответствие его чистоты в пределах требований, предъявляемых к материалу ядерной чистоты. На третий вопрос я могу сказать, что очистка и получение металлического урана производится фирмой «Нуклеар-хеми унд металлурги» (NUKEM) в Вольфганге, вблизи Ханау. У меня нет сведений о результатах, полученных фирмой.

В. ЦИГЛЕР (Франция): В связи с аэро-гамма-съемкой, упомянутой в докладе, говорится о вспомогательной установке, которая позволяет регистрировать аэромагнитные данные и т. п. Я хотел спросить, во-первых, проводится ли регистрация аэромагнитных данных систематически или лишь изредка? Во-вторых, при проведении аэромагнитной съемки каково увеличение расходов в процентах? В-третьих, регистрация положения по системе Допплера все еще используется при гамма-съемке или лишь для аэромагнитной съемки?

И. ВЕНДТ (ФРГ): На Ваш первый вопрос я сообщу, что в большинстве случаев для поисков урана требуется лишь аэро-гамма-съемка с применением сцинтилляционных счетчиков. Ответ на второй вопрос: когда производится общая аэромагнитная съемка, как правило, одновременно производится и аэро-гамма-съемка с применением сцинтилляционных счетчиков, так что увеличение расходов из-за этого дополнительного измерения почти неощутимо по сравнению с расходами на собственно магнитную съемку. По поводу Вашего третьего вопроса я могу сказать, что высота полетов обычно значительно ниже (около 50—100 *м* над уровнем земли) для съемки на уран по узкой сетке, чем для магнитной съемки. До сих пор мы применяли электронное навигационное оборудование и альтиметры лишь в магнитной или комбинированной аэросъемке.

А. ФАУР (ОАР): Рассматривалось ли применение D2EHPA (ди-2-этилгексилфосфорной кислоты) в качестве растворителя для очистки нитратного раствора от сорбционного процесса? Считается, что этот растворитель может действовать более удовлетворительно в разбавленном нитратом растворе и является более специфичным для урана.

И. ВЕНДТ (ФРГ): Предварительные эксперименты с D2EHPA были проведены, но до сих пор мы еще не имеем достаточного количества данных, чтобы представить окончательные результаты.

А. ФАУР (ОАР): Чтобы получить удовлетворительную экстракцию урана в трибутилфосфатный экстрагент, в Южно-Африканской Республике приходилось использовать концентрацию нитрата порядка 150 *г/л*. Было установлено, что эти растворы вызывают быстрое разложение ионообменных смол. Наблюдались ли подобные эффекты на Вашей опытной установке?

И. ВЕНДТ (ФРГ): Концентрация нитрата, который мы использовали, составляет 80—100 *г/л*, а чистота, полученная при вымывании, равна чистоте, получаемой при применении более высоких концентраций. При такой концентрации мы не наблюдали разложения смол.

Дж. ГЭЙБЛМЕН (США): В районах залегания радиоактивных осадочных пород, где геологические поиски оказываются безрезультатными, имеются ли признаки того, что из эродируемых материнских пород никогда не поступали большие количества урана или что большие количества урана отложились сингенетично с осадками, но просто не были сконцентрированы?

И. ВЕНДТ (ФРГ): Мы нашли в так называемой хардегсенской глине признаки того, что большое количество урана было принесено из материнских горных пород, но реконцентрация была недостаточной. Максимальные концентрации составляют лишь около 0,01%.

Доклад Р/503 (представил Х. Каррейра Пич)

ДИСКУССИЯ

Ж. ЛЕКОК (Франция): До какой производительности полупередвижная установка описанного Вами типа является более экономичной, чем обычный завод в отношении себестоимости получаемого уранового концентрата?

Х. КАРРЕЙРА ПИЧ (Португалия): Мне несколько трудно дать прямой ответ на Ваш вопрос, так как следует учесть различные параметры и особые условия, характерные для каждого случая. Так, при сравнении обычного завода и полупередвижной установки необходимо иметь в виду, с одной стороны, стоимость перевозки руды с месторождения на завод и более высокие капитальные затраты на его сооружение. С другой стороны, нужно учитывать более высокую призводительность обычного завода и стоимость недемонтируемых устройств, которые теряются при перемещении полупередвижных установок. Производительность полупередвижной установки зависит от оборудования, которое может легко транспортироваться с одного рудника на другой. Я считаю, что полупередвижную установку следует использовать в том случае, если необходимо перерабатывать руду небольших, удаленных друг от друга месторождений: короче говоря, я считаю, что эти установки будут пригодны для производительности не более 50 *т* руды в сутки.

Т. БАТЮКАС РОДРИГЕС (Испания): Мне хотелось бы указать, что с 1960 года в Испании проводились исследовательские работы по статическому выщелачиванию (естественно, путем просачивания и насыщения восходящим потоком) в лабораторном масштабе на опытной и полупромышленной установках как в части растворения урана, так и в части его извлечения из щелочных растворов. Для этой цели в Мадриде была создана лаборатория и опытная установка с производительностью до 60 *т/сутки*. Имеются также полузаводские установки для выщелачивания в Сиудад Родриго, а именно установки Валдемасканьо и Каридад производительностью 3000 и 5000 *т* соответственно и еще одна установка Карретона производительностью 750 *т* в Какоресе. Кроме того, существует передвижная экстракционная установка, работающая на аминах, производительностью 50 $м^3$*/сутки* в Андухаре. Эта установка сейчас реконструируется и будет включена в систему для выщелачивания и извлечения урана, как указано в докладе Р/494 *.

Доклад Р/353 (представил А. М. Седов)

ДИСКУССИЯ

Р. Э. РОБИНЗОН (ЮАР): По-видимому, есть расхождение между аннотацией и самим докладом в отношении зависимости между концентрацией ионов трехвалентного железа и скоростью реакции. Можно ли считать, что доклад правильно относит реакцию ко второму порядку в отношении ионов трехвалентного железа? Это положение означает, что, если удвоить концентрацию ионов трехвалентного железа, сохраняя все другие факторы постоянными, скорость реакции будет возрастать в четыре раза. Следовательно, при очень высоких концентрациях ионов трехвалентного железа возможна чрезвычайно быстрая реакция. Это не подтвердилось результатами, полученными во время работы, проводившейся в Государственных металлургических лабораториях Иоганнесбурга. Указанная работа показала, что зависимость между скоростью реакции и концентрацией ионов трехвалентного железа имеет вид

$$R = \frac{ax}{1 + bx},$$

где a, b — постоянные; x — концентрация Fe^{+++}

Данная зависимость имеет такой же вид, как и изотерма адсорбции Ленгмюра, и мы пришли к заключению, что реакцией, регулирующей скорость процесса, является реакция между комплексами трехвалентного железа, адсорбированными на поверхности окиси урана самой окисью. Эта теория объясняет, почему скорость реакции между ионами трехвалентного железа и UO_2 в среде хлорной кислоты чрезвычайно мала, поскольку не существует никаких комплексов между анионами перхлората и катионами трехвалентного железа. Этот материал подробно обсуждается П. А. Лаксеном в докладе, представленном на Международный симпозиум по гидрометаллургии, состоявшийся в Далласе, шт. Техас, в 1963 году.

А. М. СЕДОВ (СССР): К сожалению, авторы доклада не присутствуют на конференции, а вопрос д-ра Робинзона требует технического обсуждения. Поэтому я передам его замечания авторам. Но все теоретические расчеты, приведенные в докладе, находятся в хорошем согласии с практическими результатами.

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* Этот том, заседание 2.12.

Доклад P/257 (представил Дж. Гэйблмен)

ДИСКУССИЯ

Х. РОЗАЦИН (Швейцария): Я понимаю, что уран-органические соединения играют важную роль в процессе образования урановой руды. Были ли найдены какие-нибудь специфические уран-органические соединения?

Дж. ГЭЙБЛМЕН (США): Да. Асфальтит или тухолит содержит уран. В Грантсе, шт. Нью-Мексико, имеется также материал, который мы называем «хьюматом» и который, по нашему мнению, образовался из растений.

С. Х. Ю. БОЙИ (Соединенное Королевство): Если первоначальная минерализация эпигенетична, как указано в докладе, то обязательно ли комплексы переносились в окисленных состояниях? Во-вторых, какие существуют доказательства того, что органические вещества выполняли двойную функцию поглотителя и восстановителя при образовании уран-органических комплексов?

Дж. ГЭЙБЛМЕН (США): По поводу Вашего первого вопроса можно сказать, что растворы переносились не обязательно в окисленном состоянии. Они могли переноситься в окисленном состоянии в грунтовых водах, близких к нейтральному состоянию, или в восстановленном состоянии в сильно кислых водах, например при pH менее 3. В отношении второго вопроса имеются доказательства, что богатая урановая минерализация тесно связана с органическими веществами и органическое вещество, по-видимому, само содержит некоторое количество урана. Однако это может показывать только, что уран, выходящий из окружающих пород, не оставил никаких следов на пути своего движения. Некоторые органические вещества, в которых можно было бы предполагать существование урана, не содержат его, а это говорит за то, что урановые растворы по ним не проходили.

Г. БИГОТ (Франция): В докладе предполагается, что уран, встречающийся в осадочных месторождениях, мог всегда, в большей или меньшей степени, привноситься из гидротермальных или магматических урановых месторождений. Не следовало ли бы рекомендовать с точки зрения будущих поисков учитывать противоположную теорию, то есть, что уран, найденный в жильных месторождениях, мог в некоторых случаях поступить из осадочных урановых месторождений?

Дж. ГЭЙБЛМЕН (США): Да, нам известен факт, что уран из любого месторождения может перемещаться вниз в порядке вторичного обогащения и отлагаться в трещинах на больших глубинах после выщелачивания из вышележащих пород. Но можно отличить этот уран от урана, отложенного восходящими гидротермальными растворами по соотношению изотопов серы.

А. ГАНГЛОФ (Франция): Не могли бы Вы объяснить термин «подвижные пояса», использованный в докладе? Относится ли он к поздним крупным отогеническим зонам?

Дж. ГЭЙБЛМЕН (США): Этот термин относится к большим и малым подвижным поясам любого возраста. Большие подвижные пояса обычно бывают активными в течение нескольких геологических периодов, возможно даже продолжительнее одной эры. Сопутствующий зональный металлогенический цикл может продолжаться почти также долго; при этом понятно, что минерализация всегда соответственно следует за деформацией и интрузией.

С. АЛПАН (Турция): В Турции мы проводили интенсивные поиски и разведку радиоактивных минералов начиная с 1957 года. Мы провели аэро-гамма-съемки на площади в 494 000 *км*², автомобильные гамма-съемки на площади в 407 000 *км*², обычные наземные поиски на площади в 73 000 *км*², детальные и систематические поиски на площади в 9000 *км*².

Наши первые работы были посвящены проверке аномалий, встречающихся вдоль заполнения трещин и жил в граните. Была установлена отенитовая и торбернитовая минерализации, но без значительных открытий. Позднее поиски и разведка проводились по флюоритовым жилам в Кианите, также без существенных результатов. Последующие поиски в метаморфических образованиях, таких как гнейсы и сланцы Мандорезского массива, дали очень обнадеживающие результаты. Наконец, работы велись в неоценовых и поздних осадочных породах, причем с наиболее перспективными результатами.

В итоге исследований в поздних осадочных образованиях за последние несколько лет мы разведали 650 *т* урана после широких разведочных работ, включавших бурение, канавы и проходку шахт. Мы выявили 1,5 млн. *т* урановой руды со средним содержанием урана порядка 0,085—0,17%. Таким образом, мы пришли к заключению, что первичные отложения в массиве, возможно, были выщелочены и уран переотложился в окружающих неоценовых или поздних осадочных породах. Поэтому наша программа радиометрических съемок направлена теперь на изучение осадочных пород в массивах и вокруг них.

Здесь следует сказать, что мы зарегистрировали около 1000 аномалий во время аэро-гамма-съемок и до сих пор проверили лишь небольшую их часть. После того как мы проверим все важные аномалии, можно будет сделать дальнейшие заключения.

По поводу переработки руды я хотел бы сделать следующее замечание. Вторичные урановые минералы, тонко рассеянные в слабоцементированном гравии, суглинках, песчаниках и глинах, встречаются в Касарском месторождении. Результаты исследований по переработке руды были весьма удовлетворительными благодаря нахождению вторичных урановых минералов в слабоцементированных песчано-гравийных отложениях. При промывке и грохочении руды крупная почти безрудная фракция отделяется и для выщелачивания остаются лишь мелкие классы; таким образом, удается избежать стадий дробления и измельчения. В рудной пробе 65% имело размер зерен — 200 *меш* (0,8 *мм*). Содержание урана в этой части пробы составляло порядка 1,7%. При последующей обработке агитационным выщелачиванием удавалось достичь извлечения 93% металла. Около 16% пробы имело размер зерен в пределах 6—0,8 *мм* при содержании урана до 1,2%. Эта часть руды обрабатывалась дешевым способом статического выщелачивания, путем погружения в H_2SO_4 с извлечением металла 93%. Остальная часть пробы (19% руды и 11% металла) сбрасывалась в хвосты. При такой простой и дешевой переработке общее извлечение металла составило 82,5%.

Считается, что комбинированный раствор, полученный в результате статического и агитационного выщелачивания, можно далее концентрировать на сорбционной установке с получением богатого чистого раствора для осаждения желтого кека с высоким содержанием урана.

М. РУБО (Франция): Я хочу подчеркнуть большое значение исследований, которые описаны в докладе, представленном д-ром Гэйблменом. В настоящее время поиски практически ведутся в основном непосредственным методом с помощью радиометрической аппаратуры. Этот способ дал возможность определить ориентировочный размер запасов урана, которые можно предположительно ожидать во всем мире, даже с учетом территорий, где поиски не производились. Теперь эти запасы, хотя и большие по размерам, могут в один прекрасный день оказаться недостаточными. Это свидетельствует о том, что необходимо направить усилия на поиски глубоко залегающих месторождений, относительно которых на поверхности не имеется никаких признаков.

Лишь приняв в расчет общие геологические и химические соображения, основанные на теоретических научных исследованиях, мы можем найти такие месторождения. Поэтому значение таких исследований неоценимо, если в ближайшем будущем потребуется определить районы, где следует проводить поисковое бурение, как в случае нефти, по структуре, а не по наличию следов минеральных отложений.

Как д-р Мабил правильно указал в докладе Р/72 *, одним из главных достижений данной конференции должно служить ознакомление нас с масштабом задачи, которую предстоит решить в результате сильно возрастающего спроса на уран. Я полагаю, что конференция должна подчеркнуть необходимость значительного усовершенствования методов проведения поисков и научных исследований.

Доклад Р/450 (представил Э. Сабо)

ДИСКУССИЯ

П. МАЖЕ (Франция): Мне хотелось бы знать, использовался ли в промышленности радиометрический аппарат для сортировки руд, описанный в докладе?

Э. САБО (Венгрия): Аппарат для радиометрического обогащения руд еще не применялся для промышленных целей, и поэтому мы не имеем точных технических данных относительно его промышленного использования.

С. ТАТАРУ (Румыния): При проведении экспериментов, подобных тем, которые описаны в докладе, и связанных с флотационным обогащением руды и последующим выщелачиванием продуктов флотации в кислотных или содовых системах, мы установили, что реагенты флотации оказывают отрицательное воздействие на последующие фазы переработки **, главным образом поскольку они сами сорбируются ионообменными смолами ***. Мне хотелось бы спросить о том, не ухудшают ли остаточные количества флотационных реагентов сорбцию и выщелачивание урана при содовой схеме.

Э. САБО (Венгрия): Мы также наблюдали подобное явление, но сокращение емкости ионообменной смолы было небольшим и не имело сколько-нибудь значительного влияния на применение этого способа.

Доклад Р/464 (представил Р. Э. Робинзон)

ДИСКУССИЯ

А. М. СЕДОВ (СССР): Какой процент урана уносится из псевдоожиженного слоя и каков коэффициент очистки в циклоне?

Мне также хотелось бы спросить о том, происходит ли отложение NH_4 на поверхностях системы трубопроводов и какова длина трубопровода от аппарата до конденсатора в экспериментальной установке?

Р. Э. РОБИНЗОН (ЮАР): Количество урана, уносимое из псевдоожиженного слоя, зависит в значительной степени от размера частиц про-

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* Этот том, заседание 2.12.

** I. N. Plaksin and S. A. Tataru. Revista Mineral, *6* (1962); S. A. Tataru. Revista Mineral, *6* (1963).

*** S. A. Tataru. Revue roumaine des Sciences techniques. Serie Metallurgia, *1* (1964).

дукта. Оно может колебаться приблизительно от 10 до 40%. Из этого количества около 90% возвращается в слой из циклона.

На Ваш второй вопрос я могу сказать, что в трубах отлагается очень мало продукта или вообще не отлагается, потому что температура стенок труб поддерживается на таком уровне, который выше точки конденсации фтористого аммония. Трубы имеют длину не более полуметра.

Acta de la sesión 2.12

Métodos de prospección y de laboreo de minerales

Presidente: J. Neumann (Checoslovaquia)

Documento P/521 (presentado por A. W. Wylie)

DISCUSIÓN

S. ALPAN (Turquía): ¿Es aconsejable la prospección de torio teniendo en cuenta la demanda y el proceso de concentración actual?

A. W. WYLIE (Australia): Probablemente, no está justificada, en este momento, una costosa prospección del torio. Pero en Australia disponemos de un mineral de torio, la monazita, como subproducto de la industria minera de las arenas de las playas, que produce rutilo, zircón, etc. Nosotros estamos interesados también en un ciclo de combustible del torio y por lo tanto, en el desarrollo de medios para utilizar nuestro propio torio en algún momento.

J. GABELMAN (Estados Unidos de América): ¿Tiene Vd. alguna estimación sobre el coste unitario de la producción de torio de pureza nuclear, como producto principal en vez de como subproducto?

A. W. WYLIE (Australia): Los costes que se dan en la memoria son los costes de los reactivos y no incluyen los costes de conversión en la fábrica química. Representan el coste de producciòn del torio como un producto principal, y no como un subproducto.

Documento P/844 (presentado por Y. Imai)

DISCUSIÓN

P. MAGET (Francia): Me gustaría hacer al Dr. Imai dos preguntas. La primera: ¿por qué se eligió como disolvente TNCA? y la segunda: ¿cuáles son las propiedades físicas y químicas del UF_4 obtenido?

Y. IMAI (Japón): Hemos llevado a cabo un estudio bastante completo de diversas clases de aminas y encontramos que la TNCA era adecuada para nuestros propósitos en lo que respecta a estabilidad, selectividad y velocidad de separación de fases; por otra parte, en nuestro país se dispone de ella con mayor facilidad.

En cuanto a su segunda pregunta, las propiedades químicas del UF_4 son las mismas, o mejores, que las que comprende la especificación normal del UF_4. Respecto a las propiedades físicas no hemos encontrado dificultades al reducirlo con magnesio. La recuperación media de uranio metal fue superior al 95%.

R. L. FAULKNER (Estados Unidos de América): ¿En la minería por disgregación hidraúlica, la disolución de los minerales de uranio da lugar a algunos problemas? y ¿tiende el método a producir excesiva cantidad de finos con la consiguiente baja recuperación del uranio?

Y. IMAI (Japón): En la minería hidraúlica, el agua se recicla, en dos etapas, en tanques de espesamiento para evitar la pérdida de uranio disuelto y recuperar los finos.

A. FAURE (Sudáfrica): ¿Qué tratamiento se da al efluente acuoso procedente de la sección de conversión, en la cual el sulfato complejo de uranio se convierte en cloruro complejo de uranio? Me gustaría saber si han investigado la recuperación de uranio y ácido clorhídrico de esta solución.

Y. IMAI (Japón): El efluente acuoso procedente de la sección de conversión se neutraliza con una solución cáustica para recuperar el uranio. Con respecto a la recuperación y nuevo empleo del ácido clorhídrico nosotros creemos que es más económico emplearlo lo menos posible y desecharlo después de la neutralización.

F. BAZILE (Francia): ¿Qué efectos económicos se consiguen con su método, comparados con los métodos convencionales?

Y. IMAI (Japón): Nosotros estimamos que aproximadamente el coste que lleva consigo el empleo de nuestro proceso es un 25% menor que el ocasionado en el proceso convencional.

A. M. SEDOV (URSS): ¿Qué método es el que utilizan para obtener los minerales a que hace referencia en la memoria, el regular o el hidraúlico? Si es este último ¿emplean el método hidrociclónico de separación de minerales?

Y. IMAI (Japón): El método hidrociclónico ha sido investigado, pero el diagrama de flujo principal de nuestra planta piloto está basado en el sistema de espesamiento ordinario.

M. PERARNAU PERRAMÓN (España): Me gustaría saber si el mineral contiene piritas y si han observado disolución del uranio durante el lavado hidraúlico.

Y. IMAI (Japón): El mineral contiene piritas. La disolución de uranio en agua no es importante; sin embargo, el agua se recicla para evitar pérdidas de uranio.

M. PERARNAU PERRAMÓN (España): ¿Ofrece dificultades la filtración del concentrado hidraúlico y el secado sobre el filtro?

Y. IMAI (Japón): La filtración no es fácil. Puede emplearse vapor eficazmente para reducir el contenido en agua de las tortas en el filtro.

M. PERARNAU PERRAMÓN (España): ¿Permanece mucho tiempo en el mezclador la mezcla adecuada de mineral y ácido?

Y. IMAI (Japòn): Menos de diez minutos.

M. PERARNAU PERRAMÓN (España): ¿De qué está fabricado el desecador?

Y. IMAI (Japón): El desecador está hecho de acero inoxidable con un revestimiento de aleación de níquel.

M. PERARNAU PERRAMÓN (España): ¿Cuantas etapas de extracción con agua y filtrado se consideran necesarias? Me gustaría también saber cuál es la relación entre el líquido total y el mineral.

Y. IMAI (Japón): El nuevo batido de la pasta y el filtrado deben realizarse dos veces. La relación entre el líquido y el mineral es casi 1:1.

Documento P/414 (presentado por B. Bunji)

DISCUSIÓN

J. LECOQ (Francia): Yo deduzco de la memoria presentada por Vd. que los estudios en planta piloto indican que su proceso es más barato que el proceso en el que se emplean resinas cambiadoras de ion. ¿Tiene Vd. datos suficientes para decir si su proceso sería también más ventajoso para una fábrica de gran capacidad, que produjera, por ejemplo, 1 000 toneladas diarias, y cuál sería la diferencia en el precio de coste por tonelada de mineral tratado?

B. BUNJI (Yugoslavia): La fábrica de Kalna tiene una capacidad de 200 toneladas diarias y los datos obtenidos indican que el proceso de reducción es, por lo menos, un 10 % más barato, por tonelada de mineral tratado, que el coste resultante en el proceso de cambio de ion. Hemos de señalar, también, que la mayor pureza del producto ofrece posibilidades de una posterior reducción en el coste en la etapa de purificación (extracción por disolvente). Por ahora sabemos que el proceso de precipitación por reducción ofrece una solución buena y económica. Cuando la capacidad se incremente a 1 000 toneladas por día, será posible una posterior reducción en el coste.

F. BAZILE (Francia): ¿Es comparable la pureza de los productos obtenidos mediante su proceso con la de los productos obtenidos cuando se emplean los procesos convencionales?

B. BUNJI (Yugoslavia): El producto obtenido tenía una pureza de grado técnico; sin embargo, era de un grado mayor y de una mejor calidad que el que se obtiene habitualmente mediante las técnicas de cambio de ion. Las principales impurezas son carbonatos y partículas de mineral muy finas. Las demás impurezas se encuentran en el orden de trazas.

J. SCHMETS (Bélgica): Respecto a la precipitación catalítica del uranio, el texto que se refiere a la figura 4, en la parte en que se describe la fábrica de reducción, indica que la solución se satura con hidrógeno en el primer tanque; luego se transvasa a otros tanques bajo presión y se calienta a 150 °C. ¿Significa esto que la precipitación se efectúa a las velocidades mencionadas exclusivamente por difusión y disolución del hidrógeno en la solución? Si no sucede esto, ¿cómo se realiza un buen contacto?

B. BUNJI (Yugoslavia): Como indica la figura 4, la saturación de la solución impregnante se efectúa en el primer tanque de presión. La precipitación tiene lugar en los tanques siguientes que están llenos de UO_2, en forma enrollada, como catalizador. En el tanque de saturación no se ha observado precipitación. Por el momento sólo se está empleando hidrógeno hasta la etapa de saturación. Sin embargo cuando se emple el hidrógeno como agente de agitación en los tanques con el catalizador, se observó un incremento en la velocidad de reacción. Algunas dificultades técnicas hacen que esta técnica sea ligeramente más costosa.

H. HUET (Francia): ¿Han estudiado Vds. el UO_2 obtenido con su proceso desde el punto de vista de la sinterización? Parece que su pureza no es suficiente. En tal caso ¿podría Vd. darnos algunos detalles en relación con la serie de tratamientos empleados posteriormente con vistas a convertirlo bien en óxido sinterizable, bien en uranio metálico de pureza nuclear?

B. BUNJI (Yugoslavia): Se ha encontrado que el UO_2 impuro, obtenido por el método descrito, puede convertirse en UO_2 de grado nuclear, conveniente para ser sinterizado después de una purificación. En este momento, no puedo dar más detalles. Sin embargo, estamos estudiando la posibilidad de purificación disolviendo el UO_2 impuro y volviéndolo a precipitar. Sabemos que el UO_2 impuro puede disolverse y que tanto el proceso de disolución como el de reducción son selectivos para el UO_2. Sustituyendo el hidrógeno por oxígeno, y la solución estéril por agua, hemos obtenido un UO_2 de grado nuclear, pero, hasta el presente, sólo tenemos una idea aproximada del coste de producción.

Documento P/478 (presentado por I. Wendt)

DISCUSIÓN

P. MAGET (Francia): Con relación a la memoria presentada por el Dr. Wendt, yo estoy particularmente interesado en la descripción de la planta piloto de Ellweiler. La memoria indica que el líquido resultante del tratamiento con ácido sulfúrico, es decir, el denominado líquido impregnante, se trata en columnas de cambio de ion y después con disolventes, con objeto de obtener uranato nuclearmente puro. Yo quiero hacer tres preguntas. Primera: ¿qué consumo de reactivos, expresado por ejemplo en kilogramos por kilogramo de uranio tratado, es necesario para el cambio de ion, tratamiento por disolventes y precipitación? Segunda: ¿cuál es el análisis del uranato nuclearmente puro obtenido? Tercera: ¿se ha empleado el uranato obtenido para preparar uranio metal? y en caso afirmativo, ¿cómo y con qué resultados?

I. WENDT (República Federal de Alemania): No dispongo, en este momento, de todos los datos solicitados por Vd. pero puedo dar algunas cifras. Una información detallada de la planta piloto de Ellweiler puede Vd. encontrarla en la referencia [39] de la bibliografía.

Respecto a su primera pregunta, el consumo de NO_3Na en el proceso de circulación es aproximadamente 1,2-2 kg por kg de U_3O_8. Respecto a su segunda pregunta, se ha llevado a cabo un análisis químico y espectrográfico del producto final y se encontró que la pureza está dentro de los límites requeridos por un material nuclearmente puro. Por lo que se refiere a su tercera pregunta, el refino y producción del uranio metal se lleva a cabo porla Nuklear-Chemie und -Metallurgie GmbH (NUKEM) en Wolfgang, Hanau. No dispongo de información acerca de los resultados obtenidos por la compañía.

V. ZIEGLER (Francia): En relación con el reconocimiento radiométrico aéreo, a que se hace referencia en la memoria, se menciona una unidad auxiliar que permite el registro de datos aeromagnéticos, etc. Quisiera saber, en primer lugar, si el registro de datos aeromagnéticos se hace sistemáticamente o de forma esporácida. En segundo lugar, cuando se lleve a cabo el reconocimiento aeromagnético ¿cuál será el porcentaje resultante del incremento en el coste?, y, en tercer lugar, el registro de posición por sistema Doppler ¿se emplea aún en reconocimientos radiométricos, o solamente en los aeromagnéticos?

I. WENDT (República Federal de Alemania): Respecto a su primera pregunta, para la prospección de uranio solamente se requiere, en muchos casos, un reconocimiento aéreo con contador de centelleo. En cuanto a su segunda pregunta, cuando se hace un reconocimiento general aeromagnético, se lleva a cabo simultáneamente, por regla general, un reconocimiento con contador de centelleo, ya que el aumento de coste debido a esta medida adicional es prácticamente insignificante en comparación con el coste de un reconocimiento puramente magnético. Respecto a su tercera pregunta, la altura de vuelo es normalmente mucho más baja (unos 50 a 100 m sobre el terreno) para un reconocimiento de uranio con cuadrícula estrecha, que para un reconocimiento magnético. Hasta ahora nosotros hemos empleado equipos electrónicos de navegación y altímetros solamente en reconocimientos aéreos, magnéticos o combinados.

A. FAURE (Sudáfrica): ¿Se ha tenido en cuenta el empleo de D2EHPA (ácido di-2-etil hexilfosfórico) como disolvente para la purificación de la solución de nitrato procedente del proceso de cambio de ion? Se tiene la opinión de que este disolvente es más eficaz en la solución diluida de nitrato y más específico para el uranio.

I. WENDT (República Federal de Alemania): Se han llevado a cabo algunos experimentos preliminares con D2EHPA, pero hasta la fecha no hemos reunido suficientes datos para poder dar resultados finales.

A. FAURE (Sudáfrica): Con objeto de conseguir una extracción satisfactoria de uranio con disolventes TBP (fosfato de tributilo), en Sudáfrica se ha empleado una concentración de nitrato del orden de 150 g por litro. Se encontró que estas soluciones producían una rápida degradación de las resinas de cambio de ion. ¿Se han observado en su planta piloto efectos análogos?

I. WENDT (República Federal de Alemania): La concentración de nitrato empleada por nosotros tiene unos 80-100 g por litro, y la pureza obtenida en la elución es igual a la que se obtiene cuando se emplean concentraciones superiores. Con esta concentración no hemos observado ninguna degradación de las resinas.

J. GABELMAN (Estados Unidos de América): En regiones que contienen rocas radiactivas sedimentarias donde la exploración no ha tenido éxito ¿existen pruebas de que por erosión de rocas madre se hayan producido grandes cantidades de uranio o de que se hayan depositado singenéticamente grandes cantidades con los sedimentos y que simplemente no han sido reconcentradas?

I. Wendt (República Federal de Alemania): Nosotros hemos encontrado indicios en la llamada arcilla Hardegsen, de que grandes cantidades de uranio han provenido de las rocas-madre, pero no es adecuada la reconcentración. Las concentraciones máximas sólo vienen a ser aproximadamente de 100 ppm.

Documento P/503 (presentado por H. Carreira Pich)

DISCUSIÓN

J. Lecoq (Francia): ¿Hasta qué capacidad es más económica una fábrica de tratamiento semimóvil, del tipo de la que Vd. describe, que una convencional, en lo que se refiere al precio del coste del concentrado de uranio producido?

H. Carreira Pich (Portugal): Tropiezo con algunas dificultades para dar una respuesta acertada a su pregunta ya que deben tenerse en cuenta diferentes parámetros y en cada caso intervienen condiciones especiales. Así pues, en una fábrica convencional o en una semimóvil, se debe tener en cuenta, en primer lugar, el coste del transporte del mineral desde las minas a la instalación convencional y el mayor coste de ésta. Por otra parte se debe tener en cuenta la mayor producción lograda en las fábricas convencionales y el coste de las instalaciones fijas que se pierden cuando se trasladan las fábricas. Así pues, la capacidad de la planta depende del hecho de que el equipo debe ser fácilmente transportable desde una mina a otra. Mi opinión es que una instalación semimóvil debe emplearse cuando es necesario tratar pequeñas cantidades de yacimientos muy esparcidos y, hablando en términos generales, creo que estas fábricas son aconsejables para capacidades que no excedan de 50 t de mineral por día.

T. Batuecas Rodriguez (España): Yo quisiera señalar que desde 1960 se están llevando a cabo en España trabajos de investigación sobre lixiviación estática (natural, por percolación y por capilaridad) en escalas de laboratorio, planta piloto y semiindustrial, tanto en lo que concierne a la fase de disolución del uranio como a su recuperación del líquido de lixiviación. Para este fin disponemos en Madrid de un laboratorio y una planta piloto con una capacidad de hasta 60 t. Hay también instalaciones de lixiviación semiindustrial en la zona de Ciudad Rodrigo, como son las fábricas de Valdemascaño y Caridad con capacidades de 3 000 y 5 000 toneladas respectivamente y otra fábrica, La Carretona, en Cáceres, con una capacidad de 750 t. Tenemos, además, en Andújar una instalación de extracción móvil, que emplea aminas, con una capacidad de 50 m³ diarios. Esta última fábrica entra ahora en funcionamiento y se incorporará al sistema de lixiviación del uranio y su recuperación, como se menciona en el documento P/494 *.

Documento P/353 (presentado por A. M. Sedov)

DISCUSIÓN

R. E. Robinson (Sudáfrica): Parece existir una discrepancia entre el resumen de la memoria y la memoria misma en lo que se refiere a la relación entre la concentración de los iones férricos y la velocidad de reacción. ¿Puede suponerse que la memoria es correcta al establecer que la reacción es de segundo orden con respecto a los iones férricos? Esta suposición indica que si se duplica la concentración de iones férricos, manteniendo constantes todos los demás factores, la velocidad de reacción aumentaría en un factor de 4. Esto implica que para concentraciones muy altas de iones férricos serán posibles tiempos de reacción extremadamente cortos. Esto no coincide con los resultados obtenidos en el trabajo llevado a cabo en los Government Metallurgical Laboratories de Johanesburgo que indica que la relación entre la velocidad de reacción y la concentración de iones férricos era de la forma: $R = ax/(1 + bx)$, donde a y b son constantes y x es la concentración del Fe^{3+}.

Esta relación es de la misma forma que la isoterma de adsorción de Langmuir, y la conclusión a que se llega es que la reacción que controla la velocidad es la que tiene lugar entre los complejos férricos adsorbidos sobre la superficie del óxido de uranio y el propio óxido. Esta teoría explica por qué la velocidad de reacción entre los iones férricos y el UO_2 en un medio de ácido perclórico es extremadamente pequeña, ya que no existen complejos entre los aniones perclorato y los cationes férricos.

Este asunto está discutido con detalle por P.A. Laxen en una memoria presentada en un simposio internacional sobre hidrometalurgia, celebrado en 1963 en Dallas, Texas.

A. M. Sedov (URSS): Desgraciadamente los autores de la memoria no asisten a esta Conferencia y la pregunta del Dr. Robinson requiere una discusión teórica. Por este motivo yo transmitiré sus comentarios a los autores. Sin embargo, los cálculos teóricos que aparecen en la memoria están de completo acuerdo con los resultados prácticos.

Documento P/257 (presentado por J. Gabelman)

DISCUSIÓN

H. Rosatzin (Suiza): Yo entiendo que los compuestos orgánicos de uranio desempeñan un papel impor-

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* Este volumen, sesión 2.11.

tante durante el depósito de minerales de uranio. ¿Han identificado algunos compuestos orgánicos de uranio, especìficos?

J. GABELMAN (Estados Unidos de América): Sí. La asfaltita o tucholita contiene uranio. Existe también una sustancia, que nosotros llamamos *humate*, en Grants, Nuevo México, que pensamos procede de materia vegetal.

S. H. U. BOWIE (Reino Unido): Si la mineralización original es epigenética, como la memoria sugiere, ¿fueron los complejos transportados necesariamente en estado oxidado? En segundo lugar ¿qué pruebas hay de que la materia orgánica se comporte con la doble función de un agente absorbente y reductor en la formación de los complejos orgánicos de uranio?

J. GABELMAN (Estados Unidos de América): En lo que respecta a su primera pregunta, las soluciones no fueron necesariamente transportadas en estado oxidado. Pudieron haber sido transportadas en estado oxidado, en aguas freáticas aproximadamente neutras o en estado reducido en aguas muy ácidas, por ejemplo a pH inferior a 3. Respecto a su segunda pregunta, hay indicios de que los materiales muy ricos en uranio están asociados a la existencia de materia orgánica y el material orgánico parece haber captado algo de uranio. Sin embargo, esto puede indicar solamente que el uranio que ha atravesado la zona circundante no ha dejado huellas de su paso. Alguna materia orgánica, de la que debía esperarse que contuviese uranio, no lo contiene, lo que indica que ningún uranio pasó por ella.

G. BIGOTTE (Francia): La memoria sugiere que el uranio encontrado en yacimientos estratiformes debe proceder siempre, más o menos, de uranio contenido en yacimientos hidrotermales o magnéticos. ¿No podría ser aconsejable, desde el punto de vista de futuras exploraciones, considerar una teoría contraria, es decir, que el uranio filoniano puede, en ciertos casos, proceder del uranio contenido en yacimientos estratiformes?

J. GABELMAN (Estados Unidos de América): Sí; nosotros sabemos que el uranio procedente de cualquier yacimiento puede desplazarse hacia abajo como una forma de enriquecimiento secundario y depositarse en fracturas inferiores después de lixiviaciones procedentes de la parte superior. Sin embargo, es posible distinguir entre este uranio y el uranio depositado a partir de soluciones hidrotermales nacientes mediante las relaciones de isótopos del azufre.

A. GANGLOFF (Francia): ¿Puede Vd. explicar el término « zona movediza » empleado en la memoria? ¿Se refiere a las recientes grandes zonas orogénicas?

J. GABELMAN (Estados Unidos de América): El término se refiere a las grandes y pequeñas zonas movedizas de cualquier edad. Durante varios períodos geológicos —quizá durante más de una era— estuvieron activas grandes zonas movedizas. El ciclo metalogénico zonal que las acompañó pudo haber sido casi igual de duradero, entendiéndose que la mineralización sigue siempre convenientemente la deformación e intrusión.

S. ALPAN (Turquía): En Turquía hemos llevado a cabo una extensa exploración y prospección de minerales radiactivos desde 1957. Mediante reconocimientos aéreos se exploraron 494 000 km^2, 407 000 km^2 mediante prospección autoportada; 73 000 km^2 por prospección general sobre el terreno y 9 000 km^2 efectuando prospecciones detalladas y sistemáticas.

Nuestros primeros trabajos se concretaron a la investigación de las anomalías que se presentaban en los rellenos de grietas y venas de granito. Se encontraron mineralizaciones de autunita y torbernita pero no se obtuvieron resultados significativos. Más tarde, la prospección y exploración se realizó en filones de fluorita en cyanita con resultados análogos. Los resultados de la prospección en formaciones metamórficas, tales como gneis y esquistos del macizo montañoso de Menderes fueron esperanzadores y el trabajo llevado a cabo en el neoceno y sedimentos recientes dió resultados muy prometedores. Como resultado de las investigaciones en las formaciones sedimentarias recientes se descubrieron durante los últimos años 750 t de U_3O_8 después de una amplia exploración que comprendía sondeos y apertura de zanjas y pozos. Hemos encontrado millón y medio de toneladas de mineral de uranio con un contenido medio de U_3O_8 del 0,1-0,2 %. Así pues, llegamos a la conclusión de que los depósitos primarios en el macizo montañoso podían haber sido lixiviados y el uranio redepositado en el neoceno y sedimentos recientes de las proximidades. Por esta razón nuestro programa de reconocimientos radiométricos dirige ahora la atención a sedimentos de este tipo tanto en los macizos montañosos como en los alrededores del mismo.

Debo señalar que registramos unas 1 000 anomalías en la prospección aérea y hasta ahora hemos investigado solamente una pequeña proporción de ellas. Una vez hayamos comprobado todas las anomalías importantes podremos sacar posteriores conclusiones.

En relación a la recuperación de minerales me gustaría hacer el siguiente comentario. En los yacimientos de Kasar aparecen minerales de uranio secundarios, finamente dispersos en gravillas no muy compactas, areniscas, arenas y arcillas. Los resultados de los ensayos de recuperación de mineral fueron muy satisfactorios a causa de los yacimientos de minerales secundarios de uranio en la ganga de gravillas arenosas no muy compactas. Lavando y tamizando el mineral, se rechaza una porción gruesa, casi estéril, quedando solamente las fracciones más finas para el tratamiento de lixiviación; así se eliminan las etapas de trituración y molienda. El 65 % de la muestra de mineral poseía tamaños de grano comprendidos entre 1/32 pulgadas y 200 mallas. Esta porción de la muestra tenía un contenido en U_3O_8 del 17 %. Un tratamiento posterior en una instalación de lixiviación con agitación condujo a una recuperación del 93 % del mineral. El 16 % de la muestra poseía tamaños de grano comprendidos entre 1/4-1/32 pulgadas, con un contenido en U_3O_8 del 12 %. Esta porción fue tratada por el método barato de lixiviación por inmersión estática en SO_4H_2 y condujo a una recuperación de mineral del 93 %. La parte restante de la muestra (19 % en peso, con un contenido en U_3O_8 del 11 %) fue rechazada como desecho. Mediante el empleo de este simple y barato tratamiento el total de mineral recuperado fue del 82,5 %.

Se considera que la mezcla de las soluciones producidas en los procesos de lixiviación estática y con agitación puede tratarse en una instalación de concentración por cambio de ion con objeto de dar una solución limpia, de alta concentración, que por precipitación da lugar a unos concentrados de elevado contenido en U_3O_8.

M. ROUBAULT (Francia): Deseo resaltar la gran importancia que debe atribuirse a la investigación tal como ha sido descrita en la memoria presentada por el Dr. Gabelman. En la actualidad, la prospección práctica se efectúa principalmente por el método directo, empleando contadores. Este método ha permitido evaluar el orden de magnitud del tonelaje que puede razonablemente anticiparse en el mundo, aun considerando las regiones en las que aun no se ha llevado a cabo la prospección. Ahora bien, si se consideran las cifras dadas, estas cantidades, aunque elevadas, pueden, un día, ser insuficientes. Esto prueba que deben hacerse esfuerzos para alcanzar yacimientos más profundos de los que no existe indicación superficial. Solamente podemos alcanzar estos yacimientos teniendo en cuenta consideraciones generales, geológicas y químicas, basadas en una investigación científica fundamental. Esta investigación es, por esta razón, indispensable si, en un futuro próximo, han de determinarse las regiones en las que han de llevarse a cabo los sondeos como en el caso de petróleo, basados en estructuras y no solamente por la presencia de trazas de depósitos de mineral.

Como acertadamente indicó el Dr. Mabile en el documento P/72 *, uno de los principales logros de la actual Conferencia debe ser llamar la atención sobre la magnitud del problema que plantea una demanda de uranio cada vez mayor. Pienso que ello contribuirá a que nos formemos una idea de la necesidad de mejorar considerablemente los métodos que han de adoptarse en el trabajo de prospección e investigación.

Documento P/450 (presentado por E. Szabó)

DISCUSIÓN

P. MAGET (Francia): Me gustaría saber si los aparatos de clasificación radiométricos descritos en la memoria han sido empleados en la industria.

E. SZABÓ (Hungría): Los aparatos de concentración radiométrica de minerales no han sido aun empleados industrialmente y por ello no disponemos de datos técnicos precisos en relación con su aplicación industrial.

S. TĂTARU (Rumanía): Al llevar a cabo experimentos análogos a los descritos por Vd. en relaciòn con la separación de minerales por flotación con la posterior lixiviación de los productos de flotación en una instalación ácida o alcalina, hemos encontrado que los reactivos de flotación tienen un efecto negativo sobre las posteriores fases del proceso**, debido principalmente a que dichos reactivos son absorbidos por los cambiadores de ion***. Yo quisiera saber si la cantidad residual del reactivo de flotación no dificulta la absorción y la lixiviación del uranio en una instalación alcalina.

E. SZABÓ (Hungría): Hemos observado, también, un fenómeno análogo, pero la disminución en la capacidad de la resina de cambio de ion no fue lo bastante acusada para tener un efecto significativo en la aplicabilidad del método.

Documento P/464 (presentado por R. E. Robinson)

DISCUSIÓN

A. M. SEDOV (URSS): ?Cuál es el porcentaje de uranio arrastrado del lecho fluidizado y cuál es el coeficiente de descontaminación en el ciclón?

Quisiera saber también si se produce algún depósito de FNH_4 sobre las superficies de las conducciones y cuál es la longitad de éstas desde el aparato al condensador, en la instalación experimental.

R. E. ROBINSON (Sudáfrica): La cantidad de uranio arrastrado desde el lecho fluidizado depende, en gran parte, del tamaño de las partículas del material. Puede variar aproximadamente entre el 10 y el 40 %. El 90 % aproximadamente de esta cantidad es devuelta al lecho por el ciclón.

En cuanto a su segunda pregunta existe muy pequeño o ningún depósito de material en las conducciones, puesto que éstas se mantienen a una temperatura superior al punto de condensación del fluoruro amónico. La longitud de las conducciones es solamente de algunos metros.

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* Este volumen, sesión 2.11.

** Plaksin, I. N., y Tătaru, S., *Revista Minelor*, *6* (1962); Tătaru, S., *Revista Minelor*, *6* (1963).

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Session 2.10

ISOTOPE SEPARATION

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Enseignements tirés des études et réalisations françaises relatives à la séparation des isotopes de l'uranium

par C. Fréjacques et R. Galley *

La séparation des isotopes de l'uranium a continué à faire l'objet en France d'études théoriques et appliquées nombreuses, nécessitées par la construction de l'usine de Pierrelatte, donc consacrées essentiellement à la diffusion gazeuse. Parallèlement un certain nombre d'autres procédés étaient examinés, et en particulier des prototypes de centrifugeuses à gaz étaient étudiés et construits. Après un rappel rapide des réalisations déjà effectuées, et en nous basant sur l'expérience de la construction des usines de Pierrelatte, nous donnerons l'évaluation économique des différents paramètres du coût d'une usine de diffusion gazeuse produisant de l'uranium enrichi à 0,9 % ou à 3 % en fonction de sa taille, et nous la comparerons sommairement à une usine utilisant la centrifugation gazeuse.

DIFFUSION GAZEUSE

Depuis la Conférence de Genève de 1958, la construction d'une usine de diffusion gazeuse dans la vallée du Rhône, à Pierrelatte, a été entreprise et partiellement réalisée. La maîtrise d'œuvre est assurée par le Commissariat à l'énergie atomique, qui effectue également les études de base en laboratoire. L'industrie privée joue un rôle essentiel par l'intermédiaire de la Société de recherches techniques et industrielles (SRTI), société de procédé qui effectue en particulier l'expérimentation des matériels industriels, et par la société chargée de la construction des usines de Pierrelatte, dite USSI.

A la mi-1959, l'avant-projet était établi. Début 1960, les travaux de génie civil commencent, et chaque année voit s'ouvrir un nouveau chantier : début 1961, celui de l'usine basse; mi-1962, celui de l'usine moyenne; mi-1963, celui de l'usine haute; mi-1964, celui de l'usine très haute.

Fin 1962, un pilote de huit étages, dont le matériel est identique à celui utilisé dans l'usine basse, est mis en hexafluorure d'uranium (UF_6); il tourne sans interruption depuis cette date, sans variation de la perméabilité des diffuseurs, sans variation du coefficient d'enrichissement et sans remplacement de matériel, procurant ainsi une assurance sur la marche en durée de l'usine basse. Enfin, au printemps 1964, l'usine basse elle-même démarre.

L'enseignement le plus important pour la production d'énergie électrique nucléaire que l'on puisse tirer de ces réalisations concerne les coûts d'enrichissement de l'uranium en fonction des différents paramètres qui le définissent. En effet, en dehors du barème officiel américain [1, 2] dont la décomposition et les bases ne sont pas connues, aucune donnée économique détaillée en provenance des pays ayant une expérience industrielle de la diffusion gazeuse n'a été publiée.

Connaissant les coûts d'investissements des différentes usines de Pierrelatte, auxquelles correspondent des dimensions d'étages très différentes, il est possible d'en déduire une loi d'extrapolation empirique des frais fixes en fonction de la puissance de séparation d'un étage unitaire; les améliorations que l'on sait pouvoir réaliser pour une usine de deuxième génération permettent alors de définir la valeur des coûts correspondant à un étage de dimension donnée. En se donnant le prix du courant électrique et de l'hexafluorure d'uranium naturel, il est alors possible d'optimiser une cascade carrée alimentée par un certain débit d'hexafluorure d'uranium — variant de 5 000 t/an à 20 000 t/an — et produisant de l'uranium enrichi soit à 0,9 %, soit à 3 %.

L'optimisation se fait en deux temps : à partir de la loi du prix de fonctionnement de l'étage, on optimise d'abord le débit d'étage en rendant minimal le coût de l'unité de puissance de séparation de l'usine, pour la production considérée et pour une teneur de rejet donnée. Dans un deuxième temps, cette teneur de rejet est optimisée de manière à réaliser un compromis entre le prix de la séparation et celui de l'alimentation [3, 4].

Données de base

Des différentes contributions au prix de l'uranium enrichi : *a*) frais d'alimentation, UF_6 naturel; *b*) frais d'électricité; *c*) amortissement du capital investi; *d*) entretien; *e*) main-d'œuvre, les trois dernières sont regroupées pour le calcul d'optimisation sous la seule expression « frais fixes » et redécomposées ensuite.

Frais d'alimentation

Le prix de UF_6 naturel pris pour l'optimisation est de 80 F/kg, correspondant à un prix du concentré U_3O_8 de 8 \$/lb, et à un prix de transformation U_3O_8

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* Commissariat à l'énergie atomique.

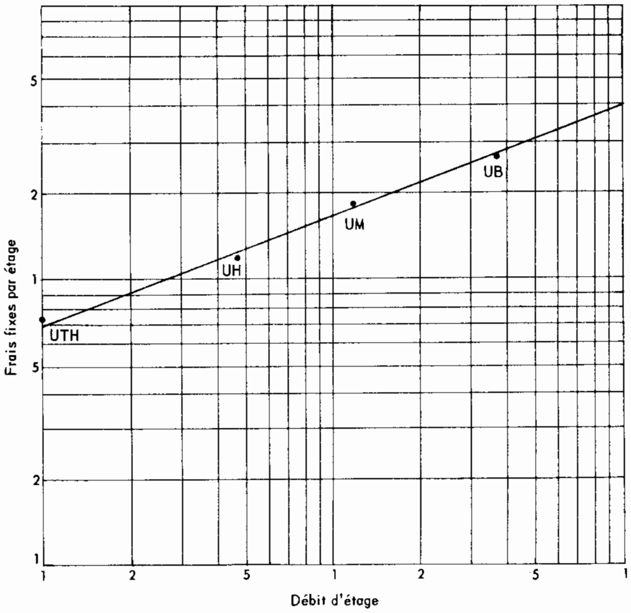

Figure 1. Loi d'extrapolation des frais fixes par étage

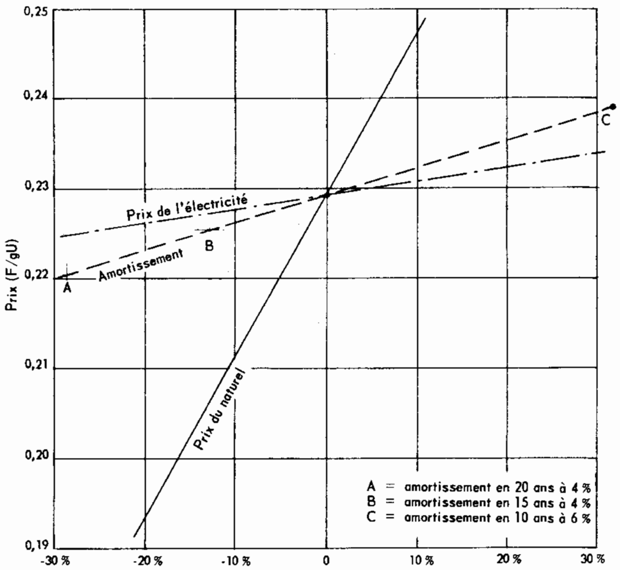

Figure 4. Sensibilité du prix aux variations des paramètres économiques

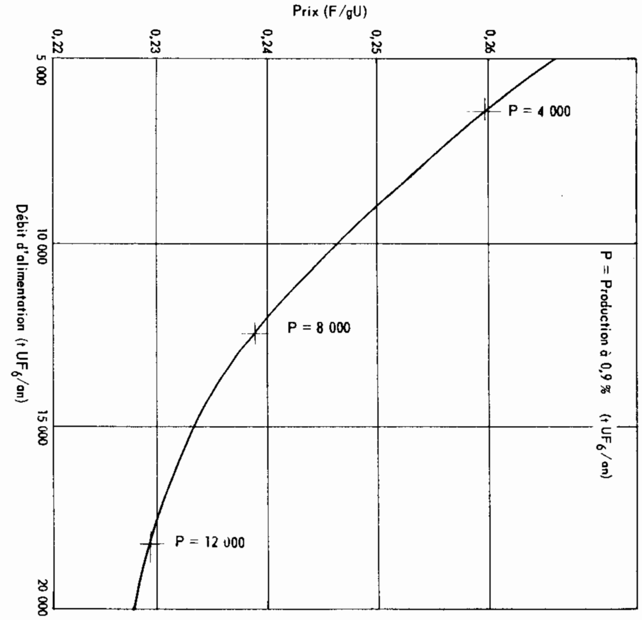

Figure 2. Prix de l'uranium enrichi à 0,9 %

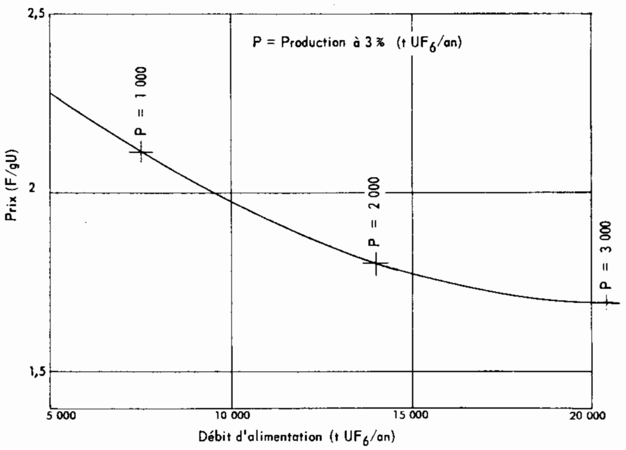

Figure 5. Prix de l'uranium enrichi à 3 %

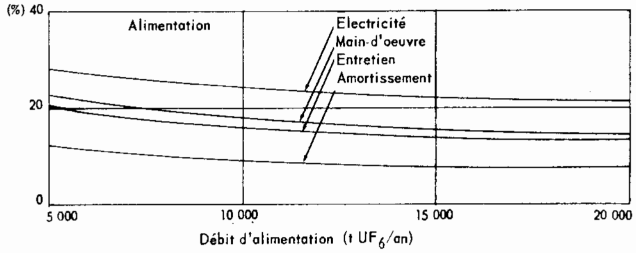

Figure 3. Décomposition du prix de l'uranium enrichi à 0,9 %

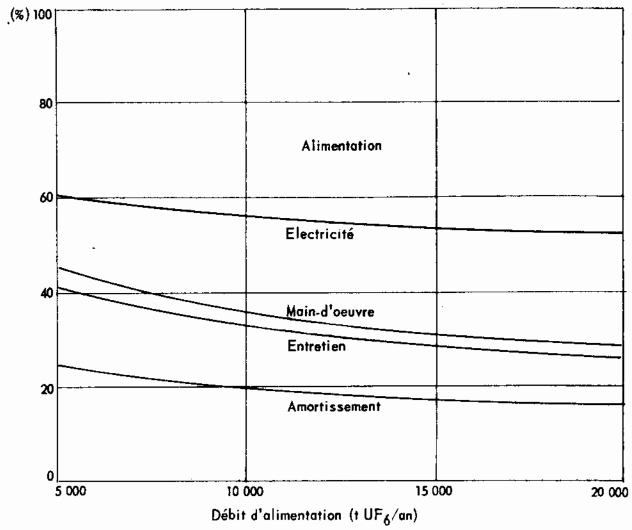

Figure 6. Décompositon du prix de l'uranium enrichi à 3 %

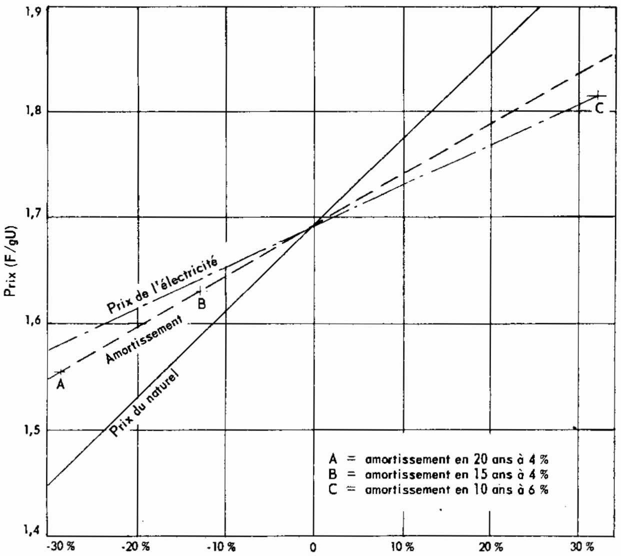

Figure 7. Sensibilité du prix aux variations des paramètres économiques

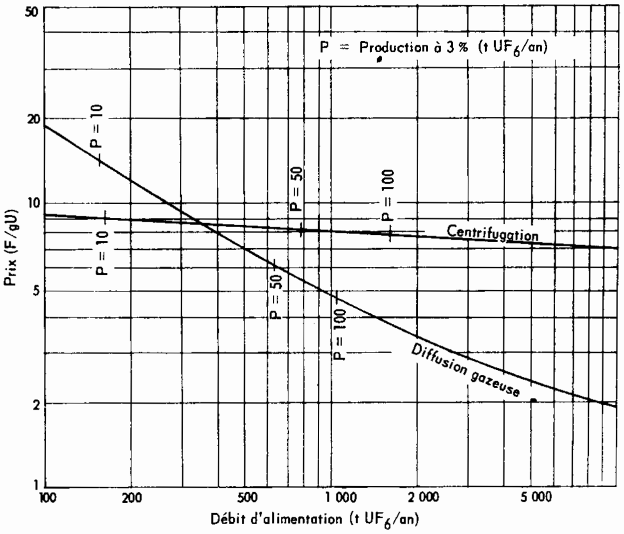

Figure 8. Prix comparés de l'uranium enrichi à 3 % par diffusion gazeuse et par ultracentrifugation

en UF_6 de 16 F/kg U qui pourrait être atteint en Europe pour les tonnages correspondant à cette étude.

Frais d'électricité

Le prix de l'électricité choisi est de 0,025 F/kWh, aux bornes des groupes motocompresseurs. Ce prix est déjà très inférieur au prix du tarif vert EDF, mais il est probablement une bonne base d'optimisation pour une usine européenne éventuelle.

Les consommations sont dues essentiellement aux groupes motocompresseurs, auxquelles s'ajoute un terme constant correspondant aux dépenses annexes (éclairage, pompes, etc.).

Si L est le débit d'étage en t/an, le coût de l'électricité rapporté à un étage et exprimé en F/an est donné par : $a_E = 0{,}214\,L + 3 \times 10^3$.

Frais fixes

Ils regroupent les trois postes main-d'œuvre, entretien, amortissement du capital investi.

La loi d'extrapolation en fonction du débit d'étage nous est donnée empiriquement par les points représentatifs des différentes usines de Pierrelatte.

On vérifie sur la figure 1 que la loi puissance : $a_I = KL^m$ est correctement vérifiée. La valeur du coefficient de puissance déduite de la pente de la droite correspondante est $m = 0{,}38$. C'est une valeur faible qui nous a nous-mêmes surpris : elle est due au fait que de nombreux frais fixes sont liés beaucoup plus au nombre d'étages qu'à la taille, et que le prix de la chaudronnerie croît beaucoup moins vite sur le débit traversant un étage. Ce coefficient est la raison essentielle de l'intérêt des très grosses usines.

L'amortissement choisi pour l'optimisation est un amortissement en 15 ans avec un intérêt de 6 %.

Les frais fixes rapportés à un étage en F/an sont alors donnés en fonction du débit d'étage L en t/an par : $a_I = 3{,}8 \times 10^3\,L^{0{,}38}$

Résultats de l'optimisation

Ils sont fournis dans les figures 2 à 7 qui donnent, pour des usines optimisées pour produire de l'uranium enrichi respectivement à 0,9 % (taux de rejet = 0,35 %) et à 3 % (taux de rejet = 0,32 %) :

Figures 2 et 5 : le coût de cet uranium en fonction du tonnage annuel d'alimentation, c'est-à-dire en fonction de la taille de l'usine;

Figures 3 et 6 : les pourcentages des coûts respectifs de l'alimentation, de l'électricité, de la main-d'œuvre, de l'entretien et de l'amortissement;

Figures 4 et 7 : les variations de ces coûts, pour des variations relatives des prix de UF_6 naturel, du kilowatt/heure, ou des frais fixes, en particulier pour d'autres conditions d'amortissement.

CENTRIFUGATION

Nous avons été amenés à développer des prototypes de centrifugeuses à gaz de différentes dimensions. La machine qui nous semble actuellement la meilleure est une centrifugeuse fonctionnant à contre-courant, de longueur 1,25 m et de diamètre 0,22 m. Les bases de comparaison avec la diffusion gazeuse sont alors les suivantes : vitesse périphérique, 360 m/s; consommation électrique, 2 kW; investissements totaux avec les annexes et rapportés à une centrifugeuse, 50 000 F.

Ces deux dernières valeurs paraîtront élevées par rapport aux estimations données par d'autres auteurs, mais la marche de très longue durée en UF_6 nécessite des tolérances de jeux aux paliers très faibles pour permettre la réalisation des dispositifs d'étanchéité convenables, et ceci se paye en consommation et en coût de la machine.

Sur les mêmes bases d'amortissement et de prix du kWh que pour la diffusion gazeuse, et compte tenu d'une baisse du prix des centrifugeuses pour les très grandes séries, nous donnons dans la figure 8 une comparaison des coûts de l'uranium enrichi à 3 % par les deux procédés, en fonction de la taille de l'installation. Les prix décroissent plus vite avec la taille pour le procédé de diffusion gazeuse, le point de croisement se situant pour une alimentation de 350 t/an environ.

CONCLUSION

Le procédé de diffusion gazeuse est le procédé le plus intéressant pour les productions importantes d'uranium faiblement enrichi. Le prix des produits obtenus diminue fortement avec la taille de l'installation. Les utilisateurs d'uranium enrichi pour réacteurs doivent savoir qu'il n'est pas possible d'aboutir à des prix économiques pour des usines de diffusion gazeuse traitant moins de 10 000 t/an d'hexafluorure d'uranium, c'est-à-dire correspondant à des programmes de puissance installée annuellement d'environ 4 000 MW(e).

Avec des conditions d'amortissement normales, et avec un prix du kWh de 2 centimes, même pour de très grandes productions, il semble difficile à une usine européenne de diffusion gazeuse d'aboutir à un coût du gramme supplémentaire d'uranium 235 inférieur à celui du barème américain, majoré de 30 %.

⁂

Les résultats contenus dans ce mémoire sont le fruit d'un travail d'équipe. Les contributions de C. Chidaine, J. Dixmier, J.-C. Guais, L. Guillaume, R. Jacques, C. Leduc, J.-C. Martin, D. Massignon, M. Pecqueur, J. Pauli, et P. Plurien ont été particulièrement importantes.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/89 France

Information derived from French studies and achievements in the field of uranium isotope separation

By C. Fréjacques and R. Galley

The work carried out in the field of uranium isotope separation, by gaseous diffusion and by ultracentrifugation, is reviewed. An economic estimate of the various parameters involved in the cost is given, and it is shown that only very large gaseous diffusion plants, corresponding to a programme of enriched uranium reactors of at least 4 000 MW(e) to be installed yearly, can give an economically acceptable enriched uranium production.

A/89 Франция

Данные, полученные на основании исследований и проведения работ по разделению изотопов урана во Франции

К. Фрежак и Р. Галли

Приводится обзор работ, проведенных в области разделения изотопов урана методом газовой диффузии и ультрацентрифугирования. Приводится экономическая оценка различных параметров, влияющих на стоимость, и доказывается, что только на очень крупных газодиффузионных заводах, соответствующих программе пуска реакторов, работающих на обогащенном уране и производящих дополнительно 4000 *Мвт* (эл.) в год, можно достичь экономически приемлемого производства обогащенного урана.

A/89 Francia

Enseñanzas deducidas de las realizaciones y estudios franceses relativos a la separación de los isótopos del uranio

por C. Fréjacques y R. Galley

En la memoria se examinan las realizaciones en materia de separación de isótopos del uranio por difusión gaseosa y por ultracentrifugación. Se presenta una evaluación de carácter económico de los diferentes parámetros que intervienen en los costos y se demuestra que solamente las instalaciones de difusión gaseosa en escala muy grande, que corresponden a un programa de instalación de nuevos reactores de uranio enriquecido a razón de 4 000 MW(e) por año, como mínimo, pueden conducir a producciones de uranio enriquecido en condiciones rentables.

Production of heavy water in the United States of America

By W. P. Bebbington,* J. F. Proctor,* W. C. Scotten* and V. R. Thayer**

Most of the world's supply of heavy water (D_2O) has come from plants in North America built and operated for the United States Government. Despite continued research and development, no more economical processes have been found than those conceived in the period 1940-1943 in the laboratories of Columbia University under the direction of H. C. Urey, the discoverer of deuterium. In 1943, dual-temperature exchange of deuterium between water and hydrogen sulfide gas was recognized as being potentially the most economical process. This conclusion was evidently also reached independently by workers in other countries at about the same time.

The early history of the development of heavy water processes in the United States of America has been described by Murphy *et al.* [1]. Plants in the United States and their operation have been described by Bebbington and Thayer [2], Morris and Scotten [3], and Thayer and DeLong [4]. The most comprehensive worldwide report of the present state of the technology was presented by Becker [5]. During the past five years, many of the world's experts in heavy water development have visited the Savannah River plant (SRP), near Aiken, South Carolina.

Research to find chemical or physical principles that would form the basis for separation of deuterium or its compounds from ordinary hydrogen or its compounds was given high priority at Columbia and other universities in the United States about 1940, when it was realized that D_2O might be the only feasible moderator for nuclear reactors to make plutonium. Before commercial production of D_2O was begun, however, the graphite-moderated reactor at Chicago had operated and D_2O was relegated to a supporting role as the moderator for the second generation of nuclear reactors.

Water distillation and electrolysis were chosen for the wartime production of heavy water because they were certain to succeed and required no scarce materials of construction. The Columbia group and the Du Pont engineers who designed the wartime plants believed that stainless steel would be the only satisfactory material of construction for the H_2S process; the quantities required would have been prohibitive. After contemplating the building of a small demonstration plant, they set the dual-temperature process aside.

In 1950, the US Atomic Energy Commission (AEC) asked Du Pont to build a large new plant to produce plutonium and tritium in heavy-water moderated reactors. Dual-temperature exchange with H_2S was still the most economical heavy water process. DeLong and his co-workers defined the conditions under which carbon steel could be used for the piping, towers and other large vessels of the plant [4]. Babcock conceived the extremely effective comparison of mid-column concentrations as an effective basis for process control [6]. A logical chemical engineering embodiment of the process was applied to a pilot plant and a production unit by engineers of the Girdler Company. Spevack, a member of Urey's group at Columbia and later a consultant for the AEC, participated in both phases of process development. He is cited as the inventor in the US Government's basic patent [7]. He holds another patent on certain aspects of the heat recovery system [8].

Two plants were built, the Dana plant near Terre Haute, Indiana, and the heavy-water facility at SRP. These plants provided the moderator for the five production reactors at SRP and subsequently have filled most of the world's heavy-water-moderated research and power reactors. The future of heavy water now depends upon the success of these latter reactors in the competition to achieve lowest-cost nuclear power. Controlled nuclear fusion could put D_2O in a uniquely important position as a source of the world's power.

The two plants in the United States tremendously increased the world's supply of pure D_2O during the years 1953-1957. For the past several years, the production from SRP has been little more than sufficient to satisfy the needs of power and research reactor programs. The history of production and use is shown in Fig. 1.

Heavy water from the plants in the United States is now used in fifteen foreign countries as is shown in Table 1.

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* E. I. du Pont de Nemours & Co., Savannah River Plant, Aiken, South Carolina.

** E. I. du Pont de Nemours & Co., Atomic Energy Division, Wilmington, Delaware.

Table 1. Tons[a] of heavy water exported
(up to 31 December, 1963)

Canada	276	Norway	25
Germany	132	Switzerland	23
France	70	Denmark	17
United Kingdom	66	Australia	13
Sweden	57	Italy	10
Japan	48	Israel	4.4
India	36	Netherlands	1.6
Euratom	28	Belgium	0.25

[a] 1 ton = 907.2 kilograms.

There are no large commercial uses for D_2O other than as a moderator. Deuterium, when substituted for ordinary hydrogen in organic compounds, including plastics and synthetic fibers, causes some interesting changes in properties, but at any present or foreseen cost, such uses of deuterium cannot be justified. As a tracer, deuterium is relatively cheap, safe and easily detected. It is an important aid to researchers in biology, chemistry and hydrology.

OPERATION (1959-1963)

Operating history and status

During the period 1957-1958, the Dana Plant was shut down permanently, and at SRP two-thirds of the H_2S - exchange (GS process) units were placed in a standby condition, operation of the electrolytic final concentration (E process) was discontinued, and nearly half of the water distillation (DW process) was diverted to the reconcentration of diluted heavy water. The present situation is summarized in Fig. 2.

Process performance and costs

Emphasis at SRP is now on minimum cost of D_2O per pound. The major process variables that affect production and cost are given in Table 2.

Table 2

Variable	Effect on production rate
Liquid-to-gas flow ratio, ± 1½% deviation from optimum	1% Decrease
Cold tower temperature, 1 °C decrease	1½% Increase
Hot tower temperature, 1 °C increase	1% Increase
Gas flow rate	Directly proportional
Gas quality (% H_2S)	Directly proportional
Gas pressure 15 psi increase (exclusive of the effect on gas flow)	1% Increase

Hot tower temperature, gas flow rate and gas pressure are interrelated in their effects on production and cost. The pressure in the steam supply headers is limited to the safe operating pressure of the GS process towers. Thus while an increase in H_2S pressure increases the mass rate of gas flow produced by the gas blowers, it also decreases the attainable hot tower temperature by decreasing the pressure differential available for steam input. Because two major costs are for steam to heat the towers and electricity to drive the gas blowers, the minimum unit cost occurs at the pressure that is the best compromise between high gas flow and high hot tower temperature. This in indicated in Fig. 3.

Process efficiency

The concentration of D_2O in effluent waste water from the GS process would be the best continuous indication of efficiency. To date, however, routine analytical methods have not been sufficiently precise to make this a useful criterion. A number of samples of waste water from SRP have been analysed by Nief at the Centre d'études nucléaires de Saclay with precision sufficient to calculate the yield of heavy water to within ± 2%. A mass spectrometer at SRP is being modified to achieve the precision and sensitivity that Nief demonstrated.

At present the calculated effects of all process variables are combined into a performance index as a measure of day-to-day operating efficiency. The performance index is a function of operating time, first stage gas flow and hot and cold tower temperatures, first and second stage mid-column concentration ratios, H_2S quality and DW process performance. Poor DW process performance causes an increase in the product concentration of the GS process; an increase from 10% to 20% D_2O causes about a 5% loss in GS production.

Process changes

The installation of a line to by-pass a portion of the process steam around the waste stripper and thereby to reduce the restriction to steam flow into the unit is the only major process change that has been made at SRP in the last five years. These steam by-passes increased the GS unit pressure by 10 psi, increased production by 5%, and decreased the unit cost by $0.80 per pound D_2O.

Mechanical performance

From 1959 to the end of 1962 the GS units operated 96.2% of the time. Half of the shut down time was for scheduled annual overhaul and safety inspection, and half was for emergency repair. In 1963, the frequency of unit overhauls was decreased to once every two years; average operating time for 1963 was 98.6%.

The only major line rupture in six years' operation at Dana and eleven years' operation at SRP occurred in 1960 at SRP. The screwed joint of a flange to the 16-inch slip tube of the first-stage gas cooler parted,

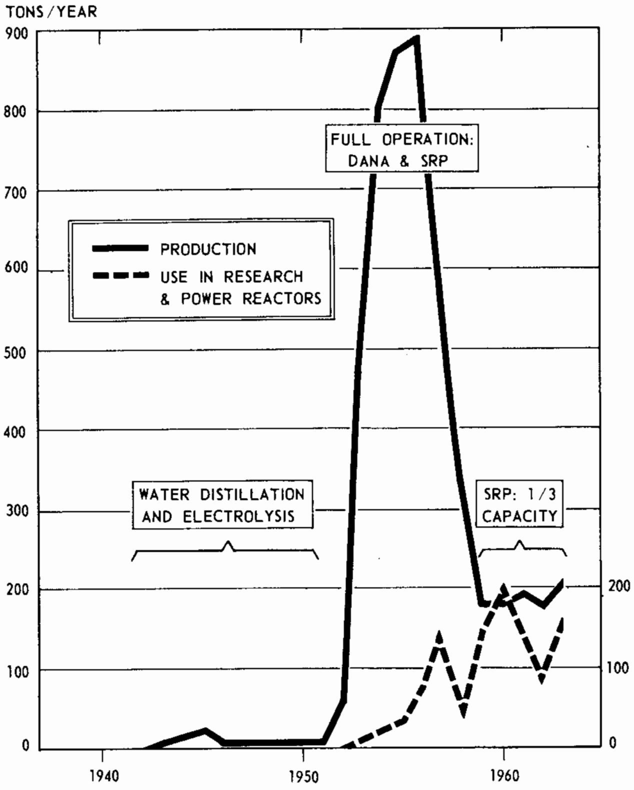

Figure 1. Production and use of heavy water

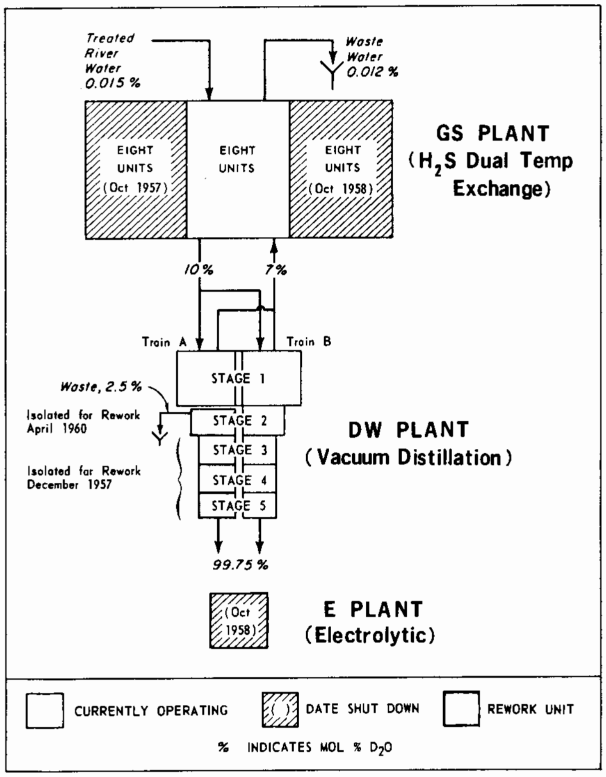

Figure 2. Operating status of heavy water facilities at SRP

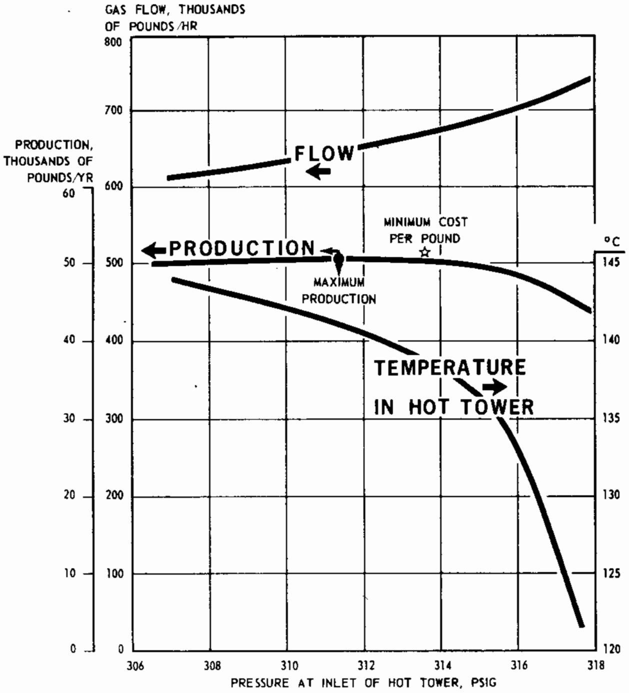

Figure 3. Operating characteristics of a GS unit at SRP

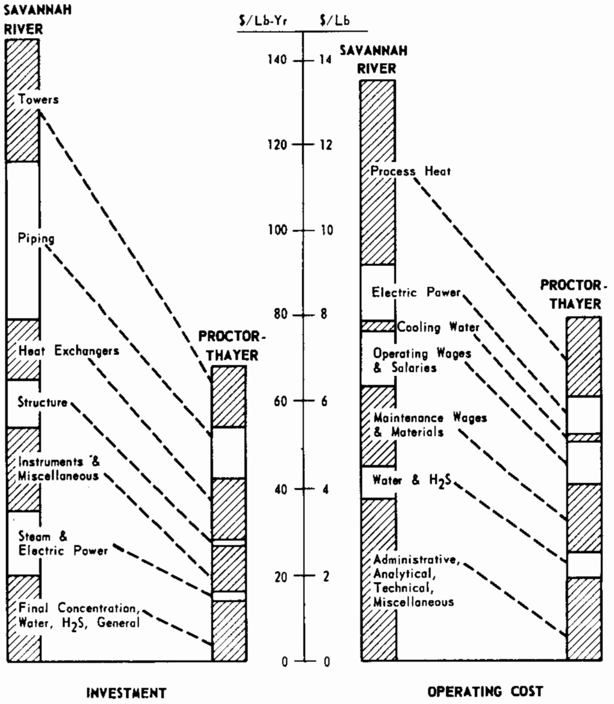

Figure 4. Economic comparisons of present plant with Proctor-Thayer design

and in 20 minutes, 46 tons of H_2S burned. The heat carried the gases up above the surrounding towers where winds dissipated the fumes; the odor of H_2S was barely detectable at ground level. Rector found that poorly-machined threads and warping of the flange by the normal bolt load caused the failure [9]. All 16-inch and 12-inch screwed flanges have been replaced with welded flanges.

Corrosion

96 of the 144 GS towers at SRP were lined with stainless steel in an effort to insure long life. The stainless lining was specified before the resistance of carbon steel to H_2S had been proved; the lining has not only proved to be unnecessary, but has caused serious weakening of the walls of some towers. Welds joining stainless steel lining sheets to each other and to the carbon-steel wall of the tower have cracked, thus reducing the effective thickness of the tower wall by as much as 0.28 inch. The remaining 48 towers and other unlined process vessels and piping have not been seriously corroded.

Some of the towers have been weakened by external corrosion as deeply as 0.19 inch. They have been attacked by chemicals that were leached by rain from the cellular glass insulation. In August 1963, when the seriousness of this corrosion was realized, nominal operating pressure was reduced from 325 psig to 260 psig until the exact condition of each tower could be determined. Additional relief valves for direct protection of the weakest towers will permit return to full pressure.

Heat exchangers in the GS process have corroded in unexpected ways:

(*a*) Upon leaking into the cooling water, H_2S is oxidized to sulfur which provides food for the growth of a bacterial slime; the slime produces sulfuric acid which attacks the tubes. More than 21% of 71 000 tubes in the water-cooled exchangers failed. Elimination of H_2S leaks has almost completely stopped this corrosion.

(*b*) Corrosion of the carbon-steel shells of the exchangers by river water continues to be a problem. Two types of sprayed-on organic coatings are being tested.

(*c*) In the gas coolers of the heat-recovery system, chloride bearing solids in the circulating liquid have precipitated on the outsides of vertical tubes at the vapor-liquid interface near the tops of the shells. These deposits have caused pitting and stress-corrosion cracking of the type 316 stainless steel tubes. During 1962, 3% of 15 000 tubes inspected were corroded enough to warrant replacement. No completely effective remedy has been found.

(*d*) In liquid-liquid heat exchangers, waste water, which has been stripped free of H_2S, leaks past the shell side baffles of the tube bundles and cuts narrow bands into the shells. This stripped waste causes severe corrosion wherever there is high turbulence.

Diligence is required to insure that all bolts that may be exposed to H_2S are below the maximum stress and hardness defined by DeLong [4]. AISI 4140 steel, the standard material for high-quality bolts in the United States, will crack when exposed to H_2S unless softened by special heat treatment. Springs in relief valves are also vulnerable to H_2S stress-corrosion cracking but can be protected by stainless steel bellows.

The Dana Plant towers and one-third of the SRP towers had bubble-cap trays of AISI 410 stainless steel which corroded almost completely away in about 5 years; the iron precipitated as iron sulfide in the tubes of waste liquid heaters. The resultant plugging of tubes was essentially eliminated at Dana by injecting sodium hydrosulfide into the feedwater to raise the pH and suppress the solubility of iron.

Bubble caps trays of AISI 304 stainless steel in the remaining two-thirds of the SRP towers show only minor pitting and metal loss after 12 years of operation.

Safety

As the result of the comprehensive and meticulous safety program at SRP, there have been no deaths or serious injuries caused directly by exposure to H_2S.

In the GS units two men always work together, staying far enough from one another so that both cannot be exposed simultaneously to a high H_2S concentration. If one member should be overcome, the other can rescue his partner.

Face masks or mouthpieces with pure air supplied from pressure cylinders are widely used. For escape from an H_2S-contaminated area, a cylinder containing a 3-minute supply of breathing air is carried by everyone. Where release of some H_2S may be expected, face masks and cylinders with 15 or 30-minute air supplies are used.

Emergency masks with 15-minute supplies are available for rescue purposes at many locations in the process area. Help can be summoned to any of these stations merely by pressing a button which sounds an alarm and identifies the location in the control room.

Air from the control room and from several points in the process area is continuously monitored for H_2S.

Reconcentration of heavy water

The four vacuum distillation towers that were isolated from the DW process in 1957 and 1960 for reconcentration of heavy water are as trouble-free as the DW process itself. The Rework Unit, as it is called, produces 99.75 mol % D_2O and discards waste to the river at a maximum concentration of

2.5 mol % D_2O.* Because the four towers do not have enough trays to span the entire concentration range from product to waste, the product and waste fractions are obtained separately from alternating product and waste campaigns, each lasting several months.

The concept of separative work, developed from the cascade theory by Cohen and Kaplan [10, 11], is used to assess the performance of the Rework Unit and is the basis for the charge for reconcentrating degraded heavy water of various concentrations [12]. The present schedule of charges is given in Table 3.

Table 3. Charges for reconcentrating heavy water
(effective September 1963)

Wt% D_2O	\$ per lb	Wt% D_2O	\$ per lb
10	11.10	70	2.25
20	6.95	80	1.80
30	5.15	90	1.30
40	3.75	95	1.00
50	3.30	99	0.40
60	2.75	99.5	0.20

This schedule is based on the current heavy water price of \$24.50 per pound and is subject to change. The charge is for the return to the customer of one pound of 99.75% D_2O for each pound of D_2O received.

The rework facilities at SRP will remove limited quantities of some chemical impurities. Purification costs are not included in Table 3.

THE FUTURE COST OF HEAVY WATER

New processes

The present AEC price for heavy water is \$24.50 per pound. The production cost at SRP, exclusive of depreciation or other capital charges, is \$13.50 per pound; the unit investment in the plant is \$145.00 per pound-year. These high costs of heavy water have provided abundant incentive to search for lower-cost processes. Barr and Drews have suggested that some completely new principles be tested [13]. Catalytic exchange of deuterium between hydrogen gas and liquid ammonia has been evaluated in the United States and France. Exchange between hydrogen gas and liquid water remains tantalizingly promising, with the lack of an economically feasible catalyst for liquid-phase exchange and the low solubility of hydrogen in water as obstacles to its success. Distillation of liquid hydrogen, the method by which Urey first concentrated deuterium, has been applied on pilot plant or moderate commercial scale in France, Germany, Switzerland and India. Other exchange reactions, including some of those first tested by Urey's group in 1943, and a variety of physical methods including fractional crystallization have been proposed. Of all these, only hydrogen distillation and ammonia-hydrogen exchange have reached the stages of design or operation of plants, and they are competitive with the GS Process only when operated as adjuncts to large-scale production of hydrogen or of ammonia or methanol gas synthesis. About 25 tons of D_2O per year might be produced from deuterium that could be separated by distillation from 50 tons of liquid hydrogen per day, an amount equivalent to about 280 tons of synthetic ammonia per day. Operation of the hydrogen distillation plant complicates and restricts the operation of the hydrogen plant.

Improvements in the GS process

Proctor and Thayer have shown that the cost of heavy water by the GS process can be reduced greatly by optimum design of the plant and by use of cheap fuel [14]. This is the only known approach that is certain to provide unlimited quantities of heavy water at much less than the present cost. The use of cheap fuel at a remote location to make heavy water provides an interesting possibility for the upgrading of a natural resource.

Operating expenses and capital charges are both large parts of the total cost of heavy water; to substantially reduce that cost, both the plant investment and the utilities and labor requirements must be attacked. Proctor and Thayer sought to eliminate from the GS process as much auxiliary equipment as possible and to use the essential hot and cold towers with maximum effectiveness. At the same time they designed for the direct application of the energy of low-cost fuel.

The effect of fuel and its cost. At SRP, coal costs \$7.35 per ton, almost half of which is for shipment by railroad from mine to powerhouse. The cost of 10^6 Btu delivered as steam to the process is \$0.36. Natural gas, even from some highly-developed fields in the United States, can be obtained for 0.15 to \$0.20 per 1000 cubic feet. The cost of 10^6 Btu delivered directly to the process by gas-fired heaters is estimated to be \$0.20 to \$0.25. Gas turbines can provide power for gas circulators, with heat recovery from the exhaust gases in process heaters, at an over-all thermal efficiency of 70 to 75 per cent.

Plant simplification. The Dana and SRP designs were two slightly different versions of one of many possible chemical engineering designs for the GS process. Both had large numbers of towers and heat

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* This dilute material is discarded because it always contains tritium which would contaminate the heavy water in the production plant. The value of the D_2O discarded is included in the cost of reconcentration; the cost could be reduced by adding another tower to the Rework Unit.

exchangers and complex interconnecting piping and valves. Proctor and Thayer propose 17 foot diameter towers, instead of the maximum of 12 foot at SRP, and the use of direct heat exchange between gas and liquid wherever possible. Their plant would have three stages instead of the five at Dana and two at SRP.

At SRP, the largest heat exchangers are for cooling gas from the hot towers by indirect exchange with water. Gas from the cold towers is heated by direct exchange in a section of ten trays at the bottom of each first-stage hot tower. Proctor and Thayer would eliminate the large gas-liquid heat exchangers by providing a direct cooling section in the bottoms of the cold towers.

These proposals would decrease the pressure drop, reduce the number of towers by 80%, and require much less piping, structural steel, and fewer operating controls. The efficiency of heat recovery is less than might be attained with indirect exchange, but with low-cost fuel the effect of this is small. A comparison of the Proctor-Thayer proposal with the situation at Savannah River is shown in Fig. 4.

Equipment and materials. Perforated stainless steel plates were installed at Dana to replace corroded AISI 410 stainless steel bubble-cap trays. The new plates were less expensive, had a higher capacity and lower pressure drop, and were more efficient. Perforated trays would be used in any new GS plant, with corollary benefits of lower energy costs for gas circulation.

Carbon steel would be used for the towers, heat exchanger shells, tanks, and piping. Thick plate for the larger diameter vessels would be carefully selected and inspected by methods similar to those used for Dana and SRP [4]. Stainless steel would be used only in regions of high velocity or turbulence namely for perforated plates, heat exchanger tubes, control valves, liquid pumps, and at a few other points of severe turbulence. Stainless steel would not be widely used as a lining for carbon steel.

The 17-foot towers proposed by Proctor and Thayer might be fabricated most cheaply at the site of the heavy water plant; larger towers than these would probably have to be fabricated on site.

Personnel. The consolidation of the GS Process into an integrated plant with its own energy supply, together with the process simplification, would permit a 50% reduction in operating and maintenance forces.

Final concentration. Vacuum distillation of water is still the best choice for concentrating heavy water from about 10 - 20 to 99.8%. The required equipment is inexpensive and dependable, and operation is extremely simple.

Analysis and control. The GS Process has proved stable and rather easy to control [3]. The original frequency of sampling and the number of mass spectrometers used have been greatly reduced. Infrared absorption spectrometry would probably be used at least for high D_2O concentrations in a new plant, with consequent lower cost of the instruments and their operation.

Automation or computer control of the critical flow ratios in the GS process have not been seriously considered. A method for continuous indication of mid-column concentrations might make such control methods feasible and attractive.

CONCLUSIONS

The Proctor-Thayer design is probably near-optimum for the situation that they assumed, and their cost of $8 per pound of D_2O and unit investment of $70 per pound-year appear to be attainable. Their study is most significant, however, in the attention it has brought to the controlling elements of D_2O cost; any new plant should be designed, with thorough attention to these elements, to make best use of resources of fuel and materials that are available where the plant can or must be erected. It should be remembered that heavy water is a valuable, readily-shipped commodity; the plant should probably be located near the source of the fuel.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/290 États-Unis d'Amérique

La production d'eau lourde aux États-Unis d'Amérique

par W. P. Bebbington *et al.*

Aux États-Unis, l'eau lourde est produite à l'installation de Savannah River, en Caroline du Sud, qui relève de la Commission de l'énergie atomique. La teneur de l'eau en D_2O naturel est normalement d'environ 0,015 %. On la concentre jusqu'à 10 à 20 % par échange à double température en présence de sulfure d'hydrogène gazeux, puis jusqu'à une concentration de 99,75 % par distillation sous vide. L'installation de Savannah River et l'installation jumelle de Dana (Indiana) ont été construites en 1950-1952 pour alimenter en modérateur-refroidisseur les cinq réacteurs de production de Savannah River. Après avoir fabriqué une quantité d'eau lourde permettant de remplir les réacteurs et de constituer une réserve suffisante, on a arrêté et démonté l'installation de Dana, et on a réduit la production à Savannah River. Depuis 1958, un tiers seulement des appareils produisant l'eau lourde à Savannah River sont en service; ils fonctionnent continuellement et d'une manière satisfaisante depuis plus de dix ans.

De 1959 à 1963, l'installation de Savannah River a produit 830 tonnes de D_2O à 99,75 %. Pendant cette période, elle en a fourni 700 tonnes pour des réacteurs de recherche et de puissance aux États-Unis et dans d'autres pays.

Toute augmentation appréciable de la demande d'eau lourde exigerait une augmentation de la production, soit à Savannah River, soit ailleurs. Le matériel actuellement à l'arrêt à Savannah River pourrait être remis en service et produire pratiquement à pleine capacité. Cet appoint serait suffisant pour remplir chaque année un réacteur de puissance d'environ 300 MW.

Dans l'état actuel des connaissances, l'échange à deux températures du deutérium entre l'eau et le sulfure d'hydrogène gazeux reste le procédé le plus rentable pour la fabrication de l'eau lourde dans des installations autonomes de taille non limitée. D'autres procédés peuvent le concurrencer lorsqu'il s'agit d'une production d'appoint dans des usines produisant de l'hydrogène ou des mélanges de gaz synthétiques pour la fabrication d'ammoniac ou d'alcool. Dix années d'expérience à l'usine de Savannah River ont permis d'envisager des perfectionnements et des simplifications qui réduiraient nettement le coût de l'eau lourde dans une installation nouvelle, en particulier si elle était placée à proximité d'une source de combustible à bon marché. Le prix actuel de l'eau lourde fixé par la CEA est de 24,50 dollars la livre. Le coût de la production, à Savannah River, sans tenir compte de l'amortissement et des autres charges financières, est de 13,50 dollars la livre; les frais d'investissement unitaire pour cette installation sont de 319 dollars par kilogramme-année. On pourrait ramener le coût de production à environ 18 dollars le kg et les frais d'investissement unitaire à 154 dollars par kilogramme-année dans une installation nouvelle d'une conception optimale située à un emplacement favorable.

Une partie de l'installation de distillation sous vide de Savannah River est actuellement utilisée pour la reconcentration de l'eau lourde qui a été diluée. Ce traitement de récupération est à la disposition de tous les utilisateurs d'eau lourde; le prix dépend de la concentration. Au cours des cinq dernières années, près de 200 tonnes d'eau lourde ont été renvoyées à Savannah River pour y subir ce traitement.

A/290 США

Производство тяжелой воды в США

У. П. Беббингтон *et al.*

Тяжелая вода производится в США на заводе КАЭ США в Саванна-Ривере, близ Эйкена, шт. Юж. Каролина. Тяжелая вода концентрируется из естественного содержания от 0,015% до 10—20% двухтемпературным обменом с сероводородом и затем до 99,75% перегонкой в вакууме. Завод тяжелой воды в Саванна-Ривере и подобный ему завод в Дане, шт. Индиана, были построены в 1950—1952 гг. для обеспечения потребностей в замедлителе и теплоносителе пяти промышленных реакторов в Саванна-Ривере. После того как достаточное количество тяжелой воды было произведено для первоначального наполнения реакторов и для достаточных резервов, завод в Дане был закрыт и демонтирован, а эксплуатация завода в Саванна-Ривере была сокращена. С 1958 года только одна треть агрегатов, добывающих тяжелую воду в Саванна-Ривере, находится в эксплуатации; эти агрегаты работают непрерывно и удовлетворительно уже более десяти лет.

С 1959 по 1963 год в Саванна-Ривере было произведено 920 *т* ($8{,}3 \cdot 10^5$ *кг*) 99,75%-ной D_2O. За это время 770 *т* было использовано для заполнения исследовательских и энергетических реакторов в США и других странах.

При любом значительном увеличении спроса

потребуется увеличение производства тяжелой воды в Саванна-Ривере или на другом заводе. Недействующие агрегаты в Саванна-Ривере могут быть восстановлены приблизительно в размере своей прежней мощности. Дополнительное количество тяжелой воды, полученное таким образом, будет достаточно для того, чтобы наполнить один энергетический реактор мощностью приблизительно в 300 *Мвт* в год.

Известно, что двухтемпературный обмен дейтерия между водой и сероводородом до сих пор является самым дешевым процессом производства тяжелой воды на самоокупаемых заводах неограниченного размера. Другие процессы могут оказаться более выгодными, когда они служат на заводах побочным методом производства водорода или смеси газов для синтеза аммиака и спирта. Опыт десятилетней эксплуатации завода в Саванна-Ривере указывает путь к улучшениям и упрощениям, которые могут значительно уменьшить стоимость тяжелой воды, производимой на новом заводе, особенно если этот завод расположен вблизи источников дешевого топлива. Нынешняя цена КАЭ на тяжелую воду составляет 54 *долл/кг*. Издержки производства на заводе в Саванна-Ривере, исключая амортизацию или другие расходы капитала, составляют 30 *долл/кг;* удельное капиталовложение на заводе достигает приблизительно 300 *долл/кг* в год. На новом заводе оптимальной производительности, расположенном в благоприятном районе, издержки производства составят, вероятно, около 17,5 *долл/кг*, удельное капиталовложение 154 *долл/кг* в год.

Часть установки для перегонки под вакуумом в Саванна-Ривере сейчас употребляется для повторного концентрирования разбавленной D_2O. Такое повторное концентрирование D_2O доступно всем потребителям тяжелой воды; стоимость зависит от концентрации D_2O. За последние 5 лет на завод в Саванна-Ривере было возвращено почти 200 *т* тяжелой воды для переработки.

A/290 Estados Unidos de América

La producción de agua pesada en los Estados Unidos

por W. P. Bebbington *et al.*

El agua pesada se produce en los Estados Unidos de América en Aiken (Carolina del Sur), en la instalación de Savannah River de la Comisión de Energía Atómica. El D_2O se concentra, por el método de intercambio bitérmico con sulfuro de hidrógeno gaseoso, hasta el 10 ó 20 % a partir del 0,015 % (abundancia natural) y se aumenta, después, hasta el 99,75 % por destilación en vacío. La fábrica de agua pesada de Savannah River y otra similar en Dana (Indiana) fueron construidas en 1950-1952 para suministrar moderador y refrigerante a los cinco reactores de producción de Savannah River. Cuando se hubo obtenido suficiente agua pesada para la primera carga de los reactores y para tener una reserva suficiente, se paró y desmontó la instalación de Dana y se redujo la producción en Savannah River, en la que desde 1958 no han trabajado más que un tercio de las unidades que han funcionado en forma continua y satisfactoria durante más de diez años.

Entre 1959 y 1963 se obtuvieron 920 t ($8,3 \times 10^5$ kg) de D_2O del 99,75 % de las que 770 t fueron suministradas a reactores de investigación y de potencia de los Estados Unidos y de otros países.

De aumentar notablemente la demanda, sería preciso incrementar la produción de agua pesada, en Savannah River o en otro lugar. Las unidades que ahora no funcionan en Savannah River podrían comenza a hacerlo a un rendimiento casi igual al que alcanzaron inicialmente con lo que la producción de agua pesada bastaría para las necesidades de un reactor de 300 MW por año.

Por cuanto se sabe, el proceso de intercambio bitérmico de deuterio entre agua y sulfuro de hidrógeno gaseoso sigue siendo el más económico para la producción de agua pesada en fábricas autónomas sin límite de tamaño. Es posible que otros procesos resulten también económicos como auxiliares en instalaciones que producen hidrógeno o mezclas de gases para la síntesis de amoniaco o alcohol. La experiencia de diez años en Savannah River ha proporcionado modos de mejorar y simplificar el proceso que reducirían considerablemente el coste en una fábrica nueva, particularmente si estuviera situada en la proximidad de una fuente de combustible barato. El precio actual de la AEC para el agua pesada es 24,50 dólares por libra. El costo de producción en Savannah River, sin incluir los gastos de depreciación ni otras cargas del capital, asciende a 13,50 dólares por libra; la inversión específica en la fábrica es de 145 dólares por libra-año. En una instalación nueva, de construcción y emplazamiento óptimos, se podría alcanzar un costo de producción de unos 8 dólares por libra y una inversión específica de 70 dólares por libra-año.

Parte de la instalación de destilación en vacío de Savannah River se utiliza hoy para reconcentrar D_2O diluido. Este servicio se encuentra a disposición de todos los usuarios de agua pesada y el coste depende de la concentración del D_2O. En los últimos cinco años se han recibido en Savannah River casi 200 t de agua pesada para proceder a su reconcentración.

Some Japanese work on chemical separation of uranium isotopes

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A THEORY OF URANIUM ISOTOPE SEPARATION INVOLVING ELECTRON EXCHANGE

(H. Kakihana and K. Kurisu)

From the quantum mechanical point of view, it is certain that there are slight isotopic effects in electron exchange reactions [1, 2] as well as in some complex forming reactions of U isotopes. However, in practical systems each of the isotopic effects is usually cancelled by the other, so any appreciably high separation factor has not yet been obtained by chemical means. An attempt to find a good combination of these isotopic effects has been carried out theoretically so as to determine the best chemical separation factor for U isotopes.

Mathematical treatment

The fundamental equation obtained by the present authors for the separation factor of isotopes A and B is as follows [3-5],

$$\ln S_{\mathrm{A}}^{\mathrm{B}} = \ln(1+\Delta_t) - \ln(1+\Delta_c) + \ln(1+\bar{\Delta}_c) \qquad (1)$$

where Δ_t is the effect caused by an isotopic exchange of a certain chemical species between two different phases, Δ_c and $\bar{\Delta}_c$ are the isotopic effects caused by chemical reactions in the first and second phases, respectively.

In a hydrochloric acid solution containing only U(IV), Δ_t and Δ_c are given by

$$\Delta_t(\mathrm{IV}) = Q_{\mathrm{UCl_4}}(Q'_{\mathrm{UCl_4}})^{-1}\bar{Q}'_{\mathrm{UCl_4}}(\bar{Q}_{\mathrm{UCl_4}})^{-1} - 1 \qquad (2)$$

$$\begin{aligned}\Delta_c(\mathrm{IV}) \\ = \sum_0^3[\mathrm{UCl_n}](a)^{-1}(Q'_{\mathrm{UCl_n}}(Q_{\mathrm{UCl_n}})^{-1}Q_{\mathrm{UCl_4}}(Q'_{\mathrm{UCl_4}})^{-1} - 1) \\ + \sum_5^6[\mathrm{UCl_n}](a)^{-1}(Q_{\mathrm{UCl_4}}(Q'_{\mathrm{UCl_4}})^{-1}Q'_{\mathrm{UCl_n}}(Q_{\mathrm{UCl_n}})^{-1} - 1) \qquad (3)\end{aligned}$$

where Q and [ ] denote the partition function and the concentration of each species respectively, a is the total concentration of ^{238}U, $^-$ represents the second phase and a prime means the lighter isotope ^{235}U.

The separation factor with a cation exchanger is

$$\begin{aligned}\ln S_{(\mathrm{IV})}^{(+)} = \ln(1+\Delta_t(\mathrm{IV})) - \ln(1+\Delta_c(\mathrm{IV})) \\ + \ln\{1 + \sum_{p=0}^{4}[\overline{\mathrm{UCl_{4-p}}}](a)^{-1} \\ (\bar{Q}'_{\mathrm{UCl_{4-p}}}(\bar{Q}_{\mathrm{UCl_{4-p}}})^{-1}\bar{Q}_{\mathrm{UCl_4}}\bar{Q}'_{\mathrm{UCl_44}})^{-1} - 1)\} \qquad (4)\end{aligned}$$

The separation factor with an anion exchanger is

$$\begin{aligned}\ln S_{(\mathrm{IV})}^{(-)} = \ln(1+\Delta_t(\mathrm{IV})) - \ln(1+\Delta_c(\mathrm{IV})) \\ + \ln\{1 + \sum_{q=1}^{2}[\overline{\mathrm{UCl_{4+q}}}](a)^{-1} \\ (\bar{Q}_{\mathrm{UCl_4}}(\bar{Q}'_{\mathrm{UCl_4}})^{-1}\bar{Q}'_{\mathrm{UCl_{4+q}}}(\bar{Q}_{\mathrm{UCl_{4+q}}})^{-1} - 1)\} \qquad (5)\end{aligned}$$

In a hydrochloric acid solution containing only U(VI), Δ_t and Δ_c are

$$\Delta_t(\mathrm{VI}) = Q_{\mathrm{UO_2Cl_2}}(Q'_{\mathrm{UO_2Cl_2}})^{-1}\bar{Q}'_{\mathrm{UO_2Cl_2}}(\bar{Q}_{\mathrm{UO_2Cl_2}})^{-1} - 1 \qquad (6)$$

$$\begin{aligned}\Delta_c(\mathrm{VI}) = \sum_0^1[\mathrm{UO_2Cl_n}](a)^{-1} \\ (Q'_{\mathrm{UO_2Cl_n}}(Q_{\mathrm{UO_2Cl_n}})^{-1}Q_{\mathrm{UO_2Cl_2}}(Q'_{\mathrm{UO_2Cl_2}})^{-1} - 1) \\ + \sum_3^4[\mathrm{UO_2Cl_n}](a)^{-1} \\ (Q_{\mathrm{UO_2Cl_2}}(Q'_{\mathrm{UO_2Cl_2}})^{-1}Q'_{\mathrm{UO_2Cl_n}}Q_{\mathrm{UO_2Cl_n}})^{-I} - 1) \qquad (7)\end{aligned}$$

The separation factor with a cation exchanger is

$$\begin{aligned}\ln S_{(\mathrm{VI})}^{(+)} = \ln(1+\Delta_t(\mathrm{VI})) - \ln(1+\Delta_c(\mathrm{VI})) \\ + \ln\{1 + \sum_{p=0}^{2}[\overline{\mathrm{UO_2Cl_{2-p}}}](a)^{-1} \\ (\bar{Q}'_{\mathrm{UO_2Cl_{2-p}}}(\bar{Q}_{\mathrm{UO_2Cl_{2-p}}})^{-1}\bar{Q}_{\mathrm{UO_2Cl_2}}(\bar{Q}'_{\mathrm{UO_2Cl_2}})^{-1} - 1)\} \qquad (8)\end{aligned}$$

The separation factor with an anion exchanger is

$$\begin{aligned}\ln S_{(\mathrm{VI})}^{(-)} = \ln(1+\Delta_t(\mathrm{VI})) - \ln(1+\Delta_c(\mathrm{VI})) \\ + \ln\{1 + \sum_{q=1}^{2}[\overline{\mathrm{UO_2Cl_{2+q}}}](a)^{-1} \\ (\bar{Q}_{\mathrm{UO_2Cl_2}}(\bar{Q}'_{\mathrm{UO_2Cl_2}})^{-1}\bar{Q}'_{\mathrm{UO_2Cl_{2+q}}}(\bar{Q}_{\mathrm{UO_2Cl_{2+q}}})^{-1} - 1)\} \qquad (9)\end{aligned}$$

For the system involving the electron exchange reaction between U isotopes as well as the complex formations, Eq. (1) has the following expression:

$$\begin{aligned}\ln S_{238}^{235} = \ln S_{(\mathrm{VI})} - \ln\{1 + x(K_e - 1)\} \\ + \ln\{1 + \bar{x}(\bar{K}_e - 1)\} \qquad (10)\end{aligned}$$

where x is the mole fraction of U(IV), $S_{(\mathrm{VI})}$ is the separation factor described previously. K_e and $\bar{K}_e$ are the equilibrium coefficients for the electron ex-

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change reaction between the isotopes in the solution and exchanger phases, respectively,

$$^{238}\mathrm{U(IV)} + {}^{235}\mathrm{U(VI)} \overset{\mathrm{K_e}}{\rightleftharpoons} {}^{235}\mathrm{U(IV)} + {}^{238}\mathrm{U(VI)}$$

and can be expressed by

$$\overline{K}_e = K_e S_{(IV)} (S_{(VI)})^{-1} = \overline{Q}_{U(VI)} (\overline{Q}'_{U(VI)})^{-1} \overline{Q}'_{U(IV)} (\overline{Q}_{U(IV)})^{-1} \quad (11)$$

Discussion

Eq. (10) indicates the important fact that the greater the difference between x and $\overline{x}$ the greater the contribution of K_e (the isotope effect of the electron exchange) to the separation factor. U(IV) is preferably absorbed by cation exchange resins and U(VI) is, reversely, better absorbed by anion exchange resins. Therefore, both cation and anion exchange resins could be good second phases giving a higher separation factor, if the electron exchange reaction, which has been believed to be very slow in the usual aqueous solution, could be accelerated by some catalyst such as the resin itself or the special compounds existing only in concentrated HCl solution.

Since $(S_{(IV)}\text{-}1)$ and $(S_{(VI)}\text{-}1)$ with cation exchange resins have the opposite sign to those with anion exchange resins, the selection of an appropriate resin could cause an effective contribution of complex formation to the separation factor. Values of S^{235}_{238} were calculated from Eq. (10) by using the experimental values of $S_{(IV)}$, $S_{(VI)}$, x and $\overline{x}$ and by assuming a set of reasonable values of K_e estimated from theoretical considerations and are shown in Fig. 1.

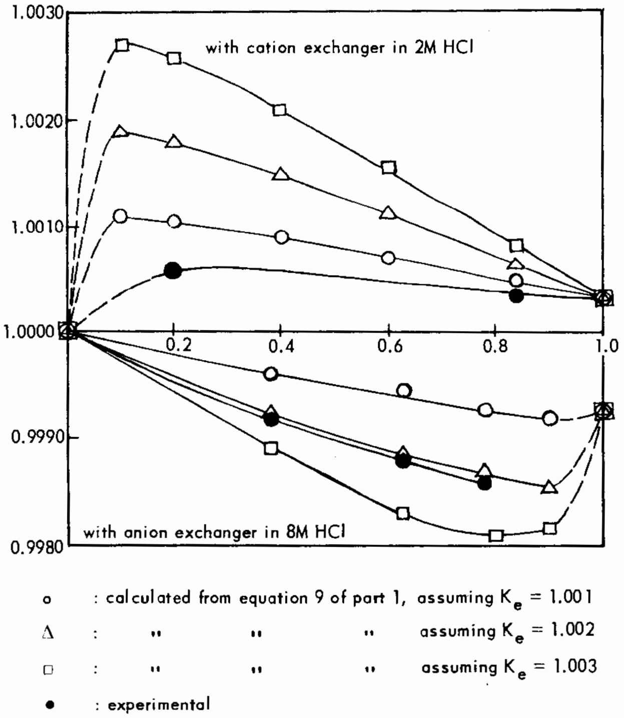

Figure 1. Separation factor of U isotopes in a mixed solution of uranic and uranyl ions

SOME REMARKS ON THE ISOTOPIC EXCHANGE REACTION BETWEEN U(IV) AND U(VI)

The isotopic exchange reaction between U(IV) and U(VI) ions in the mixed system of acidic solution and cation exchange resin

(J. Shimokawa and G. Nishio)

Experimental results and their analysis

The cation exchange resin particles containing depleted U(IV) ions (mole fraction: 0.231×10^{-2}) were mixed with a natural U(VI) solution. At the beginning of the reaction, some of the U(VI) ions entered the resinous phase from the solution, but all the U(IV) ions remained in the resinous phase in the pH range used. The change in isotopic content of the U(IV) in the resinous phase was followed by mass-analysis. The experimental detail will be described in another paper [6].

A study of this system indicates the presence of two possible exchange paths

$$[^{235}\mathrm{U(VI)}]_r + [^{238}\mathrm{U(IV)}]_r \xrightarrow{k_1} [^{238}\mathrm{U(VI)}]_r + [^{235}\mathrm{U(IV)}]_r \quad (12)$$

$$[^{238}\mathrm{U(VI)}]_r + [^{235}\mathrm{U(VI)}]_s \xrightarrow{k_2} [^{235}\mathrm{U(VI)}]_r + [^{238}\mathrm{U(VI)}]_s \quad (13)$$

From Eqs.(12) and (13), the molal balances for the ^{235}U in the resinous phase leads to a set of differential equations:

$$\frac{\mathrm{d}\,[^{235}\mathrm{U(VI)}]_r}{\mathrm{d}t} = -k_1 [^{235}\mathrm{U(VI)}]_r [^{238}\mathrm{U(IV)}]_r + k_1 [^{238}\mathrm{U(VI)}]_r [^{235}\mathrm{U(IV)}]_r - k_2 [^{235}\mathrm{U(VI)}]_r [^{238}\mathrm{U(VI)}]_s + k_2 [^{238}\mathrm{U(VI)}]_r [^{235}\mathrm{U(VI)}]_s \quad (14)$$

$$\frac{\mathrm{d}\,[^{235}\mathrm{U(IV)}]_r}{\mathrm{d}t} = -k_1 [^{238}\mathrm{U(VI)}]_r [^{235}\mathrm{U(IV)}]_r + k_1 [^{235}\mathrm{U(VI)}]_r [^{238}\mathrm{U(IV)}]_r \quad (15)$$

Table 1 gives the experimental results and the most important values of k_1 and k_2 estimated from Eqs. (14) and (15).

From this table it is seen that k_1 is very sensitive to the f-value (isotopic fraction in U(IV)) in each run, but k_2 is almost constant for all cases except G_1 and G_2. This seems to be due to the fact that k_1 is dependent mainly on the degree of hydrolysis of the U(IV) ions in the resinous phase, while k_2 is not influenced by the hydrogen ions in the resin and the external solution. The apparent activation energy is found to be 13.9 kcal mol^{-1} (E_1) for the first process and 5.84 kcal mol^{-1} for the second process. It should be noted that E_1 is smaller than the activation energy for the U(IV)-U(VI) exchange in the solution phase*. E_2 seems to be nearly equal to the activation energy of ion diffusion in the resinous phase which is generally between 4 and 7 kcal mol^{-1} [8].

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* 33-4 kcal mol^{-1} in the case of pH 0.85 [7].

Table 1. Experimental conditions and the most relevant values of the apparent exchange rate constants k_1 and k_2

	Final conc. of U(VI) in resin, U mol	Conc. of U(IV) in resin, V mol	Final conc. of U(VI) in soln. W mol	pH change in soln.		Conc. of H+ in resin 1/[H+]r mol	Rate constants		Isotopic fraction in U(IV) f %
							k_1 mol min	k_2 mol min	
A	0.0236	0.0410	0.0182	3.5	1.4	1.45	0.876	0.72	0.325
A′									0.392
B	0.0198	0.0373	0.0177	1.2	0.71	0.826	0.379	0.60	0.316
C	0.0311	0.0367	0.00527	3.6	1.5	0.625	0.161	0.60	0.319
D	0.0398	0.0546	0.0160	1.5	0.9	0.661	0.120	0.60	0.274
E	0.0317	0.0358	0.000444	3.6	1.4	0.640	0.10	0.60	0.281
F	0.0281	0.0374	0.00920	1.7	1.4	0.529	0.114	0.60	0.287
G	0.0260	0.0372	0.0112	1.5	1.1	0.629	0.110	0.60	0.286
G_1	0.0260	0.0372	0.0112	1.5	1.1	0.629	0.479	1.0	0.325
G_1'									0.383
G_2	0.0260	0.0372	0.0112	1.5	1.1	0.629	0.0287	0.31	0.250
H	0.025	0.0427	0.0175	1N	1N	0.405	0.040	0.80	0.259

Modified uranium concentration $U = U'$ (mol/l-resin) $\times$ $(1 - \varepsilon)$.

$V = V'$ (mol/l-resin) $\times$ $(1 - \varepsilon)$ $W = W'$ (mol/l-soln.) $\times$ ε where $\varepsilon = \dfrac{\text{(soln. vol)}}{\text{(soln. vol)} + \text{(resin vol)}}$

Temperature: 22.5 °C except for G_1 42.0 °C and G_2 7.0 °C.
Time: A 12 min; D, G_1 20 min; A′, B 30 min; C, E, F, G, G'_1, G_2, H 40 min.

Mechanism of isotopic exchange

The hydrolysis of the U(IV) ion is expressed by

$$U^{4+} + nH_2O \overset{K_{h,n}}{\rightleftharpoons} U(OH)_n^{(4-n)+} + nH^+ \qquad (n = 1, 2 \text{ and } 3) \quad (16)$$

Each hydrolysis constant is

$$K_{h,n} = [U(OH)_n^{(4-n)+}]\,[H^+]^n\,[U^{4+}]^{-1} \quad (17)$$

As the U(IV) concentration is held constant through the reaction therefore

$$[U(IV)] = [U^{4+}] + \sum_{n=1}^{3} [U(OH)_n^{(4-n)+}]$$
$$= [U^{4+}]\{1 + \sum_{n=1}^{3} K_{h,n}[H^+]^{-n}\} \quad (18)$$

If the $U(OH)_p^{(4-p)+}$ ion is the only species contributing to isotope exchange, Eq. (12) is rewritten as follows:

$$[^{235}U(VI)]_r + [^{238}U(OH)_p^{(4-p)+}]_r \xrightarrow{k'} [^{238}U(VI)]_r + [^{235}U(OH)_p^{(4-p)+}]_r \quad (19)$$

The concentration of p species is

$$[U(OH)_p^{(4-p)+}] = K_{h,p}\,[U^{4+}]\,[H^+]^{-p}$$
$$= K_{h,p}\,[U(IV)]\,[H^+]^{-p}\{1 + \sum_{n=1}^{3} K_{h,n}\,[H^+]^{-n}\}^{-1} \quad (20)$$

From Eqs. (12), (19) and (20),

$$k_1 = K_{h,p}\,k'[H^+]^{-p}\{1 + \sum_{n=1}^{3} K_{h,n}\,[H^+]^{-n}\}^{-1}$$
$$\approx K_{h,p}\,k'[H^+]^{-p}\ (\text{if}\,[H^+]^{-n} \gg K_{h,n}) \quad (21)$$

or $$\log k_1 = \text{const.} + p \log\,[H^+]^{-1} \quad (22)$$

Line (A) in Fig. 2 shows the relation of log k_1 vs. log $[H^+]_r^{-1}$. The similar tendency should also be obtained for the U(IV)-U(VI) exchange in the solution phase. Line (B) gives the relation of log k_{Rona}* vs. log $[H_s^+]^{-1}$. The slope of the straight line is found to be 3.0 in either case.

It becomes apparent from these analytical results that

(*a*) The U(IV)-U(VI) exchange takes place readily between $U(OH)_3^+$ and UO_2^{2+}.

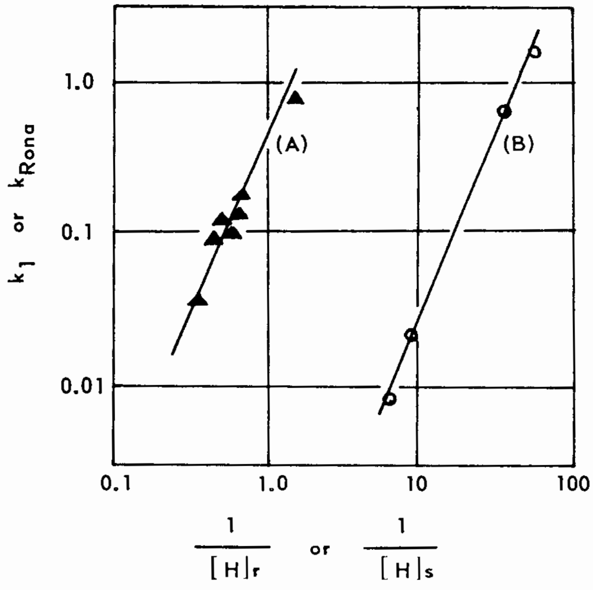

Figure 2. Basic relation of rate constant to hydrogen ion concentration

Line (A) in resinous phase; Line (B) in solution phase

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* Rona calculated the apparent exchange rate constant K' for the U(IV)-U(VI) exchange in solution phase. The relation of k_{Rona} and K' is given by $K' = -\,k_{\text{Rona}}\,(a + b)/2.303$.

Table 2. Experimental conditions and results obtained for anion exchange resin with 8*M* hydrochloric acid

Reac. time h	Conc. of U(IV) in resin mol/l	Conc. of U(IV) in soln. mol/l	Conc. of U(VI) in resin mol/l	Isotopic fraction			k_1 l/mol h	k_2 l/mol h
				Meas. $\bar{f}$(IV)	Meas. f(IV)	Calc. $\bar{f}$(VI)		
0	0.6140	0.0251	0.445	0.710	0.709	0.292		
4.5	0.6140	0.0251	0.445	0.690	0.705	0.324		
8.5	0.6140	0.0251	0.445	0.676	0.701	0.345	$2.7\ 10^{-2}$	1.3
13.5	0.6140	0.0251	0.445	0.664	0.696	0.364		

(*b*) The apparent exchange rate constant is inversely proportional to the third power of the hydrogen ion concentration. However, for the same acid concentration,

(k_1 in resinous phase)/(k_{Rona} in solution phase) = $10^3 - 10^4$

(*c*) The cation exchange resin seems to have a catalytic action for the U(IV)-U(VI) exchange.

Isotopic exchange reaction between U(IV) and U(VI) in 8*M* hydrochloric acid with anion exchange resin

(H. Kakihana and K. Gonda)

Experimental

Dowex 2 × 8 anion exchange resin samples weighing 1.00 g were immersed in 12.0 ml of 8*M* hydrochloric acid containing 112.00 g of natural U(IV) and 107.20 g of depleted U(VI) (mole fraction: 0.291×10^{-2}). After shaking for one hour in a thermostat at 30 °C, the ion exchange equilibrium was reached and very small amounts of U(VI) (about 1.08 g) remained in the solution. The distribution of U(IV) and U(VI) between the resin and the solution phases is shown in the 2nd, 3rd and 4th columns of Table 2. Regarding the time of the ion exchange equilibrium as the starting point, the change in the isotopic content of ^{235}U was followed by mass-analysis [9] with an Atlas CH4 mass spectrometer for U(IV) in the resin and for U(IV) in the solution.

Discussion

Since the amounts of U(VI) in the solution were very small, the isotopic exchange reaction could be represented by the following three paths:

$$[^{235}\text{U(VI)}]_r + [^{238}\text{U(IV)}]_r \overset{k_1}{\rightleftharpoons} [^{238}\text{U(VI)}]_r + [^{235}\text{U(IV)}]_r \quad (23)$$

$$[^{238}\text{U(IV)}]_r + [^{235}\text{U(IV)}]_s \overset{k_2}{\rightleftharpoons} [^{235}\text{U(IV)}]_r + [^{238}\text{U(IV)}]_s \quad (24)$$

$$[^{238}\text{U(VI)}]_r + [^{235}\text{U(IV)}]_s \overset{k_{12}}{\rightleftharpoons} [^{235}\text{U(VI)}]_r + [^{238}\text{U(IV)}]_s \quad (25)$$

The molal balances for ^{235}U(IV) and ^{235}U(VI) in the resin phase lead to a set of differential equations:

$$\frac{d\bar{f}(\text{IV})}{dt} = \bar{k}_1\bar{b}(\bar{f}(\text{VI}) - \bar{f}(\text{IV})) + k_2 a(f(\text{IV}) - \bar{f}(\text{IV})) \quad (26)$$

$$\frac{d\bar{f}(\text{VI})}{dt} = k_{12} a(f(\text{IV}) - \bar{f}(\text{VI})) + \bar{k}_1\bar{a}(\bar{f}(\text{IV}) - \bar{f}(\text{VI})) \quad (27)$$

where f denotes the isotopic fraction of ^{235}U, *a* and *b* the concentration of U(IV) and U(VI) respectively and $^{-}$ represents the ion exchange resin phase.

The best relevant set of values for the rate constants was estimated graphically as $k_1 = 2.7 \times 10^{-2}$ mol^{-1} hour^{-1}, $k_2 = 1.3$ 1 mol^{-1}hour^{-1} and k_{12} was negligibly small. Compared to the results obtained for a cation exchange resin [1], the rate of the exchange reaction with an anion exchange resin looks very slow. However, if the very high HCl concentration (8*M*) of the present system is remembered, the rate could be considered as high.

Conclusion

The U(IV-U(VI) exchange reaction takes place even with such a high HCl concentration as 8*M*. Further experiments are required to decide whether this derives from the catalytic action of the anion exchange resin or from the properties of complexes existing in concentrated HCl solution. If there is some isotopic effect in the U(IV)-U(VI) exchange, the effect will be accomplished within the limited reaction time even in 8*M* HCl solution.

CHEMICAL SEPARATION OF URANIUM ISOTOPES BY ION EXCHANGE IN THE SYSTEM CONTAINING BOTH U(IV) AND U(VI)

(H. Kakihana, H. Sato, K. Gonda, Y. Mori and T. Kansaki)

Experimental

Based on the theoretical considerations described in the first part, experimental work has been done to obtain the higher separation factor of the U isotopes. Dowex 50 X12 or Diaion SK-1 cation exchange resin columns have been used for breakthrough experiments with 2*M* HCl solutions containing U(IV) and U(VI) of various ratios. For each experiment the depletion of U was found at the front of the U(IV) breakthrough and very minor depletion was also observed in the U(VI) eluant [10, 11]. Similar experiments have been done through Dowex 2 X10 anion exchange resin columns of 100 cm height and 1.2 cm diameter with 8*M* HCl solutions containing U(IV) and U(VI).

Remarkably high enrichment of U was found in a few fractions of the U(IV) eluant. Some of the results are shown in Table 3. No fraction of the eluant from a system containing only U(IV) or U(VI) gave such a high enrichment [12].

Table 3. Results of mass-analysis obtained for the eluants from the anion exchange resin column with 8*M* HCl solution containing both U(IV) and U(VI)

Mole fraction of U(IV)	Eluant		r/r_0 [a]
	Vol. ml	U^{4+} mg	
	10	233	1.0009
	10	225	1.0032
	10	233	1.0009
0.78	10	240	1.0036
	100	2 150	1.0078
	100	2 050	1.0002
	100	1 230	1.0003
	100	1 000	1.0046
0.38	100	1 500	1.0050
	100	1 350	1.0016
	100	1 350	1.0003

[a] r = Isotopic ratio of each fraction; r_o = Isotopic ratio of the original sample.

Approximate values for the single process separation factor, S^{235}_{238}, were calculated using the equation [10].

$$S^{235}_{238} = [{}^{235}\overline{U}]\,[{}^{238}\overline{U}]^{-1}\,[{}^{238}U]\,[{}^{235}U]^{-1} = 1 + DQ^{-1}R_0^{-1} \qquad (27)$$

where D is the total depletion of U in the elute, Q is the total amount of uranium absorbed in the column and R_0 is the original mole fraction of U. The values obtained are shown in Table 4.

Table 4*a*. Separation factor of uranium with anion exchange resin in 8*M* HCl

Mole fraction of U(IV)	Separation factor S^{235}_{238}			
	Experimental	Theoretical		
		K_e = 1.001	1.002	1.003
100	0.9993	0.9993	0.9993	0.9993
78	0.9986	0.9993	0.9987	0.9981
63	0.9988	0.9994	0.9989	0.9983
38	0.9992	0.9996	0.9993	0.9990
0	1.0000	1.0000	1.0000	1.0000

Table 4*b*. Separation factor of uranium with cation exchange resin in 2*M* HCl

Mole fraction of U(IV)	Separation factor S^{235}_{238}			
	Experimental	Theoretical		
		K_e = 1.001	1.002	1.003
98	1.0003_3	1.0003	1.0003	1.0004
84	1.0004_8	1.0005	1.0006	1.0008
20	1.0005	1.0017	1.0018	1.0026
0	1.0000	1.0000	1.0000	1.0000

Discussion

Comparing the system containing only U(IV) with that containing U(VI), the former gave a better separation factor than the latter.

Also the value for the anion exchange resin is better than the value for cation exchange resins. These facts may be attributed to the higher degree of complex formation of U(IV) than U(VI) and to the better contribution of the third term of Eq.(5) to that of Eq. (4).

With anion exchange resins, the mixed solutions of U(IV) and U(VI) gave very high separation factors (0.9992 — 0.9986), which can be explained by the effective contribution of the electron exchange reaction described earlier. In fact, as shown in Fig. 1, all the experimental results agreed well with the theoretical values obtained from Eq. (9) by assuming K_e = 1.002. With the cation exchange resin the effect of mixing U(IV) with U(VI) has not been studied. A 2*M* concentration of HCl might be too high to realize the isotopic effect of U(IV)-U(VI) exchange even in the presence of a cation exchange resin, which was proved to be a fine catalyst in the preceding section.

EFFECT OF SUPERIMPOSING AN ALTERNATING ELECTRIC CURRENT ON THE ISOTOPE SEPARATION IN AN ION EXCHANGE RESIN COLUMN BY IONIC MIGRATION

(H. Goto, S. Suzuki, A. Sato and M. Kishimoto)

In 1950, ion exchange resins had been used effectively as a medium for electromigration for the separation of Cu and Ni by Japanese researchers [13]. Since then, several Japanese workers have tried to use ion exchange resins for the separation of isotopes by electromigration [14-17]. However, only direct current was used in their experiments. In this paper, the effect caused by superimposing an alternating electric current is described.

A cell made of borosilicate glass was divided into a few compartments with cation exchange membranes. Each of the compartments was filled with cation exchange resin, excepting the end compartments of the cell, one of which was filled with ammonium chloride solution for nitrogen isotope separation and used as an anodic cell and the other was filled with hydrochloric acid solution and used as a cathodic cell. The ion exchange electromigration of the ammonium ion was carried out by superimposing alternating current on the direct current. By this method, ammonium ions pass through the cation exchange resin to the cathode from the anode, while as the phase of the alternating current is reversed the ion proceeds in the reverse direction and as the phase is again reversed it advances again to the cathode. After the passage of the electric current for a certain time, the isotopic ratio of the nitrogen in the ammonium chloride in each

Table 5. Effect of superposing alternating electric current, its frequency and wave form

Frequency (cycles)	Direct current only	25		50		500		1 000	
Wave form.	—	Sine	Square	Sine	Square	Sine	Square	Sine	Square
Isotopic ratio of N in cathodic cell (%)	0.379	0.387	0.398	0.390	0.391	0.394	0.392	0.385	0.386

Isotopic abundance ratio of nitrogen in the original ammonium chloride sample = 0.372 ± 0.0016%
Conditions for ion exchange electromigration:
Ion exchange resin; Doxex 50 X8, 200 mesh or Amberlite CG-120, type 2, hydrogen form, 2.5 cm diameter and 20 cm long. Ion exchange membrane; Nepton CR-61; Anodic cell; 40 ml of 3.0*M* ammonium chloride solution. Cathodic cell; 40 ml of 3.0*M* HCl solution. Time of electromigration; 400 hours. Electricity; ac 4.0 V, dc 0.2 V.

Table 6. Distribution of isotopic ratio of nitrogen in the cell

Number of cell compartment		Cathodic cell	No. 1	No. 2	No. 3	No. 5	Anodic cell
Isotopic ratio of N in each compartment %	Expt. A	0.400	0.381	0.374	0.368	0.371	0.363
	Expt. B	0.413	0.384	0.367	0.372	0.369	0.367
Amounts of NH_4Cl in each compartment mg.	Expt. A	148	1.329	1.590	1.752	1.220	218
	Expt. B	125	1.251	1.542	1.764	1.413	187

Conditions for ion exchange electromigration were same as those for table 5, except electricity; ac (square wave) 50 cycles, 4.0 V, dc 0.2 V.

Table 7. Results of enrichment of uranium-235

Time of electro-migration h .	400	600	1,000
Isotopic ratio of U in anodic cell %	0.709 ± 0.005	0.715 ± 0.004	0.720 +± 0.007
Amounts of U remaining in anodic cell mg	728	63	4

Isotopic ratio of uranium in the original uranyl nitrate sample: 0.702 ± 0.005 %.
Conditions: Ion exchange resin; Amberlite CG-120 type 2, hydrogen form, 2 cm diam. and 75 cm long. Anodic cell; 40 ml of 0.5*M* uranyl nitrate solution. Cathodic cell; 40 ml of 0.5*M* nitric acid solution. Electricity; ac (square wave) 50 cycles 4.0 V, dc 0.2 V.

compartment was determined with a mass spectrometer. The ammonium chloride was purified by sublimation and completely oxidized to nitrogen gas by the hydrobromite method. From these experiments, it was found that the heavier isotope ^{15}N proceeds more quickly to the cathodic cell than the lighter isotope ^{14}N. The results obtained are shown in Tables 5 and 6.

The above method was applied to the enrichment of ^{235}U. The apparatus was the same as described above. After a definite time of passing the electric currents, the uranium remaining in the anodic cell was purified and the isotopic ratio was determined with a mass spectrometer using the thermionic method. As with nitrogen, the lighter isotope ^{235}U had tended to remain in the anodic cell. The results are shown in Table 7.

In spite of the simpleness of the apparatus and the procedure, a good enrichment of isotopes seems to be obtainable by this new method.

A NEW APPARATUS FOR CONTINUOUS ISOTOPE SEPARATION BASED ON A SIMULTANEOUS USE OF ION EXCHANGE AND IONIC MIGRATION

(H. Kakihana, T. Hoshino and Y. Mori)

Studies of isotopic separation using ion exchange chromatography or ionic migration have been carried out by many workers. Recently, a cation exchange membrane has been proved to be a very effective medium for ionic migration especially for the separation of Lithium isotopes [16], and even for uranium isotopes the appreciable enrichment of ^{235}U (e.g.

Table 8. A result with LiCl solution

Compartment No.	Li-conc. mg/l	R fraction / R feed	^{6}Li-mol fr. %	^{6}Li-conc. mol/l	Li-dist. %	Total separation factor Cut	T.S.F.
2	9	1.027 ± 0.004	7.28	0.09	0.24		
3	21	1.019 ± 0.003	7.34	0.22	0.57		
4	85	1.013 ± 0.005	7.37	0.91	2.31		
5	135	1.012 ± 0.004	7.38	1.44	3.66		
6	218	1.018 ± 0.004	7.34	2.31	5.92		
7	313	1.009 ± 0.004	7.40	3.35	8.49		
8	396	1.006 ± 0.003	7.42	4.24	10.75		
9	493	1.001 ± 0.003	7.46	5.31	13.83		
10	490	0.999 ± 0.003	7.47	5.29	13.30	0.5472 (10 ~ 14)	1.008
11	551	0.993 ± 0.004	7.51	5.98	14.95	0.4142 (11 ~ 14)	1.016
12	560	0.996 ± 0.004	7.49	6.06	15.20	0.2647 (12 ~ 14)	1.013
13	410	0.977 ± 0.004	7.63	4.52	11.13	0.1127 (13 ~ 14)	1.024
14	5	0.936 ± 0.005	7.93	0.06	0.14	0.0014 (14)	1.068
Calc. feed solution	737	—	—	7.96	—		
Calc. feed solution	720	—	7.46	7.76	100.04		

Operation conditions:
Feed solution: 0.1*M* LiCl solution; flow rate 120 ml/h cell.
Cathode solution: 0.5*N* $(NH_4)_2SO_4$ solution; flow rate 15 L/h.
Anode solution: 0.25*N* NH_4OH, 0.25*N* $(NH_4)_2SO_4$ solution; flow rate 15 l/h.
Potential between electrodes: 20 V dc.
Current through resin bed: 3A (10 mA/cm²).

$\Delta r = 0.004 \times 10^{-2}$) was observed at the front of the U-band in the membrane after about 45 cm migration [18].

For a continuous operation of these processes, a countercurrent technique was usually applied but was always accompanied by some experimental difficulties such as the control of the counterflow rate or boundary conditions. An apparatus based on the idea of combining these two processes — ion exchange chromatography and ionic migration — was devised to overcome such difficulties and to obtain their combined effect. The apparatus consists of an ion exchanger bed 20 cm wide, 100 cm high, 3 cm thick and two electrode compartments attached to each side of the exchanger bed. The exchanger bed is divided into 20 compartments of 1 cm width by Asahi Chemical CK-1 cation permselective membranes and filled with Mitsubishi Chemical Diaion SK-1 50-60 mesh cation exchange resin in the NH_4-form. One of the electrode compartments, equipped with a Pt-electrode, is used as an anode compartment and the other has a Hastelloy C electrode in the cathode compartment. A solution of the isotopes to be separated was usually introduced at the top of the 5 compartments of the anode side and an ammonium salt solution was fed in to the top of the other 15 compartments. An electric field was applied between the electrodes and cathodic and anodic solutions were circulated separately to each electrode compartment by pumps. The mechanism of continuous separation of isotopic ions by this apparatus is as follows [15]. Consider the isotopic ions I and II which are moving down through the ion exchange resin bed with velocities V_v^{I} and V_v^{II} respectively according to the flow rate of the solution and the difference in their affinities for the exchanger. At the same time, they are affected by the electric field and migrate horizontally with velocities V_h^{I} and V_h^{II} respectively in accordance mainly with their ionic mobilities. As a result, the two ions move along different directions with different velocities so that they will be separated from each other and eluted from different positions in the apparatus. Moreover, if the solution is fed continuously, the operation will become continuous.

The efficiency of this apparatus was examined by several experiments on lithium isotope separation with Li_2CO_3, LiCl and LiOH solutions. A result obtained for LiCl is shown in Table 8. The separation factors of the apparatus obtained with LiCl are shown in Table 9, together with the results obtained with

Table 9. Relation between cut and total separation factor

Cut	Total separation factor	
	Li_2CO_3 solution	LiCl solution
0.0014	—	1.068
0.0189	1.058	—
0.1127	—	1.024
0.1543	1.027	—
0.2647	—	1.013
0.3153	1.015	—
0.4142	—	1.011
0.4814	1.010	—
0.5472	—	1.008

Li_2CO_3. Apart from the benefit of continuous operation such values of a separation factor of 1.01 for cut 0.5 and 1.027 for cut 0.15 are larger than that of 1.001-1.003 obtained with LiCl or Li_2CO_3 by simple ion exchange chromatography [19], and also larger than that of 1.0038 obtained by ionic migration in an aqueous solution of $LiNO_3$.

The same apparatus has been used for preliminary enrichment tests of ^{235}U. The procedure was as follows. An acidic solution of $0.05M$ UCl_4 was fed from the top of a compartment next to the cathodic compartment, an electric field was applied horizontally, and the eluant from the bottom was led to the top of the next compartment. After passing through 5 compartments, the eluant was analysed for U-content and isotopic ratio. The first 10 fractions (1 fraction = 100 ml) had lower ^{235}U concentrations ($100 \times (r - r_0) = -0.005 - 0.01$), followed by about 30 fractions with no fractionation, and slight enrichment of ^{235}U was observed in the following 60 fractions.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/439 Japon

Quelques études faites au Japon sur la séparation chimique des isotopes de l'uranium

par H. Kakihana *et al.*

Une théorie de la séparation des isotopes de l'uranium par réaction d'échange d'électrons.

Les études théoriques ont montré que les mélanges d'uranium(IV) et d'uranium(VI) devraient constituer un système intéressant si la réaction d'échange d'électrons entre les isotopes peut être catalysée.

Les résines échangeuses d'ions, catalyseurs efficaces de la réaction d'échange d'électrons entre l'uranium(IV) et l'uranium(VI).

Il a été établi que les résines échangeuses de cations et d'anions sont d'excellents catalyseurs, par exemple :

$$\frac{\text{vitesse d'échange d'électrons dans une résine échangeuse de cations}}{\text{vitesse d'échange d'électrons dans une solution}} = 10^3 - 10^4.$$

Séparation chimique des isotopes de l'uranium par échange d'ions dans un système contenant de l'uranium(IV) et de l'uranium(VI).

Des facteurs de séparation plus élevés ont été observés pour l'uranium(IV) (1,0007) que pour l'uranium(VI) (1,0000). Des facteurs de séparation beaucoup plus élevés (1,0014) ont été obtenus pour des systèmes mixtes d'uranium(IV) et d'uranium(VI), ce qui peut s'expliquer par une contribution efficace de l'effet isotopique dans la réaction d'échange d'électrons entre l'uranium(IV) et l'uranium(VI).

Fractionnement des isotopes de l'uranium dans une membrane échangeuse d'ions par migration ionique.

Un enrichissement appréciable en uranium 235 a été observé en tête d'une bande d'uranium dans une membrane échangeuse d'ions, tout comme dans le cas de l'isotope du lithium.

Effet de la superposition d'un courant alternatif sur la séparation des isotopes par migration ionique dans une colonne de résine échangeuse d'ions.

Par la superposition d'un courant alternatif, on a obtenu des effets favorables au fractionnement des

isotopes de l'uranium, semblables à ceux observés pour les isotopes de l'azote.

Nouveau dispositif pour la séparation continue des isotopes utilisant simultanément l'élution d'échange d'ions et la migration ionique.

On a conçu un dispositif combinant les effets des deux procédés, l'élution d'échange d'ions et la migration ionique, et permettant en même temps la marche en continu. Avec ce dispositif, on a obtenu un débit continu de ^6Li enrichi (par exemple $^7Li/^6Li = 11{,}61$) à la cathode, tandis que ^6Li appauvri (par exemple 12,81) était obtenu à l'anode. Pareillement, un enrichissement de ^{235}U était observé à la cathode.

A/439 Япония

Некоторые работы по химическому разделению изотопов урана в Японии

Х. Какихана *et al.*

Часть I. Теория разделения изотопов урана с помощью реакции электронного обмена

Теоретические иследования показали, что смеси U (IV) и U (VI) являются наиболее предпочитаемыми системами для разделения изотопов U^{235} и U^{238} в случае, если можно катализировать реакцию электронного обмена.

Часть II. Ионообменные смолы как эффективные катализаторы для реакции электронного обмена между U(IV) и U(VI)

Катионо- и анионообменные смолы являются очень интересными катализаторами. Так, например,

$$\frac{\text{Скорость электронного обмена в катионообменной смоле}}{\text{Скорость электронного обмена в растворе}} = 10^3 - 10^4.$$

Часть III. Химическое разделение изотопов урана с помощью ионообменника в системе, содержащей U(IV) и U(VI)

Получены более высокие коэффициенты разделения для U (IV) (1,0007), чем для U (VI) (1,0000). Еще более высокие коэффициенты разделения (1,0014) были получены для смешанной системы, что объясняется эффективным влиянием изотопов в реакции электронного обмена между U (IV) и U (VI).

Часть IV. Разделение изотопов урана в мембранном ионообменнике при миграции ионов

Точно так же, как и в случае изотопов лития, в мембранном ионообменнике наблюдалось значительное обогащение изотопами U^{235}.

Часть V. Влияние наложения переменного тока на разделение изотопов в ионообменной колонне при миграции ионов

В результате наложения переменного тока наблюдалось аналогичное влияние на изотопы азота при фракционировании изотопов урана

Часть VI. Новая установка для непрерывного разделения изотопов, основанная на одновременном использовании ионообменного вымывания миграции ионов

Создана установка, основанная на комбинации методов ионообменного вымывания и миграции ионов при непрерывном процессе. На катоде этой установки был получен непрерывный поток обогащенного Li^7 ($Li^6 = 11{,}61$), а на аноде — обедненного Li^6 (12,89). Одновременно в потоке на катоде наблюдалось обогащение U^{235}.

A/439 Japón

Algunos trabajos japoneses sobre separación química de los isótopos del uranio

por H. Kakihana *et al.*

Una teoría de la separación isotópica del uranio que implica reacción de intercambio electrónico

Los estudios teóricos han probado que la mezcla de U^{IV} y U^{VI} sería un sistema favorable, si la reacción de intercambio electrónico entre los isótopos pudiera catalizarse.

Resina de intercambio iónico como un catalizador efectivo para la reacción de intercambio electrónico entre U^{IV} y U^{VI}

Se han encontrado resinas de intercambio de catión y de anión como catalizadores muy prometedores. Por ejemplo:

$$\frac{\text{Velocidad de intercambio electrónico en resina de cambio de catión}}{\text{Velocidad de intercambio electrónico en solución}} = 10^3 - 10^4$$

Separación química de los isótopos del uranio con cambiador de iones en el sistema conteniendo U^{IV} y U^{VI}

Se han observado mejores factores de separación para U^{IV} (1,0007) que para U^{VI} (1,0000). Se obtuvieron factores de separación mucho más altos (1,0014) para los sistemas mixtos de U^{IV} y U^{VI}, que podrían explicarse por la contribución efectiva del efecto isotópico en la reacción de intercambio electrónico entre U^{IV} y U^{VI}.

Fraccionamiento de los isótopos del uranio en membrana de intercambio iónico por migración iónica

En la membrana de intercambio iónico se observó un apreciable enriquecimiento de ^{235}U en el frente de la banda de U, exactamente como en el caso del isótopo de Li.

Efecto de superponer una corriente alterna en la separación isotópica con columna de resinas de cambio de íon por migración iónica

Superponiendo una corriente alterna se ha observado en el fraccionamiento isotópico del uranio un efecto favorable similar al que tiene lugar en los isótopos del nitrógeno.

Un nuevo aparato de separación continua de isótopos basado en el uso simultáneo de elución de cambio de ión y migración iónica

Se ha ideado un aparato en el que se combinan los dos procesos, la elución de cambio de ión y la migración iónica, en que se incorpora la operación continua. Por medio de este aparato el flujo continuo del litio-6 enriquecido (v.g. $Li^7/^6Li = 11,61$) se obtuvo en la región catódica, mientras que el de litio-6 empobrecido (v.g. 12, 81) se obtuvo en la región anódica. Análogamente se observó el enriquecimiento de ^{235}U en la región catódica.

Isotope separation by concurrent gas centrifuge

By Y. Takashima, A. Kanagawa and Y. Oyama *

The development of gas centrifuges in Japan started in 1959, when Oyama and his group at the Tokyo Institute of Technology planned to use the gas centrifuge for uranium isotope separation.

The first step was the design of a centrifuge with a rotor 20 cm id, 120 cm in length and a rotation speed of 20 000 rpm, to accumulate technical experience through running tests and preliminary separation tests of argon or other gases.

The project was formally started in April 1959 by Oyama and his co-operators at the Institute of Physical and Chemical Research, where this work was covered by JAEC contracts.

The Nippon Atomic Industry Group Co. also joined in the project to take charge of mechanical and material problems. The Toshiba Turbine Co. was delegated to make a pilot type of gaseous centrifuge. A rotor for the first centrifuge was constructed from duralumin 24S(A_3-T_4-T_3). In March 1960, the running test was successful, although there were various unsolved problems such as sealing, vibration and damping. In March 1961, it was possible to do the separation test of argon gas without serious trouble which could have been caused by the abrasion of bearings, leakage, etc.

The separation factor obtained was about 1.04 for a 0.5 l/min feed rate and 1.01 for 5 l/min with countercurrent flow and the cut 0.5 [1]. Concurrent flow reduced the separation factor to 1.01 for 1 l/min and 1.006 for 5 l/min. The test data, however, are not yet sufficient to indicate the separation performance by this centrifuge. The isotope concentration was measured by means of a mass spectrometer, Type RMI-2, made by the Hitachi Co.

During the test period, the Toshiba Turbine Co. built a second centrifuge with a bigger rotor, 30 cm id, 150 cm in length and 9 mm thick, which was constructed from duralumin 14ST. This rotor was expected to stand up to speeds of more than 20 000 rpm. However, several running tests started at the end of 1961 showed that the safe running speed would be no more than 18 000 rpm, since significant elliptical expansion of the cylindrical part was observed beyond this speed. This elliptical deformation was considered to be due to inherent stress in the duralumin before being machined. Therefore, another rotor machined from carefully heat-treated duralumin has been prepared for the next running test which will be done in the near future.

The separation test at 16 000 to 18 000 rpm was carried out on the second machine in March 1962 [2]. The results, however, were not as good as expected.

At the end of 1962, the responsibility for the project was transfered to the Atomic Fuel Corporation for further development for uranium isotope separation.

As part of this project, breaking tests of such materials as duralumins, high tension steels and fibreglass reinforced plastics (FRP) have been studied by a group at the Toshiba Central Research Laboratory [3]. A tested high tension steel rotor was destroyed at the peripheral speed of 317 m/s after about 50 h running time. A welded 75S duralumin rotor was torn off at the welded part at 350 m/s. The test of the FRP rotor is just under way. Basic studies on sealing and bearings have also been made by another group.

Some analytical calculations [4, 5, 6, 7, 8] on the separation performance of the gaseous centrifuge have been done including considerations of economical feasibility [9]. Part of the project includes the investigation of such problems as magnetic balancing and the characteristics of the hysteresis motor, using a small type of centrifuge similar to that developed by Zippe.

Experience gained during these tests suggest that the design of the centrifuge should be as simple as possible, since the mechanical and material problems are predominant so far.

Since concurrent flow does not require a circulation device the rotor design is simpler, so a reconsideration as to whether it is possible to obtain an equally good separation factor from concurrent flow rather than countercurrent flow is given in this paper.

According to Groth's [10] and Zippe's [11] experiments on countercurrent flow, the ratio of actual separative power to the theoretical maximum is 38 and 30% at the most, respectively. Therefore the concurrent flow is worth reconsidering if these values are likely in practice.

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BASIC EQUATIONS IN THE CONCURRENT TYPE OF CENTRIFUGE

As shown by Cohen [12], in the case of a two component gas mixture, assuming steady state conditions, the diffusion equation is given by

$$\frac{1}{r^*}\frac{\mathrm{d}}{\mathrm{d}r^*}\left[r^*\frac{\mathrm{d}N}{\mathrm{d}r^*}+2\delta r^*N(1-N)\right]=\frac{pwr_0}{Dp}\frac{\mathrm{d}N}{\mathrm{d}z^*}-\frac{\mathrm{d}^2N}{\mathrm{d}z^{*2}} \quad (1)$$

where $\delta \equiv (M_2 - M_1)(\omega r_0)^2/2RT$, $r^* = r/r_0$, $z^* = z/r_0$, and N is the mole fraction of desired material, D the diffusion coefficient, M the molecular weight, p the pressure, T the absolute temperature, w the axial velocity of gas stream, ω the angular velocity of the rotor and r_0 is the inner radius of the rotor.

Supposing that we have several thin streams in parallel at $r_i (i = 1, 2 \ldots\ldots, n, 0)$ and L_i is the flow rate at r_i, that is,

$$L_i=\int_{r_i}^{r_{i+1}}\frac{pw}{RT}\,2\pi r\mathrm{d}r \quad (2)$$

and integrating Eq. (1) with respect to r^* for the $(n+1)$ cylindrical thin streams, we obtain

$$\left.\begin{aligned}
&N(r_2)-N(r_1)-[\delta N(1-N)]_0\,(r_2^{*2}-r_1^{*2})\\
&\qquad\qquad =L_1^*\left(\frac{\mathrm{d}N}{\mathrm{d}z^*}\right)_{r_1}\ln\frac{r_2^*}{r_1^*}\\
&N(r_{i+1})-N(r_1)-[\delta N(1-N)]_0\,(r_{i+1}^{*2}-r_i^{*2})\\
&\qquad =\left[L_1^*\left(\frac{\mathrm{d}N}{\mathrm{d}z^*}\right)_{r_1}\cdots\cdots\cdots+L_i^*\left(\frac{\mathrm{d}N}{\mathrm{d}z^*}\right)_{r_i}\right]\ln\frac{r_{i+1}^*}{r_i^*}\\
&N(r_0)-N(r_n)-[\delta N(1-N)]_0\,(1-r_n^{*2})\\
&\qquad =\left[L_1^*\left(\frac{\mathrm{d}N}{\mathrm{d}z^*}\right)_{r_1}+\cdots\cdots\cdots+L_n^*\left(\frac{\mathrm{d}N}{\mathrm{d}z^*}\right)_{r_n}\right]\ln\frac{1}{r_n^*}
\end{aligned}\right\} \quad (3)$$

where $L_{i*} = L_i/\phi_0$, $\phi_0 \equiv 2\pi r.Dp/RT$ and $\delta N(1-N)$ is assumed to be nearly constant, also $\mathrm{d}^2N/\mathrm{d}z^{*2}$ is neglected.

From the material balance,

$$\begin{aligned}
&N(r_1)L_1^*+N(r_2)L_2^*+\cdots\cdots\cdots+N(r_n)L_n^*+N(r_0)L_0^*\\
&=N_0(r_1)L_1^*+N_0(r_2)L_2^*+\cdots\cdots\cdots\\
&\qquad\qquad +N_0(r_n)L_n^*+N_0(r_0)L_0^*
\end{aligned} \quad (4)$$

where $N_0(r_i)$ denotes $N(r_i)$ at $z = 0$.

Two parallel streams (in the case of $n = 1$)

Cohen indicated the maximum separative power in this case as

$$(\delta U)_{0c}=(\delta U)_{\mathrm{m}}\frac{(1-r_1^{*2})^2}{\ln 1/r_1^*}\,\frac{2\{1-\exp(-bZ^*/F^*)\}}{\{1+\exp(-bZ^*/F^*)\}bZ^*/F^*} \quad (5)$$

which can be obtained under the condition of

$$N_0(r_0)-N_0(r_1)=[\delta N(1-N)]_0\frac{(1-r_1^{*2})\exp(-bZ^*/F^*)}{1+\exp(-bZ^*/F^*)}$$

For a single entrance type, that is, $N_0(r_0) = N_0(r_1)$, the separative power becomes

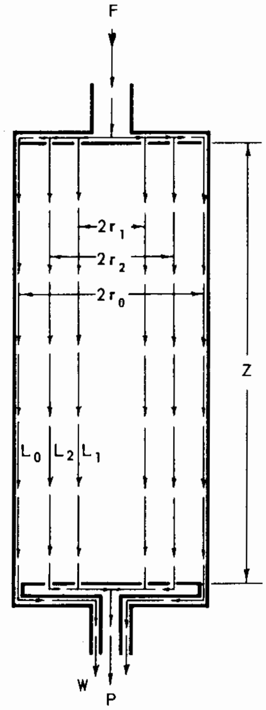

Figure 1. Inner two thin streams remixed at the exit

$$(\delta U)_{\mathrm{se}}=(\delta U)_{\mathrm{m}}\frac{(1-r_1^{*2})^2}{\ln 1/r_1^*}\,\frac{2\{1-\exp(-bZ^*/F^*)\}}{bZ^*/F^*} \quad (6)$$

where $(\delta U)_{\mathrm{m}} \equiv \pi\delta^2 ZDp/2RT$ is the theoretical maximum separative power, and $1/b = \theta_1\theta_0 \ln 1/r_1^*$, $F^* = \mathrm{F}/\phi_0$, $Z^* = Z/r_0$, $\theta_i = L_i/F$. F and Z are the gas feed rate and the rotor length, respectively. $r^* = 0.5335$, $\theta_0 = \theta_1 = 0.5$ are the most preferable condition, as already known.

Three parallel streams (in the case of $n = 2$)

We shall consider two cases for three parallel streams from a single entrance. In one case the three products are separate. In the other case the inner two streams mix at the exit, as shown in Fig. 1, and only two products are obtained. The separative power for the first can be expressed as

$$\begin{aligned}
(\delta U)_3=(\delta U)_{\mathrm{m}}\Bigg[&\mathrm{f}_{a_1}(\theta,r^*)\frac{2\{1-\exp(a_1Z^*/F^*)\}^2}{a_1Z^*/F^*}\\
&+\mathrm{f}_{a_2}(\theta,r^*)\frac{2\{1-\exp(-a_2Z^*/F^*)\}^2}{a_2Z^*/F^*}\Bigg]
\end{aligned} \quad (7)$$

and that for the latter

$$\begin{aligned}
(\delta U)_{3\mathrm{m}}=(\delta U)_{\mathrm{m}}\Bigg[&\mathrm{f}^{\mathrm{m}}_{a_1}(\theta,r^*)\frac{2\{1-\exp(-a_1Z^*/F^*)\}^2}{a_1Z^*/F^*}\\
&+\mathrm{f}^{\mathrm{m}}_{a_2}(\theta,r^*)\frac{2\{1-\exp(-a_2Z^*/F^*)\}^2}{a_2Z^*/F^*}\\
&+\mathrm{f}^{\mathrm{m}}_{a_{12}}(\theta,r^*)\\
&\frac{2\{1-\exp(-a_1Z^*/F^*)\}\{1-\exp(-a_2Z^*/F^*)}{\sqrt{a_1a_2}\,Z^*/F^*}\Bigg]
\end{aligned} \quad (8)$$

where,

$$\mathrm{f}_{a_1}(\theta, r^*) = \frac{a_1}{\xi^2 - 4\zeta}\,\Sigma\theta_i\left\{\frac{1}{a_1}(\theta_j\Delta_i - \theta_k\Delta_k) - \theta_j\theta_k d_i\right\}^2$$

$$\mathrm{f}_{a_2}(\theta, r^*) = \frac{a_2}{\xi_2 - 4\zeta}\,\Sigma\theta_i\left\{\frac{1}{a_2}(\theta_j\Delta_i - \theta_k\Delta_k) - \theta_j\theta_k d_i\right\}^2$$

$$\mathrm{f}^{\mathrm{m}}_{a_1}(\theta, r^*)$$
$$= \frac{\theta_0 \qquad a_1}{(\theta_1+\theta_2)(\xi^2-4\zeta)}\left\{\frac{1}{a_1}(\theta_2\Delta_2 - \theta_1\Delta_0) - \theta_1\theta_2\Delta_2\ln\frac{r_2^*}{r_2^*}\right\}^2$$

$$\mathrm{f}^{\mathrm{m}}_{a_2}(\theta, r^*)$$
$$= \frac{\theta_0 \qquad a_2}{(\theta_1+\theta_2)(\xi^2-4\zeta)}\left\{\theta_1\theta_2\Delta_2\ln\frac{r_2^*}{r_1^*} - \frac{1}{a_2}(\theta_2\Delta_2 - \theta_1\Delta_0)\right\}^2$$

$$\mathrm{f}^{\mathrm{m}}_{a_{1,2}}(\theta, r^*)$$
$$= \frac{\theta_0 \qquad 2\sqrt{a_1 a_2}}{(\theta_1+\theta_2)(\xi^2-4\zeta)}\left\{\xi(\theta_2\Delta_2 - \theta_1\Delta_0)\,\theta_1\theta_2\Delta_2\ln\frac{r_2^*}{r_1^*}\right.$$
$$\left.-\zeta(\theta_2\Delta_2 - \theta_1\Delta_0)^2 - \left(\theta_1\theta_2\Delta_2\ln\frac{r_2^*}{r_1^*}\right)^2\right\}$$

$$a_{1,2} = \frac{\xi \mp \sqrt{\xi^2 - 4\zeta}}{2}$$
$$\zeta = \theta_1\theta_2\theta_0(\ln r_2/r_1)(\ln r_0/r_2)$$
$$\xi = \theta_1\theta_2\ln r_2/r_1 + \theta_2\theta_0\ln r_0/r_2 + \theta_0\theta_1\ln r_0/r_1$$
$$\Delta_i = (r_j^{*2} - r_i^{*2})$$
$$d_1 = (r_2^{*2} - r_1^{*2})\ln r_0/r_2$$
$$d_2 = (1 - r_2^{*2})\ln r_2/r_1 - (r_2^{*2} - r_1^{*2})\ln r_0/r_2$$
$$d_0 = -(1 - r_2^{*2})\ln r_2/r_1$$

and i, j, k correspond to the subscripts of 1,2,0 or 2,0,1 or 0,1,2.

The best conditions are that $r_1^* = 0.48$, $r_2^* = 0.70$, $\theta_1 = 0.15$, $\theta_2 = 0.35$ and $\theta_0 = 0.5$ for the former and $r_1^* = 0.45$, $r_2^* = 0.60$, $\theta_1 = 0.19$, $\theta_2 = 0.31$ and $\theta_0 = 0.5$ for the latter [7].

Figure 2 indicates the relation between the separative power δU and the relative feed rate F^*/Z^* for either two or three streams under optimum conditions.

Of the four cases shown in Fig. 2, $(\delta U)_{\mathrm{oc}}$, $(\delta U)_3$, $(\delta U)_{3\mathrm{m}}$, $(\delta U)_{\mathrm{se}}$ is the order from highest to lowest. The first two cases, however, are hardly applicable for a cascade connection of a number of centrifuges. The third case may be worth considering, since the arrangement of the three streams and their flow control may be possible after some experimental tests.

Comparison of the separation performance through the concurrent flow and that through the countercurrent flow

Cohen [12] and the authors [4, 5, 13] have theoretically studied the separation performance of countercurrent flow.

According to the latter reports [13] either μ or $(\delta U)_p^F/K(\delta U)_{\mathrm{m}}$ can be expressed as a function of F^*Z^*. The calculated results are indicated in Fig. 3, where

$$\mu = [\ln(N_{\mathrm{p}}/N_{\mathrm{w}})_p^F]/2\varepsilon_0^* Z^*$$
$$= \sqrt{2}\,[\ln(N_{\mathrm{p}}/N_{\mathrm{w}})_p^F]/\sqrt{(K)}\,\delta Z^*$$

$$m = \sqrt{(I_3/8)}\,\frac{(pw)_a r_0}{Dp} \quad \text{and} \quad 2\varepsilon_0^* = \frac{1}{\sqrt{2}}\sqrt{(K)}\,\delta$$

$(N_{\mathrm{p}}/N_{\mathrm{w}})_p^F$ is the peak ratio of product concentration to that of waste at a given feed rate. $(\delta U)_p^F$ also is the peak value of δU at a given feed rate. K can be regarded as an evaluation factor of separation affected by flow pattern: that is,

$$K = I_2^2/I_3 \leqslant 1.0 \text{ (the larger, the better)}$$
$$I_2 = 8\int_0^1 r^*\left(\int_0^{r^*}(pw)^* r^*\,\mathrm{d}r^*\right)\mathrm{d}r^*$$
$$I_3 = 16\int_0^1 \frac{1}{r^*}\left(\int_0^{r^*}(pw)^* r^*\,\mathrm{d}r^*\right)\mathrm{d}r^*$$
$$(pw)^* = pw/(pw)_a$$

m_0 is the value of m under the optimum condition and m is mainly concerned with the circulation rate L. Under the ideal flow pattern,

$$L = 4\sqrt{2}\pi r_0\frac{Dp}{RT}m$$

then, $L_0^*\ L_0/\Phi_0 = 2\sqrt{2}\,m_0$.

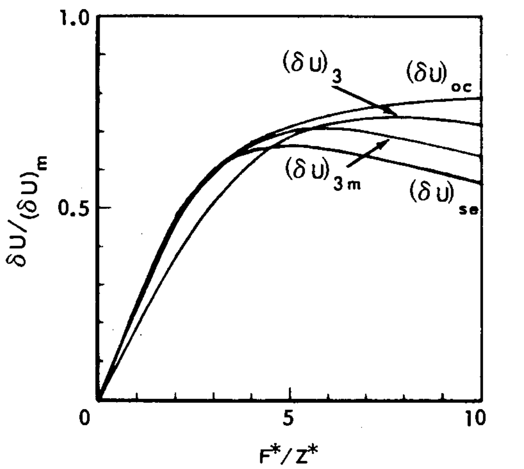

Figure 2. $\delta U/(\delta U)_{\mathrm{m}}$ versus F^*/Z^*

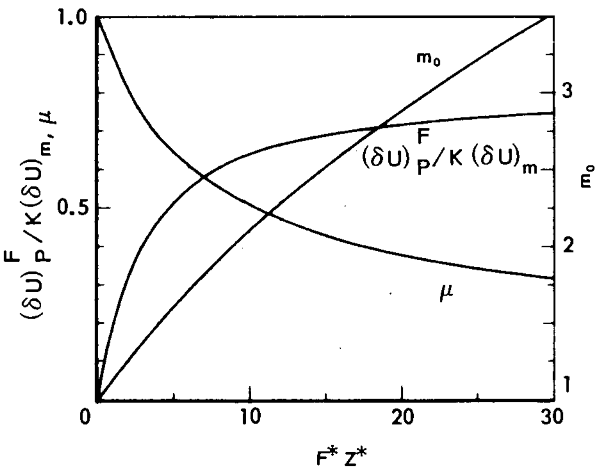

Figure 3. μ, $(\delta U)_p^F/K(\delta U)_{\mathrm{m}}$ and m_0 versus F^*Z^*

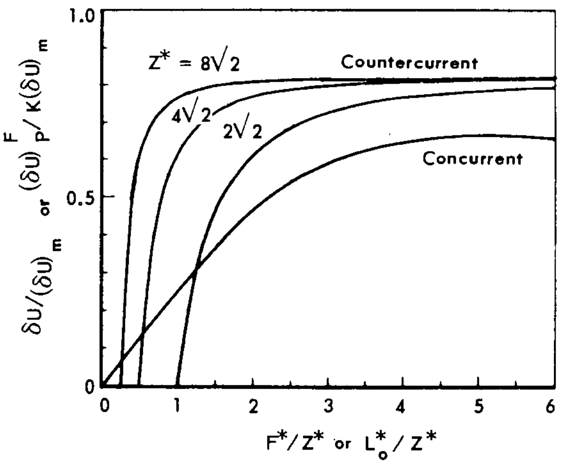

Figure 4. $\delta U/(\delta U)_m$ versus F^*/Z^* and $(\delta U)_p^F/K(\delta U)_m$ versus F^*/Z^* with Z^*

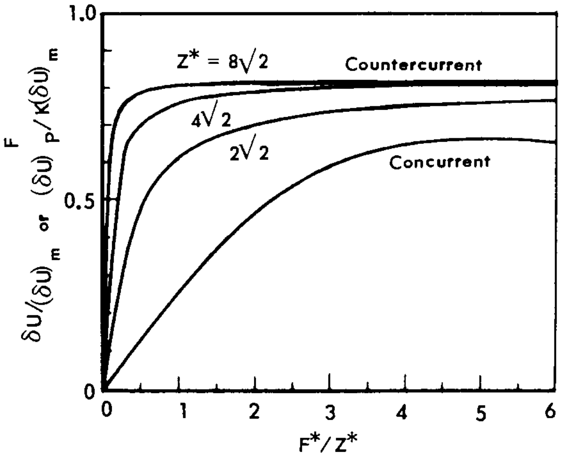

Figure 5. $\delta U/(\delta U)_m$ versus F^*/Z^*, and $(\delta U)_p^F/K(\delta U)_m$ versus L_0^*/Z^* with Z^*

Thus, we can compare the different separation characteristics of concurrent and countercurrent flow in Figs. 2 and 3.

Naturally the countercurrent flow can produce a much higher separation factor than the concurrent flow. The most important factor, however, is the separative power in view of the cascading of centrifuges for large scale production. From Fig. 4 it can be seen that a much higher feed rate is necessary for concurrent flow to obtain the same separative power compared to that for countercurrent flow, and the ratio of both flow rates must increase with $(Z^*)^2$. However, the required circulation rate in the countercurrent flow is much higher than its own feed rate and the ratio of them is proportional to Z^*.

Figure 5 compares the separative powers under the condition $F^* = L^*$ but the difference is much smaller than that in Fig. 4. As K can hardly be expected to be more than 0.7 in practice, the difference should become even less.

CONCLUSION

The countercurrent type of centrifuge is generally considered to be superior in separation performance to the concurrent type of centrifuge. Some analytical calculations have shown this. However, the requirement for a circulation device which will control a moderate circulation flow rate and give a suitable flow pattern cannot be fulfilled unless the mechanical and material problems are solved.

Unfortunately, there is little information on recent foreign work on development of the centrifuge. Therefore, the re-evaluation of the concurrent centrifuge might be necessary only from our present standpoint.

It may be worth while pointing out that a slightly better performance can be obtained from the concurrent centrifuge by using several streams instead of two streams and that the effect of stream thickness which makes it difficult to analyse the separation performance will not be detrimental, as the mixing of the inner two thin streams gives better performance than a single inner thin stream.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/440 Japon

Séparation des isotopes par centrifugeuse à gaz à courant parallèle

par Y. Takashima *et al.*

Les relations entre le pouvoir séparateur, le facteur de séparation, le débit des gaz, la longueur du rotor cylindrique, le soutirage et les rayons d'extraction ont été analysées de façon générale pour la séparation des isotopes par centrifugeuse à gaz à courant parallèle; elles ont été comparées avec celles correspondant au cas de la centrifugeuse à contre-courant.

Une équation différentielle plus générale que celle utilisée par Cohen, qui peut s'appliquer à la centrifugation avec écoulement parallèle de $(n + 1)$ courants cylindriques minces, a été obtenue et résolue pour $n = 1$ et $n = 2$.

D'abord, dans le cas $n = 1$ qui a déjà été résolu par Cohen, la relation entre le débit d'arrivée de gaz pour la longueur du rotor et le facteur de séparation ainsi que le pouvoir séparateur a été calculée et comparée avec celle correspondant au cas d'un contre-courant; on a utilisé un paramètre Z/r_0, qui est le rapport longueur/rayon du rotor. Ceci a permis de montrer quantitativement que, à mesure que Z/r_0 augmente, l'écoulement à courant parallèle doit avoir un débit plus grand pour posséder le même pouvoir séparateur que l'écoulement à contre-courant. Toutefois, le débit de l'écoulement à courant parallèle est comparable au taux de circulation de l'écoulement à contre-courant.

Dans le cas $n = 2$, un pouvoir séparateur maximal plus élevé que dans le cas $n = 1$ peut être obtenu même si les deux courants minces intérieurs se mélangent à la sortie. Les conditions optimales dans ce cas sont les suivantes : $r_1/r_0 = 0{,}45$, $r_2/r_0 = 0{,}6$, $\theta_1 = 0{,}19$ et $\theta_2 = 0{,}31$, où r_1 et r_2 sont les rayons des deux courants intérieurs, et θ le soutirage. Le pouvoir séparateur maximal est 1,066 fois celui pour $n = 1$, et le débit optimal est 1,130 fois plus grand. Les résultats de cette analyse semblent indiquer que l'épaisseur de courant que l'on rencontrera en pratique doit permettre un meilleur rendement de séparation.

A/440 Япония

Разделение изотопов на прямоточной газовой центрифуге

Й. Такашима *et al.*

Взаимосвязь между разделительной способностью, коэффициентом разделения, скоростью газового потока, длиной цилиндрического ротора, сечением потоков анализируется для случая разделения изотопов на прямоточной газовой центрифуге в сравнении со случаем использования центрифуги с противотоком.

Получено и решено для случаев $n = 1$ и $n = 2$ более общее дифференциальное уравнение по сравнению с уравнением Коэна, используемым для центрифуги с $n+1$ тонкими и цилиндрическими прямоточными потоками.

Прежде всего для случая $n = 1$, уже решенного Коэном, отношение скорости потока газа на длину ротора к коэффициенту разделения и разделительной способности было рассчитано и сравнено с отношением для случая центрифуги с противотоком, имеющей параметр Z/r_0, выражающий отношение длины ротора к радиусу. В результате этого было показано, что в количественном отношении чем выше Z/r_0, тем значительно выше должна быть скорость потока в случае прямоточной центрифуги. Только при этом условии получаются одинаковые значения разделительной способности для центрифуги с противотоком. Однако скорость потока в прямоточной центрифуге сравнима со скоростью циркуляции в центрифуге с противотоком.

Для случая $n = 2$ максимальная разделяющая способность оказывается достижимой даже тогда, когда два тонких внутренних потока смешиваются на выходе. Этого не происходит для случая $n = 1$. Оптимальные условия:

$r_1/r_0 = 0{,}45$; $r_2/r_0 = 0{,}6$; $\theta_1 = 0{,}19$; $\theta_2 = 0{,}31$, где r_1 и r_2 — радиусы двух внутренних потоков, а θ — сечение. Максимальное значение разделительной способности составляет 1,066 величины для случая $n = 1$, а оптимальная скорость потока составляет 1,130.

В результате этого анализа делается предположение, что толщина потока окажет необходимое влияние на достижение более высокого разделения.

A/440 Japón

Separación de isótopos mediante centrífuga de gases de flujo continuo

por Y. Takashima *et al.*

Las relaciones entre el poder separador, el factor de enriquecimiento, la velocidad de flujo del gas, la longitud del rotor cilíndrico, los cortes y los radios que se han extractado, generalmente han sido analizadas desde el punto de vista de la separación de isótopos por el tipo de flujo continuo de centrífuga de gases y se han comparado con las correspondientes al tipo en contracorriente.

Se ha obtenido una ecuación diferencial más generalizada que la empleada por Cohen, que puede ser aplicada a la separación centrífuga a través de $(n + 1)$ corrientes cilíndricas delgadas de flujo continuo, y resuelta en los casos de $n = 1$ y $n = 2$.

En primer lugar, en el caso de $n = 1$, que ya fué resuelto por Cohen, las relaciones entre la velocidad de movimiento del gas por la longitud del rotor y el factor de enriquecimiento y el poder separador, se ha calculado y comparado con las correspondientes al flujo en contracorriente usando un parámetro Z/r_0 que es la relación de la longitud del rotor al radio. Como consecuencia, se ha demostrado que, cuando Z/r_0 aumenta, sería necesaria una velocidad de flujo notablemente más elevada en el flujo continuo para obtener el mismo valor del poder separador que en el caso del flujo en contracorriente. La velocidad de flujo en el flujo continuo, no obstante, es comparable con la velocidad de circulación en el flujo en contracorriente.

En el caso de $n = 2$, se puede conseguir el poder separador máximo más elevado que en el caso de $n = 1$, aun si las dos corrientes delgadas interiores son mezcladas a la salida. Las condiciones optimas en este caso son como sigue : $r_1/r_0 = 0{,}45$, $r_2/r_0 = 0{,}6$, $\theta_1 = 0{,}19$ y $\theta_2 = 0{,}31$, donde r_1 y r_2 son los radios de las dos corrientes interiores y θ el corte. El valor máximo del poder separador es 1,066 veces el correspondiente a $n = 1$, entonces la velocidad de flujo óptima es 1,130 veces mayor.

Como resultado de estos análisis, se sugiere que el espesor de la trayectoria del flujo que existirá en la práctica puede producir bastante mejor resultado de separación.

Separation of stable isotopes by the gas centrifuge method : influence of the axial pressure on the separation of argon isotopes

By I. Jordan, W. Kolbe and R. Borges da Silva *

In 1959, research on isotope separation by the gas centrifuge method was initiated at the Institute of Technological Research, São Paulo, after the installation of three countercurrent gas centrifuges, developed, as model ZG-3, by Groth *et al.* [1, 2, 3]. The work done with these centrifuges was, initially, the investigation in a symmetrical separation process of the enrichment and separative power of argon isotopes as a function of the throughput rate, at a fixed axial pressure and for different countercurrent flows established by various temperature differences between the rotor covers. Later these experiments were extended to unsymmetrical separation processes. Both kinds of experiment are described in a paper by Bulang, Groth *et al.* [4], together with similar experiments done in Germany with the more recent ZG-5 gas centrifuge model, also developed by Groth and co-workers.

Continuing this work on isotope separation by gaseous centrifuging, we investigated recently the axial pressure dependence of the enrichment and separative power for the separation of argon isotopes. Enrichment experiments of argon isotopes with the centrifuge model ZG-3, in which the separation factor was measured as a function of the throughput rate for several axial pressures, have been already reported by Groth and Welge [3]. However, the axial dependence of the enrichment is not clearly stated, as can be observed from the given experimental curve. Furthermore, in our previous work done with a fixed axial pressure of 20 torr, no maxima in the separative power versus throughput rate curves, corresponding to several temperature differences between the rotor covers, could be observed for throughput rates up to 400 Ncm^3/min. On the other hand, such maxima for certain temperature differences between the rotor covers are reported by Bulang, Groth *et al.* [4] for the centrifuge model ZG-5, when working with an axial pressure of only 5 torr. Taking these facts into consideration, experiments on the separation of argon isotopes were carried out at smaller axial pressures than the formerly reported value of 20 torr, in order to gain further information about the separation process in a countercurrent gas centrifuge controlled by thermal convection. The purpose of the present paper is, therefore, the presentation of the results achieved in this investigation, as well as a description of the gas centrifuge equipment, as it stands now at this Institute.

DESCRIPTION OF THE EQUIPMENT

The gas centrifuge, model ZG-3, has been already described in detail by Groth and collaborators [1, 2, 3], so that only its most important features and the auxiliary equipment installed at this Institute will be mentioned here. Essentially, the centrifuge consists of a hollow, vertical rotor into which the gas of natural isotopic composition is fed through the inner tube of the double-walled, highly elastic and rotating upper axis. The countercurrent inside the rotor is produced by thermal convection when a temperature difference is maintained between the rotor covers. For this reason, the upper rotor cover is heated and the lower one cooled. Then the depleted fraction (waste) and the enriched fraction (product) are, respectively, withdrawn from the rotor through the outer tube of the upper axis and through the one-walled, highly elastic, rotating lower axis, by means of a vacuum pump.

The dimensions of the rotor are 66.5 cm inside length and 18.5 cm inside diameter. The peripheral velocities (ωr_2) of the three centrifuges, designated by ZG-3A, ZG-3B and ZG-3C are 296, 297 and 300 m/s, respectively. These velocities were calculated from the frequencies of the centrifuges which were measured with a cathode-ray oscilloscope by comparison with an audio oscillator.

The heating of the upper cover of the rotor is by eddy currents produced by an electromagnet in the rapidly rotating ring which is a part of the upper cover. A small d.c. power supply was built to distribute the electric current to each electromagnet of the three centrifuges. A rheostat and an ammeter were inserted, in series, in each of these electric circuits. In this way the current which circulates through each electromagnet can be independently adjusted and measured,

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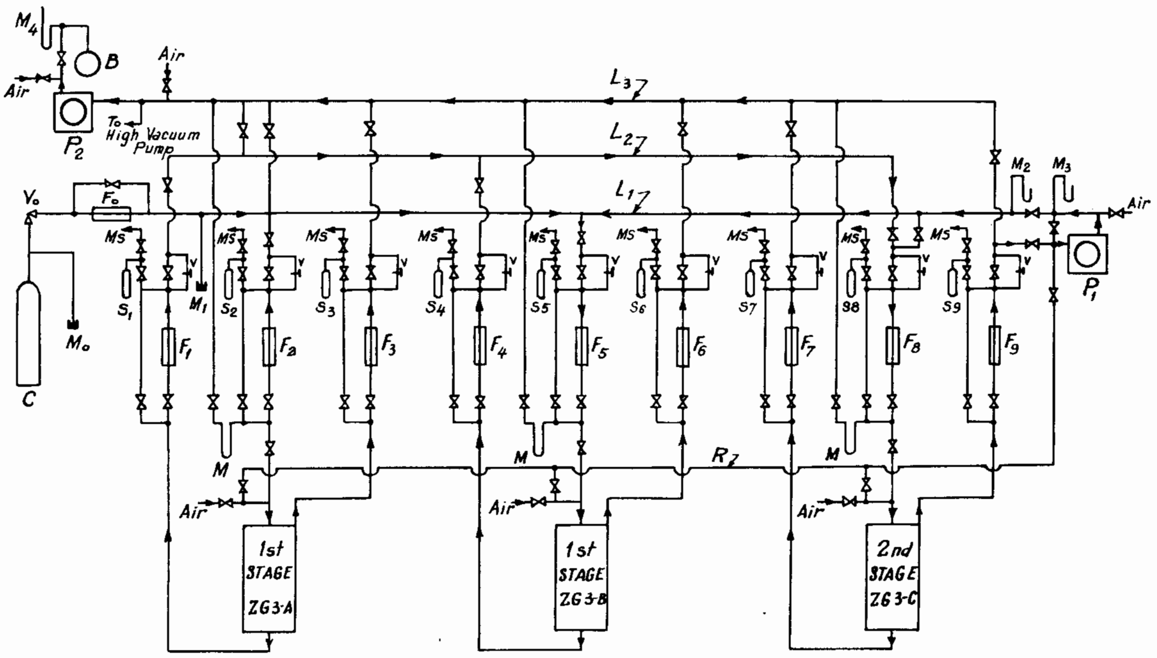

Figure 1. Diagram of the two-stage cascade for the separation of argon isotopes

up to 1 A, thus establishing the required temperature of the upper cover.

The cooling of the lower rotor cover is by a cold water coil which surrounds the cover. The cold water circulating through this coil and other parts of the centrifuge is supplied from a refrigerated water tank. The temperature of the incoming water was usually adjusted between 10 and 12 °C and could be maintained constant within 0.5 °C during the operation of the centrifuge.

The temperatures of the rotor covers are measured by calibrated electrically temperature-sensitive elements described by Groth and co-workers [2, 3] using a Wheatstone bridge. These measurements may be performed successively on the three centrifuges through a system of switches.

The centrifuges were connected in a two-stage cascade arrangement for the separation of argon isotopes, the first stage being composed of the centrifuges ZG-3A and ZG-3B and the second stage was the centrifuge ZG-3C. This experimental cascade is shown schematically in Fig. 1. Argon is stored under high pressure in cylinder C. The total feed, after leaving the cylinder at a pressure slightly higher than the atmospheric pressure and measured by manometer M_0, flows through throttling valve V_0 and flowmeter F_0 located in line L_1. The pressure of this incoming gas stream is measured by manometer M_1. The total feed is then separated into two streams which flow through valves V and flowmeters F_2 and F_5, respectively, into the rotors of the centrifuges ZG-3A and ZG-3B. The enriched fractions from these first stage units flow via valves V and flowmeters F_1 and F_4, into the line L_2 and feed the rotor of the second stage centrifuge ZG-3C, after passing through valve V and flowmeter F_8. The depleted fraction leaving this centrifuge, after passing through valve V and flowmeter F_9, is recycled by vacuum pump P_1 to the first stage of the cascade through line L_1. Manometers M_2 and M_3 are used to indicate the direction of the flow and the proper operation of this cascade section. The enriched fraction from centrifuge ZG-3C, after passing through valve V and flowmeter F_7, as well as the depleted fractions from centrifuges ZG-3A and ZG-3B, after flowing through valves V and flowmeters F_3 and F_6, respectively, are brought together in line L_3 and pumped to the atmosphere by vacuum pump P_2.

The line R is provided in order to evacuate the rotors of all the centrifuges by means of pump P_1 at the beginning of the operation.

The cascade was built of Pyrex glass tubing and all the stopcocks, shown in Fig. 1, are high vacuum glass stopcocks. The valves V, which permit the adjustment of the flows and the axial pressures, are made from rubber vacuum tubing fitted with a Hofmann clamp.

The flowmeters, based on the principle of the streaming calorimeter, were built according to the model described by Groth and co-workers [2, 3]. The flow measurements are made by these devices through a differential method of resistance determination by means of a specially built Wheatstone bridge. A double-throw three-pole knife switch establishes the electrical connection between this instrument and each pair of the ten flowmeters. The flowmeters are calibrated, after short-circuiting each centrifuge, by measuring with the manometer M_4 the pressure increase per unit time produced in the flask B of known volume (Fig. 1) by the operation of pump P_2. The calibration curves were straight lines for flows up to ca. 400 Ncm^3/min of argon. It was also verified experimentally that the flow measurements are independent of the gas pressure, according to the theory given for this kind of flowmeter by Blackett, Henry and Rideal [5, 6].

The axial pressure at the rotor of each centrifuge is measured by means of the diffusion pump oil manometers M shown in Fig. 1. The cascade also contains a mercury diffusion pump high vacuum system, which will evacuate one arm of these manometers for checking for leaks in the tubing.

For isotopic analysis of the gas of natural composition and the enriched and depleted fractions, sampling flasks S were installed for each centrifuge. These flasks are connected (through MS of Fig. 1) to a mass spectrometer, model AN 220a, type Is/spez, manufactured by Atlas-Werke A.G., Germany.

To operate the centrifuges as single elements rather than as cascade units, additional connections with stopcocks were included in the cascade, as shown in Fig. 1. By manipulating these stopcocks in a suitable manner the feed may be introduced, via the corresponding throttling valve and flowmeter, into the rotor of only one of the three centrifuges. The enriched and depleted fractions withdrawn from this centrifuge are then pumped off to the atmosphere by means of the pump P_2, after passage through the respective throttling valves and flowmeters. The present investigation was performed in this way, using only the centrifuge ZG-3B.

A general view of the cascade arrangement is given in Fig. 2, showing the upper part of the three centrifuges, each of which is mounted on two concrete pillars.

INFLUENCE OF THE AXIAL PRESSURE ON THE SEPARATION OF ARGON ISOTOPES

In order to investigate the effect of the axial pressure on the separation of argon isotopes, the experiments were carried out by determining the separation factor

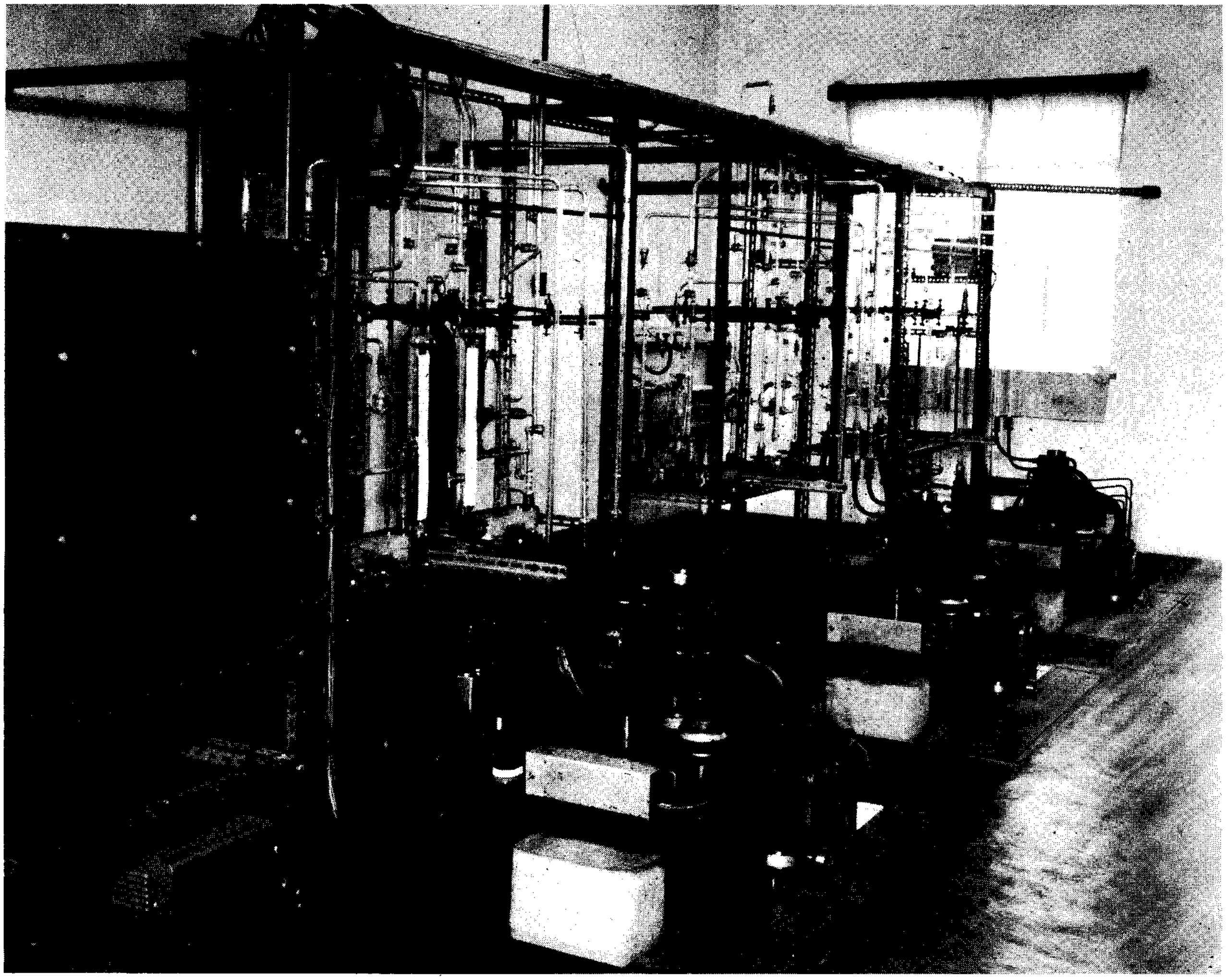

Figure 2. General view of the cascade arrangement

A as a function of the total flow or throughput rate G (Ncm^3/min) at a fixed axial pressure p_0 (torr) and for several temperature differences ΔT (°C) between the rotor covers. The experiments were then repeated in the same manner but at other axial pressures.

All experiments were carried out so as to give a symmetrical separation process (cut $\theta = 0.5$). Therefore the flows of the enriched and depleted fractions were always adjusted to the proper value, $G/2$, by means of the throttling valves V (Fig. 1). Furthermore in the experiments made at the same axial pressure this adjustment was done in such a manner as to mantain this pressure for all throughput rates. In order to obtain the temperature differences ΔT, the temperature of the lower cover was kept constant, while that of the upper cover was varied in the manner described above.

From the abundance ratios $R' = (^{36}\mathrm{Ar}/^{40}\mathrm{Ar})_\mathrm{P}$ of the enriched fraction and $R'' = (^{36}\mathrm{Ar}/^{40}\mathrm{Ar})_\mathrm{W}$ of the depleted fraction, measured with the mass spectrometer, the separation factor A was calculated by

$$A = (^{36}\mathrm{Ar}/^{40}\mathrm{Ar})_\mathrm{P}\,(^{40}\mathrm{Ar}/^{36}\mathrm{Ar})_\mathrm{W} \qquad (1)$$

All experimental values of A are averages of several mass spectrometric determinations.

For a symmetrical separation process the separation factor A is equal to α^2 where α is the separation factor of the enriched fraction. This separation factor is given by $\alpha = R'/R$, R being the abundance ratio of the isotopic mixture with natural composition.

For large values of α, according to Cohen [7], the separative power is given by

$$\delta U = G\,\frac{(\alpha - 1)\ln\alpha}{\alpha + 1} \qquad (2)$$

In the present investigation, the values of the separative power were calculated by Eq. (2), from the experimental curves of the separation factor A vs. the total flow G.

Experimental results

The experiments were performed with the centrifuge ZG-3B at a peripheral velocity of 297 m/s and with two axial pressures p_0, namely 7.4 and 9.9 torr. In each of these experiments, the enrichment A was measured as a function of the throughput rate G for five temperature differences between the rotor covers, ΔT varied from 9.8 to 27.5 °C. Owing to the great flow resistance through the inner tube of the upper axis, it was not possible to obtain symmetrical separation processes for throughput rates higher than 180 Ncm^3/min and 100 Ncm^3/min in the experiments made with axial pressures of 9.9 and 7.4 torr, respectively. In all the runs the temperature of the lower rotor cover was held constant around 21 °C. The experimental results are given in the enrichment-throughput rate curves shown in Figs. 3 and 4. For comparison and discussion purposes, the enrichment-throughput rate curves from our previous work [4], done with the centrifuge ZG-3B at an axial pressure of 20 torr and a peripheral velocity of 290 m/s, are given in Fig. 5.

The enrichments at total reflux (without production) A_0 were taken from the curves given in Fig. 3, 4 and 5, by extrapolation of the throughput rate to zero. The curves representing these enrichments as a function of the temperature difference of the covers for axial pressures of 20, 9.9 and 7.4 torr, are shown in Fig. 6.

The dependence of the separative power on the throughput rate was calculated by Eq. (2) and is given by the curves presented in Figs. 7, 8 and 9.

Discussion of the results

The curves given in Fig. 6 show that at total reflux and for each axial pressure there is an optimum temperature difference between the rotor covers, corresponding to the optimum internal flow which leads to the maximum enrichment factor. As the axial pressure is decreased this maximum becomes smaller and flatter, being also shifted in the direction of higher temperature differences between the rotor covers. The same behaviour was observed by Groth and Welge [3] for even smaller axial pressures.

According to the theory of the countercurrent gas centrifuge developed by Cohen [7], the maximum enrichment at total reflux is given, through the relation of the molar fractions $N(Z)/N(0)$ for $N \ll 1$, by the equation:

$$N(Z)/N(0) = \exp 2\varepsilon_0 Z \qquad (3)$$

where Z is the length of the centrifuge and

$$2\varepsilon_0 = \frac{(\mathrm{M}_2 - \mathrm{M}_1)\,\dfrac{\omega^2}{RT}\displaystyle\int_0^{r_2} r\,\mathrm{d}r \int_0^{r} pwr\,\mathrm{d}r}{r_2\sqrt{\left[2\displaystyle\int_0^{r_2}\frac{\mathrm{d}r}{r}\left(\int_0^{r} pwr\,\mathrm{d}r\right)^2\right]}} \qquad (4)$$

M_1 being the molecular weight of the light isotope, M_2 the molecular weight of the heavy isotope, ω the angular velocity of the centrifuge and $w = w(r)$ the velocity of the gas in the axial direction. In order to calculate the enrichment $N(Z)/N(0)$, Eq. (4) requires a knowledge of the flow profile inside the centrifuge rotor.

The exact nature of the flow profile inside the rotor of a countercurrent gas centrifuge controlled by thermal convection is not known. However, as Los and Kistemaker [8] pointed out, an estimation of this flow profile can be made by assuming the flow profile which results from the calculations of Martin [9] and is given by:

$$\int_0^{r}\frac{pw}{r}\,2\pi r\,\mathrm{d}r \approx r^{\frac{1}{2}}\exp\left(\frac{\mathrm{M}\omega^2 r^2}{4RT}\right) \qquad (5)$$

For this flow profile of Martin, Eq. (3) may be written in the form given by Groth and Welge [3]:

$$N(Z)/N(0) = \exp\left(\frac{(\mathrm{M}_2 - \mathrm{M}_1)\,(\omega r_2)^2}{2RT}\cdot\frac{\mathrm{Z}\sqrt{(2K)}}{2r_2}\right) \qquad (6)$$

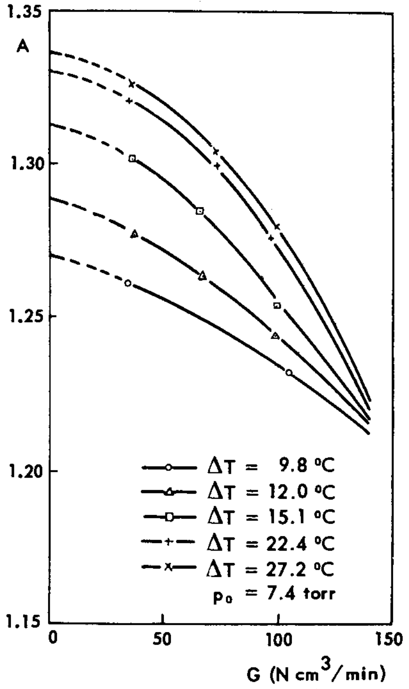

Figure 3. Variation of the enrichment *A* with the throughput rate *G*, $wr_2 = 297$ m/s

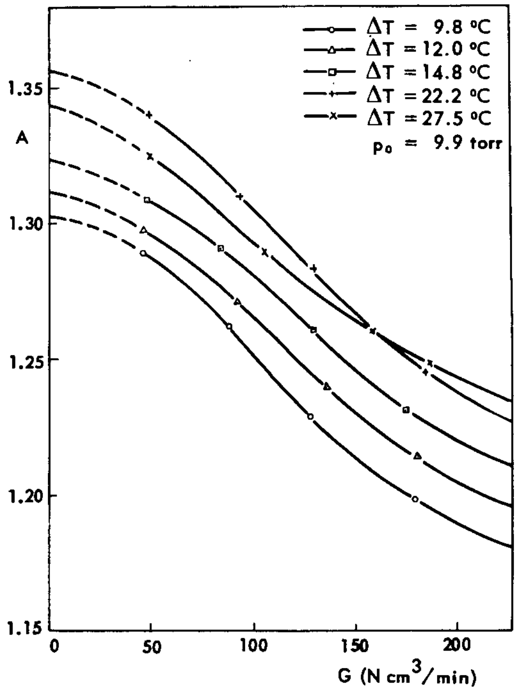

Figure 4. Variation of the enrichment *A* with the throughput rate *G*, $wr_2 = 297$ m/s

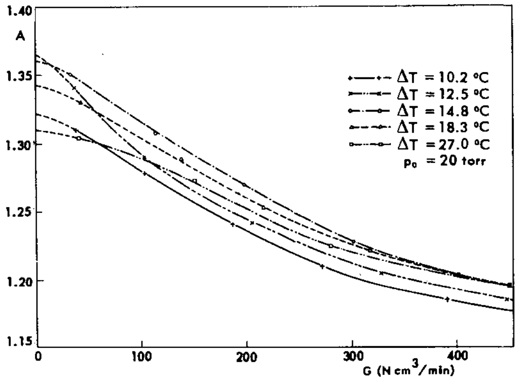

Figure 5. Variation of the enrichment *A* with the throughput rate *G*, $wr_2 = 290$ m/s

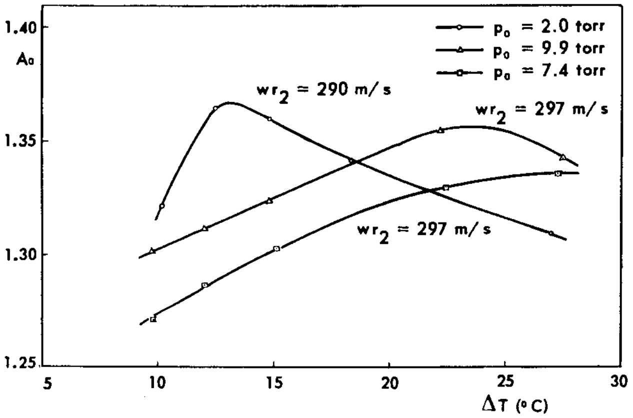

Figure 6. Dependence of the enrichment at total reflux A_0 on the temperature difference between rotor covers ΔT

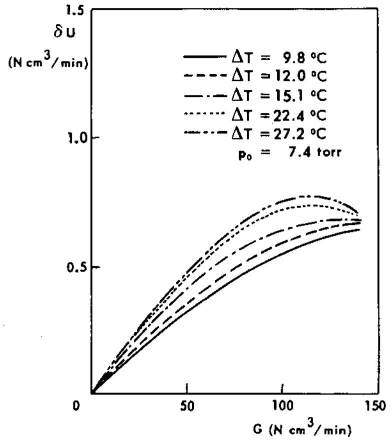

Figure 7. Variation of the separative power δU with the throughput rate *G*, $wr_2 = 297$ m/s

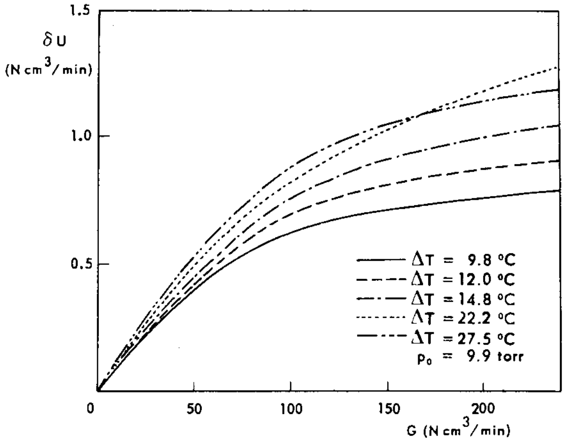

Figure 8. Variation of the separative power δU with the throughput rate *G*, $wr_2 = 297$ m/s

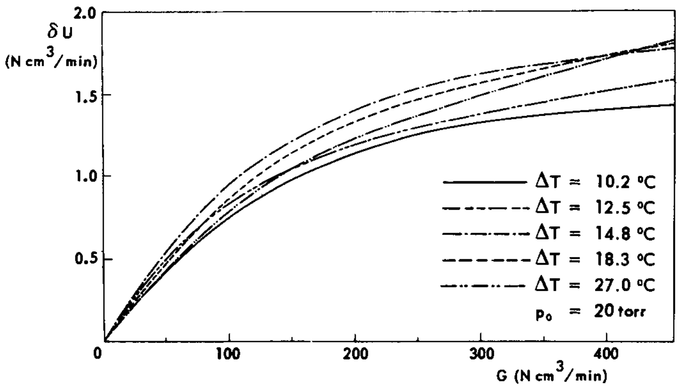

Figure 9. Variation of the separative power δU with the throughput rate G, $wr_2 = 290$ m/s

$$\text{with } K = \frac{\left(\frac{2}{r_2^2}\int_0^{r_2} r\,\mathrm{d}r \int_0^r pwr\,\mathrm{d}r\right)^2}{\int_0^{r_2}\frac{\mathrm{d}r}{r}\left(\int_0^r pwr\,\mathrm{d}r\right)^2} = \frac{\left[\frac{2}{r_2^2}\int_0^{r_2} r^{\frac{3}{2}}\,\mathrm{d}r\,\exp\left(\frac{\mathrm{M}\omega^2 r^2}{4RT}\,\mathrm{d}r\right)^2\right]}{\int_0^{r_2}\exp\left(\frac{\mathrm{M}\omega^2 r^2}{2RT}\right)\mathrm{d}r} \qquad (7)$$

Los and Kistemaker [8] also showed that the concentration gradient in the radial direction of a countercurrent centrifuge becomes equal to that corresponding to the maximum separative power when the flow profile presents the form:

$$\int_0^r pwr\mathrm{d}r \approx r^2 \qquad (8)$$

For this optimum flow profile Eq. (3) becomes:

$$N(Z)/N(0) = \exp\left(\frac{(\mathrm{M}_2 - \mathrm{M}_1)\,(\omega r^2)^2}{2RT}\cdot\frac{Z\sqrt{(2K)}}{2r_2}\right) \qquad (9)$$

The values of the maximum enrichment at total reflux $A_{0,\mathrm{M}}$ and A_0,opt corresponding to the Martin flow profile and the optimum flow profile and calculated by means of Eqs. (6) and (9), respectively, for the conditions prevailing in our experiments, are presented in Table 1. These values are compared with the experimental values $A_{0,\mathrm{exp}}$ measured at axial pressures of 7.4, 9.9 and 20 torr. Table 1 also shows the values of the equilibrium separation factor a_0 given by

$$a_0 = \exp\left(\frac{(\mathrm{M}_2 - \mathrm{M}_1)\,(\omega r_2)^2}{2RT}\right)$$

and the values of the multiplication factor f defined by $f = \ln A_{0,\mathrm{exp}}/\ln a_0$.

Table 1. Maximum enrichment at total reflux

p_0 (torr)	ωr_2 (m/s)	a_0	$A_{0,\mathrm{M}}$	$A_{0,\mathrm{opt}}$	$A_{0,\mathrm{exp}}$	f
7.4	297	1.072	1.353	1.422	1.337	4.20
9.9	297	1.072	1.353	1.422	1.357	4.40
20	290	1.069	1.337	1.403	1.367	4.68

As can be seen from Table 1, the experimental values of the maximum enrichment at total reflux are always lower than the values corresponding to the optimum flow profile, the difference becoming smaller as the axial pressure increases. On the other hand, for small and great axial pressures the experimental values are, respectively, lower and higher than the values calculated according to the Martin flow profile, becoming equal for the intermediate axial pressure. Therefore for small axial pressures the actual flow profile deviates considerably from the flow profile of Martin and from the condition that the neutral layer of the gas ($w = 0$) lies close to the rotor wall. As the axial pressure increases, the actual flow profile diverges again from the Martin flow profile, but approaches the optimum one. As might be expected the effect on the flow profile of increasing the axial pressure is similar to that of increasing the mass of the gas, studied by Groth and Welge [3].

The curves given in Figs. 3, 4 and 5 show that, when the centrifuge is operating with production, for each throughput rate, there is also an optimum temperature difference between the rotor covers which gives the maximum enrichment. These maximum enrichments and the corresponding optimum temperature differences are given by the enrichment-throughput rate curves shown in Fig. 10 for axial pressures of 9.9 and 20 torr.

The separative power-throughput rate curves given in Figs. 8 and 9 for axial pressures of 9.9 and 20 torr, respectively, do not present a maximum within the experimentally possible throughput rate range. However for an axial pressure of 7.4 torr, such maxima are observed. As can be seen from Fig. 7 these maxima become greater and are shifted toward smaller throughput rates, as the temperature differences between the rotor covers are increased up to 27.2 °C.

The theoretical maximum separative power of a centrifuge according to Cohen [7] is given by:

$$(\delta U)_{\max} = \frac{Dp}{RT}\left[\frac{(\mathrm{M}_2 - \mathrm{M}_1)\,(\omega r_2)^2}{2RT}\right]^2\frac{\pi Z}{2}\ \text{moles/s} \qquad (10)$$

$$= \varrho D\left[\frac{(\mathrm{M}_2 - \mathrm{M}_1)\,(\omega r_2)^2}{2RT}\right]^2\frac{\pi Z}{2}\ \text{grammes/s} \qquad (11)$$

where D is the diffusion coefficient and ϱ the density of the gas. The separative power of a countercurrent gas centrifuge as shown by Cohen [7] is:

$$\delta U = \frac{Dp}{RT}\left[\frac{(\mathrm{M}_2 - \mathrm{M}_1)\,\omega^2}{RT}\right]^2 \frac{\left(\int_0^{r_2} r\mathrm{d}r \int_0^r pwr\mathrm{d}r\right)^2}{\int_0^{r_2}\frac{\mathrm{d}r}{r}\left(\int_0^r pwr\mathrm{d}r\right)^2}\cdot\frac{\pi Z}{2}\cdot\frac{m^2}{1+m^2} \qquad (12)$$

where m is a measure of the total countercurrent inside the rotor. It can be shown [3, 7] that for the flow profile of Martin Eq. (12) becomes:

$$\delta U_{\mathrm{M}} = (\delta U)_{\max}\,Km^2/(1 + m^2)\ \text{moles/s} \qquad (13)$$

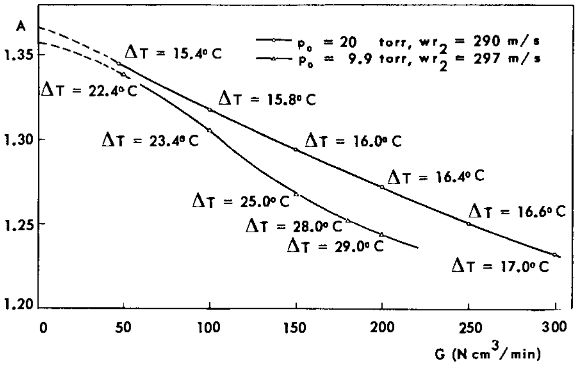

Figure 10. Dependence of the enrichment *A* for optimum temperature differences on the throughput rate *G*

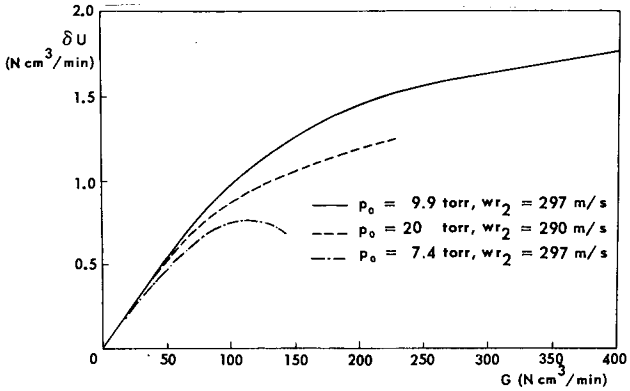

Figure 11. Dependence of the separative power δU for optimum temperature differences on the throughput rate *G*

with *K* given by Eq. (7) whereas for the optimum flow profile it is:

$$\delta U_{\text{opt}} = (\delta U)_{\max} m^2/(1 + m^2) \text{ moles/s} \qquad (14)$$

In order to compare the highest values of the separative power measured in our experiments with the theoretical maximum, the values were calculated as a function of the throughput rate by means of Eq. (2) from the values for the enrichment, corresponding to the optimum temperature differences and given in Fig. 10. The resulting separative power vs. throughput rate curves are shown in Fig. 11 for axial pressures of 9.9 and 20 torr, together with the curve resulting from the experiments performed at an axial pressure of 7.4 torr and the highest experimental temperature difference of 27 °C. Table 2 presents the values of the theoretical maximum separative power $(\delta U)_{\max}$, calculated from Eq. (11) with $\varrho = 1.78 \times 10^{-3}$ g/cm³ and $D = 0.157$ cm²/s, as well as the highest experimental values $(\delta U)_{\text{exp}}$ taken from the curves given in Fig. 11.

Table 2. Maximum separative powers

p_0 (torr)	ωr_2 (m/s)	$(\delta U)_{\max}$ (Ncm³/min)	$(\delta U)_{\exp}$ (Ncm³/min)
7.4	297	4.91	0.77
9.9	297	4.91	1.25
20	290	4.48	1.76

As can be seen from Table 2, for axial pressures of 7.4, 9.9 and 20 torr, only 15.7, 25.5 and 39.3% of the theoretical maximum separative power are attained. These results are in agreement with the previous discussion; as the axial pressure becomes smaller, the flow profile inside the rotor deviates more and more from the optimum flow profile, for which the separative power is given by Eq. (14), so that smaller values for the separation potential are to be expected.

ACKNOWLEDGEMENT

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/482 Brésil

Séparation des isotopes stables par centrifugation gazeuse — Influence de la pression axiale sur la séparation des isotopes de l'argon

par I. Jordan *et al.*

Les auteurs décrivent l'installation de séparation des isotopes stables par centrifugation gazeuse de l'Institut de recherches techniques de São Paulo, et rendent compte de recherches sur l'influence de la pression du gaz suivant l'axe du rotor de la centrifugeuse sur la séparation des isotopes de l'argon. Cette installation comprend trois centrifugeuses à contre-courant (superposition d'une circulation thermique) du modèle ZG-3 mis au point par Groth et ses collaborateurs. Ces centrifugeuses sont disposées en une cascade à deux étages pour la séparation des isotopes de l'argon. Les auteurs donnent aussi une description de cette cascade, dans laquelle chaque centrifugeuse peut également fonctionner isolément.

L'étude de l'influence de la pression axiale sur la séparation des isotopes de l'argon a été faite au moyen de l'une de ces centrifugeuses dans laquelle on a mesuré l'enrichissement en fonction du débit total de gaz pour diverses différences de températures entre les pales du rotor et pour diverses pressions axiales du gaz dans le rotor même. Au moyen des données obtenues au cours de ces expériences, les auteurs ont déterminé l'enrichissement pour un reflux total, ainsi que le pouvoir de séparation de la centrifugeuse en fonction du débit de gaz. Les résultats obtenus montrent que l'enrichissement et le pouvoir de séparation diminuent avec la pression axiale et que les différences de températures optimales entre les pales du rotor doivent être plus grandes lorsque les pressions axiales sont plus faibles. Pour certaines différences de température, on a observé un maximum des courbes exprimant le pouvoir de séparation en fonction du débit; ces courbes avaient été obtenues lors d'expériences sur la plus basse des pressions axiales ayant fait l'objet de recherches. Les auteurs examinent en outre les résultats, compte tenu du fait que le pouvoir de séparation varie selon le profil de circulation du gaz à l'intérieur du rotor.

A/482 Бразилия

Разделение стабильных изотопов методом газовой центрифуги. Влияние осевого давления на разделение изотопов аргона

И. Иордан *et al.*

В докладе описаны установка для разделения стабильных изотопов методом газовой центрифуги, построенная в Институте технологических исследований, а также эксперименты по определению влияния давления газа вдоль оси ротора центрифуги на разделение изотопов аргона. Установка состоит из трех термически регулируемых противоточных газовых центрифуг модели ZG-3, разработанных Гротом и и сотрудниками. Эти центрифуги установлены в виде двухступенчатого каскада для разделения изотопов аргона. Приведено описание этого каскада, в котором каждая центрифуга может работать и самостоятельно.

На одной из этих трех центрифуг влияние осевого давления на разделение изотопов аргона было исследовано путем измерения обогащения в зависимости от количества пропускаемого газа для различных разностей температур между крышками ротора и для нескольких осевых давлений газа в роторе центрифуги. Данные, полученные в этих экспериментах, были использованы для расчетов обогащения при полном обратном потоке, а также разделительной способности центрифуги в зависимости от пропускания газа. Результаты показывают, что обогащение и разделительная способность уменьшаются с уменьшением осевого давления и что при меньших осевых давлениях необходимы бóльшие оптимальные разности температур между крышками ротора. Для некоторых разностей температур наблюдалось наличие максимума на кривых зависимости разделительной способности от пропускания газа, которые были получены в экспериментах с наименьшими исследованными осевыми давлениями. Результаты рассматриваются в связи с зависимостью разделительной способности от профиля потока газа внутри ротора центрифуги.

A/482 Brasil

Separación de isótopos estables por centrifugación gaseosa: Influencia de la presión axial en la separación de isótopos de argón

por I. Jordan *et al.*

Se describe la instalación de separación de isótopos por el método de las centrífugas de gas existente en el Instituto de Pesquisas Tecnológicas de São Paulo, Brasil, y los experimentos efectuados para investigar, en la separación de isótopos de argón, el efecto de la presión axial del gas en el rotor de la centrífuga. La instalación comprende tres centrífugas de gas a contracorriente controladas térmicamente, de modelo ZG-3, desarrolladas por Groth y colaboradores. Las centrífugas están ligadas en una cascada de separación de isótopos de argón formada de dos etapas. Esta cascada fue construida de tal menera que cada una de las centrífugas puede ser también operada como un elemento simple. Se presenta la descripción de la cascada.

El estudio de la influencia de la presión axial en la separación de isótopos de argón fue realizado con una de estas centrífugas a través de medidas del enriquecimiento en función del flujo total del gas, para distintas diferencias de temperatura entre las tapas del rotor y diferentes presiones axiales del gas en el mismo rotor. Con ayuda de los datos obtenidos en estas experiencias fueron calculados los enriquecimientos en reflujo total, así como los valores de los potenciales de separación de la centrífuga en función del flujo de gas. Los resultados obtenidos muestran que el enriquecimiento y el potencial de separación disminuyen con la disminuición de la presión axial, siendo necesarias mayores diferencias de temperaturas óptimas entre las tapas del rotor para las presiones menores. Para ciertas diferencias de temperatura se observó la existencia de un máximo en las curvas del potencial de separación en función del flujo, correspondientes a la menor de las presiones axiales investigadas. Se discuten, además, los resultados en vista de la dependencia entre el perfil de circulación del gas en el interior del rotor y el potencial de separación.

P/637 Netherlands

The separative power of short countercurrent centrifuges

By C. Ouwerkerk * and J. Los **

In separating isotopes by means of centrifuges, three different methods can be employed. Both the evaporative and the countercurrent method are characterized by relatively large feed rates and small separation factors. In countercurrent centrifuges, the simple process factor is multiplied several times in one centrifuge, thus giving rise to large separation factors and small feed rates. This puts a high premium on the use of countercurrent centrifuges, not only from a cascade standpoint but also from the standpoint of operating the centrifuges. Provided the countercurrent can be established internally in the centrifuges, the problem of extracting product and waste is considerably simplified. A countercurrent centrifuge may be considered as a cascade of a certain number of small simple process centrifuges. Because this number is roughly equal to the length to diameter ratio, the feed rate of a countercurrent centrifuge as compared to the feed rate of a simple process centrifuge is inversely proportional to the square of this ratio. At a peripheral speed of 350 m/s, the length to diameter ratio of a subcritical centrifuge is about 5, so the feed rate is diminished by a factor 25 for a countercurrent process.

As was already indicated in an earlier paper [1] a countercurrent centrifuge can be operated in two different ways. In the centrifuges of Beams *et al* [2], the countercurrent is established by feeding into and respectively drawing off the total countercurrent flow at both end caps. The flow of the countercurrent centrifuge is part of the total flow of the cascade. In this type of centrifuge, with an externally driven countercurrent, no use has been made of the possibility of small feed rates in the single unit. In the centrifuges of Groth [3] and Zippe [4], however, the countercurrent is internal. The up and downstream are connected at both end caps thus forming a closed loop. The feed is introduced somewhere in the middle of the centrifuge, while the product and waste are withdrawn at the two opposite end caps. This configuration has to be considered as a combination of a rectifier and a stripper, connected at the feed point. It was shown that this centrifuge has a separative power which amounts to 80% of the theoretical maximum separative power. The loss is due to the fact that at both ends the net desired material transport becomes zero, thus reducing the effective length of the centrifuge.

There are however more factors which reduce the separative power in a countercurrent centrifuge. In the above-mentioned case it has been assumed that the column parameters are equal for the rectifying and the stripping part. However, in the centrifuges of Groth and Zippe the feed is introduced through a tube which is placed in the axis of the rotating drum and which does not necessarily rotate. In this way, most of the feed will be introduced in the forward flow, thus giving rise to an asymmetry in the column parameters between the rectifying and the stripping part. This asymmetry leads to a further reduction of the separative power.

THEORY

The separation factor

According to Cohen [5], the equation which describes the concentration field in a countercurrent centrifuge can be transformed to a general column equation. For a centrifuge consisting of a stripping part and a rectifying part, the differential equations are analogous but not identical for the different parts. If P and W refer to the product and waste of the centrifuge and N_{p} and N_{w} are the corresponding mole fractions, while N denotes the mole fraction as a function of the length co-ordinate z, the two equations for the stripper and the rectifier are respectively

$$W(N - N_{\mathrm{w}}) = c_{1\mathrm{w}}\, N(1 - N) - c_{5\mathrm{w}} \frac{\mathrm{d}N}{\mathrm{d}z} \quad (1)$$

$$P(N_{\mathrm{p}} - N) = c_{1\mathrm{p}}\, N(1 - N) - c_{5\mathrm{p}} \frac{\mathrm{d}N}{\mathrm{d}z} \quad (2)$$

The column parameters c_1 and c_5 which are different for stripper and rectifier, are given by Cohen in an integral form. Introducing the flow function Q and the profile factor γ they can be written as

$$c_1 = (2\varepsilon_0 \ell)\, \frac{c_2}{\ell}\, 2m\gamma^{\frac{1}{2}} \quad (3)$$

$$c_2 = \pi\varrho D r_2^2 \quad (4)$$

$$c_5 = (1 + m^2)\, c_2 \quad (5)$$

where

$$2\varepsilon_0 \ell = (\Delta \mathrm{M}\omega^2 r_2^2/2RT)\,(\ell/r_2\sqrt{2}) \quad (6)$$

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$$m = (\sqrt{2}/\varrho D r_2)\left(\int_0^{r_2} (Q^2/r)\, dr\right)^{\frac{1}{2}} \tag{7}$$

$$2\pi Q = \int_0^r \varrho W 2\pi r dr \tag{8}$$

$$\gamma = 4\left[\int_0^{r_2} Q r dr\right]^2 \Big/ r_2^4 \int_0^{r_2} (Q^2/r)\, dr \tag{9}$$

The radius and the length of the centrifuge are given by r_2 and ℓ, while W denotes the axial gas velocity and ω refers to the angular velocity.

We now assume that the feed is introduced into the forward flow. If the feed is not negligible as compared to the countercurrent flow, the column parameters of rectifier and stripper are different. The flow function of the rectifying section is found by adding the feed, with a given distribution over the cross-section, to the stripper flow function. If the flow function in the stripper is characterized by

$$Q_{\mathrm{w}} = A r^n \tag{10}$$

and the feed is introduced into the forward flow in a thin coaxial cylinder with radius r_1 then the flow function of the rectifier can be written as

$$0 < r < r_1 : Q_{\mathrm{p}} = Q_{\mathrm{w}} = A r^n$$

$$r_1 < r < r_2 : Q_{\mathrm{p}} = Q_{\mathrm{w}} + \frac{F}{2\pi} = A r^n + \frac{F}{2\pi} \tag{11}$$

Given the flow functions Q_{w} and Q_{p} the dimensionless parameters m and γ can be found with the aid of Eqs. (7) and (9)

$$m_{\mathrm{w}} = \frac{1}{\varrho D r_2 \sqrt{n}} A r_2^n \tag{12}$$

$$\gamma_{\mathrm{w}} = 8n/(n+2)^2 \tag{13}$$

$$\left(\frac{m_{\mathrm{p}}}{m_{\mathrm{w}}}\right)^2 = 1 + \frac{2}{\sqrt{n}}\left[1 - \left(\frac{r_1}{r_2}\right)^n\right] \cdot \left(\frac{\phi}{m_{\mathrm{w}}} \frac{r_2}{\ell}\right) + \tfrac{1}{2} \ln \frac{r_2}{r_1} \cdot \frac{\phi}{m_{\mathrm{w}}} \frac{r_2}{\ell}\Bigr)^2 \tag{14}$$

$$\left(\frac{\gamma_{\mathrm{p}}}{\gamma_{\mathrm{w}}}\right)^{\frac{1}{2}} = \frac{1 + \dfrac{n+2}{4\sqrt{n}}\left[1 - \left(\dfrac{r_1}{r_2}\right)^2\right] \cdot \left(\dfrac{\phi}{m_{\mathrm{w}}} \dfrac{r_2}{\ell}\right)}{\dfrac{m_{\mathrm{p}}}{m_{\mathrm{w}}}} \tag{15}$$

where

$$\phi = F\ell/\pi\varrho D r_2^2 \tag{16}$$

is the dimensionless feed rate.

Calculating now the separation factor

$$a_{\mathrm{p}}\, a_{\mathrm{w}} = N_{\mathrm{p}}(1 - N_{\mathrm{w}})/N_{\mathrm{w}}(1 - N_{\mathrm{p}}) \tag{17}$$

it will be assumed for convenience that $N \ll 1$, although this is by no means essential to the argument. Consequently the separation factor can be written as

$$a_{\mathrm{p}}\, a_{\mathrm{w}} = N_{\mathrm{p}}/N_{\mathrm{w}} \tag{18}$$

In the stripper of length $\ell_{\mathrm{w}} = \lambda\ell$ the enrichment from the waste concentration N_{w} to the concentration at the connection of stripper and rectifier N^* is found by integration of Eq. (1):

$$\Delta_{\mathrm{w}} = \frac{N^*}{N_{\mathrm{w}}} - 1 = 2\varepsilon_0 \ell \frac{2 m_{\mathrm{w}} \gamma_{\mathrm{w}}^{\frac{1}{2}}}{1 + m_{\mathrm{w}}^2} \lambda \frac{1 - \exp\left[-\left\{\dfrac{(1-\theta)\phi\lambda}{1+m_{\mathrm{w}}^2} - 2\varepsilon_0 \ell \dfrac{2 m_{\mathrm{w}} \gamma_{\mathrm{w}}^{\frac{1}{2}}}{1+m_{\mathrm{w}}^2} \lambda\right\}\right]}{\dfrac{(1-\theta)\phi\lambda}{1+m_{\mathrm{w}}^2} - 2\varepsilon_0 \ell \dfrac{2 m_{\mathrm{w}} \gamma_{\mathrm{w}}^{\frac{1}{2}}}{1+m_{\mathrm{w}}^2} \lambda} \tag{19}$$

while the increase of concentration from N^* to N_{p} in the rectifying part of length $\ell_{\mathrm{p}} = (1 - \lambda)\ell$ follows from Eq. (2):

$$\Delta_{\mathrm{p}} = 1 - \frac{N^*}{N_{\mathrm{p}}} = 2\varepsilon_0 \ell \frac{2 m_{\mathrm{p}} \gamma_{\mathrm{p}}^{\frac{1}{2}}}{1 + m_{\mathrm{p}}^2} (1-\lambda) \frac{1 - \exp\left[-\left\{\dfrac{\theta\phi(1-\lambda)}{1+m_{\mathrm{p}}^2} + 2\varepsilon_0 \ell \dfrac{2 m_{\mathrm{p}} \gamma_{\mathrm{p}}^{\frac{1}{2}}}{1+m_{\mathrm{p}}^2} (1-\lambda)\right\}\right]}{\dfrac{\theta\phi(1-\lambda)}{1+m_{\mathrm{p}}^2} + 2\varepsilon_0 \ell \dfrac{2 m_{\mathrm{p}} \gamma_{\mathrm{p}}^{\frac{1}{2}}}{1+m_{\mathrm{p}}^2} (1-\lambda)} \tag{20}$$

Finally, combination of the Eqs. (18), (19) and (20) results in

$$a_{\mathrm{p}}\, a_{\mathrm{w}} = 1 + \Delta_{\mathrm{w}}/1 - \Delta_{\mathrm{p}} \tag{21}$$

It should be noticed here that if there is no mixing at the feed point the feed concentration N_{F} is equal to the concentration N^* at the connection of the stripping and rectifying part.

The separative power

For a cascade consisting of infinitesimal separation elements, according to Cohen [5] the elementary value function $\mathrm{V}(N)$ is given as a function of the mole fraction N.

$$\mathrm{V}(N) = (2N - 1) \ln \frac{N}{1 - N} \tag{22}$$

Using this elementary value function the separative power of a non-infinitesimal element in an ideal cascade of infinitesimal elements could be defined as

$$\delta U = P\, \mathrm{V}(N_{\mathrm{p}}) + W\, \mathrm{V}(N_{\mathrm{w}}) - F\, \mathrm{V}(N_{\mathrm{F}}) \tag{23}$$

where P, W and F refer to product, waste and feed of the element and N_{p}, N_{w} and N_{F} designate the corresponding concentrations.

The conservation of matter for the element is expressed by

$$F = P + W$$

$$F N_{\mathrm{F}} = P N_{\mathrm{p}} + W N_{\mathrm{w}} \tag{24}$$

In the general case, not limited to small concentrations, the separation factors for rectifier and stripper of the element are defined as

$$a_{\mathrm{p}} = N_{\mathrm{p}}(1 - N_{\mathrm{F}})/N_{\mathrm{F}}(1 - N_{\mathrm{p}})$$

$$a_{\mathrm{w}} = N_{\mathrm{F}}(1 - N_{\mathrm{w}})/N_{\mathrm{w}}(1 - N_{\mathrm{F}}) \tag{25}$$

Substituting (24) and (25) in Eq. (23) for δU, the separative power is found to be a function of the separation factors for rectifier and stripper and of the feed concentration:

$$\frac{\delta U}{F} = \{\alpha_w - N_F(1+\alpha_w)\}\frac{\alpha_p - 1}{\alpha_p\,\alpha_w - 1}\ln\alpha_w$$

$$-\{1 - N_F(1+\alpha_p)\}\frac{\alpha_w - 1}{\alpha_p\,\alpha_w - 1}\ln\alpha_p \quad (26)$$

Although the separative power should be independent of the concentration, the expression can be used in limited concentration regions. For some special cases, the formula can be reduced to a much simpler one.

For a symmetric process that is if $\alpha_p = \alpha_w = \alpha$

$$\frac{\delta U}{F} = \frac{\alpha - 1}{\alpha + 1}\ln\alpha \quad (27)$$

In this case the formula is identical to Cohen's [5] expression.

If $N_F \ll 1$

$$\frac{\delta U}{F} = \frac{\alpha_w(\alpha_p - 1)\ln\alpha_w - (\alpha_w - 1)\ln\alpha_p}{\alpha_p\,\alpha_w - 1} \quad (28)$$

And if $(1 - N_F) \ll 1$

$$\frac{\delta U}{F} = \frac{\alpha_p(\alpha_w - 1)\ln\alpha_p - (\alpha_p - 1)\ln\alpha_w}{\alpha_p\,\alpha_w - 1} \quad (29)$$

Both expressions are independent of the concentration and they can be derived from each other by changing α_p and α_w. It should be pointed out that Eq. (29) is the same expression for δU as derived by Bulang, Groth, *et al.* [6] for an asymmetric non-infinitesimal element. However the choice they made of separating the value function into a concentration dependent and a concentration independent part is rather arbitrary. Indeed if $N_F \ll 1$ another choice is much more suitable, leading to Eq. (28).

Making use of Eq. (24) combined with the assumption $N_F \ll 1$ and Eq. (28) it is possible to express $\delta U/F$ a sa function of the total separation factor $\alpha_p\alpha_w$ and the cut $\theta = P/F$

$$\frac{\delta U}{F} = G(\alpha_p\,\alpha_w, \theta) = \ln\{1 + \theta(\alpha_p\,\alpha_w - 1)\} - \theta\ln\{1 + (\alpha_p\,\alpha_w - 1)\}$$

$$= \tfrac{1}{2}\theta(1-\theta)(\alpha_p\alpha_w - 1)^2\{1 - \frac{2(1+\theta)}{3}(\alpha_p\alpha_w - 1) + \frac{1+\theta+\theta^2}{2}(\alpha_p\,\alpha_w - 1)^2 \ldots\ldots\ldots\} \quad (30)$$

Finally the separation efficiency η, based on

$$\delta U_{\max} = \varrho D\left\{\frac{\Delta m\omega^2 r_2^2}{2RT}\right\}^2\frac{\pi\ell}{2} = (2\varepsilon_0\ell)^2\frac{c_2}{\ell} \quad (31)$$

can be written as

$$\eta = \frac{\delta U}{\delta U_{\max}} = \phi\,\frac{G(\alpha_p\,\alpha_w, \theta)}{(2\varepsilon_0\ell)^2} \quad (32)$$

It is found from numerical calculations that η is within certain limits independent of $2\,\varepsilon_0\ell$ and consequently of the peripheral velocity of the centrifuge.

Numerical calculations

One can say that the separation efficiency is a function of several variables. In the first place the geometrical variables r_2/ℓ and ℓ_w/ℓ are mentioned. Furthermore the efficiency depends on the magnitude and the pattern of the flow in the stripper, characterized respectively by m_w and γ_w or n, while the distribution over the cross-section and the magnitude of the feed, r_1/r_2 and ϕ influence the efficiency. Finally the cut $\theta = P/F$ is a variable. With given values of n, r_1/r_2, θ and r_2/ℓ the maximum value of the efficiency with the corresponding optimal values of λ, m_w and ϕ can be calculated by trial and error with the aid of the derived equations.

For our calculations we have chosen an ideal profile in the stripper ($n = 2$, $\gamma_w = 1$), a distribution of the feed over the cross-section characterized by $r_1/r_2 = \frac{1}{2}$ and a cut $\theta = \frac{1}{2}$. In Table 1 the maximal efficiency with the optimal conditions are given for two values of r_2/ℓ.

Table 1

$\frac{r_2}{\ell}$	$\eta_{\max}$	Optimal values of $\lambda = \frac{\ell_w}{\ell}$	m_w	m_p	$\phi = F\,\frac{\ell}{\pi\varrho D r_2^2}$
$\frac{1}{10}$	0.63	0.3	2	4.1	40
$\frac{1}{15}$	0.68	0.4	3	5.1	57

The dependence of the separation efficiency on the dimensionless feed ϕ at the optimal feed point location $\lambda = \ell_w/\ell$ is shown in Figs. 1 and 2 for $r_2/\ell = \frac{1}{10}$ and $\frac{1}{15}$ respectively.

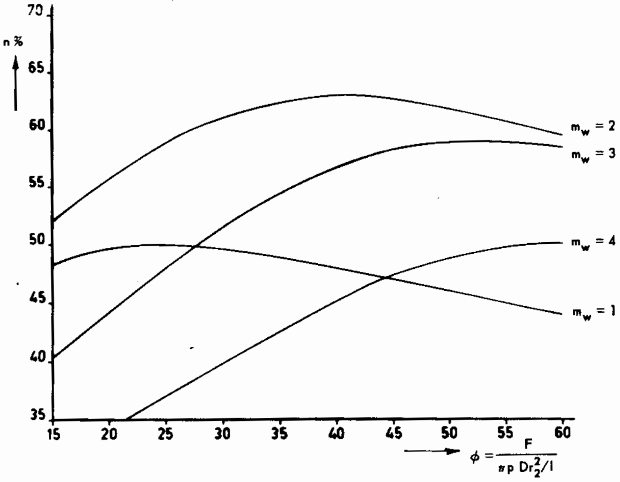

Figure 1. The separation efficiency η as a function of the dimensionless feed ϕ at $\gamma_w = 1$, $r_1/r_2 = 1/2$, $\theta = 1/2$ and the optimal feed point location $\lambda = 0.3$ for $r_2/\ell = 1/10$

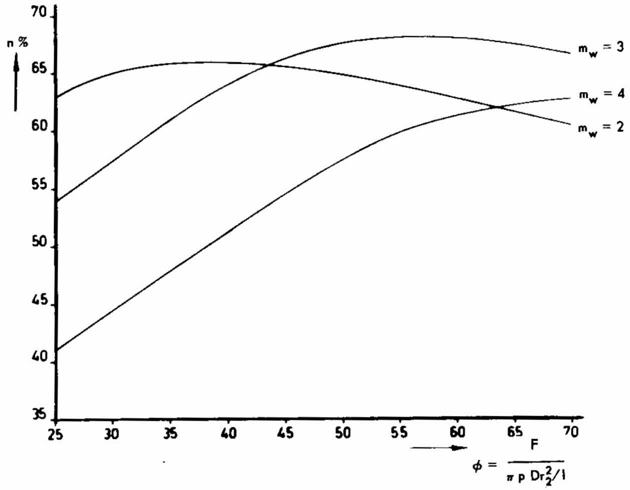

Figure 2. The separation efficiency η as a function of the dimensionless feed ϕ at $\gamma_w = 1$, $r_1/r_2 = 1/2$, $\theta = 1/2$ and the optimal feed point location $\lambda = 0.4$ for $r_2/\ell = 1/15$

DISCUSSION

At a smaller r_2/ℓ ratio the feed becomes smaller as compared to the flow-strength of the countercurrent and consequently the column parameters of both column sections equalize. Los [1] derived for a symmetrically operated centrifuge with equal column parameters in both parts

$$\eta_{\max} = 0.81 \gamma \frac{m^2}{1 + m^2} \tag{33}$$

$$P_{\text{opt}} = (\sqrt{5} - 1)\, 2(1 + m^2) \frac{\pi \varrho D r_2^2}{\ell} \tag{34}$$

$$\ell_p \approx \ell_w$$

In relatively short centrifuges, where the feed is introduced into the forward flow, the flow strength in the rectifier is much higher than in the stripper. As we have seen, this circumstance causes a considerable reduction of the separation efficiency, while the optimal location of the feed point is shifted into the direction of the waste end of the centrifuge.

The behaviour of short centrifuges can be understood by means of Cohen's column equations and of the separation characteristics for a centrifuge with equal column parameters.

At total reflux and constant dN/dz, the increase of the concentration in the rectifier is given by

$$N_p - N^* = \frac{c_{1p}}{c_{5p}} \ell_p N(1 - N) \tag{36}$$

while for the stripper

$$N^* - N_w = \frac{c_{1w}}{c_{5w}} \ell_w N(1 - N) \tag{37}$$

Furthermore, the conservation of matter in the centrifuge leads to

$$\frac{N_P - N_F}{N_F - N_W} = \frac{1 - \theta}{\theta} \tag{38}$$

In order to avoid mixing at the feed point, the concentration N^* at the connection of both column parts should be equal to the feed concentration N_F. Together with the last three equations, this results in the no-mixing condition

$$\theta \frac{c_{1p}}{c_{5p}} \ell_p \approx (1 - \theta) \frac{c_{1w}}{c_{5w}} \ell_w \tag{39}$$

or

$$\theta \frac{2 m_p \gamma_p^{\frac{1}{2}}}{1 + m_p^2} \ell_p \approx (1 - \theta) \frac{2 m_w \gamma_w^{\frac{1}{2}}}{1 + m_w^2} \ell_w \tag{40}$$

This equation shows the shift of the feed point due to the higher flow strength in the rectifier. Calculations were made for cuts not equal to a half. It was found that only the location of the feed point shifted according to Eq. (40), the separative power remained the same.

Generalising Eq. (34), the condition for optimal extraction from the rectifying part can be written as

$$\theta F_{p_{\text{opt}}} \approx (\sqrt{5} - 1) \frac{\pi \varrho D r_2^2}{\ell_p} (1 + m_p^2) \tag{41}$$

while the waste for an optimally operated stripper is equal to

$$(1 - \theta) F_{w_{\text{opt}}} \approx (\sqrt{5} - 1) \frac{\pi \varrho D r_2^2}{\ell_w} (1 + m_w^2) \tag{42}$$

To show that it is impossible to operate both column sections optimally at the same time, we combine the last two equations with the non mixing condition (40) which results in

$$\frac{F_{p_{\text{opt}}}}{F_{w_{\text{opt}}}} = \frac{m_p}{m_w} \left(\frac{\gamma_p}{\gamma_w}\right)^{\frac{1}{2}} \tag{43}$$

We may conclude that the discrepancy between the dimensionless flow strengths of the sections causes a reduction of the separation efficiency. To diminish the influence of the back-diffusion, a high value of m is required. On the other hand, this demands a higher feed which causes a greater discrepancy between the flow strengths.

Finally, it should be noticed that Cohen's column equations hold better for longer centrifuges. It is remarkable that these equations describe the separation behaviour of short countercurrent centrifuges in a correct way.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/637 Pays-Bas

Pouvoir séparateur des centrifugeuses à contre-courant court

par C. Ouwerkerk et J. Los

Dans la plupart des cas, les centrifugeuses à contre-courant fonctionnent comme des unités fermées, alimentées vers le centre de l'appareil, tandis qu'on retire les fractions séparées aux extrémités. Ces centrifugeuses pourraient être considérées comme la combinaison d'une section de rectification et d'une section d'épuisement. Dans une publication récente, on a montré qu'une centrifugeuse à contre-courant fonctionnant symétriquement possède un rendement équivalent à 80 % du pouvoir séparateur maximal. On a démontré que cette diminution du pouvoir séparateur est due au fait qu'un gradient de concentration radial optimal ne peut être maintenu sur toute la longueur de la centrifugeuse. Aux deux extrémités, le gradient de concentration radial approche du gradient de concentration à l'équilibre parce que le transport net de matière désiré approche de zéro.

Dans le mémoire, on considère l'influence de l'alimentation sur le pouvoir séparateur. Dans la plupart des expériences, l'alimentation est faite dans le sens avant du contre-courant provoquant une asymétrie dans les paramètres de colonne des sections de rectification et d'épuisement. Cette asymétrie ne peut être corrigée que partiellement en avançant le point d'alimentation.

On montre que cette asymétrie cause une diminution supplémentaire de 15 % du pouvoir séparateur.

A/637 Нидерланды

Разделительная способность коротких противоточных центрифуг

К. Оуверкерк, Дж. Лос

Вообще противоточные центрифуги представляют собой установки, действующие непрерывно по замкнутому циклу; питание осуществляется обычно через ввод посередине центрифуги, в то время как с обоих концов центрифуги выгружают разделенные фракции. Эти центрифуги характеризуются сочетанием ректификационной и перемешивающей частей. В недавно опубликованной работе[1] было показано, что в симметрично действующей противоточной центрифуге коэффициент полезного действия составляет 80% максимально допустимой разделительной способности. Показано также, что уменьшение разделительной способности обусловлено тем, что нельзя поддерживать оптимальный градиент радиальной концентрации по длине центрифуги. На обоих концах центрифуги градиент радиальной концентрации приближается к градиенту равновесной концентрации вследствие того, что величина массопередачи приближается к нулю.

В докладе рассматривается влияние способа подачи материала на разделительную способность. В большинстве экспериментов материал подавался в переднюю часть против направления противотока; это приводит к увеличению асимметрии параметров ректификационной и перемешивающей частей колонны. Эта асимметрия может быть уменьшена только частично, путем смещения точки подачи материала назад за поток.

Показано, что дальнейшее уменьшение разделительной способности (~ на 15%) объясняется наличием вышеупомянутой асимметрии.

A/637 Países Bajos

Poder de separación de las centrífugas cortas en contracorriente

por C. Ouwerkerk y J. Los

Las centrífugas en contracorriente suelen funcionar como unidades cerradas: la alimentación se efectúa aproximadamente en la parte central de la centrífuga, mientras que las fracciones separadas se extraen por los dos extremos. Se puede considerar a estas centrífugas como una combinación de una sección de rectificación y otra de separación. En una publicación reciente, se señaló que una centrífuga en contracorriente que trabaje simétricamente tiene un rendimiento igual al 80 % del máximo efecto de separación

que es posible alcanzar. Se demostraba también que la disminución del poder de separación se debe al hecho de que nos es posible mantener un gradiente de concentración radial óptimo a todo lo largo de la centrífuga. En ambos extremos, el gradiente de concentración radial se acerca al gradiente de concentración de equilibrio, porque el transporte neto de material deseado tiende a cero.

En la presente memoria se examina la influencia de la alimentación sobre el poder separador. En la mayoría de los experimentos es preciso introducir la sustancia a separar en la corriente progresiva del sistema en contracorriente, originándose de ese modo una asimetría de los parámetros de la columna entre la parte de rectificación y la de separación. Esta asimetría sólo admite correcciones parciales, desplazando el punto de alimentación aguas arriba.

Se demuestra que esta asimetría provoca una nueva reducción del poder de separación, que disminuye aproximadamente en un 15 %.

The management of heavy water for research and power reactors

By J. A. Morrison,* M. H. Thomas,* L. C. Watson* and L. W. Woodhead**

Canadian experience with large volumes of heavy water in reactor systems began in 1945 with the operation of the low-power reactor ZEEP, in which 10 tonnes of heavy water was used [1]. The NRX reactor [1-3] which came into operation in 1947 has 16 tonnes of heavy water in a sealed moderator system. Most of the heat is removed from the reactor by light water flowing through the fuel rods. The reactor power, originally 10 MW, was increased after modifications and improvements until operation at 40 MW was reached in 1954. The 200-MW NRU reactor [2, 4, 5], with 65 tonnes of heavy water as both moderator and coolant, and a second low-power reactor, ZED-2 [6], with 30 tonnes of heavy water, were commissioned in 1957. The Nuclear Power Demonstration reactor (NPD) [7, 8], whose electrical output is 20 MW, is located 40 km from the Chalk River Nuclear Laboratories (CRNL). It came into operation in 1962 and is moderated and cooled with 70 tonnes of heavy water. The heat-transport system, which contains 10 tonnes of heavy water and is segregated from the moderator system, operates at 275 °C and 75 kgf/cm^2. Both the NRU and NPD reactors are refuelled at full power routinely. The inventory of heavy water in the five reactors is about 200 tonnes.

The principal objectives in the handling of heavy water are containment and the preservation of the isotopic purity. Since neither of these objectives can be fully realized, provision must be made to recover heavy water that escapes from the reactor systems and, if it is downgraded, to reconcentrate it. Many problems, including those involving the radioactive isotope tritium, have been encountered in these reclamation operations. These aspects of Canadian experience with heavy-water reactors will be discussed in this paper.

SOURCES OF DOWNGRADED HEAVY WATER

The reactors

The isotopic concentration of the heavy water in the NRX reactor has remained fairly constant around 99.84 wt% D_2O since 1959. Since the 550 kg of water added annually to replace losses, samples and drainings has averaged about 99.85 wt% D_2O, light water is entering the system at a rate of 200 g each year. This quantity of light water in 16 tonnes of heavy water is equivalent to about 10 ppm or a decrease in the isotopic concentration of 0.001 wt%.

The heavy-water system in the NRU reactor is more complex and many assemblies, such as fuel rods and control rods, are inserted and removed while the reactor is operating. As a result the degradation is considerably greater than that in the NRX reactor and has averaged 0.007 wt% annually for the last seven years. For short periods, the rate has been much higher; for example, in June 1958, during the decontamination of the NRU reactor following the fuel-rod incident of 23 and 24 May [9], 14 kg of light water was introduced into the heavy-water system. This was nearly 50% of all the light water added in the last seven years and it reduced the isotopic concentration of the heavy water by 0.02 wt%.

The source of light water in the NPD reactor is mainly in the air ($\approx$ 15 cm^3/s) that leaks into the gas space above the moderator in the reactor vessel. If the water content of this air were uncontrolled, it would cause a yearly degradation of 0.01 wt%, a value that agrees with limited data obtained in 1962. Although the current degradation rate cannot be measured directly since an isotopic reconcentration program is in progress, it is believed to be less than this figure because the light-water content of the inleaking air has been reduced significantly.

The low-power reactors also use reactor-grade heavy water (99.75 wt% D_2O). The reactor vessels in these reactors are opened frequently and many assemblies are in contact with the heavy water during the experimental programs. As a result there is a continuous downgrading of the heavy water which averages about 0.06 wt% annually in the ZED-2 reactor and 0.02 wt% in ZEEP.

The quantities of heavy water recovered in a downgraded condition during routine operation are about 0.5 tonne/year for the NRX reactor and 6 tonne/year for the NRU reactor. This latter quantity is 10% of the heavy-water inventory in the reactor and

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agrees with the figure given for the heavy-water reactors at the Savannah River plant [10]. Similar data are not yet available for the NPD reactor. The reclamation of about half of this downgraded heavy water is simple because it is recovered by established procedures and techniques which minimize contamination and downgrading.

Ion exchangers

The deuterization and dedeuterization of the ion-exchange resin which is done outside the heavy-water systems is another source of down-graded heavy water. Generally 1.5 to 2 kg of heavy water must be reconcentrated for each kilogram of resin installed in the heavy-water system. The quantity at the NRX reactor is less than 10 kg annually, but in the NRU reactor it amounts to 550-700 kg. This water is normally contaminated with organic material which must be removed before isotopic reconcentration can be undertaken.

Air systems

The recovery of heavy water from reactor ventilation systems is a difficult problem. No attempt has been made to recover heavy water from the once-through ventilation system used in the NRU reactor because the volume of air discharged is too large, about 4 m^3/s. Since leakage of heavy water into the reactor vault of the NPD reactor was expected, a recirculating air system was installed. The vault is kept under negative pressure by removing 10 liters of air per second from the recirculating air system and this air is dried before it is discharged to the building exhaust system. The original drying unit, a refrigerator type, was undersized and was replaced with a commercial air-drying unit using activated alumina as the drying agent. The air discharged to the exhaust system has a dew point below —30 °C and the total quantity of water released daily has been reduced from 12 to about 0.4 kg. The water collected on the alumina is returned to the recirculating air system during its regeneration cycle and thus the water entering the vault gradually accumulates in the scrubber used to clean and cool the circulating air. The final isotopic content of the water in the scrubber depends on the water initially loaded into the scrubber and on the relative quantities of light and heavy water that leak into the vault.

PURIFICATION

The first operation in the reclamation of the recovered heavy water is the purification, or decontamination, step. Ion exchange and distillation are used most frequently but other methods, such as filtration, have also been used. The most frequent impurities are the soluble inorganic compounds but the most troublesome are the organic compounds and the suspended solids which often present problems in both the purification and the reconcentration steps (see later). In particular, the electrolytic reconcentration plant requires that the specific conductance of the feed water be less than $10^{-5} \Omega^{-1}$ cm^{-1} and the organic residue less than 1 ppm. The radioactive residual (exclusive of tritium) must be very small because the plant is unshielded.

Ion exchange

The frequency with which ion-exchange resins have been applied to the problems encountered in the purification of heavy water has increased steadily since the first ion-exchange column was installed in the heavy-water system of the NRX reactor in 1949. Today, mixed beds of the strongly acidic and strongly basic ion-exchange resins are used in most applications. The effectiveness of these resins in removing ionic impurities from water was recognized many years ago but more recently they have been used to reduce the water-soluble fraction of the simple aliphatic and chlorinated hydrocarbons, and to break some types of organic-water emulsions.

Distillation

Originally distillation was used almost exclusively to purify contaminated heavy water and it remains one of the most effective methods. A rising-film evaporator is used for all water which cannot be purified by ion exchange alone. The heat exchanger, de-entrainment section, condenser and the settling tank for the concentrate, are all stainless steel. If necessary the feed is neutralized with NaOH or, if an oxidizing medium is required, the feed is made alkaline and sufficient potassium permanganate is added to ensure a slight excess in the concentrate stream. The short residence time (1-2 min) in the hot zone is one disadvantage of this type of evaporator. The throughput of the evaporator is 90 l/h with a volume reduction of 5. The specific conductance of the distillate is measured continuously and if it exceeds $5 \times 10^{-5} \Omega^{-1}$ cm^{-1} the distillate is recycled. As it is discharged to a clean receiver, the distillate is passed through a mixed-bed resin column to remove the small quantities of impurities carried over by entrainment. The concentrate is recycled by mixing it with the feed in a ratio of 1 : 5 until the solids content of the feed is increased to about 1 wt%. Since continued operation with this concentration of solids will accelerate the corrosion of the tubes in the heat exchanger, the contents of the settling tank are transferred to a mild-steel pot evaporator and taken to dryness. When the solids in this evaporator reduce the heat transfer to a level that makes further use impractical, a quantity of light water is added and evaporated. More heavy water can be recovered by this method than by the application of heat alone. The pot is then detached and sent for burial.

Filtration

Insoluble and suspended materials can be removed by filtration in many cases, but not organic material or colloids like the gibbsite ($Al_2O_3 . 3H_2O$) found in the heavy water in the NRU reactor [11, 12]. Organic contaminants were first encountered in 1947, when about a tonne of heavy water in the NRX reactor displaced the oil in an oil seal. The majority of the oil was removed by centrifuging and the remainder by evaporating the water from an alkaline permanganate solution. The centrifuging step was very cumbersome and was replaced by filtration using a diatomite filter-aid. This method reduced the oil content of the water to less than 5 ppm in a single step. Another combination, a felt filter followed by filtration with a cellulose filter-aid, is being used to remove the oil from heavy water collected from the pump seals at the NPD reactor. These filter-aids are also effective in breaking oil emulsions, but it has not been necessary to use them in this way because, in the particular cases encountered, ion exchange was equally effective.

Specific problems with large volumes of downgraded heavy water

Very large quantities of heavy water ($>$ 10 tonnes) were downgraded on four occasions in the last twelve years. Since different problems were encountered in three of these incidents, and since each was a major recovery effort, a very brief account is included here.

In an accident with the NRX reactor in December 1952 [2], 15 tonnes of heavy water were downgraded from 99.8 to 92 wt% D_2O and one tonne from 99.8 to 20 wt%. The water as recovered contained approximately 0.5 curies of fission products per liter. The water was first passed through a mixed-bed resin column. The radioactive content of the water containing 92 wt% was reduced by a factor of 4×10^4, but with the water containing 20 wt% the factor was only 5×10^2. The radioactive impurity was ^{140}La which was complexed by an organic impurity in the river water which caused the downgrading. As the final step, the water was evaporated and a product suitable for isotopic reconcentration was obtained.

In 1960, leakage of heavy water into the J-rod annulus, an annular region immediately outside the NRU reactor vessel, was detected. Two years later, the leaks were found in a number of small pipes radiating out from the top header deep inside the reactor shielding. In the meantime, over 50 tonnes of water were collected, the majority containing less than 10% D_2O. Light-water leaks into the annulus were responsible for the downgrading. Water containing less than 2 wt% D_2O was discarded because it could not be reconcentrated economically in the existing facilities.

The recovered water was badly contaminated. In the J-rod annulus, it had come in contact with large quantities of aluminum corrosion products. These formed a suspension in the water that could be removed only by distillation. To reduce the handling problems, the low-grade water (2-10 wt% D_2O) was reconcentrated to 15-20 wt% in the distillation unit (see later) before it was decontaminated. Periodic plugging of the lower plates of the first column was experienced during this reconcentration but no difficulties were experienced during the subsequent evaporation and reconcentration steps. The decontamination was done in the rising-film evaporator described above.

The most recent incident occurred in December 1962, during the final stage of the development program for on-power fuelling of the NPD reactor [7]. A heavy-water leak developed at the seal between a fuelling machine and a pressure tube and it could not be repaired immediately. Since the cooling of the fuel could not be interrupted, the spilled heavy water was recycled from the sumps. In the course of this recycling, the heavy water in the reactor was downgraded from 99.7 to 99.1 wt% D_2O and contaminated with about 25 l (350 ppm) of oil and an undetermined quantity of polymerized acrylamide which was the principal ingredient in a chemical grout used as a seal in the reactor vault and adjacent areas. Most of the contaminated water was first passed through an ion-exchange column; then it was distilled and passed through a second column. When there was free oil present in the water, a physical separation was made. The water was then evaporated from a permanganate solution and the condensate passed through an ion-exchange column. Both methods reduced the oil content to less than 5 ppm, but it was discovered later that the acrylamide was only partially removed. The heavy water was removed from the reactor in 2- to 3-tonne batches, decontaminated, and then returned to the reactor. Seventy tonnes of water were processed in seven days, reducing the oil content in the heat-transport system to 5 ppm and in the moderator system to 50 ppm. When reactor operation was resumed, these residuals disappeared, presumably being oxidized to the carbonate, or some other ionic species, which were removed by the ion-exchange resins [13]. The same batch method is being used for the isotopic reconcentration, with 4 to 5 tonnes of water being processed monthly through the electrolytic plant at CRNL.

ISOTOPIC RECONCENTRATION

After the NRX reactor came into operation in 1947, the need for a reconcentration facility at the laboratories became increasingly apparent and the design of an electrolytic plant was begun in 1951. The downgrading of 16 tonnes of heavy water in the accident of December 1952 accelerated this program and a plant with four electrolytic cells was put into operation early in 1953. Four more cells were added in 1963.

The problem was somewhat different at the NRU reactor, which was scheduled for uninterrupted operation. A leak that daily introduced as little as 200 grams of light water into the heavy water would be very difficult to locate but would soon make reconcentration necessary. The problem of handling large volumes of tritiated heavy water could best be overcome by installing a reconcentration unit in the reactor building. A distillation unit designed for automatic on-stream operation was chosen and was integrated with the reactor heavy-water system. Schematic lay-outs of the electrolytic plant and the distillation unit are shown in Figs. 1 and 2.

Electrolytic plant

With the exception of the electrolytic cells and burners, the equipment used in the electrolytic plant is conventional. The cells [14] are about 30 cm in diameter and 1.5 m high. The mild-steel cathode is watercooled and there is no diaphragm between the cathode and the nickel anode. The operating volume is 56 l. The electrolyte is prepared by dissolving 8 wt% K_2CO_3 and 0.2 wt% KOH in the feed water. A current of 1 000 amperes (0.07 A/cm² with the cell full) is passed through four cells connected in series. Approximately 0.35 kilogram of water is electrolyzed per hour per cell. The voltage drop is 3 volts per cell. The hydrogen and oxygen evolved are collected in a common header and fed to a burner. When the conetnts of the cells reach the desired isotopic concentration, they are transferred to an evaporator where the water is removed from the electrolyte.

The original burner had a small nozzle, 0.28 cm in diameter, and required a steady gas pressure, around 1.3 kgf/cm² absolute. Unsteady pressure and overheating of the burner caused explosions, or flashbacks, in the cells and the small nozzle was easily plugged by material entrained in the off-gases. These difficulties were overcome with a new burner which has a large nozzle, 0.8 cm in diameter, and operates at a lower pressure, 1.1 kgf/cm².

The isotopic composition of the water can be predicted during the electrolysis with the Rayleigh equation.

$$\ln(A/A_0) = \alpha \ln(B/B_0)$$

where

A_0, B_0 = the moles of light and heavy water respectively originally in the cell, and

A, B = the moles of light and heavy water respectively at any later time, and

α = separation factor.

Since the quantity of water electrolyzed and removed from the cell can be determined accurately from the aggregate ampere-hours, an isotopic analysis of the water originally in the cell and of the water at some later time will provide an accurate estimate of α. Once the separation factor has been established,

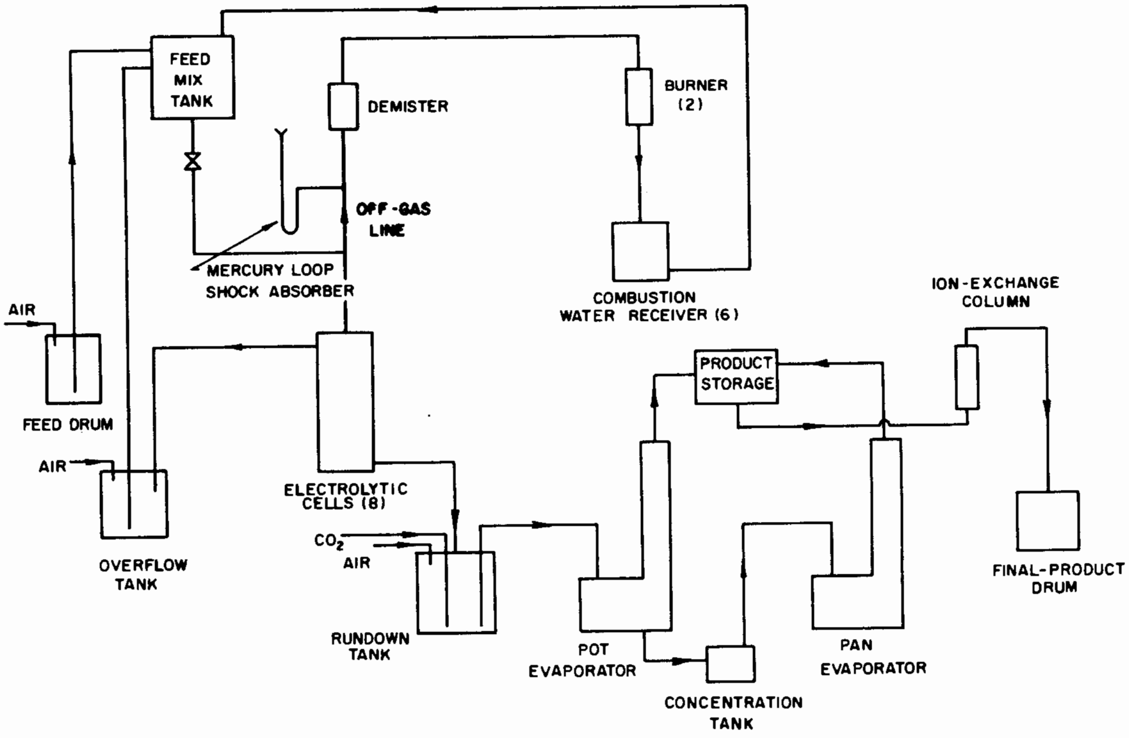

Figure 1. Simplified flowsheet of the electrolytic reconcentration plant

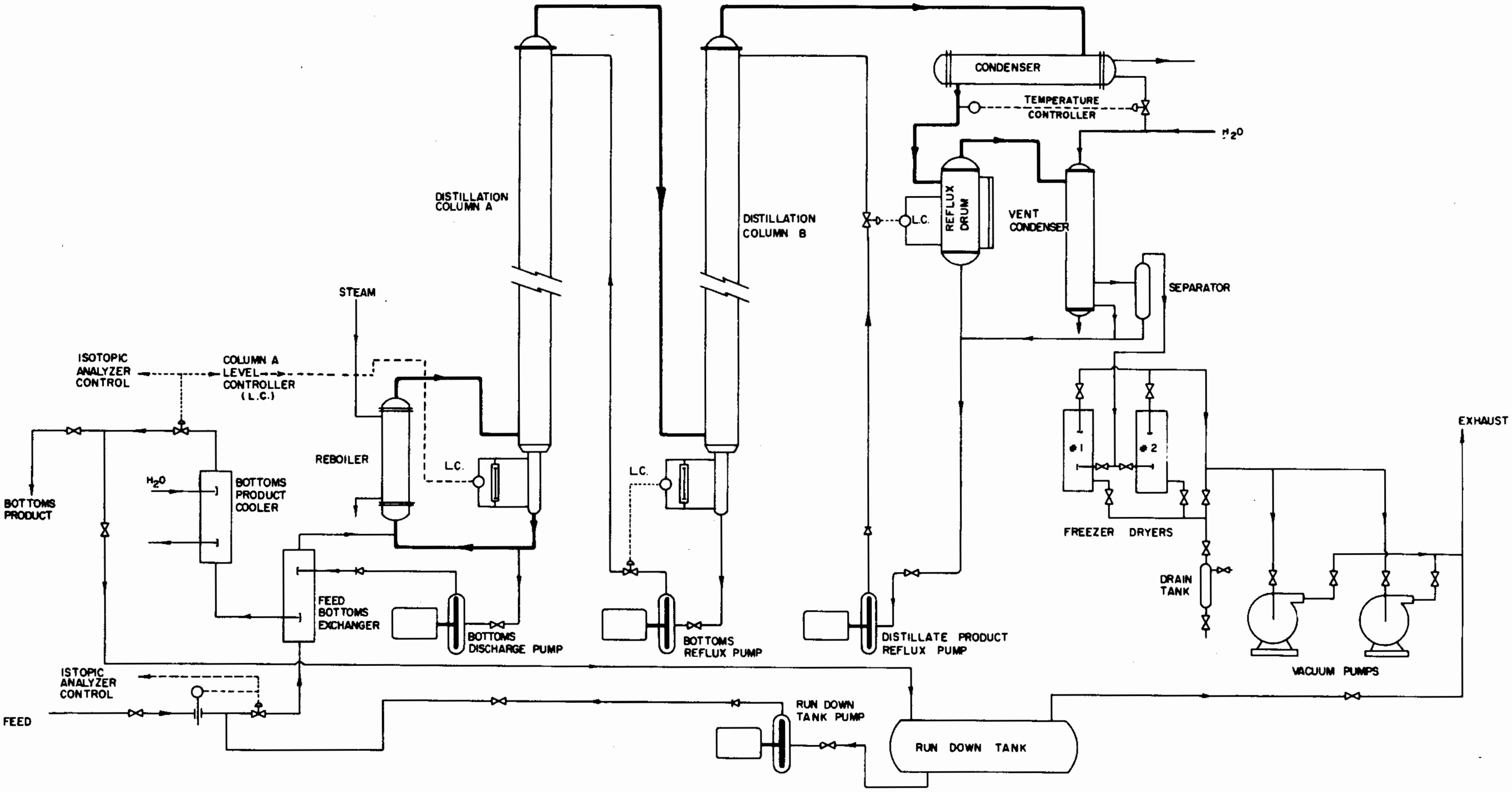

Figure 2. Simplified flowsheet of the distillation unit

the above equation will predict accurately the isotopic composition at any stage of the electrolysis if the initial composition is known.

For good efficiency, the separation factor should be 10 or higher. Many variables including electrolyte composition are known to affect α. In this plant, it has ranged from 4 to 11, but for most operations it has been above 10. The low separation factors are believed to have been caused by impurities in the feed water but only one impurity, molybdenum polysulfide, has been identified. In each case the cathode surfaces, normally dull in appearance, were bright and shiny, indicating that the oxide layer had been removed. The separation factor was restored to 10 after the electrodes were etched with 6*M* hydrochloric acid and allowed to oxidize in air for a day.

When the isotopic content of the heavy water in the two low-power reactors, ZEEP and ZED-2, is reduced to a level which is unacceptable for the experimental program, the heavy water is removed and reconcentrated in a single batch. Since the water is kept very clean a purification step is not required and the only problem is to keep the heavy water free of tritium. This is achived by flushing the electrolytic plant with light water to remove the tritium.

NRU distillation unit

Two distillation columns, each with 75 sieve plates and similar to those described by Bertsche [15], and the auxiliary equipment necessary to heat, cool and transfer the water make up the distillation unit. Stainless steel was chosen as the construction material to eliminate corrosion problems and the possibility that foreign material might be transferred into the reactor system. The columns are 61 and 76 cm in diameter and 24 m high. Operation is automatically controlled by flow, pressure, and level controllers and an isotopic analyser. The total power requirement is 375 kW of which 360 kW is supplied by high-pressure steam. The unit was designed to remove 0.5 kg of light water daily when the feed contained 99.7 wt% D_2O and the distillate 95 wt%. The feed rate is such that the water is upgraded 0.005 wt% before it is returned to the reactor system upstream of the ion-exchange resins. Some typical operating data with a throughput of 450 kg/h and a boil-up rate of 500 kg/h are:

Feed wt% D_2O	Distillate wt% D_2O	H_2O removal rate kg/d
99.78	96.4 - 97.0	0.4 - 0.5
99.75 - 99.79	95.5 - 96.5	0.25

The distillate is stored for further processing if it contains over 2 wt% D_2O. If it contains over 90 wt% it may be reconcentrated in the electrolytic plant. The column can be used as a recovery unit. For example in 400 days of operation 4.5 tonnes of water at 93 wt% D_2O was recovered from 55 tonnes of water containing from 2 to 50 wt% D_2O.

Relative advantages

The electrolytic plant is a very efficient unit for the isotopic reconcentration of water containing more than 90 wt% D_2O. At lower concentrations the volume of the feed becomes a limiting factor. If the concentration is less than 50 wt% D_2O the volume of water may be large and large volumes can be processed more efficiently in a distillation unit. An automatic distillation unit can be integrated easily with a heavy-water system for onstream operation and is also a very satisfactory reconcentration unit. For water containing over 90 wt% D_2O, either the electrolytic plant or the distillation unit can be used but the adaptability of the electrolytic plant makes it more suitable for establishments with a small heavy-water inventory.

ISOTOPIC AND CHEMICAL ANALYSES

The development of the infra-red method for the isotopic analysis of water [16, 17] has greatly increased the precision and accuracy with which this analysis can be done. With proper care very accurate analyses can be made but under normal laboratory conditions the accuracy is about $\pm$ 0.01 wt% at 99.75 wt% D_2O, $\pm$ 0.05 wt% at 99 wt% D_2O and $\pm$ 0.2 wt% at 90 wt% D_2O. Impurities, such as carbonates and nitrates, will cause low results and any sample whose specific conductance is greater than $10^{-5}\,\Omega^{-1}\,\text{cm}^{-1}$ is purified before an isotopic analysis is done. Downgrading or fractionation of the sample during purification is prevented by a slow but complete distillation under vacuum. It is often necessary to account for the heavy water in a volume of downgraded heavy water and this is commonly done by applying the results of isotopic analysis to the weights of water recovered. The figures obtained by this method can be in error by 5-10% because the impurities in the water may introduce errors into both the analytical results and weights of water.

RADIATION HAZARDS

In many cases the recovered water contains sufficient radioactive material (exclusive of tritium) to be a radiation hazard to personnel. The radioactive material is removed by distillation or by ion exchange (see earlier). These operations are done in shielded rooms in equipment which can be operated remotely. Accordingly the reboiler and the lower third of the first column of the distillation unit are located in shielded, ventilated rooms. This arrangement permits heavy water to be fed directly from the reactor system with no preliminary purification. The dose received by the operators of the distillation unit and the electrolytic plant from gamma radiation averages less than 0.3 roentgen/year while the operators in the purification area receive about 1.3 roentgens/year. The maintenance of the distillation unit results in an aggregate exposure of 5 man-roentgens/year to the maintenance crew.

The major hazard in handling irradiated heavy water is tritium. The concentration of this isotope in the heavy water has increased steadily and is now over 5 curie/l in both the NRX and NRU reactors. In the NPD reactor, the concentration has reached 1.7 curie/l. With continued operation and normal turnover of the heavy water, the tritium concentrations in these reactors will exceed 10 curie/l within a few years.

The electrolytic plant illustrates the techniques which are used to control the tritium hazard. These techniques more than fulfil the economic need to conserve heavy water. Ventilation is most important; the electrolytic plant has an air change every two minutes. The air is exhausted from those areas (e.g., the evaporators, the feed tank, and the rundown tank) in which leakage has been most frequent. All equipment vents are connected directly to the exhaust system. Welded connections are used whenever possible to minimize water leakage. Transfers of heavy water are made by gravity, or by air pressure, to eliminate pumps. Good housekeeping is a vital factor; water which escapes from the equipment is collected as soon as it is detected. Floors and walls are kept clean and painted to reduce absorption of the water. The plant is carefully maintained to minimize equipment failures and leakage. The tritium monitors [18] which will detect tritium concentrations in air as low as 5×10^{-6} microcurie/cm^3 are used to search for leaks in the plant equipment as well as for personnel protection. If the equipment has to be opened, the plant is drained, rinsed with light water, and steamed out before maintenance is begun. Protective plastic clothing and air masks [19] are used whenever the tritium concentration exceeds 5 microcurie/m^3 and the exposure is for more than two to three minutes. If there is exposed heavy water, as in a spill, the wearing of protective clothing is mandatory.

The record of radiation exposure from tritium in the electrolytic plant and purification area is a measure of the success of the operating procedures. A continuous check is maintained on personnel who are exposed to tritium by analysis of urine specimens submitted weekly. During 1963, 492 persons at CRNL received a measurable radiation dose from tritium as determined by urinalysis. Of these, 82% received less than 500 milli-rem and less than 2% received in excess of one rem. The thirteen operators who work in the electrolytic plant and the purification area averaged 380 milli-rem and the maximum exposure was 900 milli-rem.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/29 Canada

Gestion de l'eau lourde pour les réacteurs de recherche et de puissance

par J. A. Morrison *et al.*

L'expérience canadienne en matière de gestion d'eau lourde provient de plusieurs installations de réacteurs, y compris une installation opérant à haute pression et à haute température. Ces installations sont complexes et, dans les plus grandes, le combustible peut être changé quand le réacteur est en marche. Il est inévitable que de l'eau lourde s'échappe, de sorte que les circuits ont été conçus pour que les fuites soient minimes. Comme le tritium est toujours présent dans l'eau lourde irradiée, des mesures préventives sont nécessaires pour assurer la protection du personnel contre le danger d'une augmentation de la concentration de ce gaz dans l'air à la suite d'une fuite.

Pendant les six dernières années, la quantité de H_2O dans les circuits de D_2O des réacteurs NRX et NRU a été inférieure à 100 ppm par année. Le problème le plus important a été la récupération d'eau lourde échappée, surtout quand celle-ci était diluée par H_2O (diminution de teneur isotopique) ou contaminée par d'autres impuretés. La quantité d'eau lourde diluée recueillie durant l'opération normale des réacteurs n'a pas été très appréciable (3 000 kg/an dans le cas de NRX et de NRU) mais, à quatre occasions, des quantités très importantes ($>$ 10 000 kg) ont été diluées et dans trois cas, les problèmes de la récupération ont été très différents. La récupération de D_2O des systèmes de ventilation n'est ordinairement pas rentable; un appareil commercial utilisant l'alumine comme agent dessiccateur a été efficace, cependant, dans un des systèmes de ventilation à la centrale NPD (Nuclear Power Demonstration). La plupart des impuretés, à l'exception de substances organiques, sont enlevées efficacement sur des résines échangeuses d'ions. En se servant de substances de filtration, on peut réduire la quantité d'huile à environ 5 ppm.

Les méthodes de distillation et d'électrolyse ont été utilisées pour améliorer la concentration isotopique de l'eau contenant moins de 99,75 % en poids de D_2O. La distillation est préférable quand on peut tirer pleinement profit des avantages d'un système automatique, c'est-à-dire, pour extraire de petites quantités de H_2O à partir de grands volumes de D_2O ou pour reconcentrer de grands volumes d'eau à faible teneur ($<$ 65 % en poids de D_2O). Le procédé électrolytique est plus souple et, en particulier, il est mieux adapté pour l'eau contenant plus de 90 % en poids de D_2O; la charge peu élevée, de l'ordre de 50 kg par cellule, est un avantage en discontinu. Le facteur de séparation isotopique a, qui mesure l'efficacité d'une installation électrolytique, a été normalement supérieur à neuf et a souvent dépassé dix.

La concentration du tritium dans le D_2O des réacteurs NRX et NRU a été environ 5 Ci/l pour plusieurs années. En 1963, 492 personnes ont été exposées au tritium; 82 % du groupe ont reçu moins de 0,5 rem et moins de 2 % ont reçu plus d'un rem. Dans la zone de purification et l'installation électrolytique, le personnel a reçu en moyenne moins de 0,5 rem. L'exposition maximale a été de 900 mrem. Une bonne ventilation, la propreté, un équipement bien conçu, et une bonne technique d'opération, sont les facteurs clés pour le contrôle de ce risque professionnel.

A/29 Канада

Подготовка тяжелой воды для исследовательских и энергетических реакторов

Дж. А. Моррисон *et al.*

В Канаде накоплен опыт работы с несколькими тяжеловодными реакторными системами, в том числе с одним реактором, работающим при высоком давлении и высокой температуре. Все системы являются сложными, более крупные реакторные системы позволяют производить замену топлива во время работы реактора на мощности. При этом неизбежно происходит некоторая утечка тяжелой воды. Сконструированы системы, в которых такая утечка сводится к минимуму. Тритий ассоциируется с любой облученной тяжелой водой; в связи с возникновением высоких концентраций при утечке необходимо принимать меры для предотвращения опасности для персонала.

В течение последних шести лет количество H_2O, попавшей в системы, заполненные D_2O на реакторах NRX и NRU, составляло менее 0,01% в год. Большой проблемой являлось восполнение тяжелой воды после утечки из реакторов, в особенности когда она разбавлялась H_2O (то есть пониженного качества) или загрязнялась нежелательными примесями. Количество тяжелой воды пониженного качества, собранной в течение периода обычной эксплуатации реактора, было невелико (7000 *кг/год* на реакторах NRX и NRU), однако в трех случаях понижалось качество очень большого количества тяжелой воды (свыше 10 000 *кг*). В каждом

случае проблемы восстановления необходимого количества тяжелой воды имели различную трудность. Процесс извлечения D_2O из системы вентиляции обычно является неэкономичным, однако промышленная установка с глиноземом в системе вентиляции демонстрационной атомной электростанции (NPD) оказалась весьма эффективной. Большая часть примесей, за исключением органических, успешно удаляется с помощью ионообменных смол. Масляные загрязнения с помощью порошков для фильтрования доводились до концентрации $5 \cdot 10^{-6}$ %.

Вода, содержащая менее 99,75 вес. % D_2O подвергается дистилляции и электролизу. Применять дистилляцию лучше тогда, когда можно полностью использовать преимущества автоматической системы, то есть для удаления небольших количеств H_2O из больших объемов D_2O и для реконцентрации больших объемов воды с меньшим содержанием D_2O (менее 65 вес. %). Электролитический процесс является более универсальным, и он особенно хорошо подходит для воды с содержанием свыше 90 вес. % D_2O. Преимуществом является небольшая величина загрузки (до 50 *кг*) одной ванны. Коэффициент α, который является мерилом эффективности электролитической установки, обычно превышал число девять и часто был выше десяти.

Концентрация трития в D_2O на реакторах NRX и NRU составляла около 5 *кюри/л* в течение нескольких лет. В течение 1963 года облучению тритием подверглось 492 человека, из них 82% получили дозу менее 0,5 *бэр* и менее 2% — дозу свыше 1 *бэр*. Операторы электролитической установки получили в среднем дозу менее 0,5 *бэр*. Максимальная доза облучения составила 900 *мбэр*. Надлежащая вентиляция, хороший уход, соответствующим образом сконструированное оборудование и разумные методы эксплуатации — таковы основные факторы в деле устранения этой опасности.

A/29 Canadá

Administración del agua pesada en los reactores de investigación y de potencia

por J. A. Morrison *et al.*

En el Canadá se adquirió experiencia con varios sistemas de reactores de agua pesada, incluso uno que trabaja a alta presión y elevada temperatura. Todos ellos son complejos y en los más grandes es posible acceder al interior para cambiar el combustible con el reactor en marcha. Es inevitable que se produzcan pérdidas de agua pesada y los sistemas se han proyectado de manera que dichas pérdidas se reduzcan a un mínimo. La irradiación del agua pesada entraña siempre la formación de tritio y las concentraciones que se registran cuando se produce un escape obligan a adoptar medidas tendientes a evitar riesgos radiológicos.

En el curso de los últimos seis años la cantidad de H_2O que ha penetrado en los circuitos de D_2O de los reactores NRX y NRU ha sido inferior a las 100 partes por millón, por año. El principal problema ha consistido en recuperar el agua pesada que escapa de los reactores, particularmente cuando se diluye con H_2O (es decir, queda empobrecida) o se contamina por efecto de impurezas perjudiciales. La cantidad de agua pesada empobrecida que se recogió durante la explotación normal del reactor no fue muy grande (1 000 kg/a, para los reactores NRX y NRU) pero en cuatro casos se empobrecieron cantidades muy considerables de agua pesada (más de 10 000 kg) y los problemas que hubo que resolver en tres de esos casos para purificarla fueron diferentes en cada caso. La recuperación de D_2O a partir de los sistemas de ventilación suele ser antieconómica, pero en un circuito de ventilación del reactor NPD (Nuclear Power Demonstration) dio buenos resultados una instalación comercial a base de alúmina. La mayor parte de las impurezas, salvo las orgánicas, se eliminan satisfactoriamente con resinas de intercambio iónico. Mediante agentes coadyuvantes de la filtración, es posible rebajar la proporción de aceite hasta cinco partes por millón, aproximadamente.

Para la reconcentración isotópica del agua que contiene menos de 99,75 % de D_2O en peso se ha recurrido a la destilación o a la electrólisis. Conviene más la primera cuando es posible aprovechar cabalmente las ventajas de un sistema automático, es decir, cuando se trata de eliminar pequeñas cantidades de H_2O de grandes volúmenes de D_2O, o bien de reconcentrar grandes volúmenes de agua pobre (con menos de 65 % en peso de D_2O). El proceso electrolítico es más flexible y, en particular, se presta para tratar agua que contenga más de 90 % de D_2O en peso; la carga mínima, que puede reducirse hasta 50 kg para una célula, representa una ventaja de este proceso. El factor de separación α, que constituye una medida del rendimiento de una planta electrolítica, excede generalmente de 9 y a veces de 10.

La concentración del tritio en el D_2O en los reactores NRX y NRU ha sido de unos 5 curios/l, durante varios años. En 1963, quedaron expuestas a la actividad de tritio 492 personas; el 82 % de este total estuvo expuesto a menos de 0,5 rem y la dosis superó a 1 rem en menos del 2 % de los casos. Los operarios de la instalación electrolítica y de la zona de purificación recibieron un promedio de menos de 0,5 rem. La exposición máxima fue de 900 mrem. Una ventilación adecuada, una buena limpieza, un equipo correctamente proyectado y procedimientos racionales de explotación son la clave de la prevención de este riesgo.

Étude sur la production d'eau lourde en France

par B. Lefrançois*, J. M. Lerat** et E. Roth**

Depuis la communication de Genève de 1958 donnant l'état des travaux en France [1], il a été reconnu que deux procédés primaires de production d'eau lourde seulement pouvaient être économiquement viables : celui basé sur l'échange entre hydrogène sulfuré et eau, et celui d'échange entre ammoniac et hydrogène. Les distillations d'hydrogène, d'eau et d'ammoniac peuvent servir de procédé de finition. L'électrolyse de l'eau n'est viable que lorsqu'elle est justifiée par la production d'hydrogène pour la synthèse de l'ammoniac, ce qui est maintenant une exception.

PROCÉDÉ D'ÉCHANGE AMMONIAC-HYDROGÈNE

La connaissance de ce procédé a été améliorée par des études dont nous parlerons plus loin, les détails de ce procédé étant moins publiés que ceux du procédé d'échange entre hydrogène sulfuré et eau.

Ces études, menées en commun au départ par les Houillères du bassin du Nord et du Pas-de-Calais et le Commissariat à l'énergie atomique, ont été pour-

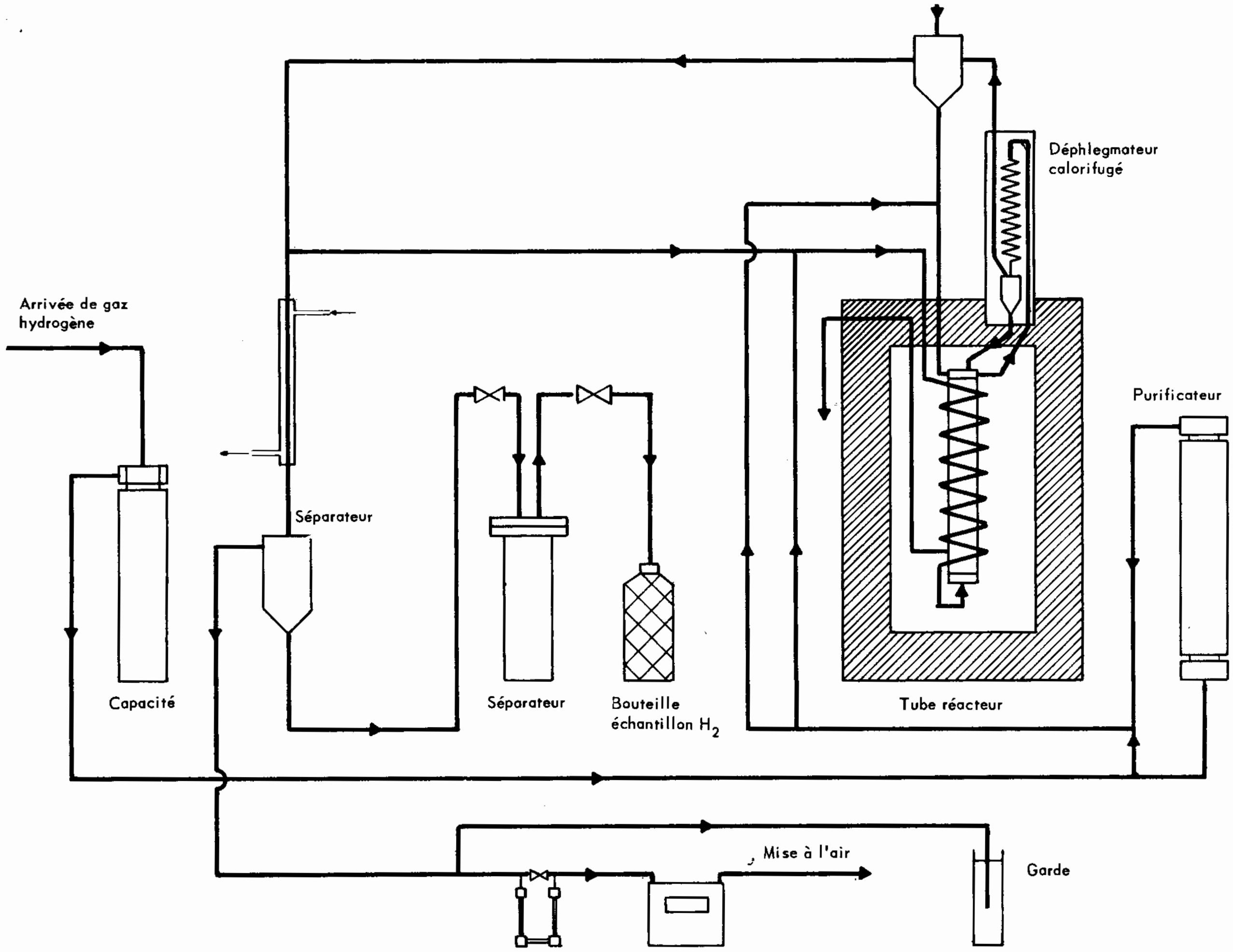

Figure 1. Petit pilote UCMa

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* Houillères du bassin du Nord et du Pas-de-Calais.

** Commissariat à l'énergie atomique, Service des isotopes stables, Saclay.

suivies à partir de 1960 dans le cadre d'un groupe comprenant en outre la Société Air Liquide et la Compagnie de Constructions mécaniques (procédés Sulzer).

Études expérimentales sur petit pilote

Dès les premiers mois de 1957, un petit pilote a été construit à la station d'essai de UCMa*, où, dès le début, les expériences furent faites sous haute pression (500 kg/cm²) et basse température (+ 15 à — 50 °C).

Description du pilote

L'installation est schématisée à la figure 1. Le réacteur proprement dit a un diamètre intérieur de 40 mm environ, sa longueur intérieure utile est de 1 m. Le fonctionnement de l'installation était discontinu et permettait d'étudier l'influence, sur l'enrichissement obtenu, de la température, du débit, de la pression, de la nature du contact employé, etc.

Le débit gazeux était mesuré, après détente à l'atmosphère, à l'aide d'un compteur; le réglage, approximatif mais rapide, étant fait par un débitmètre à diaphragme. Des couples thermoélectriques permettaient de connaître la température à l'intérieur de l'enceinte isotherme et dans le réacteur lui-même. Des manomètres, situés à l'entrée du gaz dans l'enceinte, donnaient la pression de service. Un tube de soutirage piqué dans la partie basse du réacteur servait de prise d'échantillons d'ammoniac liquide. Les mesures de teneurs isotopiques furent faites d'abord à l'infra-rouge sur l'ammoniac liquide, puis par spectrométrie de masse sur le gaz et le liquide, suivant les techniques maintenant classiques [1].

Conditions expérimentales

Le réacteur pouvait être traversé par un débit G de gaz total (azote et hydrogène) de 7 à 100 m³ (TPN) par heure, contenir une quantité d'ammoniac liquide L_0 de 125 à 600 cm³ dont la concentration en catalyseur était en général de 40 g d'amidure de potassium par litre d'ammoniac.

Systèmes de contacts essayés

Les premiers essais furent faits avec des plaques frittées de porosité 20, 50 et 100 microns et poursuivis par une expérimentation systématique de plateaux de perforation variée, plus commodes à mettre en œuvre industriellement.

Les résultats montrèrent :

a) Que l'efficacité d'échange est d'autant meilleure que le diamètre des trous est plus faible. En particulier elle est excellente pour les plaques frittées;

b) Que l'efficacité augmente lorsque le rapport G/L_0 diminue. Ainsi, tant que l'efficacité n'est pas trop forte, celle-ci est proportionnelle à la hauteur de liquide sur le plateau;

c) Que, cependant, l'efficacité reste très faible à basse température pour des submergences de liquide de quelques centimètres. Ainsi à — 50 °C pour 5 cm de liquide clair sur le plateau et des trous de $\varnothing = 1$ mm, l'efficacité est égale à 1 % environ pour un débit de gaz $N_2 + 3\ H_2$ de 13 m³/h (TPN), une concentration en catalyseur de 4 % et une pression de 500 kg/cm².

D'autres campagnes furent alors entreprises pour trouver des systèmes de contact à rendement plus élevé. On se tourna alors vers les systèmes à agitation mécanique. Entre autres, différents systèmes d'éjecteurs construits par Sulzer Frères (Suisse) se révélèrent particulièrement efficaces.

On peut, en utilisant par exemple la notion du temps de contact t_0 définie par J. Bigeleisen [3], classer les systèmes en fonction de leur efficacité.

Le choix s'est finalement porté sur l'éjecteur Sulzer, et le type d'appareil pouvant être adapté et mis en œuvre pour une installation industrielle fait l'objet du brevet français [10].

On peut citer, à titre indicatif, les efficacités d'échange (au sens de Murphree, côté gaz) obtenues dans les conditions indiquées au tableau 1.

Tableau 1. Efficacités d'un éjecteur obtenues sur petit pilote

Débit gaz (m^3/h [TPN])	Température (°C)	Quantité NH_3 introduite (cm³)	Efficacité (%)
50	— 30	225	20
50	— 30	375	50
50	— 50	225	9
50	— 50	375	20

Études expérimentales sur grand pilote

Nécessité d'expériences à plus grande échelle

Les essais sur le petit pilote correspondent à une échelle très petite par rapport à la taille de l'usine. Des essais grandeur nature, réalisés dans une nouvelle installation, ont alors porté sur un éjecteur taille usine dont la gamme de débits est comprise entre 0 et 3 500 m³/h de gaz $N_2 + 3\ H_2$ (TPN).

Le pilote, en service depuis le printemps 1963, a fourni les données définitives de fonctionnement et de géométrie de l'appareil grandeur nature essayé dans les conditions de la future usine. Ce « grand » pilote permet de plus l'expérimentation, échelle usine, de plateaux perforés employés dans certaines parties de l'installation fonctionnant à température plus élevée (tour de lavage du catalyseur).

Notons de plus que l'étude en pilote du contact avait été précédée d'essais sur un pilote de caractéristiques hydrodynamiques.

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* UCMa : Usines chimiques de Mazingarbe.

Caractéristiques générales

L'ensemble des installations du pilote est visible sur la figure 2, et comprend en particulier la préparation et le stockage de l'amidure de potassium qui permettent de définir grandeur usine l'atelier « catalyseur » de l'usine. Le réacteur proprement dit a un diamètre intérieur de 350 mm et une hauteur utile de 2,5 m environ. La pression peut être portée à 500 kg/cm² et la température abaissée aux environs de — 30 °C.

Après mise en froid et introduction de liquide, la durée de l'expérience proprement dite ne peut pas excéder 3 ou 4 min. (y compris le temps nécessaire aux prélèvements). Ce réglage du débit gazeux s'obtient en quelques secondes, grâce à un personnel particulièrement bien entraîné.

Autre expérimentation

En plus de l'expérimentation à petite et grande échelle actuelle, a eu lieu toute une série d'essais et d'expériences indispensables. Les expériences de laboratoire furent principalement menées à bien au CEA et aux HBNPC. Elles ont porté sur : la détermination

Figure 2. Grand pilote

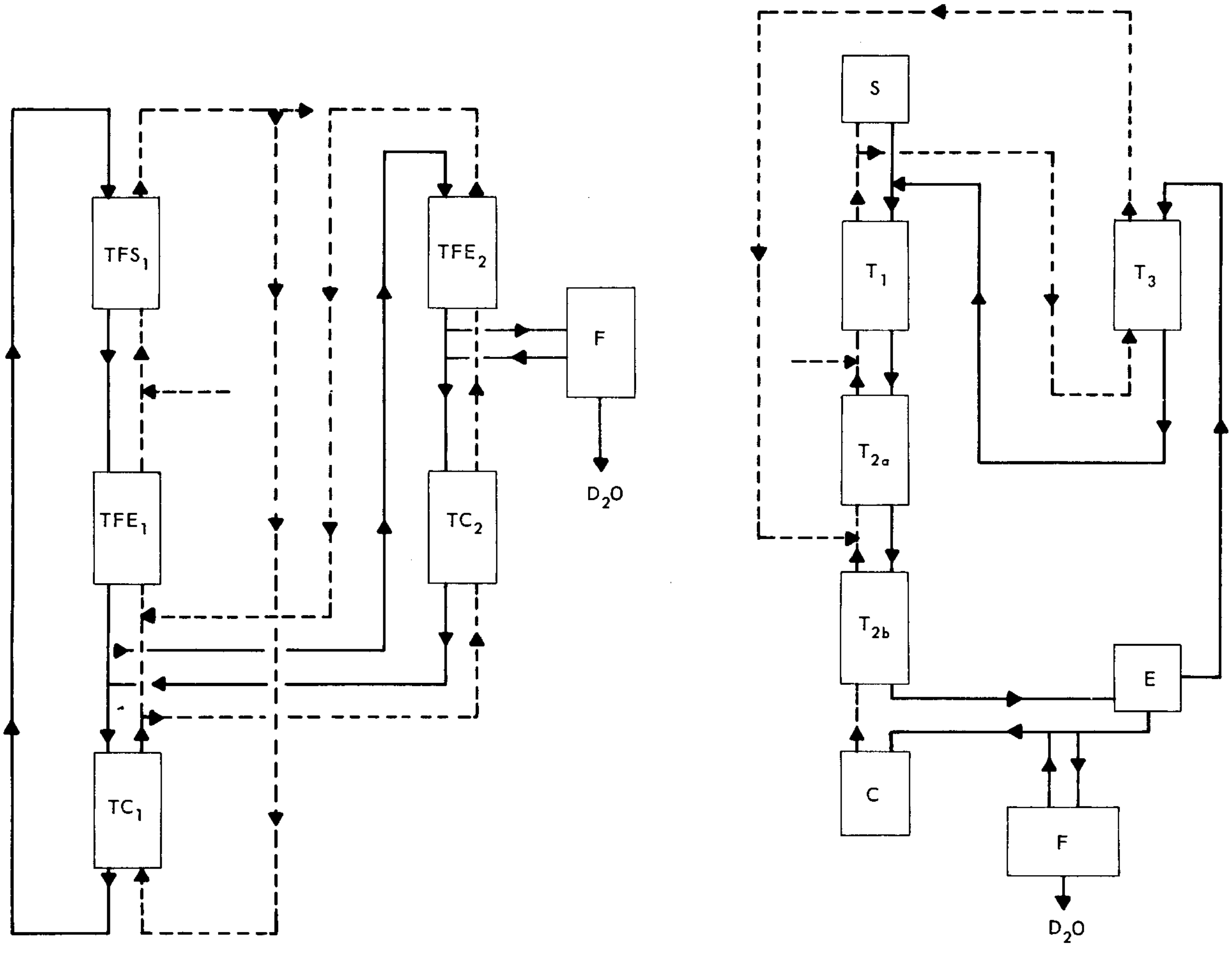

Figure 3. Schéma des procédés
A gauche : bitherme, cas A; *à droite :* monotherme, cas B

précise des facteurs de séparation de la réaction d'échange [4]; la détermination en fonction de la température de la solubilité de l'amidure dans l'ammoniac [5]; la cinétique de la réaction d'échange [6]; la cinétique de cracking, sous pression, de l'ammoniac; l'étude de la corrosion, sous tension ou non, de différents matériaux pouvant être utilisés dans la construction de l'usine : métaux, plastiques, joints, etc.; la détermination des impuretés dans le gaz de synthèse; la détermination de la teneur moyenne en deutérium dans le gaz et ses variations au cours du temps.

En outre, des mesures ont été effectuées sous haute pression, donc à la station d'essai de Mazingarbe, pour : la détermination de la quantité d'ammoniac de saturation dans le mélange $N_2 + 3\ H_2$ en fonction de la température [7]; la solubilité de $N_2 + 3\ H_2$ dans l'ammoniac liquicde, avec ou sans amidure, en fonction de la température également [8].

Des essais technologiques furent enfin réalisés aux UCMa portant sur : l'étude des constantes physiques des fluides (viscosité, densité, tension superficielle, etc.); l'étude des réactions de destruction de l'amidure dissous dans l'ammoniac par des composés oxygénés (O_2, H_2O, CO, CO_2); la préépuration et l'épuration finale du gaz [9]; la concentration de l'amidure par évaporation de l'ammoniac de dissolution; la recherche et la mise au point de pompes de compression et de circulation d'ammoniac contenant de l'amidure; l'étude du cracking de l'ammoniac sur pilote semi-industriel.

Installations industrielles et économie du procédé

Données de bases

En traitant le gaz de synthèse d'une usine produisant 500 t d'ammoniac par jour, correspondant à une quantité annuelle d'engrais contenant 145 000 t d'azote, la quantité d'eau lourde produite par an sera de l'ordre de 30 t. Ce chiffre est basé sur un taux d'extraction de 75 %, une teneur en deutérium de l'ordre de 135 ppm dans l'hydrogène et 8 000 h de production par an.

La concentration des usines d'ammoniac en unités de 1 000 à 1 500 t de production journalière permettrait d'utiliser à l'avenir le procédé d'échange ammoniac avec l'hydrogène pour des usines d'eau lourde d'une capacité unitaire approchant 100 t/an.

Schéma du procédé

On sait que deux principes de mise en œuvre peuvent être retenus [1] : le premier, analogue à une distillation (fig. 3), n'utilise qu'une seule température d'échange et est dit monotherme; le second, analogue au principe de l'échange hydrogène sulfuré-eau, dit procédé bitherme, doit, dans ce cas particulier, être accompagné d'un « surépuisement » (fig. 3); il acquiert ainsi un rendement d'extraction isotopique élevé.

Mais, pour obtenir avec ce système un bon enrichissement isotopique, 100 à 200 fois la teneur naturelle par exemple, il est nécessaire de prévoir deux étages, contre un seul dans le cas du monotherme. Or, lorsque la température froide du bitherme, pour une température chaude pas trop élevée (+ 30-50 °C, par exemple), n'est pas inférieure à — 30 °C, il se présente une difficulté de couplage, d'un étage à l'autre, lorsque le premier seul est surépuisé. Par ailleurs, cette difficulté est d'autant plus grande que l'enrichissement total du premier et du deuxième étage est plus fort. Ainsi, pour — 30 °C de température froide et un enrichissement total de 200 fois la teneur naturelle, l'enrichissement du premier étage seul étant de 15 fois cette teneur, le second étage traite des débits qui représentent à peu près la moitié de ceux circulant dans le premier étage. Au total, on arrive à un ensemble excessivement important. Il en résulte qu'il est nécessaire d'abaisser la température froide, ce qui impose en retour de disposer de systèmes de contact suffisamment efficaces à ces températures et relativement économiques, vu le grand nombre de plateaux théoriques d'un bitherme « à surstripping » comportant deux étages au moins.

Les expériences pilotes n'ayant pas été conduites à des températures inférieures à — 50 °C, on a limité à cette valeur la température froide des bithermes étudiés. Pour un rendement isotopique du même ordre (70-75 %) et un même enrichissement primaire Q_P de 100, la comparaison entre un monotherme dont la température est de — 30 °C et un bitherme surépuisé à deux étages, fonctionnant entre — 30 °C et + 50 °C, est la suivante :

Les investissements dans le cas de ce système bitherme seront beaucoup plus élevés du fait des plus grands volumes à traiter et du plus grand nombre de contacts nécessaires.

Toutefois le chapitre isolé des dépenses d'énergie est nettement plus faible dans le cas du système bitherme. Ces dépenses sont principalement dues à l'installation frigorifique, aux soufflantes de circulation des gaz et à leur saturation avant admission en tour chaude. Elles représentent : 800 kWh/kg de D_2O pour l'électricité (finition non comprise), soit 40 F/kg de D_2O environ, et 1 t de vapeur/kg de D_2O, soit 14 F/kg de D_2O environ, pour les besoins de la saturation du gaz.

Ces dépenses d'électricité semblent pouvoir être réduites par un meilleur schéma de récupération de chaleur et un abaissement de la température froide au voisinage de — 60-70 °C, abaissement qui réduit notablement les débits des fluides en circulation.

Les frais d'exploitation du monotherme sont dus en particulier au cracking d'ammoniac assurant le reflux gazeux en bas des tours d'enrichissement et à la recompression du gaz. Ils représentent environ : $2{,}5 \times 10^6$ kcal/kg de D_2O, soit 20 à 40 F/kg de D_2O

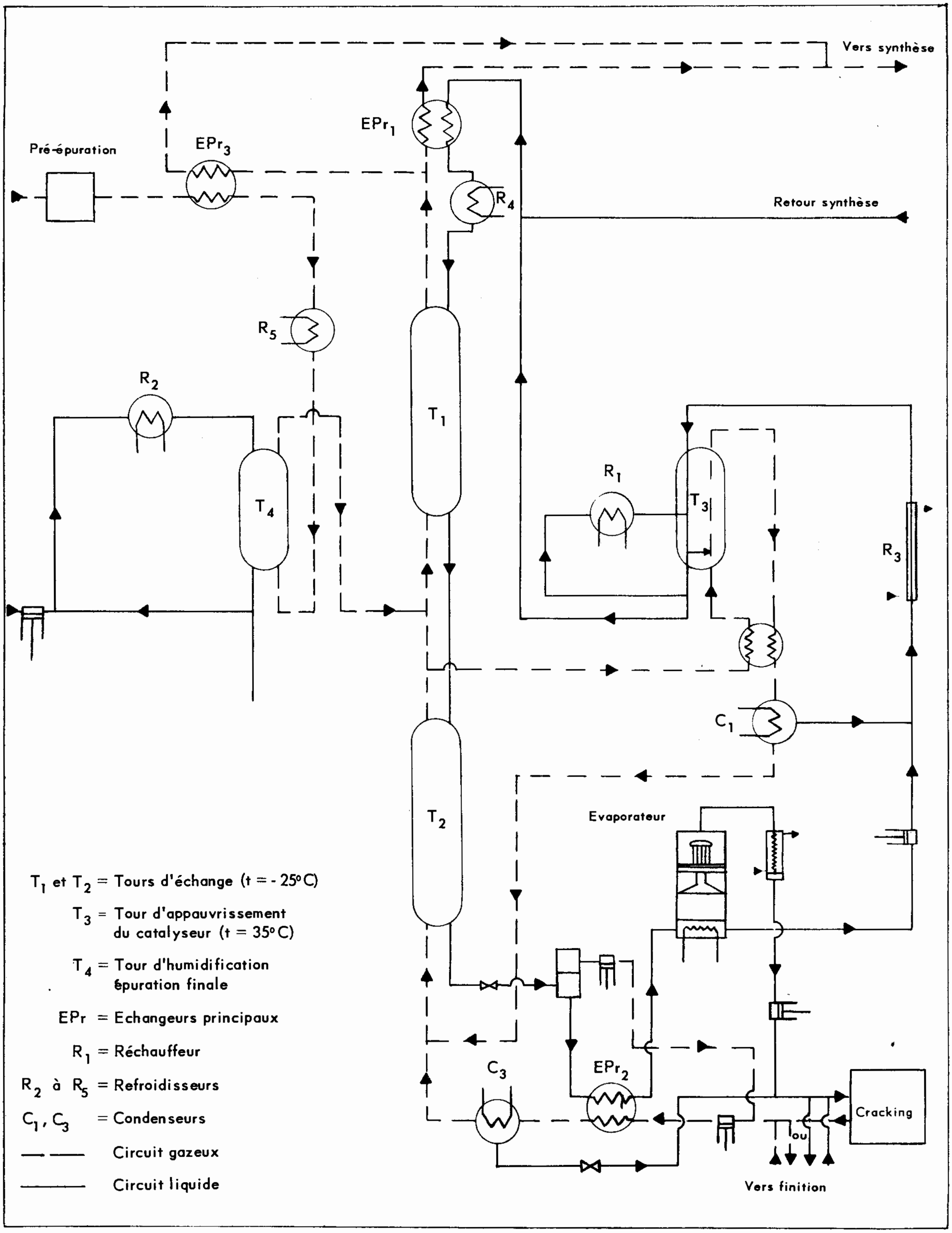

Figure 4. Procédé NH_3 — H_2, installation monotherme

suivant le prix de la calorie, et environ 1 100 kWh/kg de D_2O consommés, soit 55 F/kg de D_2O pour l'électricité (finition non comprise).

Donc, en se limitant à une température froide de — 50 °C, la seule solution envisageable pour une usine basée sur l'échange NH_3-H_2 repose sur le procédé monotherme, bien que les dépenses d'énergie soient plus élevées que pour le procédé bitherme.

Mais, dans l'avenir plus lointain, le procédé bitherme peut devenir intéressant si l'étude de l'échange à des températures de l'ordre de — 70 °C donne des résultats favorables.

Schéma du procédé monotherme

Un avant-projet d'usine, lié à une production d'ammoniac fréquemment rencontrée en France, soit 300 t/j, a été étudié.

Les caractéristiques retenues étaient les suivantes :

a) La synthèse supplémentaire nécessaire pour recombiner l'ammoniac cracké en vue d'assurer le reflux de gaz est réalisée par le même tube à une capacité totale ne dépassant pas 375 t/j (300 + 75);

b) On prévoit une boucle séparée, indépendante de l'ammoniac circulant dans le monotherme proprement dit, pour la tour de saturation et d'épuration finale T_4 (fig. 4), permettant ainsi de localiser les produits de destruction des impuretés résiduaires se trouvant dans le gaz d'alimentation.

Pour ces raisons, il est nécessaire d'abaisser la température de fonctionnement. Mais, afin de ne pas faire appel à des aciers nobles pour la construction de l'usine, n'utiliser qu'une installation frigorifique simple, disposer de systèmes de contact suffisamment efficaces, et ne pas arriver à un prix de revient trop élevé, les études furent basées sur une température ne devant pas descendre en dessous de — 30 °C, la température de la tour T_3 de lavage du catalyseur devant être optimisée, puisque celle-ci travaille comme une tour chaude de bitherme.

Des améliorations et optimisations successives conduisirent à une installation fonctionnant dans les conditions suivantes :

Enrichissement primaire : 200 fois la teneur naturelle (2,74 % D/H + D);
Rendement d'extraction : 85 % donnant une production de l'ordre de 20 t/an D_2O;
Température tour T_3 : + 35 °C;
Température tours T_1 et T_2 : — 25 °C;
Nombre de plateaux théoriques de T_1 : 9,7; de T_2 : 5,5; de T_3 : 13,6;
Reflux liquide en tête de T_1 : 75 t/j.

Ceci dans le cas d'une alimentation de 300 t/j de gaz $N_2 + 3\ H_2$.

Le *flow-sheet* de l'installation est donné à la figure 4.

CONCLUSION

Le procédé NH_3-H_2 renferme encore, sinon des certitudes, du moins de fortes possibilités d'améliorations ultérieures, et il permet donc la construction d'une usine dont l'avenir montrera si elle est la première réalisation d'une nouvelle « filière » d'ateliers de production d'eau lourde, en particulier dans les pays ne disposant que d'énergie relativement chère.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/91 France

Study of the production of heavy water in France

by B. Lefrançois *et al.*

Since 1958, several processes for the production of heavy water have been under study. Each was examined in reasonably complete detail, and attention was finally concentrated on isotopic exchanges between hydrogen sulphide and water and between ammonia and synthesis gas, pilot plant experiments having shown that the distillation of hydrogen, though technologically satisfactory, is not competitive.

Research was continued on the NH_3-synthesis gas exchange process, and led to the decision to build a production unit in which the process was combined with the synthesis of ammonia.

From among the various possible schemes for carrying out the process, the single-temperature system was chosen, in spite of certain technological problems, because it ensured high enrichment with a smaller number of contact devices. These have now been perfected after large-scale pilot-plant tests. The initial industrial trials, which are about to start, will supply useful information for second-generation plants, whether they keep to the single-temperature lay-out or revert to the two-temperature system.

A/91 Франция

Производство тяжелой воды во Франции

Б. Лефрансуа ***et al.***

Начиная с 1958 года было исследовано несколько способов получения тяжелой воды. Каждый из них был изучен более или менее полно. В конечном счете все усилия были сконцентрированы на методе изотопного обмена сероводород — вода и аммиак — синтетический газ, после того как полупромышленный опыт показал, что дистилляция водорода, хотя этот процесс и совершенен с технологической точки зрения, не является конкурентоспособной.

Метод изотопного обмена аммиак — синтетический газ. Результаты исследования этого метода подтвердили необходимость создания промышленной установки, непосредственно связанной с заводом по синтезу аммиака.

Среди различных возможных схем осуществления этого процесса выбор пал на однотемпературную схему, несмотря на некоторые технологические трудности. Эта схема обеспечивает высокое обогащение с меньшим количеством контактных аппаратов. Обширные опытные испытания показали перспективность этого метода в промышленном масштабе. Первый промышленный опыт после пуска промышленной установки позволит собрать ценные сведения для будущих заводов и определить наиболее целесообразную схему одно- или двухтемпературного процесса.

A/91 Francia

Estudios sobre la producción de agua pesada en Francia

por B. Lefrançois *et al.*

Desde el año 1958 se vienen estudiando diversos procedimientos de producción de agua pesada. Se profundizó en mayor o menor grado el examen de cada uno de ellos y, en definitiva, la labor se concentró en los métodos de intercambio isotópico ácido sulfhídrico-agua y amoníaco-gas de agua después de que los experimentos en escala piloto demostraron que la destilación del hidrógeno, si bien no ofrece mayores problemas tecnológicos, distaba de ser rentable.

Las investigaciones efectuadas condujeron a la decisión de construir una unidad de producción combinada con una instalación de obtención de amoníaco sintético.

Entre los diversos esquemas posibles para la aplicación del procedimiento, se optó por el « monotérmico » que, salvados ciertos problemas tecnológicos, ofrecía la ventaja de proporcionar un alto enriquecimiento con un número reducido de dispositivos de contacto. Estos están ya terminados, después de una serie de ensayos piloto en gran escala. La instalación industrial de carácter experimental que se pondrá en marcha, proporcionará fructuosas enseñanzas para las instalaciones de segunda generación, sea que se adopte en ellas el sistema monotérmico o el sistema bitérmicos.

Commercial technical methods for reconcentration and purification of downgraded and contaminated heavy water for nuclear reactors

By T. Saito,* S. Sonoda,* Y. Kurihara,* T. Takamatsu ** and T. Morita ***

With nuclear power generation being increasingly put to practical use, heavy water reactors have recently been extensively evaluated in such countries as Canada, the United States, the United Kingdom, the Soviet Union, Sweden, and others. It has become necessary to improve the economics of the heavy water reactor by establishing a reliable and inexpensive method for re-enrichment of downgraded heavy water which has been substantially reduced in concentration by use in a power reactor.

The concentration of downgraded heavy water varies widely with the operating conditions of the reactor which cause the decrease in concentration. The amount of downgraded heavy water depends on the reactor capacity involved.

The following are three conditions demanded of the reconcentration apparatus:

(*a*) It should permit safe operation, minimize deuterium losses, and ensure the recovery of heavy water at a very high efficiency;

(*b*) It should involve low recovery costs;

(*c*) It should respond easily to changes in the feed concentration.

A specially designed recovery apparatus [1,2] was attached to the main equipment, and the electrolytic concentration method and the perforated column rectification method studied. The basic conditions for both methods have been established by operation of a pilot plant. The special recovery apparatus can be operated with a very high degree of safety and is substantially free from gas leakage because recovery is conducted within a closed circuit, the recovery being approximately 100%.

For the rectification method, calculations were made by the gradient method to optimize the whole system on the basis of the theory of an ideal cascade. Thus a new rectification method has been developed involving low recovery costs. The retreatment or reconcentration of the downgraded heavy water discharged from the reactors JRR-2 and JRR-3 of the Japan Atomic Energy Research Institute is now being undertaken by the electrolytic method at a 5-tons per year plant.

A purification method for heavy water containing boron, fats and oils, cations and anions has been studied and purification of about two tons of such contaminated heavy water carried out. This report is being made, since the results have been more successful than had been expected.

ELECTROLYTIC PROCESS

To meet the various conditions of the above-mentioned reconcentration method, a safer technique has been established by improving the conventional electrolytic process. In June 1963 we set up a 5-tons per year plant, which is now operating smoothly.

Outline of apparatus

Electrolytic cell

An efficient electrolytic cell should have a large separation factor and be capable of providing a high ratio of the initial volume to the reduced final volume. To obtain a high separation factor, a study was made of the following:

(*a*) Uniform composition of electrolyte;

(*b*) Cooling of cathode surface;

(*c*) Selection of electrode material;

(*d*) Cleaning of electrode surface;

(*e*) Prevention of losses of liquid and gas in electrolytic cell and ancillary equipment.

To raise the ratio of the initial volume to the reduced final volume, a study was made of the cell structure and electrolyte used. The commercial apparatus is a cylindrical, non-diaphragm cell which is 0.4 m in diameter and 2.0 m in height and has a 1 000 A current capacity and an 8 to 10 separation factor.

Recovery apparatus

Since the explosive mixture of gas released from the non-diaphragm electrolytic cell contains large volumes of deuterium, it is important to recover the gas safely and at a high efficiency. The techniques already published

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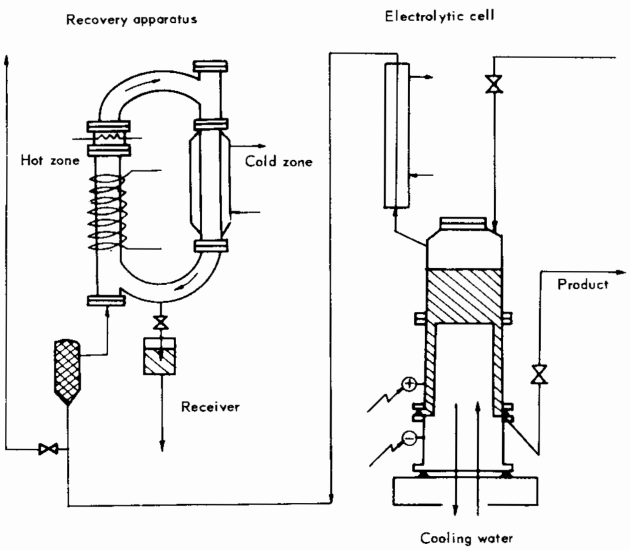

Figure 1. Flowsheet for electrolytic process

include the direct burning method [3], the burning method with air dilution [4], and the catalytic burning method [5]. A new technique has been developed which has advantages over the above-mentioned techniques in respect to safety, ease of operation and economics.

The flowsheet of the process developed is presented in Fig. 1. The burning apparatus consists of a hot zone heated to about 500 °C and a cold zone cooled to room temperature. The air or oxygen sealed in the hot and cold zone tubes circulates in the direction of the arrows due to natural convection. When the explosive gas mixture is charged into the system, it is diluted by the air or oxygen to below the explosive limit, and burns at a steady rate. Ignition takes place at the heating wire above the hot zone. The heavy water steam produced is condensed in the cold zone and discharged from the system at the bottom. The foregoing cycle is repeated continuously in the closed apparatus safely and at a high recovery efficiency. Table 1 shows the outstanding features of the technique compared to the direct burning method which is a conventional technique for the electrolytic process.

In designing the recovery apparatus, an analysis of the tube diameter and circulating gas velocity was made as follows. Assuming that the driving force for circulation by natural convection is due to the difference in the density of the material in the cold zone compared to that in the hot zone and ideal gas behaviour applies, the following equation is obtained.

$$\varrho_0 T_0 \left[\left\{\int_0^l (1/T)\,\mathrm{d}\ell\right\}_c - \left\{\int_0^l (1/T)\,\mathrm{d}\ell\right\}_h\right] = 4f\{(L/d) + C\}(\varrho v^2/2g) \quad (1)$$

This was used as the basic equation. The coefficient C was determined by actual measurements.

Table 1. Comparison of electrolytic processes

	Direct burning method	New method
Electrolytic current capacity	1 000 A	1 000 A
Construction cost	Due to the direct burning of the explosive gas, it is necessary to control strictly the pressure, velocity and temperature of the gas. This results in higher costs for instrumentation and other equipment.	A substantial margin can be allowed in the operating conditions. Consequently neither recovery apparatus nor instrumentation requires any special techniques.
Recovery efficiency	Since the apparatus is rather complicated, care should be taken in handling the liquid or gas.	Since the apparatus is completely closed, the recovery efficiency is 100%.
Electrolytic separation factor	= 8 to 10	= 8 to 10
Operation	(*a*) To insure complete burning, it is necessary to install a catalytic burning cylinder next to the burner. (*b*) It is always necessary to keep a close control over the velocity, pressure and temperature of the gas. (*c*) At the time of start-up, stoppage or sudden failure, particular care must be taken.	(*a*) Complete recovery is possible and the apparatus is simple. (*b*) Operation is very easy. (*c*) No particular care is required.

Table 2. Dimensions of 5 tons per year plant

Electrolytic cell:

Type: non-diaphragm electrolytic cell
Number of units: 2
Current density: 10 A/dm^2
Initial charge: 100 1
Separation factor: 8 to 10
Current capacity: 1 000 A
Size: 0.4 m diam 2.0 m

Recovery apparatus:

Type: burning apparatus
Number of units: 2
Capacity: the amount of gas released from the 1 000 A electrolytic cells
Size: diameter 0.5 m diam
height 1 m

Calculation method for the cascade [6, 7]

Definition of the separation factor (α)

$$\alpha = X(1-X)/Y(1-Y) \qquad (2)$$

and the theory of the batch-process of the electrolytic concentration leads to the following equation:

$$(\ln X_D/X_F) - 1/\alpha \ln (1 - X_D)/(1 - X_F) = (1 - 1/\alpha) \ln F/D \qquad (3)$$

This Eq. (3) was used in calculating the cascade. When the equation is applied to the first stage:

$$\ln (X_D)_1/(X_F)_1 - 1/\alpha \ln 1 - (X_D)_1/1 - (X_F)_1 = (1 - 1/\alpha) \ln (D_2 + F)/D_1 \qquad (4)$$

For the *i*th stage the following equation can be established:

$$\ln (X_D)_i/(X_D)_{i+1} - 1/\alpha \ln 1 - (X_D)_i/1 - (X_D)_{i-1} = (1 - 1/\alpha) \ln D_{i+1} + W_{i-1}/D_i \qquad (5)$$

By the theory of the optimum cascade and material balance

$$X_F = (X_D)_2 \qquad (6)$$

$$F + D_2 = D_1 + W_1 \qquad (7)$$

$$(X_D)_{i+1} = (X_W)_{i-1} \qquad (8)$$

$$D_{i+1} + W_{i-1} = D_i + W_i \qquad (9)$$

With $\alpha = 8$, W_n and $(X_W)_n$ were determined by solving the above equations in succession.

The flowsheet of the optimum cascade is shown in Fig. 2.

Notation used in Eqs. (1-9)

C : coefficient
c : suffix of cooling zone
D : production rate (kg mol/y)
d : tube diameter (m)
F : feed rate (kg mol/y)
f : friction coefficient
h : suffix to the heating zone
i : suffix to stage number
L : total tube length of the burning apparatus (m)
l : length of the cooling or heating zone
n : stage number
v : circulating gas velocity (m/s)
W : waste rate (kg mol/y)
X : concentration of deuterium in liquid (D atom %)
X_D : concentration of deuterium in product (D atom %)
X_F : concentration of deuterium in feed (D atom %)
X_W : concentration of deuterium in waste (D atom %)
Y : concentration of deuterium in gas (D atom %)
α : separation factor
ϱ_0 : density of circulating gas at NTP (kg/m^3)
ϱ : density of circulating gas (kg/m^3)

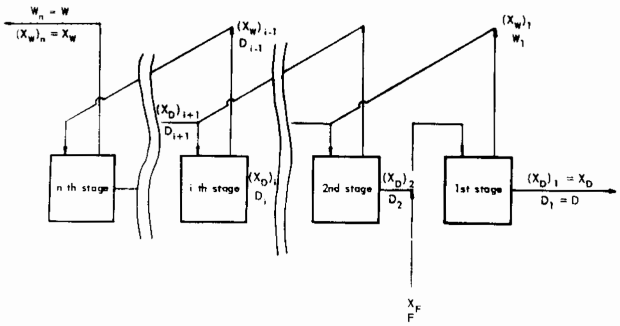

Figure 2. Flowsheet of optimum cascade for electrolytic process

RECTIFICATION PROCESS

Another process has been studied as a means for recovery and reconcentration of heavy water. This is the distillation method. As regards the optimum design of the distillation column cascade, several reports have already been published [8-12]. But they were based on approximate calculations assuming the gas-liquid ratio to be unity for all the columns. In this paper we attempt to optimize the general cascade plant, avoiding such an assumption as much as possible.

Type of cascade

The most general type of distillation column cascade is considered to be the one illustrated in Fig. 3a. For convenience in calculation, such a cascade system as is given in Fig. 4 was studied. In this system, feed plates A and B are placed in equivalent positions and the condition of no-mixing should be satisfied in this plate. It is clear that in the well-known cascade system as presented in Fig. 3b, it is impossible to

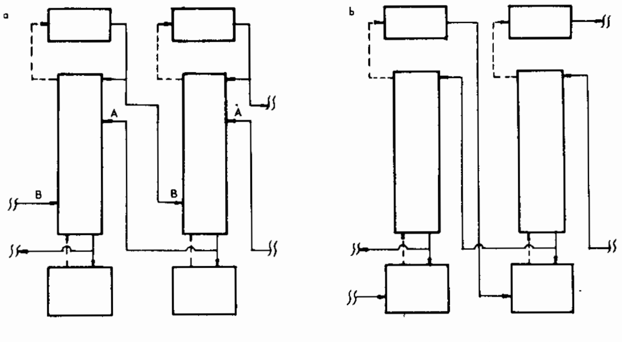

Figure 3. Distillation column cascades

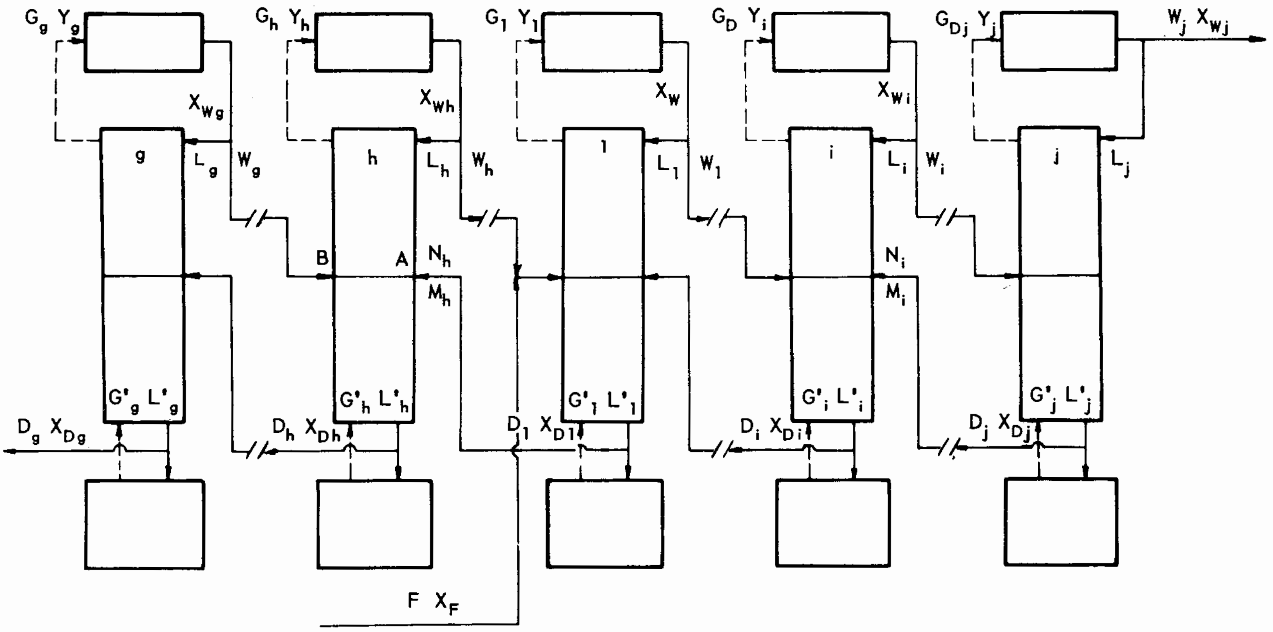

Figure 4. Distillation column cascade

provide widely different vapour rates at each stage from a consideration of the mass balance. Also it is known that where there are fewer stages, there is no appreciable difference from the effect observed in the single column system. As the result of the foregoing observations, the cascade system in Fig. 4 was compared with a single column by undertaking an optimum design for each of them.

Theoretical formula

For the cascade system in Fig. 4, assuming that the plant is operated in a steady state and that the vapour rate in the column is constant, the theoretical number of plates for that section of column *i* where light water is concentrated is given by the following equation:

$$N_i = \ln \frac{(X_{\mathrm{W}i} - h_i)\,(X_{\mathrm{F}i} + h_i + a_i + b)}{(X_{\mathrm{F}i} - h_i)\,(X_{\mathrm{W}i} + h_i + a_i + b)} \Big/ \ln\left(-\frac{h_i + a_i}{h_i + b}\right) \qquad (10)$$

Where,

$$R_i = L_i/W_i, \qquad a_i = [B_i(\alpha - 1) - a]/A_i(\alpha - 1)$$
$$b = 1/(\alpha - 1), \quad C_i = B_i/A_i\,(\alpha - 1) \qquad (11)$$
$$A_i = R_i/(R_i + 1), \; B_i = X_{\mathrm{W}i}/(R_i + 1)$$
$$h_i = \text{Root of } h_i^2 + (a_i + b)\,h_i + C_i = 0$$

Similarly, the theoretical number of plates for that section of column *i* where light water is recovered is indicated by:

$$M_i = \ln \left[\frac{(X_{\mathrm{D}i} - h_{i'})\,(X_{\mathrm{F}i} + h_{i'} + a' + b_{i'})}{(X_{\mathrm{F}i} - h_{i'})\,(X_{\mathrm{D}i} + h_{i'} + a' + b_{i'})}\right] \Big/ \ln\left(-\frac{h_{i'} + a'}{h_{i'} + b_{i'}}\right) \qquad (12)$$

Where,

$$\theta_i = D_i/L_{i'}$$
$$a' = 1/(\alpha - 1)$$
$$b_{i'} = [\alpha + (\alpha - 1)\,Q_i]/P_i\,(1 - \alpha),$$
$$C_{i'} = Q_i/P_i\,(1 - \alpha) \qquad (13)$$
$$P_i = 1/(1 - \theta_i)$$
$$Q_i = X_{\mathrm{D}i}\,\theta_i/(1 - \theta_i)$$
$$h_i = \text{Root of } (h_{i'})^2 + (a_{i'} + b_{i'})\,h_{i'} + C_{i'} = 0$$

For the light water recovery section of the cascade, the subscript *i* is substituted by *h*.

From the mass balance throughout the whole cascade system

$$W_i = F\,(1 - \gamma)/(\delta - \gamma) \qquad (14)$$
$$D_g = F\,(\delta - 1)/(\delta - \gamma) \qquad (15)$$

Where,

$$\gamma = \prod_{h=1}^{g} \gamma\mathrm{k} = X_{\mathrm{D}g}/X_{\mathrm{F}} \qquad (16)$$
$$\delta = \prod_{i=1}^{j} \delta_i = X_{\mathrm{W}j}/X_{\mathrm{F}} \qquad (17)$$
$$\delta_i = X_{\mathrm{W}i}/X_{\mathrm{F}i}, \gamma_i = X_{\mathrm{D}i}/X_{\mathrm{F}i}, \; \delta_h = X_{\mathrm{W}h}/X_{\mathrm{F}h}, \; \gamma_h = X_{\mathrm{D}h}/X_{\mathrm{F}h}$$

From the mass balance between a given column *i* and column *j* at the light water concentration end of the cascade, W_i is represented by the following equation:

$$W_i = W_j\,(X_{\mathrm{W}j} - X_{\mathrm{D}(i+1)})/(X_{\mathrm{W}i} - X_{\mathrm{D}(i+1)}) \qquad (18)$$

Assuming at this point the following relation for the condition of no-mixing,

$$X_{\mathrm{F}i} = X_{\mathrm{W}(i-1)} = X_{\mathrm{D}(i+1)},$$

Eq. (18) leads to the following.

$$W_i = W_j \left[\prod_{k=i}^{j} \delta_k - 1\right] /(\delta_i - 1), \qquad (19)$$

and D_i is as follows:

$$D_i = W_j \left[\prod_{k=i}^{j} \delta_k - 1 \right] / (1 - \gamma_i) \quad (20)$$

From the mass balance in column *i*, $G_{i'}$ is given by the following equation:

$$G_{i'} = L_{i'} - D_i = W_j \left[\prod_{k=i}^{j} \delta_k - 1 \right] (1 - \theta_i)/(1 - \gamma_i)\theta_i \quad (21)$$

Similarly with the recovery section of the cascade

$$W_h = D_g \left[\prod_{k=h}^{g} \gamma_k - 1 \right] / (1 - \delta_h) \quad (22)$$

$$D_h = D_g \left[\prod_{k=h}^{g} \gamma_k - 1 \right] / (\gamma_h - 1) \quad (23)$$

$$G_{h'} = L_{h'} - D_h = D_g \left[\prod_{k=h}^{g} \gamma_k - 1 \right] (1 - \theta_h)/(\gamma_h - 1)\, \theta_h \quad (24)$$

Now if the performance index for optimum design is taken as the sum of the cost of heavy water recovery and the cost of additional heavy water to be purchased so as to make up for losses in recovery, then

$$F_c = C_v < V > + C_g < G > + C_D W_j (1 - X_{Wj})/(1 - X_{Dg}) \quad (25)$$

Where,

$$< V > = K \left[\sum_{i=2}^{j} G_{i'} (N_i + M_i) + G_{h=1'} (N_{i=1} + M_{h=1}) + \sum_{h=2}^{G} G_{h'} (N_h + M_k) \right. \quad (26)$$

$$< G > = \sum_{i=2}^{j} G_{i'} + \sum_{h=1}^{g} G_{h'} \quad (27)$$

For the optimum design of a heavy water plant, therefore, it is necessary to determine a value which will minimize Eq. (25).

Notation used in Eqs. (10-25)

Y : concentration of light water in vapour (mole fraction)
X : concentration of light water in liquid (mole fraction)
X_D : concentration of light water in production (mole fraction)
X_W : concentration of light water in waste (mole fraction)
X_F : concentration of light water in feed (mole fraction)
F : feed rate (ton/year)
W : waste rate (ton/year)
D : production rate (ton/year)
LL' : liquid rate (kg mol/year)
GG' : vapour rate (kg mol/year)
NM : number of theoretical plates
V_G : vapour velocity (250 mm Hg) (m/s)
ρ_G : vapour density (250 mm Hg) (kg/m^3)
E : Murphree plate efficiency
R : reflux ratio
θ : cut
h : vertical distance between plates (m)
V : plant volume (m^3)
$< V >$: total plant volume (m^3)
$< G >$: total vapour rate (ton/year)
δ, γ : concentration ratio (ton/year)
C_V : cost factor proportional to volume (yen/m^3)
C_G : cost factor proportional to vapour rate (yen/kg-mol)
C_D : cost factor of D_2O (yen/kg-mol)
K : coefficient (m^3 year/ton)

Numerical calculations

As an example of the numerical calculations, it is assumed that the cascade system consists of three columns in which the feed will be charged into a given plate of the column containing the most concentrated light water (this column is referred to as column 1 and consequently the column from which enriched heavy water is discharged is column 3).

If the amount and concentration of the feed and the concentration of enriched heavy water are specified, the independent variables, obtained from the above equations would be θ_1, θ_2, θ_3, X_{D1}, X_{D2} and X_{W1}. The values of C_v, C_g, C_D and K required in the cost calculation have been determined and are given in Table 3. The calculation of the C_v value is based on the assumption that as the column diameter grows smaller, the plant cost rises in proportion to the 0.6 power of the cross-sectional area, and the C_G value is computed on the assumption that the operating cost would be proportional to the total vapour throughout. The K value is selected from the results of experimental work on the perforated column which is 40 cm in diameter and has 100 plates.

While dynamic programming [12, 13] may be available for the numerical calculation of the optimum value the present case involved six variables and so the steepest ascent method or .method of gradient [14, 15] was applied.

The results obtained from the single column are presented in Table 3. As can be seen from this table, the cascade does not offer much advantage where the number of stages is small. Table 3 contains changes in the price of the recovered product in relation to the amount treated.

Economic discussion

While it is logical to reduce the losses of heavy water so as to improve the economics of a heavy water reactor, some losses of heavy water and reductions in its concentration are unavoidable due to the following: (*a*) leakage from the heavy water loop including the pump; (*b*) losses in the regeneration and replacement of ion-exchange resin in the heavy water purification system.

Naturally, it is important to carry out the reconcentration of heavy water which has been thus reduced in concentration at low cost and to minimize the amount of make-up heavy water required. The optimum economic conditions have been investigated and the results are presented in Table 4. Labour costs and general administrative expenses are not included. If these factors are added, the electrolytic process will be economically preferable up to several tons per year. Beyond this level, it could be envisaged that the rectification process would provide the greater advantage.

The electrolytic process is characterised by the fact

Table 3. Cost estimation

Variables	F tons/year		
	5	10	30
X_W mole fraction	0.83014	0.91635	0.96111
θ	0.02405	0.02473	0.02554
R	304.51	330.88	337.73
δ	8.3014	9.1635	9.6111
G ton/year	179.13	351.40	1 028.8
L ton/year	178.55	351.40	1 025.8
L' ton/year	183.55	361.40	1 055.77
D ton/year	4.4136	8.9380	26.963
W ton/year	0.58635	1.0620	3.0372
N	137.56	164.17	191.27
M	213.47	222.55	234.51
F_c 1 000 yen/year	17 492	19 927	33 924

Numerical value of factors

V_G : 0.5 m/s at 250 mm Hg

h : 0.1 m

E : 70%

C_V : 1.60×10^6 yen/m^3 for F = 5
1.10×10^6 yen/m^3 for F = 10
0.57×10^6 yen/m^3 for F = 30

C_G : 1 460 yen/ton (vapour)

C_D : 1.70×10^7 yen/ton (D_2O)

K : $h/\varrho_G V_G = 3.4 \times 10^{-5}$ m^3 year/ton

Table 4. Economical comparison of electrolytic method and rectification method

	Distillation method			Electrolytic method		
Feed ton/year	5	10	30	5	10	30
Depreciation on construction cost[a] yen 1 000/year	4 000	5 690	9 060	2 200	3 300	6 450
Utility yen 1 000/year	750	1 470	4 560	640	1 050	3 070
Cost of make-up heavy water yen 1 000/year	300	400	780	1 050	1 510	3 210
Total expenses yen 1 000/year	5 050	7 560	14 400	3 890	5 860	12 730
Unit price yen/g[b]	1.12	0.84	0.53	0.86	0.64	0.47

[a] Depreciation on the construction cost covers a 5-year period. If the period is extended to 10 years, the depreciation cost will be reduced.

[b] The unit price of purchased heavy water is estimated at 17 million yen per ton.

that it can readily respond to changes in the amount treated per year as well as changes in the concentration of the feed stock. If, however, such changes occur, operation of an ideal cascade would be somewhat difficult from a practical standpoint. In contrast, the rectification process essentially represents a continuous process, so that it is difficult to operate under optimum conditions when excessive variations occur in the concentration and volume of feed. But the rectification method is a very effective means whereby considerable quantities can be treated annually for a constant supply for reprocessing and if the concentration only varies within closely defined limits.

PURIFICATION OF CONTAMINATED HEAVY WATER

Removal of boron by ion-exchange resin

The purification of about 2 tons of heavy water by the removal of the dissolved boric acid has been carried out. The boric acid and other impurities were completely removed with an extremely high yield and also without reducing the concentration of deuterium.

The purification was separated into the following four stages:

(*a*) Regeneration of the spent ion-exchange resin;
(*b*) Deuterization of the resin;
(*c*) Removal of boron;
(*d*) Removal of deuterium from the resin.

The results of this purification process are very satisfactory.

Removal of oils, fats and other impurities

The heavy water actually used in a reactor or in a manufacturing plant is sometimes contaminated by oil, fats and other impurities if leakages occur. While heavy water is generally purified by distillation, this process presents difficult problems if the heavy water has been contaminated by such impurities.

The purification of such contaminated heavy water was carried out by a combination of filtration, adsorption and distillation. The removal of oil from the heavy water involved the use of a synthetic resin foam as a filtering agent, and activated alumina as the adsorbent. The results of this purifying process have proved to be sufficient for use in the reactor.

CONCLUSION

The foregoing is a discussion on the economical retreatment of heavy water for use in a reactor. The electrolytic method of reconcentration has already operated in a 5-tons per year plant with more successful results than had been expected. Pilot plant tests have been completed on the rectification method and a novel concept has been introduced into the plant design and the cascade arrangement. The authors trust that this new technique will contribute substantially to the improvement of the economics of the heavy water reactor in the near future.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/433 Japon

Procédés industriels pour reconcentrer et purifier l'eau lourde dégradée et contaminée des réacteurs nucléaires

par T. Saito *et al.*

Des recherches pour la mise au point de réacteurs à eau lourde ont été récemment effectuées au Canada, aux États-Unis, en France, au Royaume-Uni, en Suède, en URSS, etc., et l'économie de ces réacteurs a suscité un renouveau d'intérêt au cours des dernières années. L'eau lourde qu'ils utilisent s'appauvrit ou risque de se contaminer selon les conditions. Son enrichissement et sa purification dans des conditions économiques sont donc essentiels pour l'exploitation des réacteurs à eau lourde.

Le procédé d'électrolyse sans diaphragme avec dispositif spécial de récupération et le procédé de rectification ont fait l'objet d'essais dans une installation

pilote, et de nouvelles techniques pour les deux procédés ont été établies. La nouvelle technologie a été mise au point, y compris les conditions nécessaires pour la réalisation à plus grande échelle (1, 2); on a élaboré la théorie de la cascade optimale et effectué une évaluation économique. Les procédés considérés sont indispensables pour améliorer l'économie des réacteurs à eau lourde. Pour empêcher la contamination et la dégradation de l'eau lourde en cours de traitement, on se sert d'un circuit de gaz et d'un système de récupération de conception particulière. Le fonctionnement est très sûr et le rendement atteint près de 100 %. La distillation s'effectue dans une colonne à plateaux-tamis conçue selon le principe de la cascade idéale, et de fonctionnement peu coûteux. Ce système a joué un rôle important dans l'exploitation des piles JRR-2 et JRR-3 de l'Institut de recherche sur l'énergie atomique du Japon. La reconcentration et la régénération de l'eau lourde se font dans de bonnes conditions économiques avec une installation d'une capacité annuelle de 5 tonnes.

Le mémoire présente les résultats expérimentaux et les calculs relatifs à une installation d'une capacité annuelle de 30 tonnes pour de traiter de plus grandes quantités d'eau lourde. Le procédé électrolytique est économiquement favorable jusqu'à 5 tonnes; au-dessus, c'est le procédé de rectification qui convient.

L'emploi d'une installation pilote a permis d'acquérir l'expérience d'une méthode particulièrement efficace de purification de l'eau lourde, notamment pour la débarrasser des huiles et des ions solubles. On a pu ainsi élaborer un procédé peu coûteux de régénération de l'eau lourde et l'utiliser pour un réacteur.

A/433 Япония

Промышленные методы обогащения и очистки обедненной и загрязненной тяжелой воды, использованной в ядерных реакторах

Т. Саито *et al.*

В течение последних лет была проведена переоценка экономичности реакторов на тяжелой воде. Исследования в области тяжеловодных реакторов проводились в Канаде, Франции, США, Великобритании, СССР, Швеции и других странах. В процессе работы тяжеловодного реактора утечка тяжелой воды или другие причины вызывают уменьшение ее концентрации или загрязнение. Обогащение и очистка тяжелой воды являются жизненно необходимыми операциями при работе тяжеловодного реактора.

На опытной установке авторами проведены испытания бездиафрагменного метода электролиза с использованием специального аппарата для извлечения примесей и процесса очистки, во время которых удалось разработать методику этих процессов. Авторы завершили разработку новой технологии, включая определение условий, необходимых для перехода к полномасштабным установкам V,[1,2] рассчитали оптимальную теорию каскада и провели экономическую оценку методов. Эти методы приведут к повышению экономичности тяжеловодных реакторов.

Для предупреждения загрязнения и обеднения тяжелой воды во время обогащения и очистки применяются системы циркуляции газа и извлечения примесей специальной конструкции, которые обеспечивают надежную безопасность в эксплуатации и почти 100%-ный выход. Процесс дистилляции осуществляется в колонке с ситчатыми тарелками, конструкция которой основывается на идеальной теории каскада, стоимость ее эксплуатации очень низка. В Японском научно-исследовательском институте по атомной энергии была построена установка мощностью 5 *т/год,* на которой производится экономичное концентрирование тяжелой воды, использованной в японских реакторах JRR-2 и JRR-3.

В докладе описаны результаты экспериментов, а также приведены расчеты установки мощностью 30 *т/год* по концентрированию больших количеств тяжелой воды. Отмечаются экономические преимущества метода электролиза для мощности ниже 5 *т/год* и метода очистки для более высокой мощности.

Для удаления таких примесей, как масло и растворимые ионы, находящиеся в тяжелой воде, разработан высокоэффективный метод ректификации с использованием опытной установки. Разработан и опробован дешевый метод регенерации тяжелой воды, использованный в ядерном реакторе.

A/433 Japón

Métodos técnicos y comerciales para el enriquecimiento y purificación de agua pesada contaminada y degradada, para reactores nucleares

por T. Saito *et al.*

En el Canadá, Francia, los Estados Unidos, el Reino Unido, la Unión Soviética, Suecia, etc., se han efectuado investigaciones sobre el desarrollo de reactores de agua pesada, y se ha revisado con renovado interés en años recientes la economía de dicho tipo de reactor. El agua pesada en un reactor, en función de sus condiciones de manejo, reduce su concentración o está sujeta a contaminación. Su enriquecimiento y purificación económicos son cuestiones vitales con respecto a la operación de estos reactores.

Hemos hecho ensayos en planta piloto sobre procesos de electrólisis sin diafragma con aparatos especiales de recuperatión y sobre procesos de rectificación, y hemos establecido nuevas técnicas operatorias en ambos procesos. Hemos completado la nueva tecnología incluyendo las condiciones necesarias para el cambio de escala de los aparatos (1, 2), hemos desarrolado la teoría de la cascada óptima y efectuado una valoración económica. Estos procesos son indispensables para mejorar la economía del reactor de agua pesada. Para impedir la contaminación y degradación del agua pesada durante el tratamiento, se utiliza un sistema de recuperación y circulación del gas de diseño especial. Las condiciones de operación son muy seguras y el rendimiento es próximo al 100 %. El proceso de destilación utiliza una torre de platos perforados. El diseño se basa en la teoría de la cascada ideal y el costo de operación es muy bajo. Dentro del Japón hemos prestado un servicio apreciable en la operación del JRR-2 y JRR-3 del Instituto Japonés de Investigación de Energía Atómica. Actualmente se está efectuando la reconcentración y regeneración económicas del agua pesada en una instalación de 5 t/año.

La memoria contiene resultados de esta experiencia y el cálculo del proyecto referente a una instalación de 30 t/año capaz de tratar cantidades mayores de agua pesada. El proceso de electrólisis mencionado es económicamente ventajoso para una capacidad de menos de 5 t/año y el proceso de rectificación para una capacidad más alta.

Con respecto a la supresión de impurezas del agua pesada, incluyendo aceite e iones solubles, hemos adquirido experiencia en la purificación de alta eficacia mediante operación en planta piloto. Hemos establecido un proceso de bajo coste para la regeneración del agua pesada que se ha usado en un reactor.

Enrichment of low-level tritium by thermal diffusion for hydrological applications

By B. Th. Verhagen and J. P. F. Sellschop *

The sensitivity attainable for tritium measurements has been improved in recent years by the use of specially designed proportional counting systems [1-3]. The most common feature of these is the use of a multi-wire annular shielding counter, which either forms part of the central or sample counter or is separated from it by a thin membrane. The ultimate background in such systems is generally taken as 0.2 cpm. A one litre counter with such a background would therefore have a minimum detectable activity of about 10 T.U. (A tritium unit $= [T]/[H] = 10^{-18}$.)

Counting by coincidence liquid scintillation, after benzene synthesis of water, has been reported to give a minimum detectable activity also of 10 T.U. [4].

To extend the range of measurements to 1 T.U. and less, isotopic fractionation or enrichment of tritium relative to protium has to be employed. In early work, multi-stage electrolysis has been used to obtain enrichments of 10^3 times and more [5, 6], but recently it has been recognized that there are inherent difficulties in achieving reliable reproducibility using this method. The standard procedure now seems to be to enrich electrolytically by about 10 times, under controlled conditions, and to detect with the most refined techniques. At least one large, high-enrichment electrolysis plant is, however, in operation at present, giving reproducible results [7].

Other enrichment techniques which have been investigated are thermal diffusion [8, 9], gas chromatography [10, 11], and fractional distillation [12, 13]. Of these, thermal diffusion has already been translated into practical systems. Taking into account the relatively long running times for distillation, gas chromatography seems perhaps the most promising of the latter two techniques at present.

MULTI-STAGE THERMAL-DIFFUSION COLUMNS

A thermal-diffusion column consists essentially of two vertical, concentric cylinders, the inner of which is heated, the outer cooled. The mixture of gases contained in the annular space between them is subjected to the superposition of thermal diffusion and convection, whereby the heavier molecules concentrate at the bottom, the lighter at the top.

Such a column was first devised by Clusius and Dickel [14] who mounted a heated wire axially in a water-cooled tube. They used a series of similar columns in their initial experiments on the separation of the isotopes of chlorine [15] and neon [16].

Since the appearance of the papers of Furry, Jones and Onsager [17] and of Jones and Furry [18], in which the whole problem of the application of thermal diffusion to the separation of isotopes is thoroughly discussed, multi-stage operation (i.e. a cascade of columns gradually diminishing in size) has been employed by several authors to obtain large separations in comparatively short times. In this instance we refer only to the work on ^{3}He [19, 20] where oil-well helium and atmospheric helium, in which the ^{3}He concentration is 10^{-6}-10^{-7}, were used in three-stage systems, to produce small amounts of gas containing several per cent of ^{3}He.

A small thermal-diffusion plant was constructed by Gonsior [8] for enriching tritium in natural hydrogen samples. It consisted of a series of four hot-wire columns. Though the plant is capable of attaining high enrichments, it is slow and mostly used in the static condition, when it will enrich about 8 times.

The two-stage thermal-diffusion tritium separator described in this paper has the advantages of good reproducibility, short running times and a relatively high yield. Moreover, the difficulties of feeding the system, sampling and purifying the product have been overcome, and the apparatus is proving a flexible and useful tool in a tritium laboratory.

DESCRIPTION OF SEPARATION PLANT

The tritium separator of the University of the Witwatersrand was designed on the basis of the theory of Jones and Furry [18]. A brief outline has previously been given by the authors [9]. To accommodate it, a framework was built to protrude through the roof of the laboratory and weatherproofed to form a tower.

The system consists of two columns. The uppermost or first stage is a concentric-tube column, and the

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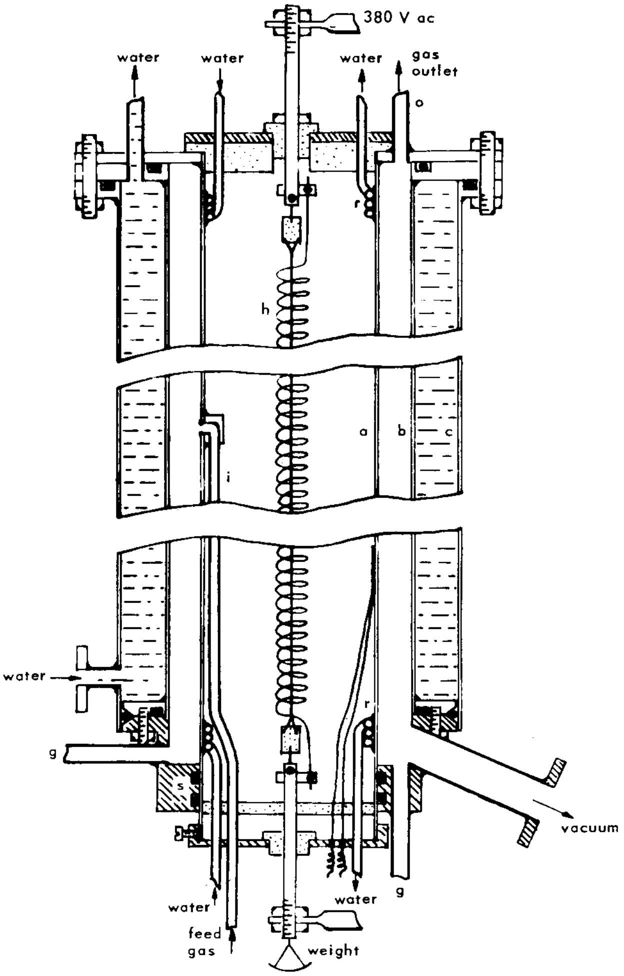

Figure 1. Section of first stage concentric tube column

lower or second stage a smaller hot-wire column. Diagrammatic sections are shown in Figs. 1 and 2.

Tube a in Fig. 1 is heated by a nichrome heating spiral, h, operating on 380 volts AC. On expanding, this tube can slide through gland s; it is water cooled at either end at r to protect the neoprene seals. Tube b is the cold wall, with cooling water circulating between it and the water jacket c. Feed gas is introduced through tube i, which enters the column at its mid-point, and gas can leave the column at o. The connection to the second stage is at points g.

The hot wall a in Fig. 2 is a DC heated tungsten wire, attached to a sliding-seal electrode, f; b is the cold wall and c the water jacket. Connections to the first stage at the top, and to a purification/extraction system at the bottom are at g.

Table 1 gives the principal dimensions and operating conditions of the two columns.

A gas-flow diagram of the whole separation plant is shown in Fig. 3.

The system is first evacuated to 10^{-4} mm Hg, with the heaters on. Feed gas is introduced at A at a rate of about 2 l/min, flowing through the freeze trap to enter the system at B. The power of the heaters is gradually increased to compensate for the additional

Table 1. Principal dimensions and operating conditions of the two thermal diffusion columns

	Concentric tube column	Hot-wire column
Length	7.20 m	2.75 m
Radius, hot wall	6.30 cm	0.02 cm
Radius, cold wall	8.76 cm	1.50 cm
Volume (cold)	80 l	2 l
Temp.: Hot wall	600 °K	1 200 °K
Temp.: Cold wall	300 °K	300 °K
Power consumption	18.5 kW	1.66 kW
Equil. sep. factor (theor.)	23.2	432.
Operating pressure	1 atm	1 atm

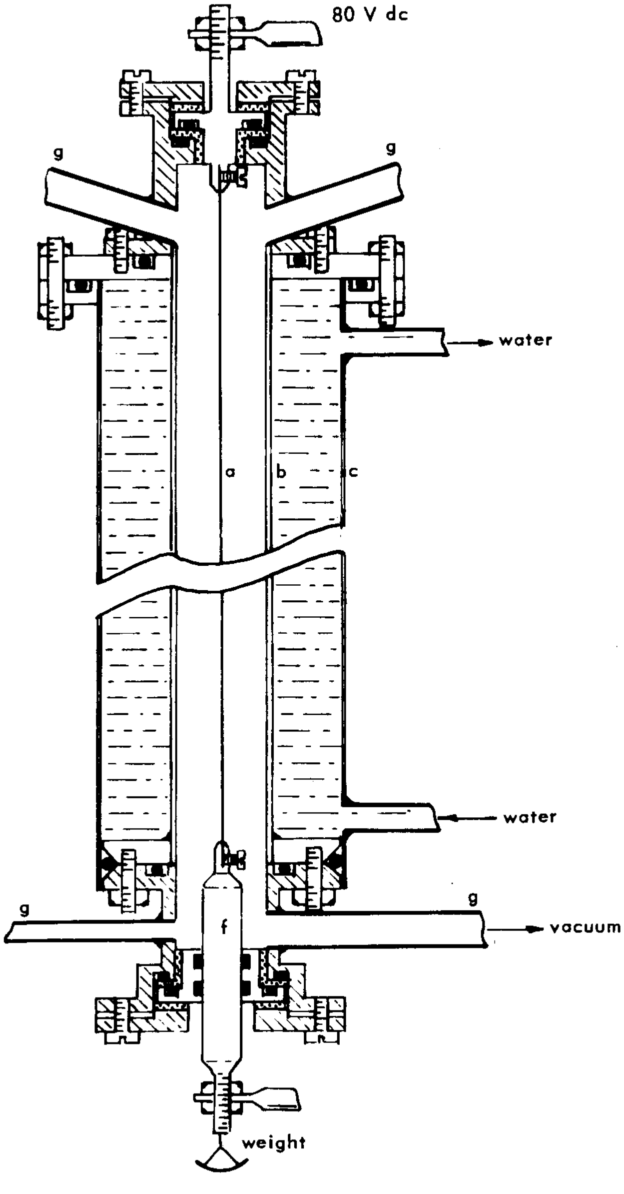

Figure 2. Section of second stage hot-wire column

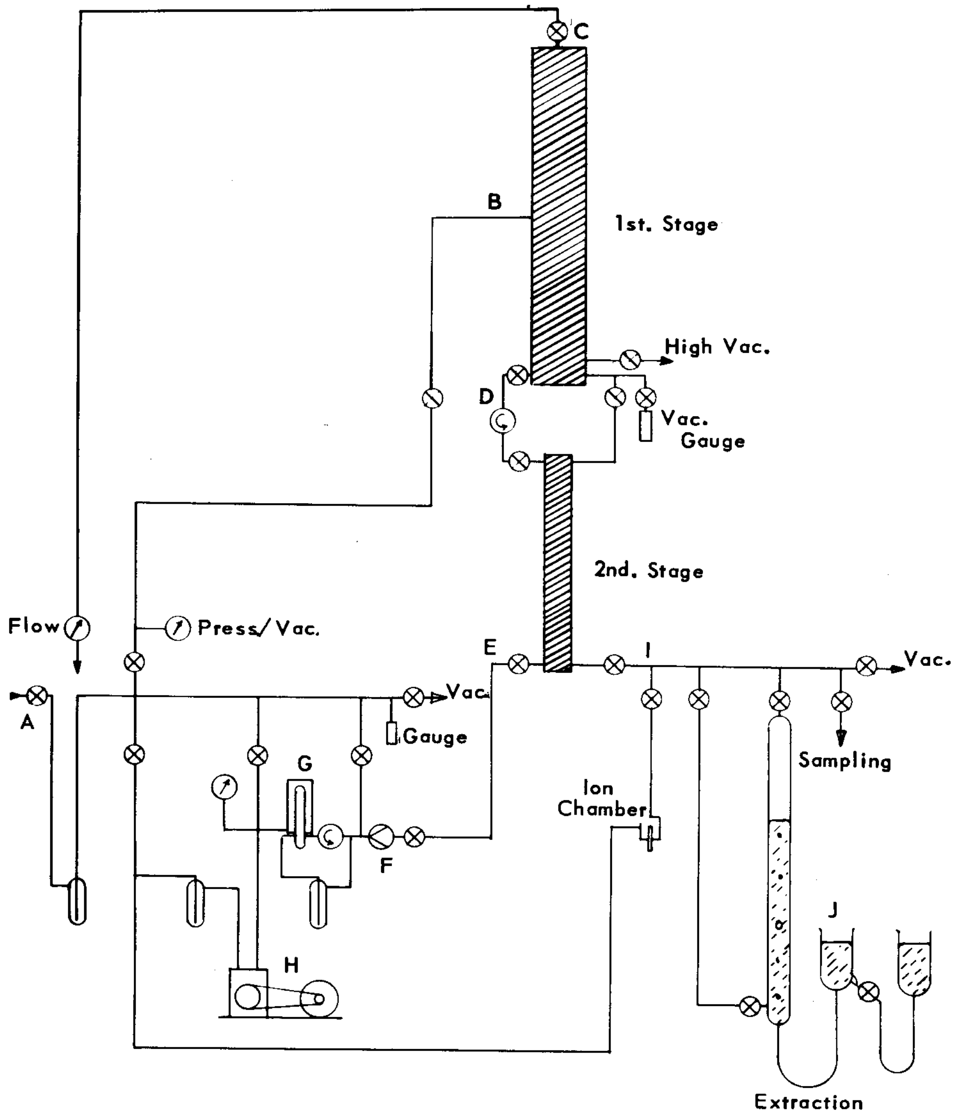

Figure 3. Gas-flow diagram of separation plant

conductive heat loss. When operating pressure (1 atm) is attained, the gas flow is reduced to 350 ml/min. This flow is determined by the stripping efficiency of the first stage (see later), the gas being displaced through C at the top, whence it flows to waste through a flow meter. The top half of the first stage acts as a stripper, the gas flowing from the top being depleted in tritium. The point of entry, B, is therefore *clamped* at the concentration of the feed material, and the bottom half of the first stage enriches over and above this value. This enriched gas is circulated past the top of the second stage by the circulating blower D. This stage then provides the final enrichment.

All impurities such as air in the feed gas and entering the system through small leaks, will be more rapidly enriched than the desired molecules (HT), as the thermal-diffusion factor is a function of $(m_2 - m)_1/(m_2 + m_1)$, where m_1 and m_2 are the masses of the two molecular species. This was borne out by gas chromatographic analysis of enriched samples, which were taken without purification, and which showed O_2 and N_2 concentrations of several per cent, even though the feed-gas impurities lay well below 0.01%.

Under such conditions, tritium enrichment necessarily suffers. As is pointed out by Jones and Furry [18], it is important to keep the impurity concentration $\ll 1$. The system is able to operate efficiently only if the rate of introduction of the feed gas is high. The effective elimination of heavy impurities consequently becomes impossible, and it was therefore decided to collect the impurities at the bottom of the second stage, whence they are gradually removed during operation. This is done by the purification loop shown in Fig. 3. Gas leaves the column at E, is drawn through non-return valve, F, and through palladium-silver alloy barrier, G, by pump H — which recompresses the gas to operating pressure — and is reintroduced into the system at I. The impurities collect between F and G and are kept at low vapour pressure by a liquid nitrogen trap. A flow ion chamber in the line enables the performance to be continuously monitored during calibration with spiked samples.

Gas can be withdrawn from the system by diverting it at tap I and collecting it over mercury in a calibrated extractor J.

The speed of extraction can be varied by changing the heater supply to the palladium purifier. The volume and rate of extraction can thus be accurately measured.

FEED-GAS PRODUCTION

The tritium samples to be assayed are in the form of water. A simple but effective self-regulating water-to-hydrogen converter has been devised, shown diagrammatically in Fig. 4.

It consists of a stainless steel vessel with a lid, through which two tubes are passed, the one being the water inlet with a sharp point and holes at the end, and the other the gas outlet tube. The lid is sealed with a neoprene ring and is protected by water cooling coils. The vessel contains magnesium turnings. It is heated under vacuum in a temperature-regulated furnace to just below the melting point of magnesium (600 °C). A glass vessel containing the water sample is mounted on the water inlet tube. Commercial hydrogen under pressure (approx. 5 psi) is introduced into this vessel, forcing the water through a small glass nozzle, where it is vaporized and reacts with the magnesium. When the pressure in the reaction vessel rises to just above the injection pressure, the droplets on the nozzle are compressed so that no further water will enter the reaction vessel until the pressure has dropped slightly owing to the flow of gas. In this way any required pressure can be maintained over a wide range of flow rates, ranging from several ml/min to 2 l/min. To achieve this regulation, the shape of the nozzle is of the utmost importance and must be determined empirically. The efficiency is good; depending on the charge of magnesium in the vessel, several hundred ml of water can be converted at varying rates with not more than a few milligrams condensing in a freeze trap. Isotope fractionation is therefore negligible.

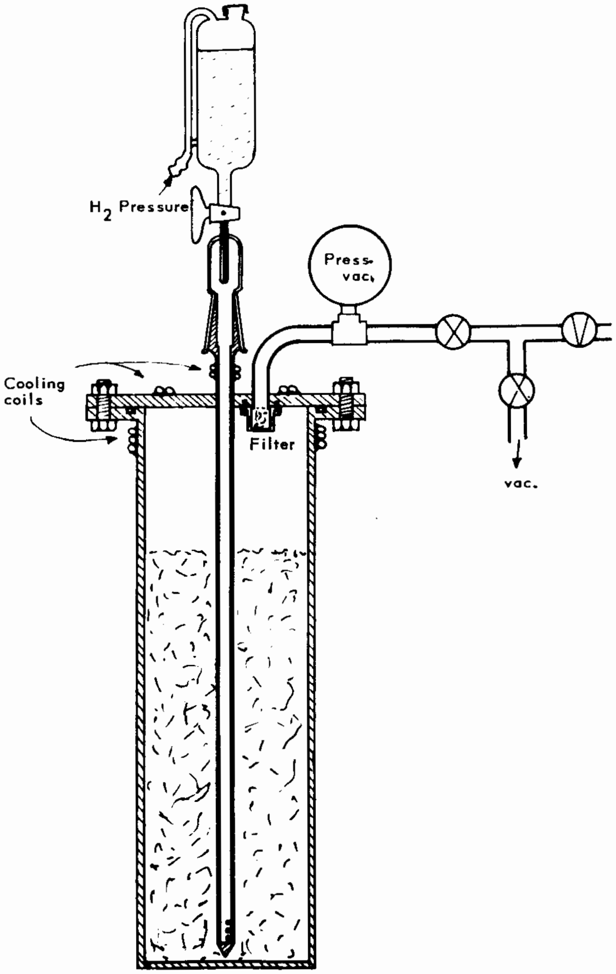

Figure 4. Water to hydrogen converter

This converter is capable of filling the separator within 20 min and giving a constant flow of gas of 350 ml/min for several hours without attention.

SOME RESULTS FROM CALIBRATION EXPERIMENTS

Figure 5 shows a typical result of an enrichment run in which the column was fed with hydrogen spiked with tritium to 4.8 × 10^5 T.U. The resulting enrichment was observed with the flow ionisation chamber mounted in the purification line. The initial curved part of the graph represents the period in which the first-stage column separates material faster than it is withdrawn by the second stage. Eventually steady state conditions are reached, and the enrichment becomes linear with time. The curve shown in Fig. 5 can be used as a calibration curve to find the enrichment after a certain running time,

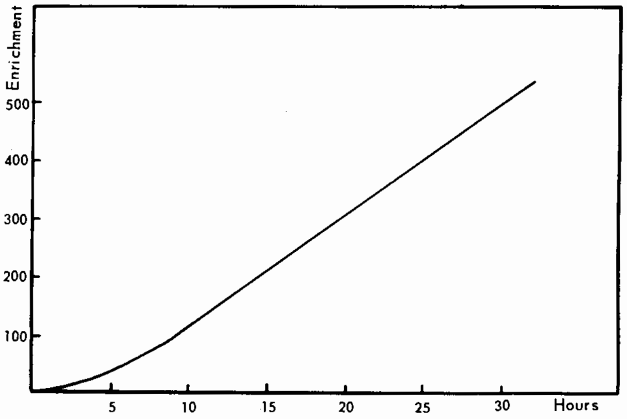

Figure 5. Typical enrichment curve for whole plant

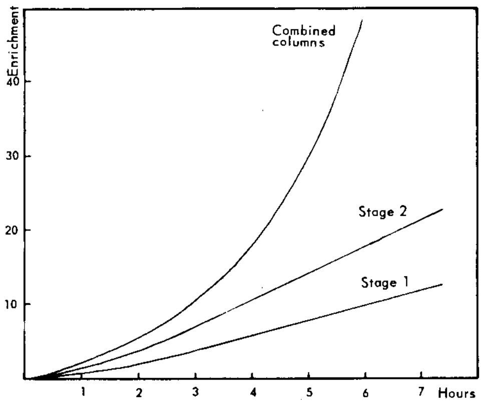

Figure 6. Comparison of the initial parts of enrichment curves

as this curve is reproduced closely in independent runs.

In Fig. 6 the initial parts of enrichment runs carried out on the two columns combined and on the individual columns are compared.

Even though the activity of 4.8 × 10^5 T.U. still strictly conforms to the assumption in the design formulae [21] of the system, *viz.* that the concentration of the desired isotope shall be $\ll 1$, a few short runs were made with lower activities to check the validity of the calibrations to values of interest (1 — 1 000 T.U.).

The results are shown in Table 2 for runs of 9 hours.

Table 2. Enrichments obtained in calibration runs using different feed gas concentrations

Feed concentration (T.U.)	Initial ion current (A)	Final ion current (A)	Enrichment
4.8×10^{5}'	4.5×10^{-16}	$(46.0 \pm 0.3) \times 10^{-15}$	102 ± 1
4.8×10^{4}	[a]4.5×10^{-17}	$(4.5 \pm 0.2) \times 10^{-15}$	100 ± 4
4.8×10^{3}	[a]4.5×10^{-18}	$(0.5 \pm 0.2) \times 10^{-15}$	111 ± 40

[a] Inferred from dilution factor.

The third result is inaccurate, mainly owing to the very small ion current that could be observed after 9 hours' enrichment. The results, however, show that there is no significant dependence of enrichment on concentration and therefore that the calibration curve is valid for all concentrations of interest.

STRIPPING EFFICIENCY

To determine the efficiency with which tritium is retained in the system, the first-stage column was filled with spiked material whilst cold. This gas was also passed through a flow ion chamber and the ion current recorded. The heater was switched on, and the gas, as it expanded, was allowed to flow from the top of the column and pass through the same ion chamber. As the column attained operating temperature, this flow diminished and new feed gas was introduced, displacing gas from the top. A record of this experiment is shown in Fig. 7. As the column temperature rose, the activity of the overflow became less, until it could no longer be measured above ion-chamber background. During the next 4½ hours, several varying flow rates were sent through the column, and, only at a flow rate appreciably greater than 600 ml/min (the maximum which could be recorded on the flow meter), did activity begin to break through the stripper. The selected stripping flow of ml/min therefore lies well within the range of maximum stripping efficiency, which is estimated at 95 % or better.

PRODUCTION RATE

The system was designed to give an equilibrium separation factor* of 10^4, at which value the total flow σ, or maximum production rate, is 1.41×10^{-7} g/s or 0.103 ml/min(STP). It is, however more practical in most cases to run the system at much lower enrichments thus obtaining appreciably higher production rates. As was pointed out by Jones and Furry [18], the most efficient production is achieved when the separation is just the square root of equilibrium separation.

The maximum withdrawal rate at constant enrichment when a certain separation has been attained, is computed as follows:

The transport equation for a thermal diffusion column is:

$$T = Hc\,(1 - c) - K({}^{dc}/_{dz}) \qquad (1)$$

where:

T = transport of the heavy isotope in g/s;
c = concentration of the heavy isotope;
z = a co-ordinate along the vertical axis of the column;
H = transport coeff of thermal diffusion in g/s;
K = total remixing coeff in g cm s^{-1}.

For equilibrium, i.e. when $T = 0$, Eq. (1) becomes, on integration:

$$c/(1 - c) = \exp 2A(z - z_0) = \exp 2AL \qquad (2)$$

where $A = H/2K$ and L is the length of the column.

Eq. 1 can have several solutions. When gas is to be withdrawn at constant enrichment, the process is called continuous, and the solution for $c \ll 1$ is:

$$q = (1 + n)/(\exp\,[-y\,(1 + n)] + n) \qquad (3)$$

where $$y = 2AL \qquad (4)$$

and $$n = \sigma/H \qquad (5)$$

σ is the available flow of enriched gas in g/s.

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* The separation factor q is defined as: $q = (c/1 - c)_b/(c/1 - c)_t$, where c is the concentration of the desired (heavy) isotope and b and t refer to the bottom and top of the apparatus respectively.

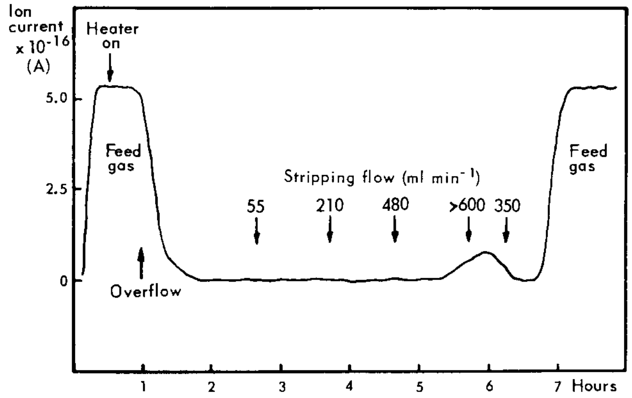

Figure 7. Activity vs time record for different stripping flow rates

Equation 3 will be applied to the second stage, as the rate of withdrawal will depend on its value of H as well as of n, according to Eq. 5. The value of q to be used will, of course, be q_2, where

$$q_{\text{tot}} = q_1 \cdot q_2 \qquad (6)$$

q_1 therefore has to be known to find q_2 for a certain q_{tot}, because the rise in concentration at the bottom of the first stage when feeding the second will differ appreciably from that shown in Fig. 6. During a number of calibration runs, the activity at this point was measured and found to increase to 5 times the initial value in about 6 hours and then to remain essentially constant. This is borne out by the performance of the whole system. (See earlier and Fig. 5.) As long as running times of 6 hours and more are envisaged, the value of q_2 can be taken as $0.2q_{\text{tot}}$, and the corresponding value of σ determined. Fig. 8 shows a graph of σ (in ml/min) against q_2, using Eqs. (3) and (5) and the two parameters:

$$H_2 = 6.8 \times 10^{-5} \text{ g/s} \qquad (7)$$
$$y_2 = 8.32$$

for the second stage. This graph can now be used to read off the appropriate draw-off rate for a certain separation of stage 2.

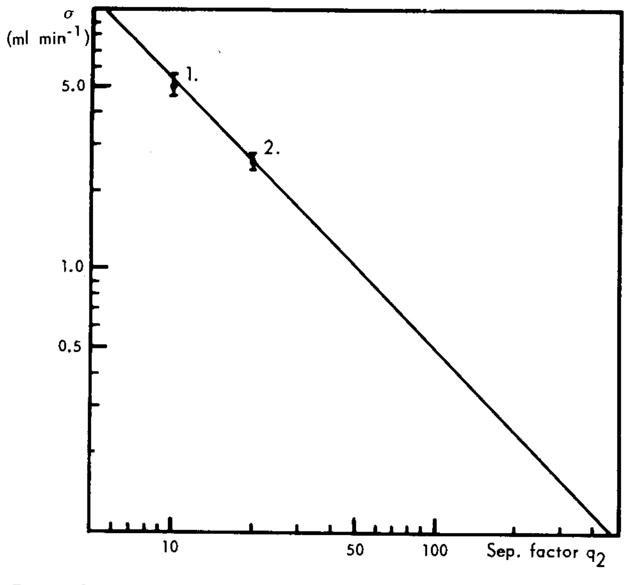

Figure 8. Theoretical graph of σ against q_2 for the second stage

To check the validity of this graph, two measurements were made, one at $q_{\text{tot}} = 50$ and the other at $q_{\text{tot}} = 100$. Aliquots of 100 ml were removed from the system at such a rate as to exceed somewhat the values prescribed by the graph. From these results, the rate at which the activity would remain constant was computed and plotted on the graph. These two experimental points (1 for $q_{\text{tot}} = 50$ and 2 for $q_{\text{tot}} = 100$) show good correlation with theory. They also confirm the theoretical value of H, Eq. (7), for the second stage.

DETECTION

The low-level counting system in this laboratory consists of a 500 ml proportional counter with an anti-coincidence ring and 4 inches of 60 year-old lead shielding. The full spectrum count, using the anti-coincidence system, is 12 cpm. With a window set at the E_{max} for tritium, this is reduced to 6 cpm.

The hydrogen obtained from the column is converted to ethane [22]. Thus two molecules of hydrogen are incorporated in every molecule of counting gas, and a 1 litre yield from the separator can be held in the counter.

At 50 times enrichment the minimum detectable activity of the system lies at about 5 T.U. This can be extended to 1-2 T.U. by longer enrichment runs.

The authors hope to obtain a commercial screen-wall counter soon which will reduce the minimum detectable activity to 0.5 T.U.

DISCUSSION

The separation system described above shows good reproducibility, and can give a range of enrichments to suit the activity of the feed material. Withdrawal experiments correspond well to theory and provide a convenient means of collecting enriched material in any required amount. To simplify the procedure, experiments are under way to attach a reservoir to the system, in which the enriched material can be collected during the run.

The production of enriched material at higher enrichments (say > 100,) becomes prohibitively small (see Fig. 7). A redesigned system, in which the values of H for both stages would be larger and the lengths smaller, would be able to produce material at enrichments of $\approx$ 100 at much greater rates and within shorter periods.

Although electrolysis is essentially a much simpler technique, thermal diffusion has proved to be a powerful tool where lower tritium activities and therefore higher enrichments have to be handled.

ACKNOWLEDGEMENTS

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/465 Afrique du Sud

Enrichissement de tritium à faible concentration par diffusion thermique en vue d'applications hydrologiques

par B. Th. Verhagen et J. P. F. Sellschop

On a mis au point un système à colonnes de séparation par diffusion thermique à deux étages pour l'enrichissement du tritium. On décrit les paramètres critiques du système et les caractéristiques de son fonctionnement. Des facteurs d'enrichissement de 800 fois pendant des périodes d'équilibre de 30 heures ont été réalisés. L'emploi de telles colonnes, dans un laboratoire pour la préparation de tritium destiné à être employé pour la datation et comme traceur, fait l'objet d'une discussion et est comparé à d'autres techniques.

A/465 ЮАР

Обогащение трития путем термодиффузии для гидрологических применений

Б. Т. Верхаген и Я. П. Ф. Сельшоп

Была разработана двухкаскадная система термодиффузионной колонки для обогащения трития. В докладе дается описание критических параметров и рабочих характеристик системы. Данная система позволила достигнуть 800-кратных коэффициентов обогащения при равновесных периодах в 30 *ч*. Критически обсуждается и сравнивается с другими методами использование таких колонок в лабораториях по датированию и индикации с помощью трития.

A/465 Sudáfrica

Enriquecimiento en tritio poco concentrado por difusión térmica para aplicaciones hidrológicas

por B. Th. Verhagen y J. P. F. Sellschop

Se ha construído una columna de difusión térmica de dos etapas para el enriquecimiento en tritio. Se describen los parámetros críticos del sistema y las características de funcionamiento. Se han logrado factores de enriquecimiento de 800 veces con un período de equilibrio de 30 horas. Se efectúa una discusión crítica y se compara con otras técnicas el empleo de estas columnas en un laboratorio de determinación de edades con tritio y de trabajo con trazadores.

Estudios realizados en la JEN sobre la obtención de agua pesada por electrolisis y reacción de intercambio isotópico

por J. Alvarez, M. Gispert, A. Maria, J. L. Otero y J. L. Rojas *

La producción de agua pesada a escala industrial está condicionada a la existencia de un plan de reactores de potencia que la utilicen como moderador. En tanto que este plan no exista, los estudios sobre los procesos posibles de obtención de agua pesada han de efectuarse a una escala razonable para conocer las características de los mismos. De acuerdo con este criterio la JEN ha desarrollado el siguiente plan de trabajo : *a*) estudio previo de métodos posibles de obtención; *b*) cálculo de cascadas cuadradas a las que podría ajustarse la pequeña instalación de hidrógeno electrolítico de EIA; *c*) proyecto, montaje y puesta en marcha de la instalación de EIA modificada para la producción de un concentrado al 2 %; *d*) proyecto, montaje y puesta en marcha de las instalaciones piloto de electrolisis con quemadores y rectificación en Madrid; *e*) puesta a punto de los métodos analíticos necesarios.

De esta forma, se ha adquirido experiencia en el cálculo y trabajo de las cascadas y en los procesos de electrolisis y quemadores y rectificación, así como en la reconcentración del agua degradada en un reactor.

ESTUDIOS TEÓRICOS

Cascada electrolítica con reactores

Se estudiaron las cascadas electrolizadores-reactores de intercambio isotópico hidrógeno-vapor de agua [1-3]. Una etapa de las diferentes variantes de la cascada está representada en la figura 1. La figura 1.a corresponde a la forma más sencilla : un electrolizador con condensadores en la corriente de hidrógeno (el oxígeno no se representa), para que una vez desprovisto del vapor de agua que sirve de alimentación a la etapa siguiente de la cascada, pueda reaccionar con vapor sobre un lecho catalítico. Este vapor que es de agua natural después del intercambio se condensa para formar parte de la alimentación de la etapa correspondiente. La variante de la figura 1.b corresponde a dos reactores por etapa con condensación y nueva alimentación de vapor intermedia. En la figura 1.c, se presenta la posibilidad de sustituir la condensación y nueva alimentación por una torre alimentada por agua natural. Por último en la figura 1.d, se representa la variante con lavadores en el hidrógeno y en el oxígeno, con agua de alimentación.

Estos cálculos se realizaron inicialmente con máquina de calcular eléctrica y posteriormente en la UNIVAC–VCT se prepararon los programas con los que se pudo ampliar el estudio de las variantes de diagramas de flujo indicadas.

Como final de estos estudios se planteó con la cascada cuadrada [4] montada en Sabiñánigo, las variantes para estudiar la influencia de los diferentes parámetros variables sobre la producción de la misma. Tambien se estudiaron los posibles desequilibrios en la potencia de las etapas de la cascada motivados por la conexión eléctrica de los electrolizadores y por la pequeña potencia total de la instalación.

Cascada electrolítica con quemadores

Se realizó este estudio dándole importancia fundamental a la utilización de lavadores con el mismo criterio que en la variante de la figura 1.d. Estos trabajos están pendientes de publicación.

Columnas de rectificación y cascadas

El cálculo del número de pisos teóricos se ha realizado mediante la máquina UNIVAC–VCT variando la volatilidad piso a piso [5]. En dicho cálculo se realiza una serie de tanteos hasta que la pérdida de carga por piso teórico coincida con la encontrada experimentalmente con error menor de 1 mm Hg entre la pérdida de carga observada y la calculada.

Cascada electrolítica, con quemadores, semicontinua

Para producir agua exenta de deuterio con fines analíticos se calculó en la UNIVAC–VCT los parámetros que definen la cascada.

DESCRIPCIÓN DE LA PLANTA JEN-EIA DE OBTENCIÓN DE CONCENTRADO AL 2 %

Instalación electrolítica

El conjunto de la instalación electrolítica de EIA utilizado consta de los siguientes elementos :

a) 6 electrolizadores Oerlikon tipo filtro prensa, de 120 celdas con una potencia máxima de 2 160 kW

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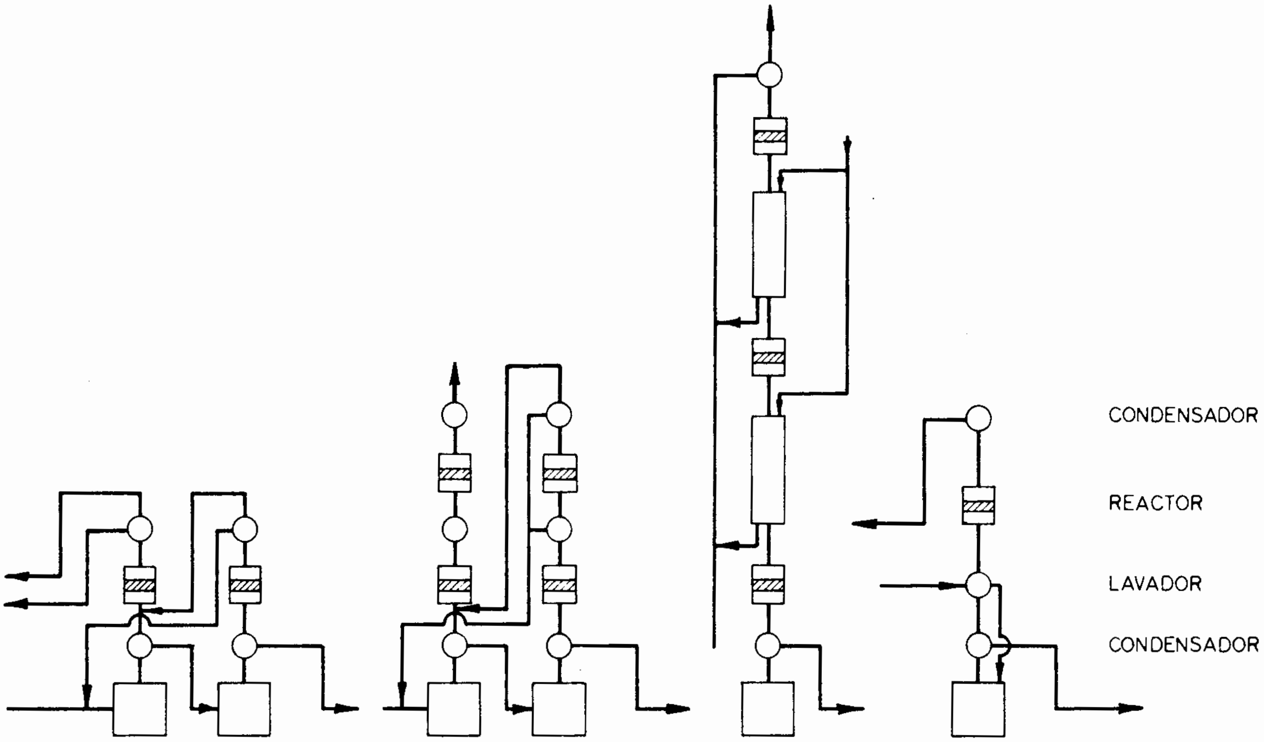

1.a 1.b 1.c 1.d

Figura 1. Diagramas de flujo estudiados

por electrolizador. El suministro eléctrico se efectúa por tres rectificadores de mercurio alimentándolos dos a dos;

b) 2 electrolizadores Oerlikon más antiguos de 104 celdas con una potencia de 1 870 kW por electrolizador;

c) 1 electrolizador Oerlikon de 32 celdas iguales a las anteriores, con una potencia de 580 kW.

Los tres últimos electrolizadores descritos están conectados en serie a un rectificador de mercurio de la misma potencia que los anteriores.

La distribución más aproximada a la ideal para una cascada con 6 etapas que da una complicación mecánica reducida, aunque no corresponde exactamente a una cascada de máximo rendimiento, viene dada en la tabla 1.

Tabla 1. Distribución de potencias

Grupo	Potencia máx. (kW)	Núm. de celdas
1	9 600	532
2	4 300	240
3	1 900	104
4	940	52
5	410	23
6	160	9

Los electrolizadores de menos potencia que forman los últimos grupos de la cascada están divididos de tal manera que el electrolito y los gases producidos circulan independientemente. Para su correcto funcionamiento se ha modificado la refrigeración del electrolito de todos los electrolizadores de acuerdo con la casa Oerlikon.

El rio Gállego suministra el agua a 138 ppm necesaria para la alimentación purificándose en una instalación de filtración y posterior columna de resina de intercambio. El agua desmineralizada alimenta la caldera de vapor de la instalación de recuperación de deuterio, las torres de intercambio de vapor de esta instalación y las de lavado de los gases del primer grupo.

Instalación de recuperación de deuterio

A partir del 2.º grupo (figuras 2 y 3) de la cascada de electrolisis, se inicia la recuperación del deuterio en el hidrógeno en una sala auxiliar, a la que llegan 5 tuberias por las que circula el hidrógeno de los 5 últimos grupos, enfriado y lavado. La recuperación se realiza como sigue : cada una de las corrientes de hidrógeno se mezcla con vapor de agua natural (saturación 75 °C) para cada grupo. La mezcla de hidrógeno y vapor de agua se homogeniza y se manda al correspondiente reactor precalentándola unos 10 °C por encima de su temperatura de saturación.

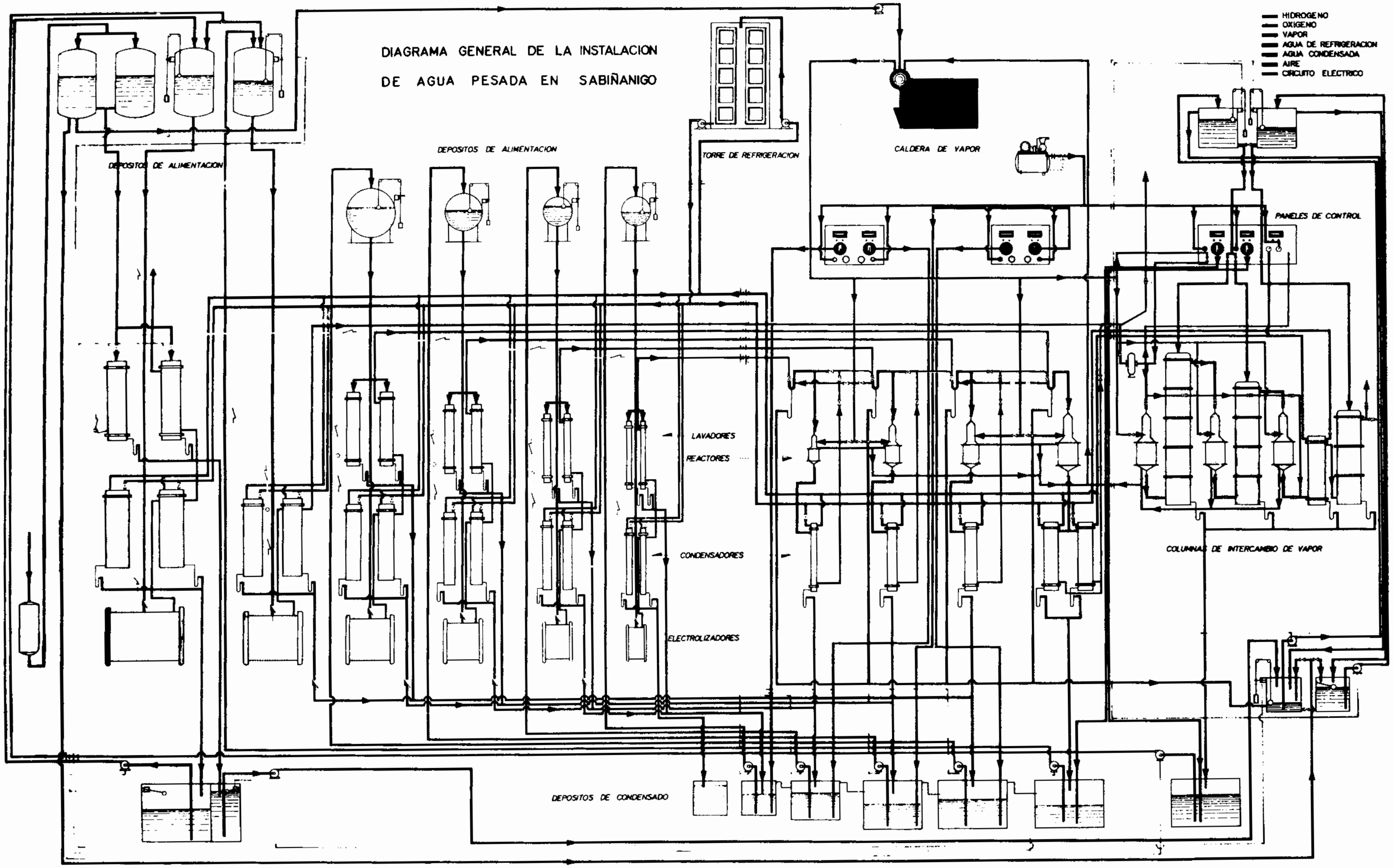

Figura 2. Diagrama de flujo

Dentro del reactor atraviesa el lecho catalítico alojado en una bandeja con fondo de tela metálica.

A la salida del reactor, el vapor de agua se separa en un condensador a 25-30 °C, y el hidrógeno se une con el del grupo siguiente y así recibe una serie de tratamientos en sucesivos reactores y condensadores que van rebajando gradualmente su concentración en deuterio hasta llegar a reunirse todo con el procedente del 2.º grupo. El vapor condensado después de cada reactor se envía en la etapa de la cascada adecuada.

El hidrógeno del 2.º grupo y el procedente de los grupos anteriores se hace circular mediante un compresor de anillo hidráulico a través del circuito siguiente.

Para el tratamiento de este hidrógeno se le añade vapor de agua hasta saturación a 75-80 °C, atraviesa la mezcla un reactor y luego entra en una torre de borboteo en contracorriente con agua natural para intercambiar el vapor de agua enriquecido por vapor de agua natural. A la salida, la mezcla regenerada atraviesa otro reactor y otra columna de borboteo de análogas características. Finalmente, después de atravesar un último reactor, se separa el vapor de agua en un condensador y el hidrógeno se lava en una tercera columna.

Instalaciones auxiliares

Depósitos de regulación. — La capacidad de los depósitos cubre las oscilaciones de demanda de alimentación, realizándose muy pocas veces al año diluciones.

Bombas. — Todo el sistema de bombeo está automatizado en función de la alimentación.

Contadores. — Se dispone de contadores en cada etapa de la cascada para realizar los oportunos balances.

Seguridad. — Cierres hidráulicos a la atmósfera o en recirculación para cubrir sobrepresiones o depresiones.

Servicios

Agua de refrigeración. — Se dispone de una torre de refrigeración con una capacidad para 200 m^3/h. Tiro natural. Salto de temperatura 4-6 °C.

Energía eléctrica. — El consumo de energía eléctrica para los compresores, bombas y servicio eléctrico de la caldera de vapor está próximo a los 100 kW. Existe una instalación de transformación un 50 % superior en potencia.

Vapor. — La caldera de vapor trabaja a 6 kg/cm^2 quemando antracita y produciendo vapor saturado. Capacidad máxima de 1 250 kg/h. En el primer año

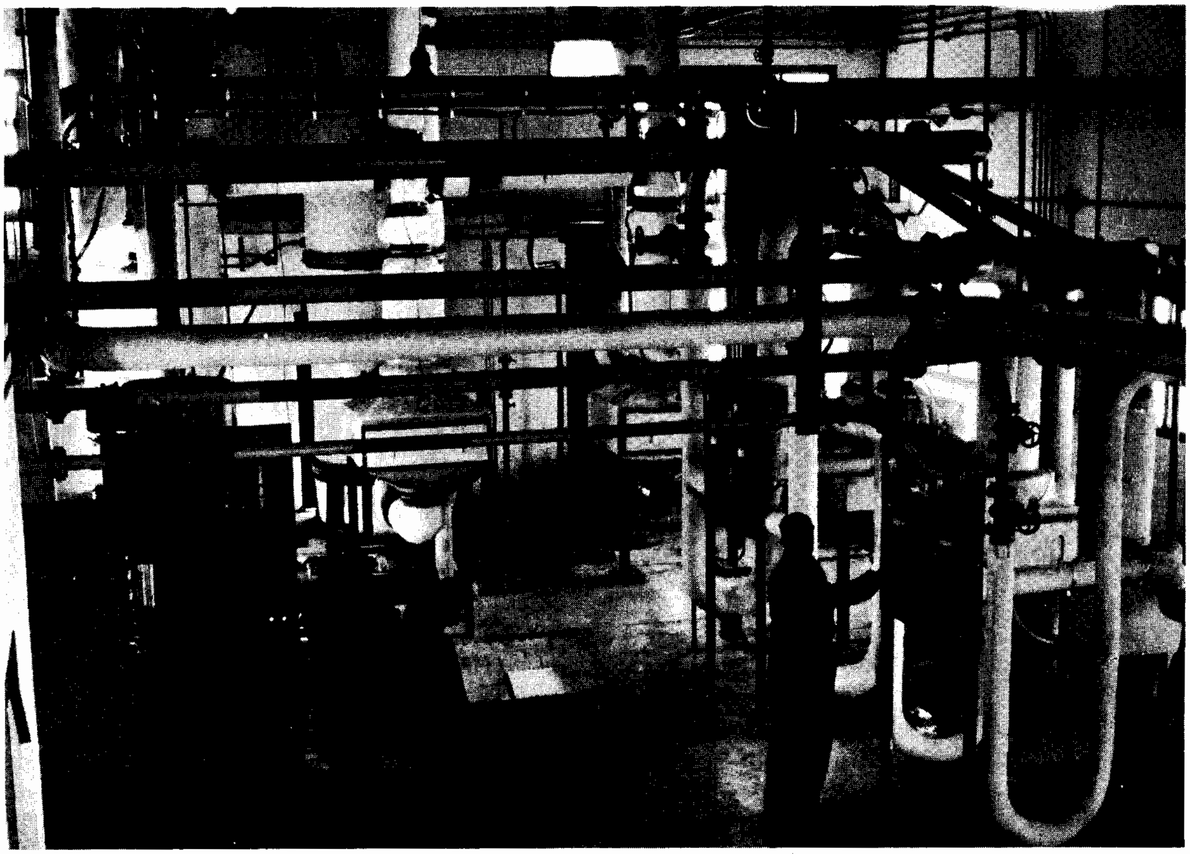

Figura 3. Vista parcial de la instalación de Sabiñánigo

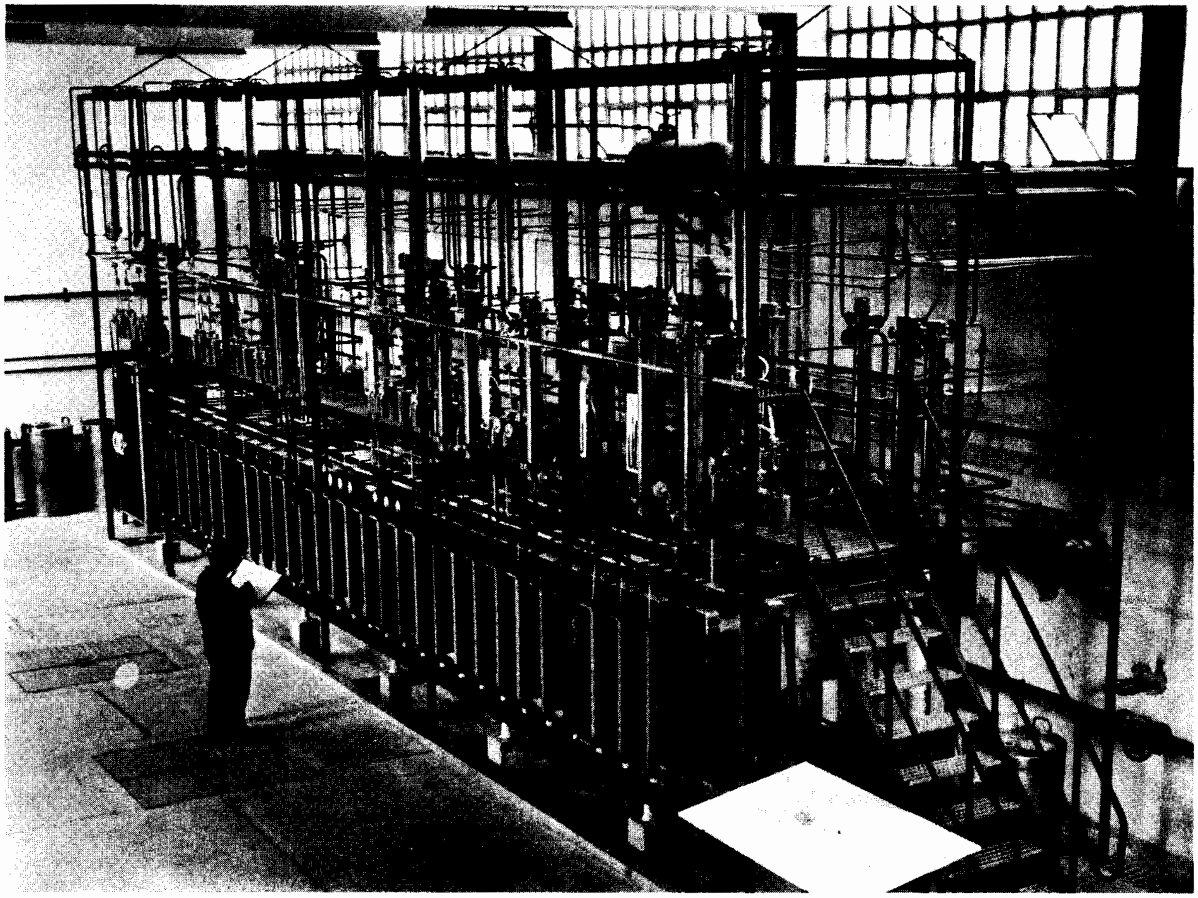

Figura 4. Batería electrolítica con quemádores

de funcionamiento se puede fijar en 8 kg vapor/gr D_2O (al 2 %) el consumo unitario de vapor. La producción media annual es actualmente de 500 kg D_2O, esperando que pueda sobrepasarse.

En cada turno trabajan dos operarios y para el control analítico un analista por día.

PLANTAS PILOTO PARA LA CONCENTRACIÓN 2-99,8 %

Para tratar el concentrado obtenido en Sabiñánigo en la planta descrita anteriormente, se diseñaron dos plantas piloto, una electrolítica con quemadores y otra de rectificación. Ambas plantas se han proyectado sobre la base de darles grandes posibilidades de modificación para conocer además las características fundamentales de ambos procesos.

Por otra parte, para caudales de 25 t/año y por razones de seguridad y vigilancia de los aparatos, fué aconsejable este montaje en Madrid para supervisar funcionamiento y experimentación. Las dos plantas piloto funcionan en serie. La electrolítica con quemadores trata el agua al 2 % y la lleva hasta el 20-30 %. Este producto se trata a continuación en la planta de rectificación dando un concentrado superior al 95 % y un residuo al 2 %. La operación final de concentración se realiza por cargas de 200-300 kg para tener garantia en cuanto a la posible contaminación por la humedad atmosférica.

Planta piloto de electrólisis y quemadores

Se utilizan celdas de cuba (figura 4) en número de 30 para mayor versatilidad en cuanto a agrupaciones en cascada. El número de quemadores, 9, es superior al de etapas por el nismo motivo. La cascada tiene zona de enriquecimiento y agotamiento con rendimientos superiores al 95 % sobre alimentación.

Descripción de la planta electrolítica con quemadores

Las celdas electrolíticas son monopolares, cerradas, con recirculación del electrolito. La tapa es de CPV y la misma cuba actúa como cátodo siendo el ánodo una chapa niquelada suspendida en la tapa. Una tela de amianto permite la separación de los gases producidos siendo el tanto por ciento de O_2 en el H_2 del orden de 0,1–0,2 %. La superficie de cada cuba es de 2 m^2 aproximadamente con un espesor de 45 mm. Las 30 cubas se reunen en 5 grupos de potencia diferente, con sus correspondientes rompedores de espuma, refrigerantes, lavadores, gasómetros de plástico y quemadores. Las cubas están conectadas entre sí eléctricamente en serie. Los refrigerantes estan calculados ampliamente con un gasto global de 25 m^3 de agua/hora. Los lavadores llevan un lecho de 1 m de altura de relleno de anillos Raschig de porcelana de 15 mm; el agua de lavado procede de los quemadores del grupo siguiente y sirve a su vez para alimentación del grupo cuyos gases lavan. Los gasómetros que estabilizan la presión de los gases son bolsas de doble pared de polivinilo transparente de unos 300 litros de capacidad.

Los gases, a la salida de los gasómetros, atraviesan unos cortafuegos y luego entran en la boquilla del quemador, el hidrógeno por el centro y el oxígeno por la periferie, dónde se combinan en presencia de aire atmosférico, para asegurar la combustión total del hidrógeno. El quemador lleva una camisa de refrigeración más un serpentín situado encima de la llama. El agua condensada, que es ácida por el NO_3H formado en la llama por el tiro natural de aire, atraviesa una columna de resina Dowex 21 K para desmineralizarla antes de recircularse al grupo anterior.

La alimentación de la cascada entra en el tercer grupo, que es el de mayor potencia, estableciéndose así dos grupos de agotamiento y tres de enriquecimiento. La alimentación de cada etapa se efectúa con el condensado de los gases enfriados de la anterior. Se han montado unos evaporadores, conectados en las tuberías de recirculación de electrolito para poderlos llenar y vaciar cómodamente. Estos evaporadores complementan la alimentación deficiente por la baja temperatura de las cubas evitándose fugas en los cierres por la deformación del PCV a temperaturas más elevadas.

La caida de tensión por cuba es de 2,0 V con una intensidad de 700 A. Los factores de separación medidos son $S_1 = 7$; $S_2 = 7{,}5$; $S_3 = 8$; $S_4 = 8$ y $S_5 = 8$. La temperatura del electrolito es de unos 50 °C. El rendimiento de las cascadas es del 97 %.

Planta piloto de rectificación

La rectificación es una operación totalmente convencional que presenta para la obtención de agua pesada las dos características perfectamente conocidas : elevado número de pisos teóricos necesarios y consumo de vapor alto.

Como esta instalación ha de alimentarse con una cantidad del orden de 10 veces menor que el de la planta electrolítica, ambos problemas se simplifican en parte desde el punto de vista de experimentación. Fundamentalmente la cantidad de vapor horaria es pequeña y solamente es importante la altura o el número de pisos de las columnas.

El problema fundamental era el de conseguir un relleno con eficacia conveniente. Se proyectó y construyó una máquina para fabricar anillos Dixon con tela de bronce fosforoso. Este relleno se ha utilizado junto con el adquirido a la casa Eggman & Co., en las dos columnas de 9 m de altura en las que se trata la alimentación indicada y en las de experimentación de 1 m con las que se sigue el comportamiento de las primeras.

Descripción de la planta piloto de rectificación

La primera columna montada tiene 10 cm de diámetro. El calderín, de unos 25 litros de capacidad, proporciona vapor mediante calofacción eléctrica. La presión en cabeza es alrededor de 125 mm Hg. El conjunto va equipado con los correspondientes dispositivos para toma de muestras, regulación de vacío, vaporización y medida de caudales. El retenido del condensador de cabeza y del calderín pueden variarse a voluntad intercalando los oportunos depósitos para trabajar en producción por cargas.

Antes de llevar a producción la columna se realizaron una serie de experiencias encaminadas a conocer y aumentar la eficacia del relleno. El relleno Dixon inicial tenía 10 mm de diámetro y dió una HETP de 20 cm a reflujo total prácticamente independiente de la velocidad de vaporización. Este relleno se trató previamente con un detergente y después con benceno y etanol.

La segunda serie de experiencias se efectuó reduciendo el tamaño del relleno a 8 mm y se trató su superficie oxidándola con una solución diluida de hidróxido sódico. La HETP bajó hasta 15 y 13 cm con pequeñas modificaciones en la distribución del reflujo, para caudales de vaporización de 12 kg/h.

Terminada esta segunda serie se consideró que el relleno dejaba demasiado espacio libre y se redujo su tamaño de forma que se pasó de 1 400 anillos/litro a 2 200. La tercera serie de experiencias se efectuó previo un tratamiento de oxidación análogo al anterior y se alcanzaron HETP de 9 cm. Se repitió la operación de oxidación y se consiguió alcanzar HETP próxima a 7 cm. Por último al someter a la columna a unas condiciones de inundación inicial más fuerte que las utilizadas se alcanzaron HETP de 5,5 y 5 cm para vaporizaciones de 14 y 10 kg/h respectivamente.

En general el tiempo requerido para alcanzar el régimen estacionario oscila entre las 48 y 62 horas.

La segunda columna de 7 cm de diámetro es análoga a la anterior en calderín y accesorios. Utiliza anillos Dixon de 3 mm, con 25 000 piezas/litro. Las experiencias realizadas previa oxidación han dado HETP inferior a los 4 cm y actualmente se sigue la experimentación intentando mejorar este número.

MÉTODOS DE ANÁLISIS

De todos los métodos descritos en la bibliografía para el análisis de deuterio se han utilizado en nuestros laboratorios los basados en la determinación de la densidad del agua, método del flotador, y la espectrofotometría de infrarrojo.

Método del flotador

Se ha seguido la variante superida por Sapirstein [6] y modificada por Silvestri *et al.* [7] que empleaban pequeños flotadores de vidrio y trabajaban a temperaturas alrededor de 25 °C. Según este método se han efectuado en nuestros laboratorios y en la planta de Sabiñánigo más de 10 000 análisis de rutina sobre muestras cuyos contenidos en D_2O oscilan entre el 0,05 y el 5 % molar, con una dispersión de ± 25 ppm.

En este rango de concentraciones el método indicado en [7] da resultados satisfactorios.

Bajas concentraciones

Al intentar mejorar la sensibilidad del método, montamos el aparato en cámara oscura y proyectamos las imágenes de la escala termométrica y del flotador en sendas pantallas con un aumento de unas 100 veces. Se ha conseguido así obtener sobre la pantalla, junto al extremo del flotador, la imagen de este extremo, por reflexión en el fondo del depósito que lo contiene. De este modo la velocidad de despegue es el doble de la real de ascenso (método de la doble imagen). Trabajando según esta técnica y a 25 °C se han obtenido resultados con un error máximo de ± 6 ppm [8]. Después se han realizado experiencias a 10 °C con la misma técnica y los errores obtenidos son de ± 1 ppm.

También se han preparado flotadores con temperaturas de despegue en agua natural de 6 °C y con ellos se han obtenido errores de ± 0,5 ppm, si bien a esta temperatura de trabajo surgen inconvenientes de tipo experimental que aconsejan la temperatura de 10 °C, como la más conveniente para la determinación.

El equipo actualmente en funcionamiento permite trabajar a cualquier temperatura. Se han efectuado unas 2 000 determinaciones de muestras cuyos contenidos en D_2O oscilan entre 0 y 500 ppm con resultados altamente satisfactorios.

Todas las concentraciones

Para poder trabajar con el método del flotador en todas las concentraciones, después de la oportuna revisión bibliográfica se ajustaron los datos de densidad de agua ligera y agua pesada para poder extrapolar con garantias hasta 90 °C los existentes hasta 60 °C, así como realizar el cálculo de la densidad de las mezclas H_2O–D_2O a 25,50 y 75 % con ayuda de la UNIVAC-VCT.

Se divide entonces el intervalo de concentraciones en cuatro zonas y con la fórmula usual para calcular la densidad en función de la concentración y la temperatura, se programó el cálculo de las curvas de calibrado que se dan en la figura 5. En ellas puede comprobarse que en los intervalos 25-30 y 75-80 % es posible utilizar la misma muestra para definir la curva típica de los flotadores para 0-25 y 25-50, y 50-75 y 75-100 % respectivamente.

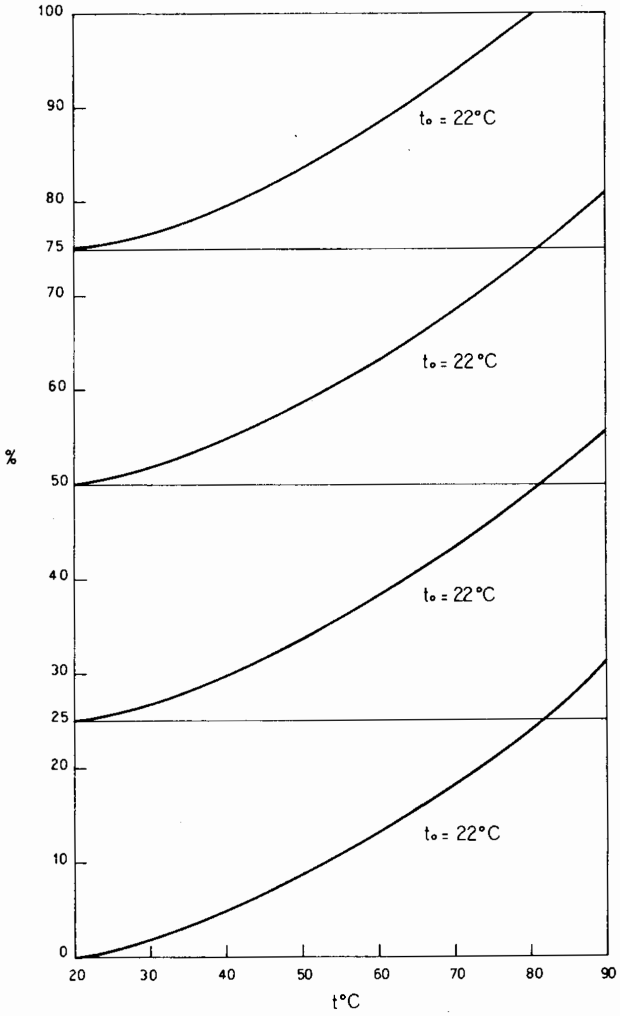

Figura 5.

Para comprobar la extrapolación efectuada se prepararon cuatro flotadores, de densidad adecuada para cada una de las zonas de trabajo.

Se han preparado unas 50 muestras de concentraciones conocidas y de distintas concentraciones entre 5 y 99,7 % D_2O, para comprobar las curvas y el error del método.

Las extrapolaciones son suficientemente buenas dentro del error del método que es de ± 100 ppm en las zonas de baja temperatura y 400 ppm en las altas.

El tiempo que se invierte en preparar la muestra y su lectura es de unos 20 minutos.

Concentraciones próximas a 100 %

Como este error de ± 400 ppm es excesivo para muestras cuyo contenido es superior al 99 % en D_2O, se ha preparado un flotador con una temperatura de despegue de 25,00 °C para una muestra del 99,95 % en peso de D_2O.

Estas muestras se toman mediante una combinación de vacío y N_2 seco para evitar que en ningún momento esté en contacto con el ambiente. La destilación previa se hace en atmósfera saturada en agua pesada y la lectura de la temperatura de despegue también.

El método se ha contrastado con muestras analizadas mediante espectrometría de masas y picnometría. El error obtenido es de ± 30 ppm.

Método de espectrofotometría de infrarrojo

Dadas las grandes posibilidades que ofrece la determinación de D_2O mediante espectrofotometría infrarroja, se ha puesto a punto este método con un espectrofotómetro Perkin–Elmer NIR 17G Infracord.

Mediante muestras conocidas se han trazado las curvas de calibrado correspondientes a los siguientes rangos :

N.º	Long. de onda	Conc. agua pesada	Error
I	1,46	0 — 80 % D_2O	± 1 % D_2O
II	2,0	70' — 99 % D_2O	± 1 % D_2O
III	2,94	99' — 100 % D_2O	± 0,01 % D_2O
IV	3,98	0 — 10 % D_2O	± 0,03 % D_2O

El método, aunque con menor exactitud que el del flotador, ofrece la ventaja de su rapidez (unos 5 minutos por muestra), que permite un satisfactorio control de las cascadas de producción de D_2O.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/496 Spain

JEN Studies on heavy water production by electrolysis and isotopic exchange reaction

by J. Alvarez *et al.*

The studies carried out by the JEN on heavy water production by electrolysis and isotopic exchange reaction in order to utilize the facilities of a water electrolysis plant owned by the fertilizer company EIASA are described.

The studies were developed in the following stages:

(*a*) A theoretical study of the ideal cascade with electrolysers and reactors for the isotopic exchange reaction H_2O/H_2 utilizing as feed water vapor with a natural deuterium concentration;

(*b*) The theoretical study of square cascades by means of the computer UCT-UNIVAC;

(*c*) Commissioning and starting up of the modified industrial electrolysis plant;

(*d*) Commissioning and starting up of the electrolysis and burner pilot plant and of the rectification pilot plant to enrich the product of the industrial plant;

(*e*) Analytical methods of control for all the ranges of concentration.

A/496 Espagne

Études faites à la Junta de Energía Nuclear en vue de la fabrication d'eau lourde par électrolyse et échange isotopique

par J. Alvarez *et al.*

Les auteurs décrivent les études faites par la JEN en vue de fabriquer de l'eau lourde par électrolyse et réaction d'échange isotopique en utilisant une petite installation d'électrolyse espagnole appartenant à la société EIASA, qui fabrique des engrais.

Le mémoire décrit les différentes étapes de ces études, entre autres : *a*) étude théorique de la cascade idéale — arrangement d'électrolyseurs et d'appareils pour la réaction d'échange isotopique H_2O/H_2 — alimentée par de la vapeur d'eau naturelle (concentration naturelle en deutérium); *b*) étude théorique de cascades carrées en projet et en service, à l'aide d'une calculatrice UCT-UNIVAC; *c*) étude, montage et mise en marche de l'installation industrielle d'électrolyse modifiée; *d*) étude, montage et mise en marche des installations pilotes d'électrolyse et des brûleurs; rectification de l'eau pour traiter la production de l'installation industrielle; *e*) méthodes analytiques de contrôle utilisées dans tout l'intervalle des concentrations.

A/496 Испания

Производство тяжелой воды методами электролиза и изотопного обмена

Т. Альварец *et al.*

Описываются исследования, проведенные Комиссией по ядерной энергии, методов производства тяжелой воды электролизом и изотопным обменом с целью определения возможности использования установки по электролизу воды, принадлежащей фирме по производству удобрений EIASA в Испании.

В докладе описываются различные аспекты исследований, а именно: теоретическое исследование идеального каскада с электролизерами и реакторами в целях получения реакции изотопного обмена H_2O/H_2 с использованием водяных паров с концентрацией дейтерия, как это имеет место в природе и квадратных каскадов с помощью счетно-решающего устройства UCT-UNIVAC; проект, конструирование и сдача в эксплуатацию усовершенствованной промышленной электролизной установки, опытной электролизной установки камеры для сжигания и опытной очистительной установки для обогащения тяжелой воды, полученной на промышленной установке; аналитические методы контроля концентрации воды.

Technical and economic considerations for producing 200 t/year of heavy water in India

By P. G. Deshpande, D. C. Gami and S. Nagaraja Rao *

The first stage of India's nuclear power development programme is mainly based on heavy-water moderated reactors. The first such reactor of the CANDU type, is to be built at Rana Pratap Sagar and is expected to be commissioned in 1970. It is planned to construct 5 similar reactors in various parts of India by 1974. The quantity of heavy water required for each of the reactors is 200 tonnes. Thus, by 1974 about one thousand tonnes of heavy water will be required. This will necessitate a supply of 200 tonnes per year beginning in 1970. There is, therefore, a need to build a larger heavy water plant in India.

In a large plant, the largest portion of the capital as well as the operating costs is required for the pre-enrichment section (up to 1% deuterium). Of the various available processes the H_2S-H_2O exchange process is the only one for which a long operating experience in a large plant is available [1, 2]. This process has generally been improved [3] upon. Moreover, it seems to be the most economical process under present day technology [4, 5]. Some of the important improvements suggested by Proctor and Thayer [4] to reduce the cost of the H_2S-H_2O exchange process are given below:

(*a*) The use of sieve plates instead of bubble plates for exchange towers. Sieve plates are 10% more efficient and can take up 15% more vapour flow. Moreover, they are cheaper.

(*b*) The use of a liquid-liquid instead of a gas-gas or gas-liquid heat exchange system. This will reduce the heat transfer area by about a factor of two.

(*c*) The use of large diameter towers to reduce the number of parallel units in a stage. This will reduce the capital cost by a reduction in fabrication and installation charges as well as reducing the cost of instruments and equipment.

(*d*) The use of the cheapest available fuel as the main source of heat.

A pilot plant incorporating the first two improvements has been constructed at Trombay. Installation is complete and the testing of individual items of equipment is being carried out. The pilot plant operation will give first hand experience on process and operational problems besides yielding valuable data on the allowable liquid and vapour rate, plate efficiency, equipment size, safety problems, etc.

SITE SELECTION

Improvements (*a*), (*b*) and (*c*) above reduce the capital cost whereas improvement (*d*) reduces the operating cost of the plant. Improvements (*a*) and (*b*) are strictly matters of design and can be incorporated in a plant located anywhere, whereas improvement (*c*) can be incorporated only in a plant where the necessary facilities for handling, fabrication and testing of large towers are available. An analysis of the operating costs of the Savannah plant indicates that the higher cost is due to the fuel. Since no raw material except water is required, the plant can be conveniently located near a source of plentiful and cheap thermal energy. Thus a site near such a source, with an established heavy engineering industry, would be ideal.

The principal sources of thermal energy at present in India are coal and oil. Natural gas may be available at Jwalamukhi — about 80 kilometers from Nangal where deep drilling is being tried. Until the availability of gas is confirmed and the price pattern established, only coal and oil can be considered as fuel sources. Fuel oil is more expensive than coal except in coastal regions. Since the bulk of the fuel oil is still imported and surplus middling coal is available from coal washeries, coal constitutes the most suitable fuel. Large quantities of middling coal at a comparatively low price are available from coal washeries in Bihar. Moreover, heavy engineering industries have been established in this area. This area, would therefore, provide a suitable site for a large-sized heavy water plant.

At present heavy water is being produced by the distillation of hydrogen, combined with pre-enrichment, in an electrolytic cascade [6] at Nangal (Punjab). Operating experience of the hydrogen distillation plant [7] indicates that it is possible to produce 40 tonnes of heavy water without any modifications to the existing plant provided that the feed gas is suitably enriched. The existing capacity can be raised to 67 tonnes per year if minor modifications are carried out

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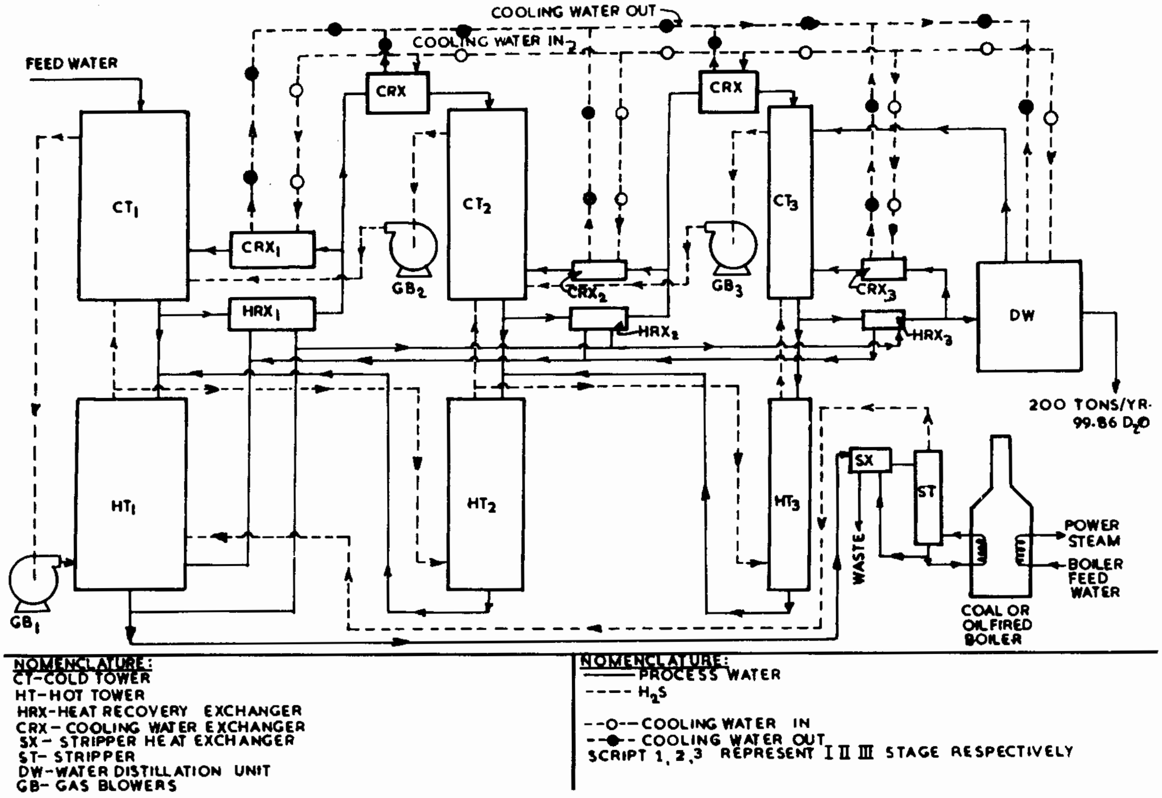

Figure 1. Flow diagram for a 200 t/yr heavy water plant in Bihar

on the existing distillation plant and up to 200 tonnes per year with major modifications. The technical feasibility in respect of the latter requires further study. If a pre-enrichment unit of requisite capacity is installed, it is possible to produce 67 tonnes of heavy water per year by hydrogen distillation and another 133 tonnes per year by water distillation, making a total of 200 tonnes per year. Thus, neglecting the possible availability of gas, two locations are considered for installation of a 200 tonnes per year plant in India.

PROCESS DESCRIPTION

Bihar

A schematic diagram of the process to be followed is shown in Fig. 1. Pre-enrichment of water will be carried out in a H_2S-H_2O dual temperature exchange process. This will be further enriched to obtain 99.86% heavy water in a water distillation section.

The H_2S-H_2O section is divided into three stages. Water is enriched fivefold in the first stage, fiftyfold in the second stage and a thousand-fold (14.4% D_2O) in the third stage.

Since no specific site has been selected for the location of the heavy water plant, design criteria are based on the general conditions prevailing in the area. Design bases assumed for the location are given in Table 1 for the H_2S-H_2O section and in Table 2 for the water distillation plant.

Table 1. Comparison of the H_2S-H_2O sections of the Bihar and Nangal plants

	Nangal Scheme	Bihar Scheme
Natural concentration of water ppm deuterium . .	14	14
Average temperature of water °C	22	30
Cold tower temperature °C	30	35
Hot tower temperature °C	130	135
Operating pressure psia		
cold tower	300	310
hot tower	315	325
Recovery		
maximum theoretical %	28.5	28.75
of feed %	18	18
Liquid to gas ratio		
cold tower	0.485	0.4915
hot tower	0.555	0.567
Stream factor h/yr	7 200	7 500
Flows mol/h		
liquid cold tower	115 556	105 498
gas cold tower	238 260	214 645
liquid hot tower	153 259	143 052
gas hot tower	275 962	252 200
Fuel (coal)		
cost Rs/ton	53.12	16.8
calorific value BTU/lb. .	9 000	7 000
Power nP/kWh	1.813	3.5

Table 2. Water distillation plant at Bihar

Feed concentration	14.4% D_2O
Waste concentration	5.0 % D_2O
Product concentration	99.86% D_2O
Operating pressure mm Hg at column top	100
Separation factor	1.037

Nangal

The schematic diagram of the process to be followed is shown in Fig. 2. The existing hydrogen distillation plant will be operated in the same way as at present except that the feed sent to the hydrogen distillation plant will be enriched by a factor of 15.6 instead of 2.1 to 2.8 as at present. Under these conditions this plant would produce 67 tonnes of heavy water after suitable minor modifications, such as a larger D_2 oxidation system and larger scrubbing towers in the electrolysis plant, are incorporated. For this purpose 4.26 tonnes per hour of water, enriched by a factor of 17.7 will be required as feed for the third stage of the existing electrolysis plant. An additional 133 tonnes of heavy water will be produced in a water distillation section. This will require feed enrichment by a thousand-fold. Requirements for the enriched feed for both the hydrogen distillation and the water distillation sections will be met from the three stage H_2S-H_2O dual temperature-exchange pre-enrichment plant. Water will be enriched fivefold in the first stage of this plant. This water will then be fed appropriate proportions into two parallel units of the second stage. Water will be enriched to 17.7 times in the first tower CT'_2 of the second stage and fiftyfold in the second tower CT''_2 of the second stage. The latter will be fed to the third stage tower where it will be further enriched to 1 000 times. The assumed design criteria, based on actual conditions prevailing at Nangal are given in Table 1 for the H_2S-H_2O section.

Since the quantity of condensate available from the electrolytic cascade is small compared to the total requirement and in view of the fact that the H_2S-H_2O section is quite sensitive to variation in flow, it is felt that it will not be desirable to feed enriched water into the mid point of the first stage of the H_2S-H_2O section. It has therefore been assumed, for design purposes, that the requirement for enriched water for both the hydrogen distillation and the water distillation sections will be met by the H_2S-H_2O plant and that no enriched water will be taken from the existing cascade, though arrangements will be made to feed the enriched water into the second stage of the H_2S-H_2O plant.

SELECTION OF IMPORTANT PROCESS CONDITIONS

Temperature

Since the cold tower has to be operated above 28.9 °C to prevent solid H_2S hydrate formation, and

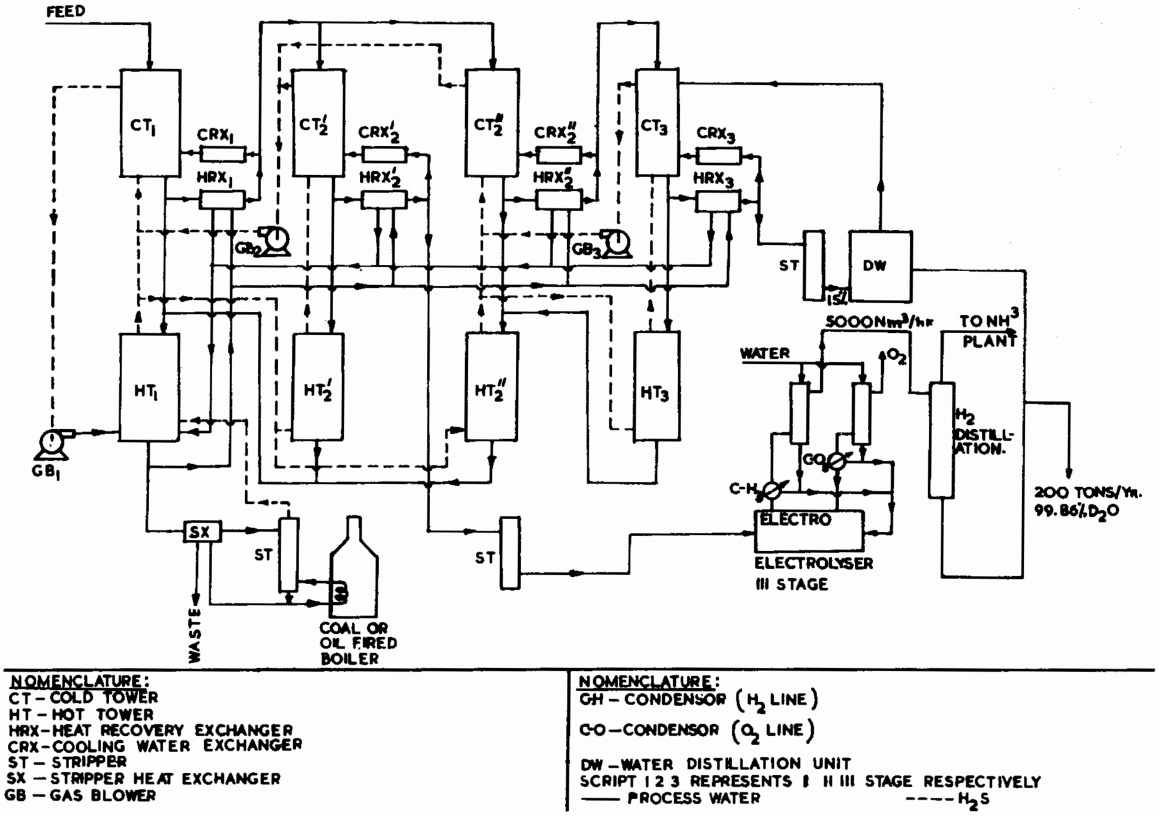

Figure 2. Flow diagram for a 200 t/yr heavy water plant in Nangal

as water is available at Nangal at an average temperature of 22 °C, the cold temperature is fixed at 30 °C and the hot tower temperature is accordingly fixed at 130 °C as an optimum value [4, 5]. On the other hand, in Bihar these towers will have to be operated at 35 °C and 135 °C because of the higher temperature of the water.

Pressures

The operating pressures have been fixed at a slightly lower pressure than the liquefaction pressure of H_2S for cold tower temperature. As the maximum pressure favours the throughput, the operating pressure at Bihar is higher than that at Nangal, so that a decrease in production rate due to higher operation al temperature of the cold tower is partially compensated.

Liquid/gas ratio

The ratio of liquid to gas in the cold tower has been fixed in such a way that the number of plates is approximately the same in the cold and hot towers, which is necessary for an optimum plant volume for any stage.

Stream factor

The stream factor for Nangal is assumed to be 7 200 hours per year as against 7 500 hours in Bihar. This 300 hours reduction in stream factor is allowed for maintenance in the electrolysis plant. If an additional spare cell line in the electrolysis plant were available, the stream factor could be increased to 7 500 hours per year.

COMPARISON OF THE TWO SCHEMES

Important technical data such as temperatures, pressures, gas ratio, flows and recoveries are given in Table 1.

Staging of the columns in the H_2S-H_2O plant for both the schemes are varied to suit individual requirements. In both cases, however, the enrichment of the water in the first stage is fivefold as this figure has been found to be the optimum for this process. It can be seen from Table 1, that gas flows are higher for Nangal than for Bihar in spite of the fact that higher gas flow rates, necessitated by higher operating temperatures and pressures are required in Bihar. This is due to the following:

(*a*) Leakage of the enriched water in an electrolysis plant or carry-over of rich vapours requires more feed containing a higher deuterium concentration. This increases the liquid as well as the gas rate in H_2S-H_2O plant.

(*b*) The low stream factor at Nangal requires a higher flow per unit of time and, therefore, correspondingly an increase in the size of H_2S-H_2O plant.

The cost of coal at Nangal is higher, due to heavy transportation charges, than in Bihar.

ESTIMATION OF CAPITAL AND OPERATING COST

Capital cost

Capital costs are calculated on the basis that the largest portion of the equipment, including exchange towers and heat exchangers, will be fabricated in India while most of the rotating machinery such as compressors, boosters, pumps and other important items and materials such as valves, stainless steel, instruments etc. will be imported. The cost of modification of the hydrogen distillation plant is estimated at Rs.5 lakhs and is added to the actual cost of the existing plant. As the specific location of the plant in Bihar has not been selected, the costs of site development, housing colony etc. have not been taken into consideration.

Operating cost

The cost of materials and utilities at Nangal are based on the actual cost whereas those for Bihar have been estimated. Depreciation is assumed to be 14% of the capital cost. The capital and operating costs for the two schemes are given in Table 3.

Table 3. Estimated cost of production for a 200 t/year heavy water plant

	Nangal Scheme	Bihar Scheme
Capital investment (in lakhs of rupees)		
H_2S-H_2O plant	1 800	1 900
Water distillation plant	100	100
Hydrogen distillation plant		
Existing	240	—
Additional	5	—
Total	2 145	2 000
Estimated cost of production per kg. D_2O :		
Direct operating cost:		
Services :		
Cooling water	0.9	1.1
Electricity	10.8	15.4
Cost of fuel (coal)	58.3	18.1
Raw materials :		
Process water	13.9	13.9
H_2S	2.2	2.2
Wages and overheads	12.1	11.0
Maintenance materials	23.8	22.0
	122.0 ($25.6)	83.7 ($17.6)
Depreciation at 14% (per kg. D_2O)	166.0	154.0
Total cost of production per kg. D_2O	288.0 ($60.5)	237.7 ($49.9)

CONCLUSION

A comparison shows that the capital costs for both the sites are about the same and that the fuel cost, at a given location, mainly determines the final cost of the heavy water produced. Under the circumstances when coal is the only available fuel, a suitable location at a developed site in an industrial area in Bihar will definitely have an advantage over Nangal. If, however, gas is available at Nangal from Jawalamukhi, so that the fuel cost for one million BTUs delivered to the process plant is about Rs.1.25, the cost of production at both sites will be comparable.

ACKNOWLEDGEMENTS

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/753 Inde

Considérations techniques et économiques sur la production de 200 tonnes d'eau lourde par an en Inde

par P. G. Deshpande *et al.*

Le mémoire expose les considérations techniques et économiques qui se rapportent à un programme de production de 200 t/an d'eau lourde en Inde, avec du charbon de qualité moyenne comme source principale de chaleur, l'usine étant implantée près d'une mine de charbon ou une laverie de charbon. Dans le procédé que l'on envisage pour cette usine, on se sert de l'échange de H_2S-H_2O, à deux températures, pour l'enrichissement préalable, suivi par la distillation d'eau pour l'enrichissement final, jusqu'à l'eau lourde de qualité exigée pour le fonctionnement du réacteur. L'implantation de l'usine près d'une source de combustible à bon marché a une grande influence sur les frais de production car les frais relatifs à l'énergie constitue la plus grande partie des frais d'utilisation de ce procédé.

On a évalué les frais qu'entraînera l'extension de l'usine actuelle d'eau lourde (14 t/an) à Nangal pour permettre une production de 200 t/an par enrichissement préalable de l'alimentation aux électrolyseurs au moyen d'un procédé d'échange de H_2S-H_2O et l'installation de capacité additionnelle au stade de l'enrichissement final de la distillation d'hydrogène.

Une comparaison des frais d'utilisation pour ces deux usines montre que l'implantation de l'usine près d'une mine de charbon ou d'une laverie de charbon permettra d'abaisser le coût de l'eau lourde.

A/753 Индия

Технические и экономические соображения по производству в Индии 200 *т/год* тяжелой воды

П. Г. Дешпанде *et al.*

В докладе обсуждаются технические и экономические соображения по производству в Индии 200 *т/год* тяжелой воды с использованием низкосортных углей в качестве основного источника тепла для систем при условии расположения завода вблизи угольной шахты или обогатительной фабрики. Приемлемый для такого завода процесс состоит в предварительном обогащении путем двухтемпературного обмена H_2S — H_2O, после чего следует дистилляция воды для окончательного обогащения тяжелой воды реакторной чистоты. Поскольку стоимость энергии составляет значительную часть эксплуатационных расходов для этого процесса, расположение завода вблизи источников дешевого топлива имеет важное значение при оценке стоимости производства.

Определены ориентировочные затраты на расширение существующей установки по производству тяжелой воды (производительность 14 *т/год*) в Нангале до производительности 200 *т/год* путем предварительного обогащения поступающей в электролизеры воды при помощи обменного процесса H_2S — H_2O и обеспечения дополнительной производительности на конечной стадии дистилляции водорода.

Сравнение эксплуатационных расходов для

этих двух установок показывает, что установка, расположенная вблизи угольной шахты или обогатительной фабрики, позволит получить тяжелую воду по более низкой стоимости.

A/753 India

Consideraciones técnicas y económicas relativas a la producción de 200 t anuales de agua pesada en la India

por P. G. Deshpande *et al.*

En la memoria se examinan las consideraciones técnicas y económicas relativas a la producción de 200 t anuales de agua pesada en la India, utilizando carbón de mediana calidad como fuente principal de energía para una fábrica a situar en las proximidades de una mina o de un lavadero de carbón. El procedimiento que se seguirá será el de intercambio H_2S-H_2O a dos temperaturas para el enriquericimiento previo, seguido de destilación del agua para su enriquecimiento final hasta obtener agua pesada para reactores. Dado que el costo de la energía representa la parte más importante de los gastos de obtención del agua pesada, la localización de la fábrica en las proximidades de una fuente de combustible económico repercute sensiblemente en el costo de producción.

Se ha calculado lo que costaría ampliar la actual instalación de producción de agua pesada (14 t anuales) de Nangal para obtener 200 t anuales enriqueciendo previamente por el proceso H_2S-H_2O el agua para el proceso electrolítico y aumentando la capacidad en la fase de enriquecimiento final por destilación del hidrógeno.

La comparación de los gastos de explotación de estas dos instalaciones muestra que la situada en las proximidades de una mina o lavadero de carbón producirá agua pesada a un costo más reducido.

Analysis of operating experience of a hydrogen distillation plant

By D. C. Gami and A. S. Rapial *

Production of heavy water by the distillation of hydrogen has evoked considerable interest among research workers in various countries [1]. The feasibility of using this process has been actively considered for more than 20 years [2]. Five plants have been built [3-7] based on this process. Some data have been published on the process and the design of equipment. The purpose of this paper is to provide operational data in respect of the plant at Nangal.

PROCESS

The process in simplified form is shown in Fig. 1. The feed gas, after compression, is passed through Evasil and Deoxo at a temperature of 67 °C to remove potassium hydroxide and oxygen respectively. The gas is then transferred to regenerators where it is cooled to a temperature of 65 °K, it is then cooled to 30 °K in a second set of regenerators during which process practically all of the impurities are also removed. The purified feed hydrogen then passes into the triple distillation column where it is enriched to 2-4% HD. This is then fed to the hydrogen deuteride (HD) column, where it is further enriched to nearly 100% HD. This gas is warmed to room temperature and converted to an equilibrium mixture of HD, D_2 and H_2 by passing it through a Deoxo type M catalyst. The mixture, after cooling, is fed to the denterium (D_2) column for further enrichment to 99.98% D_2. The D_2 is catalytically reacted with pure oxygen to produce 99.9% heavy water vapour which is condensed by ammonia cooling. The heavy water is put into stainless steel drums under an atmosphere of pure oxygen after it has been analysed for pH, conductivity and deuterium concentration by continuously recording instruments.

PRODUCTION HISTORY

Trial runs including tests of the individual units were started in February 1962 and the plant as a whole was started on 20 July 1962. Fig. 2 shows the production as a function of time. The output up to December 1962 was below normal as the entire fertilizer factory, of which the heavy water plant forms a part, was operating at only two-thirds capacity. The plant was shut down in early October 1962 for inspection prior to conducting guarantee tests. For this purpose it was warmed to room temperature and all the equipment was thoroughly inspected. Some minor modifications were carried out at this stage. The plant was restarted towards the end of October 1962; but had to be shut down again due to a fire caused by leakage of the high pressure hydrogen into the atmosphere. It was in continuous operation from December 1962 to September 1963 except for shutdowns of short duration due to water and power failures. In September 1963 it was suspected that the main bearings of the hydrogen recycling compressor were showing signs of wear. To check this and to carry out an annual maintenance, the plant was shut down. It was restarted towards the end of October 1963 and has been running smoothly since then. The variations in monthly production are due to fluctuations of load in the fertilizer factory and maintenance in the heavy water plant.

OPERATIONAL DIFFICULTIES

Difficulties encountered during the first 20 months of the plant's operation are given in a separate report [8]. The major difficulties are discussed below:

Choking of liquid nitrogen line and instrument impulse lines

Soon after the plant was started, the level indicators and the vacuum gauges on the vacuum nitrogen system stopped functioning. On investigation it was found that the temperature of that portion of the cold box through which the liquid nitrogen line passed, was below the freezing point of nitrogen. The vacuum N_2 system had, therefore, to be stopped. The nitrogen lines were re-routed and the impulse lines were jacketted and warm hydrogen circulated round them to prevent their freezing.

Choking of the heat exchanger between the HD and D_2 columns and the feed line to the D_2 column

The heat exchanger and the feed line to the D_2 column were found to choke periodically. It was

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Work carried out at the Heavy Water Plant, Fertilizer Corporation of India, Nangal (Punjab).

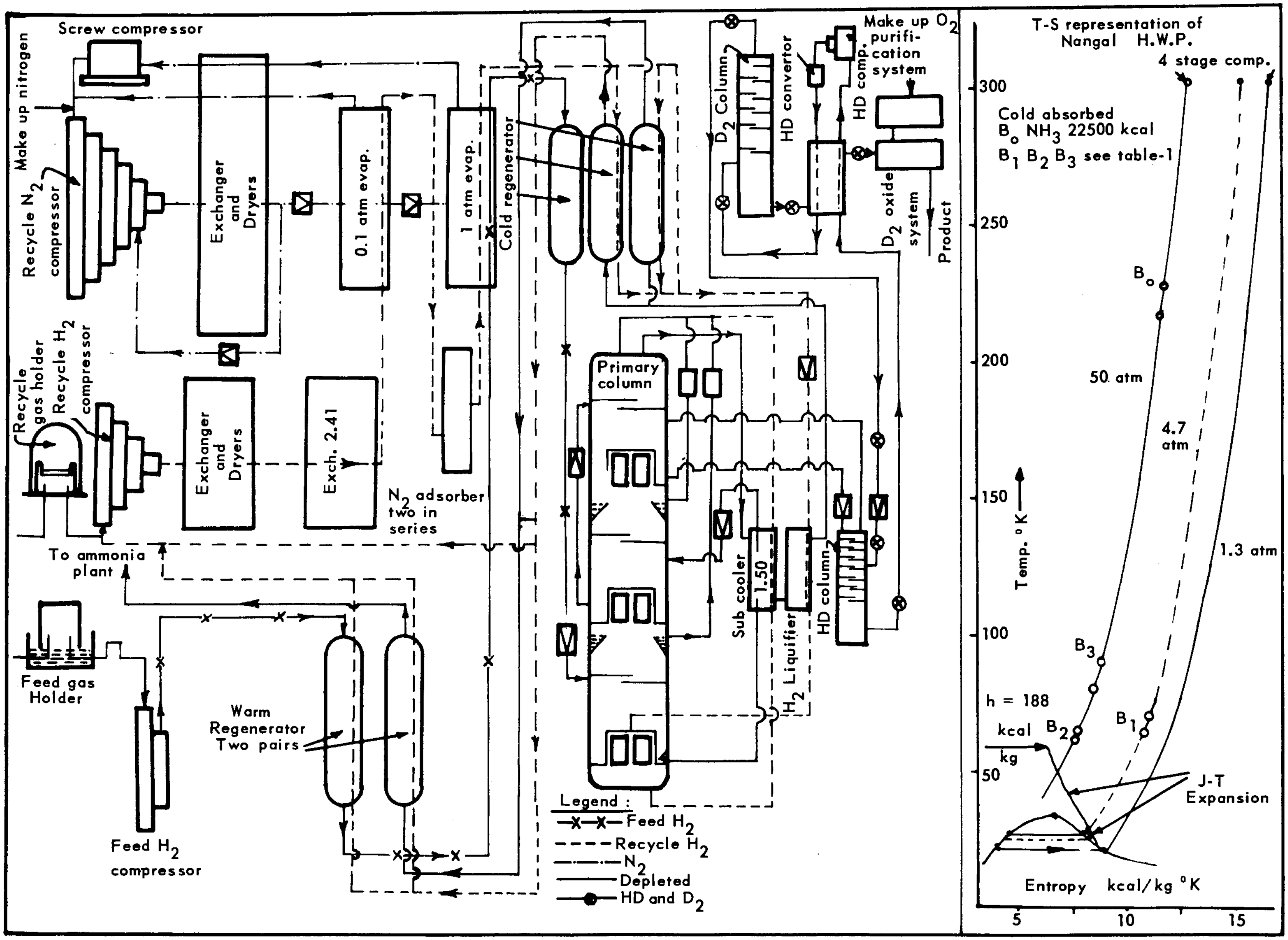

Figure 1. General flowsheet of the heavy water plant

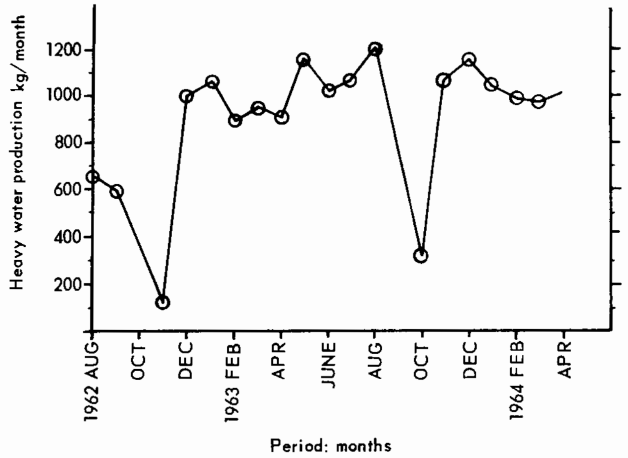

Figure 2. Production as function of time

suspected that air was diffusing into the HD gas holder through the rubber seal. Moreover, some minute leaks were detected on the HD compressor cylinder head flanges which permitted the seepage of the cooling water. Moisture was solidifying in the exchanger and air was solidifying in the feed line to the D_2 column. These difficulties were completely eliminated by by-passing the HD gas holder and running the compressor directly on the HD column and by lowering the cooling water level below that of the cylinder flange.

Deposition of solid nitrogen and oxygen in the piping, valves and equipment at very low temperature

Nitrogen and oxygen in the hydrogen gas cannot be fully eliminated in any purification system. The residual nitrogen and oxygen can, therefore, give trouble when they are deposited in cold regions. We have experienced such difficulties in the non-return valves of the cold regenerators, in the expansion valve of the feed hydrogen and in the valve leading from the low pressure (LP) column to the HD column. It was found that solid nitrogen/oxygen did not stick to the metal and could be easily blown off by mechanical manipulation of the valve spindle.

The amounts of residual oxygen and nitrogen deposited in the cold regions determine the period for which such a plant can be continuously operated. A smooth and continuous operation of the plant over a period of 10 months has indicated that these solids are deposited uniformly throughout the plant rather than at one spot. Heavy choking was not, therefore, observed at any time. Another factor of importance in this connection is the quantity of oxygen which can be safely stored with the hydrogen at liquid hydrogen temperatures. From analyses it has been estimated that a maximum of 1.1 kg of oxygen and 6.5 kg of nitrogen are deposited in the plant in a month. On the assumption that the oxygen in the cold parts can combine stoichiometrically with the available hydrogen, the explosion potential of such accumulation over a period of one month, calculated by the formula given in NASA Hydrogen Safety Manual [9], is equivalent to that of 1.15 kg TNT. However, even if an explosive mixture of oxygen and hydrogen is present in the colder part of the equipment, the chances of an explosion occurring are remote in the absence of a source of ignition. Nevertheless, the situation is potentially dangerous. The period for which a plant can be run continuously under such conditions is determined by safety considerations. At Nangal it has been decided to derime the entire plant once a year.

Deuterium oxidation system

The oxidation of deuterium into heavy water is carried out with the help of a Deoxo catalyst. This type of catalyst is commonly used in industry for the purification of hydrogen as well as oxygen. At Nangal, this system has worked very smoothly except for three occasions when the D_2 gas ignited to produce flames. A flame, however, is produced only in the mixing zone, before the mixture of D_2 and O_2 enters the catalyser. It immediately creates a vacuum in the system as a result of the rapid consumption of oxygen. The fall in pressure reduces the oxygen flow which immediately actuates the magnetic valves in the deuterium and oxygen lines, shutting them off in less than a second. Nevertheless, the heat of the flame is so intense that the entire mixing zone becomes red to white hot. A flame can occur at the time of the start-up, due to inadequate preheating or improper mixing. Since a proper mixing of D_2 and O_2 is not easy to achieve, the D_2 in O_2 is limited to 1% even though the catalyser is designed to work at 4% D_2 in O_2.

TECHNICAL STUDIES

The size of the distillation columns and the requirements of reflux and refrigeration determine the capital and operating costs of a hydrogen distillation plant. The purification of hydrogen was once considered to be a major problem. But it can now be easily done by adsorption on silica gel at liquid nitrogen temperature or by regenerators or by reversible heat exchangers. Silica gel and cold regenerators seem to be equally efficient for the removal of oxygen and nitrogen. The residual oxygen and nitrogen, after purification in both the systems, vary between 0.05 to 0.15 ppm and 0.1 to 0.6 ppm respectively.

Refrigeration and power consumption

An analysis of power consumption has revealed that 19% of it is consumed in the compression of the feed stream, 45% in the hydrogen recycling stream and 36% in the refrigeration system. Distillation calculations have shown that the necessary separation of HD + H_2 can be achieved with a lower reflux.

There is, therefore, a possibility of saving power by a reduction in the hydrogen recycling flow.

Feed hydrogen and recycled hydrogen absorb heat from the N_2 system at 80 °K and 65 °K. This refrigeration is required to meet thermal losses in the cold box. All heat losses can be determined except those due to ortho-para conversion and an ingress of heat through the insulation. The latter can be calculated by subtracting calculated heat losses from the refrigeration required as shown in Table 1.

Table 1. Data on heat leakage and refrigeration required

	kcal/h
A. *Heat leakage*	
Warm end enthalpy difference for 5 500 m³ of feed hydrogen/h (*STP*)	3 900
Warm end enthalpy difference for 7 500 m³ of recycled hydrogen/h (*STP*)	11 300
Production withdrawal	300
Regeneration of nitrogen adsorber (average)	2 300
Purge hydrogen	800
Purge nitrogen	800
	19 400
B. *Refrigeration required*	
5 500 m³ of feed hydrogen/h (*STP*) at 65 °K	5 000
7 500 m³ of recycle hydrogen/h (*STP*) at 65 °K	Nil
7 500 m³ of recycle hydrogen at 80 °K (*STP*)	22 000
	27 000
C. *Heat leakage due to insulation and ortho-para conversion*	
B — A (27 000 — 19 400)	7 600

Detailed calculations of the refrigeration balance have revealed that 2 800 kcal/h of refrigeration were lost due to a very low temperature at the warm end of the vacuum N_2 system. The enforced shut down of the screw compressor has indicated that the refrigeration requirement could be adequately met without a supply from the vacuum N_2 system.

A systematic plant study was, therefore, undertaken to find out the minimum power consumption with or without a vacuum N_2 system and with a varying flow of recycled H_2.

When observations were made with the vacuum nitrogen system in operation and with a gradual reduction of recycled H_2, it was noticed that both the power consumption and the refrigeration supply from the nitrogen system were progressively decreasing until a recycle flow of 6 000 m³/h (*STP*) was reached. Below this rate of flow, the refrigeration supplied by the N_2 system remained constant possibly because the reduction in the refrigeration was transferred to the ammonia system which operated at a lower temperature. This may perhaps be due to the limitations of the heat exchange equipment. By the provision of a valve to by-pass the high pressure hydrogen from the nitrogen evaporator, it may be possible to reduce the load on the nitrogen system and to increase the load on the NH_3 system and thus supply refrigeration still more economically.

When observations were made without the vacuum nitrogen system, the maximum permissible pressure in the recycled hydrogen compressor was found to be a limiting factor. It was, therefore, not possible to reduce the flow below 6 000 m³/h (*STP*).

Operation of the plant with a low reflux and refrigeration presents difficulties. As the reflux and refrigeration are reduced, operational flexibility is also reduced and additional vigilance is required by operating personnel. Particularly, the D_2 column operation changes due to a reduction in its reboiler and reflux requirements.

The present recycled H_2 compressor is not equipped with a continuous unloading device. Though, theoretically, it is possible to use suction unloaders to control the flow, in practice it has been found that the discharge pressure of the first stage fluctuates due to use of the unloaders for flow control. Moreover, a reduction in the flow increases the amplitude of vibration in the compressor. No such difficulty was observed in the N_2 compressor when the flow was controlled through such unloaders.

Thus a compromise has to be obtained between the maximum operating flexibility, power consumption and maintenance. The best compromise at Nangal would be to run the plant without a vacuum system and with the reflux reduced to 6 200 m³/h (*STP*). This will allow a reduction in the power consumption to the extent of 4 200 kWh/d without sacrificing operational flexibility of the distillation column or increasing maintenance on the compressor. If a proper control device is introduced, there will be a further reduction of 1 800 kWh/d.

Distillation

The low pressure column is 1 250 mm in diameter with a 400 mm hollow shaft for supporting 65 plates. Of these, 25 are bubble-cap plates below the feed point, and 40 sieve plates above the feed point. The feed concentration to the LP column is 2 800 ppm HD. The reflux ratio is estimated to be 0.82 above the feed point and 1.0 below the feed point. The HD column is 400 mm in diameter with a 125 mm hollow shaft. There are 44 plates with the feed at the top. The depleted gas from the D_2 column enters the HD column between the 14th and the 15th plates. The D_2 column is 150 mm in diameter with 80 bubble-cap plates. The feed is introduced between the 46th and the 47th plates.

The number of theoretical plates for the triple column was determined by using the following formula:

No. of theoretical plates above the feed plate = n

$$n = \log\left(\frac{Y + Bn}{1 + Bn}\right) \Big/ \log a$$

where

$$Y = \frac{X_f}{a X_0}$$

$$Bn = \frac{B}{a - 1}$$

$$a = \frac{La}{V}$$

$$B = 1 - \frac{L}{V}$$

No. of theoretical plates below the feed plate = m

$$m - 1 = \frac{\log\left[\left(\frac{B_m}{a} - 1\right) \Big/ \left(\frac{B_m \cdot A_m \cdot X_f}{X_p} - a_m\right)\right]}{\log a_m}$$

where

$$A_m = \frac{L_m}{V_m}; \quad a_m = A_m a$$

$$B_m = \frac{P}{V_m (a - 1)}$$

X_f = Concentration of HD in feed
X_0 = Concentration of HD in depleted stream
X_p = Concentration of HD in product
L = Mols. of liquid
V = Mols. of vapour
a = Relative volatility of volatile components

These formulae are based on the usual assumptions as in the Macabe-Thiele calculation, and the equilibrium relationship is assumed to follow $X/Y = a$ up to 3% HD concentration. The plate to plate calculations are made for higher concentrations.

The values of a published by Wolley *et al* [10] have been used, after making the necessary corrections for non-ideality [11].

The calculations have shown that the over-all plate efficiency was 35-40%. This low figure was attributed to an under utilization of the column. This was confirmed by two methods: (*a*) by gradually increasing the concentration of the LP column product to 21% HD, which is by no means the maximum possible, without affecting the concentration of the depleted stream; and (*b*) by enriching the feed concentration from the normal 600-800 ppm HD to 3 300 ppm HD. This was done by injecting pure HD into the feed stream and raising its concentration. Both the triple and the HD columns were operated under these conditions for a period of 48 hours by feeding an enriched gas containing, on an average, 3 300 ppm of HD. The concentration in the LP column product was 11.5% HD, in the depleted stream 5 ppm HD and in the HD column 98% HD. The study has revealed that the overall plate efficiency for these columns could be at least 50%. This is better than the 30-35% efficiency reported by Malkov *et al.* [3] and compares favourably with the correlation reported by Timmerhaus [12].

Assuming a plate efficiency of 50% and the full quantity of reflux, it was calculated that 5 500 m^3/h (*STP*) of feed hydrogen, containing 12 000 ppm HD, could be separated in the primary and HD columns to obtain a product containing 95% HD and 5% H_2. The depleted gas leaving the primary column would contain 60 ppm HD. This means that it could produce the equivalent of 200 tonnes of heavy water per year.

A study of the D_2 column efficiency is rather difficult as (*a*) the vapour/liquid flows for the column cannot be estimated reliably, (*b*) a large quantity of HD is not available for feeding into the D_2 column and (*c*) the limitation on the capacity in the D_2 oxidation system. For the latter two reasons it is not possible to study the D_2 column experimentally. The only feasible course was to make a theoretical study assuming that the characteristics and the efficiency of the D_2 column would be similar to that of the HD and the primary columns. These assumptions, however, may not be absolutely correct as the D_2 column has bubble-cap plates, whereas the other columns have sieve plates in the stripping section and bubble-cap plates in the enriching section. It was further assumed that the heat transfer coefficient in the reboiler of the D_2 column would be the same as that calculated from the correlations for reboilers of the HD and the primary columns. From the known heat transfer area and temperature difference across the reboiler, the total heat transfer from the reboiler, and hence the vapour flow in the D_2 column, was calculated and found to be 56 m^3/h (*STP*). Moreover, assuming that the pattern of flow in all the columns would be similar, the vapour flow in the D_2 column was calculated from the known pressure drop per plate in the D_2 column. This calculation showed the vapour flow to be 64 m^3/h (*STP*). Assuming an average vapour flow of 60 m^3/h (*STP*), 50% over-all plate efficiency, a feed concentration of 22.5% D_2, 50% HD and 27.5% H_2 and a product concentration of 99.98% D_2, it was found that the D_2 column could produce a maximum of 6 m^3 D_2/h equivalent to about 40 tonnes of heavy water/year.

The columns have also been studied from the point of view of reflux duty. They have been operating satisfactorily with as high as 5 900 m^3/h (*STP*) of feed at a full reflux of 7 500 m^3/h (*STP*) of hydrogen. Under these conditions, however, it was found that the operating pressures of the columns were quite high and, perhaps, the maximum possible in the Nangal plant. Thus, a total flow of 13 400 m^3/h (*STP*) can be handled in the present column. This can be suitably divided into reflux and feed depending upon the feed concentration. The columns have also been operated at as low a flow as 2 800 m^3/h (*STP*) of feed and 5 500 m^3/h (*STP*) reflux. They operate smoothly at this load provided the refrigeration system, column levels, and pressures are adjusted suitably.

The operating experience and the above mentioned calculations show that hydrogen distillation is an extremely flexible process from the operational point of view. Even when the feed gas is not available for processing, a plant can be maintained in steady state conditions for a maximum period of 10-12 hours, and for an indefinite period if make-up hydrogen and nitrogen are available to supply the normal loss from the plant.

Heat transfer coefficient

The calculations of the heat transfer coefficients for the reboilers and condensers of the various distillation columns have yielded some interesting results. The heat transfer coefficients have been measured with varying liquid levels and temperature differences between the reboiler and condensers. The limitations of these measurements in an operating plant are (*a*) the liquid level cannot be varied over a wide range; (*b*) the liquid level (heat transfer area) and ΔT are inter-related, and (*c*) those tubes not covered by liquid may also contribute to the heat transfer. Thus at low levels we can get only the apparent heat transfer coefficients. The data have been obtained over a long period at varying feed and reflux conditions. The data for the primary column reboilers and the condensers are plotted in Fig. 3. The coefficients of heat transfer obtained are much higher than those reported by Timmerhaus [12] and Malkov [3]. However, a later study by Drayer and Timmerhaus [13] indicates values of the same magnitude as those obtained at Nangal.

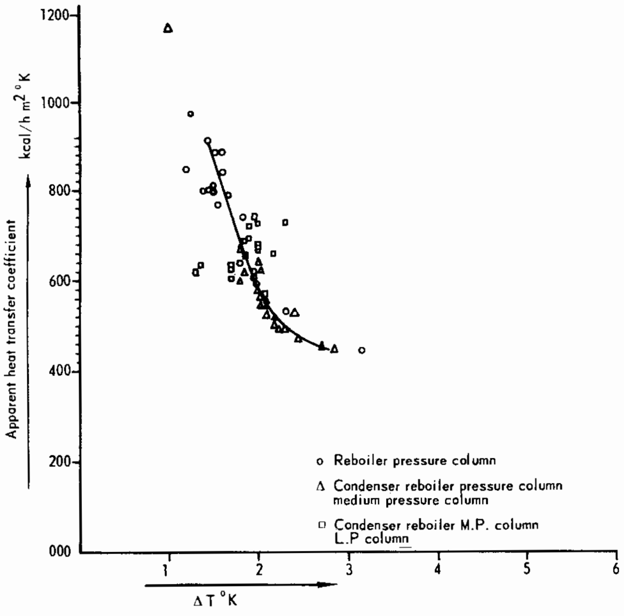

Figure 3. Boiling-condensing heat transfer coefficient for hydrogen

PLANT FLEXIBILITY

The plant is laid out in a single line except for the provision of two 50% capacity feed compressors and one standby each for the HD and screw compressors. It has been found that all running equipment, except the recycled H_2 compressor in the plant, can be shut down for varying periods without affecting plant operation. The N_2 compressor can be shut down for about an hour, the ammonia compressor for about 4 hours and one of the feed compressors, as well as both the screw compressors, for an indefinite period. The HD compressor and the D_2 oxidation system can be shut down for 3 days during which time the product can be stored in the columns and can be tapped off at a higher rate later on.

In the pre-cooling section, pairs of exchangers have been provided, so that if one of the exchangers chokes up the other can be put in line without shutting down the plant. Silica gel driers have been provided at the end of the pre-cooling section to ensure that a properly purified gas enters the cold box. These can be by-passed for 3 days without any adverse effect.

No standby equipment has been provided in the cold box except an H_2 liquefier after the Joule Thompson expansion valve. A liquid hydrogen wash column is provided after the cold regenerators to remove any solid nitrogen or oxygen carried over from the feed gas. However, it has not been found necessary so far to use this device.

Three nitrogen adsorbers have been provided, two working in series and one under regeneration. If required, one adsorber can adequately meet the needs instead of the two in series. All the valves on the adsorbers have to be leak-tight to the high pressure hydrogen. In view of the frequent operation and the possibility of the presence of silica gel dust, these valves might not remain leak-tight for a long period. It might then be necessary to operate with only two adsorbers. An alternative would be to shut down the plant, warm it up and repair these valves. As these valves are not easily accessible, any shut-down period would have to be very long.

The empty spaces in the two cold boxes are not filled completely with insulation, but only in the outer and inner boxes to a thickness of 1.5 m and 0.6 m respectively. All the equipment, however, is lagged individually. This mode of insulation simplifies maintenance.

As is characteristic of any low temperature plant, any maintenance required on equipment inside the cold box necessitates a prolonged shut-down. In the present plant, production loss for a minimum of 25 days has to be allowed, if any maintenance work is to be done inside the cold box. Since most of the difficulties which may be encountered in such plants are due to choking, provision has been made to supply hot hydrogen and nitrogen to all equipment, valves, etc. This arrangement has been found to be useful and has been used on more than one occasion.

Additional facilities

The plant produces extremely pure H_2, HD and D_2 gases. Facilities have been provided to put these gases under a pressure of 30 kg/cm², into a cylinder by adsorption at liquid nitrogen temperature. In special cases the cylinders can be filled to 120 kg/cm².

DEUTERIUM RECOVERY AND CONSUMPTION

The over-all recovery of D_2 in the plant is 85-90%, whereas the loss of deuterium due to non-recovery in the columns is 1 to 1.5%. The other main losses are (*a*) about 5% due to loss of enriched gas during the pressure equalization in the warm and cold regenerators, (*b*) about 2-3% due to consumption of enriched gases for analytical purposes and (*c*) the balance is due to leakage of hydrogen. Any estimate of D_2 recovery is subject to an error of ± 20 ppm HD in the analysis of the feed hydrogen representing ± 3% of the total input of D_2.

The consumption of materials, power and other facilities depends upon the total quantity of the feed hydrogen processed and not on its HD concentration. Therefore, the practice of indicating it in terms of kg of D_2O produced in a H_2 distillation plant does not accurately reflect the efficiency of the plant, especially when the feed gas is pre-enriched. If consumption is based on the quantity of feed hydrogen processed, it will be found that a hydrogen distillation plant using a triple distillation column combined with an orthodox refrigeration system employing the Joule Thompson expansion, will require low power consumption. This is due to the fact that a greater hydrogen circulation is required when turbines are used.

A typical consumption of power, facilities and materials is given in Table 2.

Table 2. Consumption of power, utilities and materials

	Unit	Total consumed/h	Unit cost Rs.	Total cost Rs./h
Power consumption	kWh	2 610	0.01812	47.3
Hydrogen	m³ (*STP*)	145	0.15	21.8
Nitrogen	m³ (*STP*)	45	0.03	1.4
Cooling water	1 000 gal (imp)/h	81	0.054	4.4
Oxygen	m³ (*STP*)	0.72	—	—
Steam	kg.	14.9	—	0.2
Ammonia	kg.	0.0625	—	—
Lubricants	litre	4.1	1.1	4.5
Labour	Rs.	—	—	59.1
				118.7

Feed quantity	5 400 — 5 900 m³/h (*STP*)
Feed concentration	600 — 800 ppm HD
Heavy water production	1.4 — 1.8 kg/h

SUGGESTED IMPROVEMENTS AND MODIFICATIONS

The recovery of deuterium from the present plant can be improved by 2% if, during the pressurising period of the warm and cold regenerators, the feed gas is transferred to the gas holder instead of to the depleted system through the second regenerator. This improvement will be extremely valuable when a more enriched gas is treated in a hydrogen distillation plant.

Hydrogen distillation plants employing different refrigeration and distillation systems have been installed in different parts of the world. From the data published so far it can be said that it may not be possible to reduce power consumption by employing a system which is thermodynamically more efficient. It has been found that the capital cost as well as the power consumption are mainly dependent upon the quantity of recirculated hydrogen necessary for reflux or refrigeration. This has been reduced at Nangal by employing a triple distillation column. The reduction in the circulation gained by employing a quadruple column is not adequate. Attention has, therefore, been focused on increasing the relative volatility by a reduction in pressure. If a new plant is built, using a similar design as at Nangal, with the low pressure column working under a pressure of 0.4, the medium pressure column at 0.56 and the high pressure column at 0.83 kg/cm² absolute, 1 300 m³ (*STP*) of recycled H_2 will be required to process 5 000 m³/h (*STP*) of feed gas. The power consumption will then be 1 600 kWh/h and the diameter of the column 1 200 mm.

The main problem will be to prevent an ingress of air into the parts of equipment which are under vacuum. The distillation column, the sub-cooler, the liquefier and the cold and warm regenerators can be kept under a hydrogen atmosphere, as in Nangal, so that even if there is any leakage, only hydrogen will leak in. To doubly ensure against leakage, jackets with a cold hydrogen circulation may be provided round each part of the plant. Once the gas is warmed to —50 °C and transferred to the pre-cooling section, no special precautions need be taken, except for the provision of bellow seal valves, as any small ingress of air can be removed by employing a Deoxo unit installed after the vacuum pump. Our present experience with similar systems using nitrogen indicates that the ingress of air can be controlled within reasonable limits.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/754 Inde

Analyse de l'expérience d'exploitation d'une usine de distillation d'hydrogène

par D. C. Gami et A. S. Rapial

Une usine de distillation d'hydrogène pour la production d'eau lourde est en service à Nangal depuis août 1962. On décrit les problèmes principaux qui se sont posés au début de la mise en exploitation et dans les opérations ultérieures. La consommation d'énergie, les besoins de refroidissement, les pertes de gaz et les rendements de colonne ont été analysés et on les a comparés avec la littérature qu'on peut trouver dans ces domaines.

En se basant sur les données obtenues et l'expérience acquise actuellement grâce à l'exploitation de cette usine à eau lourde, on considère que des frais de production plus bas pourraient être obtenus si la distillation d'hydrogène était entreprise sous vide. Dans le mémoire sont également exposés des problèmes divers susceptibles de se présenter, les solutions proposées ainsi que le projet et l'estimation des frais d'exploitation d'une nouvelle usine.

A/754 Индия

Анализ опыта эксплуатации установки для дистилляции водорода

Д. К. Гами, А. С. Рапиал

Установка для получения тяжелой воды путем дистилляции водорода работает в Нангале с августа 1962 года. Описаны основные проблемы, с которыми столкнулись во время первоначального пуска и последующей эксплуатации установки. Данные по потреблению электроэнергии, условиям охлаждения, потерям газа и коэффициенту полезного действия колонны были проанализированы и сравнивались с имеющимися в литературе данными.

На основе полученных данных и накопленного опыта эксплуатации тяжеловодной установки делается заключение, что стоимость производства может быть снижена, если проводить дистилляцию водорода под вакуумом. В настоящем докладе представлены различные проблемы, с которыми, возможно, придется столкнуться, и возможные решения этих проблем, а также порядок протекания процесса и расчетная стоимость эксплуатации новой установки.

A/754 India

Experiencia adquirida en la explotación de una fábrica de destilación de hidrógeno

por D. C. Gami y A. S. Rapial

En Nangal funciona desde agosto de 1962 una fábrica de destilación de hidrógeno para la producción de agua pesada. Se examinan los principales problemas planteados por la puesta en servicio y explotación subsiguiente de esa instalación. Se estudian el consumo de energía eléctrica, las necesidades en materia de refrigeración, los escapes de gases y el rendimiento de las columnas, y se comparan con los datos facilitados en publicaciones sobre esta materia.

A juzgar por los datos obtenidos y la experiencia adquirida con la explotación de la fábrica, se considera posible reducir el costo de producción si la destilación del hidrógeno se efectuá al vacío. En la memoria se examinan diferentes problemas que suelen plantearse y se proponen las soluciones correspondientes; también se expone el diseño de una nueva instalación y se calculan los gastos que su explotación entraña.

Séparations physico-chimiques d'isotopes stables — réalisations et études de petites productions

par F. Botter, P. Molinari, G. Dirian *

Nous passerons successivement en revue :

a) Des réalisations concernant la séparation des isotopes de l'hydrogène par diffusion thermique et par chromatographie; l'enrichissement du xénon 124 par diffusion thermique;

b) Des études en vue de l'enrichissement du lithium 6 ou 7 par échange chimique et par échange sur résines échangeuses d'ions et du calcium 46 par électromigration en milieu sels fondus.

SÉPARATION DES ISOTOPES DE L'HYDROGÈNE

Diffusion thermique (P. Molinari)

Une installation a été réalisée permettant de produire du tritium de pureté élevée (90-100 %) à partir d'un mélange dont la teneur atomique peut varier entre 5 et 30 % selon l'origine [1-3].

Elle peut servir aussi à préparer du deutérium très riche (95 à 100 %) ou de l'hydrogène très appauvri en deutérium (moins de 0,1 ppm) et en tritium (non mesurable).

Considérations techniques

a) Le rayonnement bêta du tritium ** oblige à placer l'installation dans une enceinte étanche, en dépression et puissamment ventilée. Elle est entièrement télécommandée; le risque d'absorption de tritium par des opérateurs, en cas de fuite de l'installation, est donc minimal;

b) Le comportement des matériaux habituellement inertes vis-à-vis de l'hydrogène (huiles, graisses plastiques) a été examiné du point de vue des réactions chimiques qui se produisent en présence de tritium. Ces réactions provoquent une dilution et une contamination du tritium et modifient les caractéristiques physiques des matériaux constituant les clapets et les joints.

L'utilisation de vannes à soufflet à clapet en Kel-F, et de joints métalliques semble avoir réduit ces inconvénients.

Enfin, toute la construction métallique bridée ou soudée est en acier inoxydable.

Séparation du tritium

Elle se fait à l'aide d'une cascade dont on trouvera figure 1 les caractéristiques.

Cette cascade opère à débit quasi continu, et les opérations automatiques de soutirage et d'alimentation ne font varier sa pression que du 1/25 autour de la valeur de 1 atm.

Le stockage des produits d'alimentation, préalablement épurés de l'hélium qu'ils contiennent, et parfois de production, se fait sur charbon actif pouvant adsorber à la température de l'azote liquide 10 l de gaz par litre de charbon avec une pression résiduelle de 1 Torr.

Le gaz épuisé en tritium, s'il n'est pas stocké, peut être rejeté à l'atmosphère.

L'introduction et le prélèvement des gaz de l'installation se font par détente entre des pressions comprises entre 6 atm et le vide à travers des tubes capillaires de 0,4 mm de diamètre. Dans la cascade, le déplacement du gaz est réalisé au moyen de thermosiphons.

Pour pouvoir traiter des gaz d'alimentation de titres différents, trois points d'alimentation ont été prévus qui permettent d'utiliser au mieux le facteur d'enrichissement, égal à 10^{10}, assuré en régime par la cascade entre l'extrémité riche et l'extrémité pauvre.

Séparation du deutérium

On a pu récupérer à une teneur comprise entre 95 % et 100 % le deutérium que contenaient des mélanges avec de l'hydrogène à un titre voisin de 30 %.

Production d'hydrogène très pauvre en deutérium ou en tritium

Une telle production a été obtenue en n'utilisant que la moitié de la longueur de la cascade, à partir d'hydrogène contenant 32 ppm de deutérium. La teneur en deutérium était inférieure à 0,1 ppm; celle en tritium n'a pu être mesurée

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* Commissariat à l'énergie atomique, CEN, Saclay. Ces travaux doivent beaucoup à la participation de Mme S. Grunspan et F. Menes, E. Saito et J.-M. Lerat, et ils ont été effectués sous la direction générale d'E. Roth.

** La radioactivité du tritium pur est voisine de 2 500 Ci/l TPN et la dose de tolérance de tritium dans l'air pour une journée de 8 h de travail est de 5×10^{-6} Ci/m³.

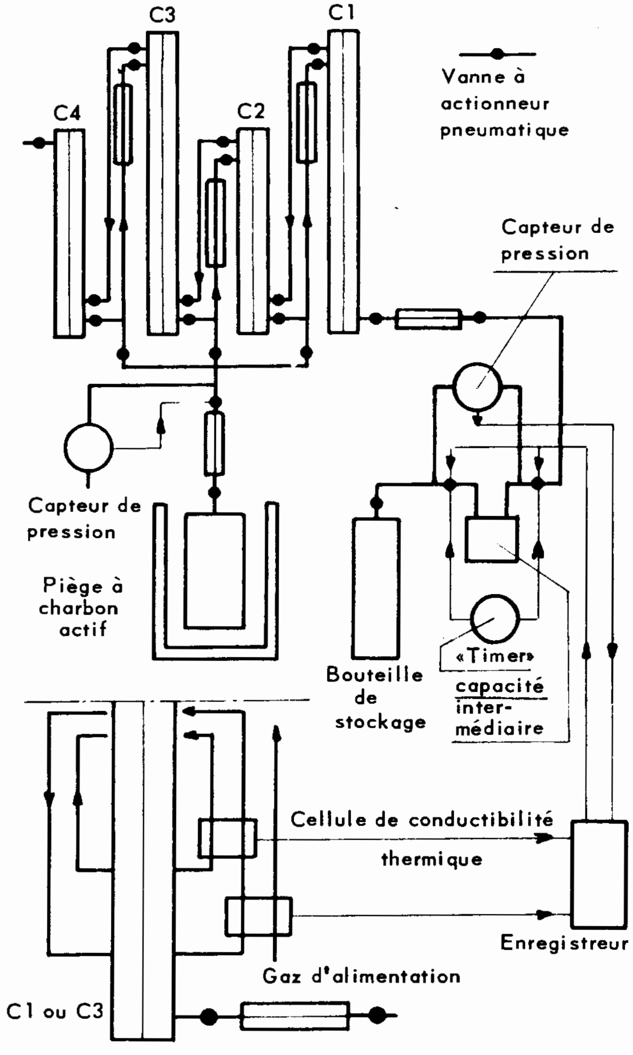

Figure 1. Séparation des isotopes de l'hydrogène par diffusion thermique

Nombre de colonnes en série	4	
Circulation de gaz par thermosiphon		
Longueur (2 × 240 cm + 2 × 360 cm)	1 200 cm	
Section d'enrichissement	$360 < L < 600$ cm	
Section d'épuisement	$600 < L < 840$ cm	
Fil chaud :		
Diamètre	0,08 cm	
Température	1 000 °K	
Matière	Nichrome V	
Tube froid :		
Diamètre	3 cm	
Température	288 à 300 °K	
Matière	Acier inox	
Électricité (courant redressé) :		
Intensité	15 A	
Voltage	30 V/m	
Pression de fonctionnement	1 atm	
Retenue gazeuse (y compris les thermosiphons)	12 l (TNP)	
Concentration :	Deutérium	Tritium
Alimentation	$25 < x_A < 35$	$5\% < x_A < 20\%$
Production	$95 < x_P < 99{,}9$	$91\% < x_P < 99{,}3\%$
Rejet	< 10 ppm	10 ppm
Débit de production maximal	$1\ \text{l/j} < D < 10\ \text{l/j}$	

Les mesures

L'établissement des bilans-matières précis exige :

a) Des mesures de pression, volume, température : les pressions sont mesurées à ± 1 % en 10 points de l'installation au moyen de capteurs de pression absolus ou différentiels et sont enregistrées;

b) Des analyses isotopiques de deux types : premièrement, de façon continue, au moyen de cellules de conductibilité thermique, on compare la teneur du gaz du niveau d'une colonne avec celle du gaz d'alimentation d'un autre niveau de la colonne (fig. 1), et, deuxièmement, de façon discontinue, des échantillons prélevés en quatre points de l'installation sont analysés par spectrométrie de masse ou par chambre à ionisation avec une précision de ± 0,5 %.

L'erreur sur les bilans est alors de ± 2 %.

Chromatographie (F. Botter)

Nous avons séparé les isotopes de l'hydrogène par chromatographie frontale et par déplacement de bande sur des masses palladiées. Ces séparations ont été étudiées avant nous par E. Glueckauf et G. P. Kitt [4] et J. Chadwick [5].

Interprétation des résultats

Nous avons adopté un modèle simplifié d'échange isotopique à contre-courant. Ce modèle qui néglige la diffusion longitudinale en phase gazeuse et latérale en phase adsorbée est déjà une bonne approximation [6]. Un modèle plus élaboré [7] pourra expliquer, entre autres, la légère dissymétrie observée dans les chromatogrammes qui n'est pas conforme avec la courbe symétrique en tangente hyperbolique prévue pour le « profil isotopique » par le modèle simplifié [6]. Nous donnons ici une méthode nouvelle de calcul des plateaux théoriques en chromatographie.

A l'aide de la masse d'alumine palladiée reconnue la plus efficace, nous avons fabriqué une colonne d'une capacité d'environ 2 l, s'adaptant sur un prototype d'appareil préparatif dont on trouvera la description en [8]. Sur cet appareil a été réalisée la séparation de D_2 et de T_2, par déplacement de bande à partir de mélanges H_2-D_2 et H_2-T_2.

Les principales grandeurs et définitions utilisées sont résumées dans le tableau 1. On trouvera en [6] le mode de détermination du facteur de séparation, la justification de l'existence des « fronts d'adsorption » et des deux profils isotopiques, et l'établissement des taux de charge dans le cadre d'un exposé général des chromatographies de déplacement et frontales.

Pour développer l'analogie avec un échange à contre-courant, on lie un plan référence à chaque profil isotopique. Le plan référence lié au premier profil est alors traversé dans le sens du débit gazeux par un débit de gaz $G_1 = d - (V_1/L)\,B\ \text{cm}^3/\text{s}$ et en sens inverse par un débit d'« adsorbé » de $F_1 = (V_1/L)\,A\ \text{cm}^3/\text{s}$. Le plan référence lié au profil 2 est traversé à contre-

Tableau 1

y : teneur en deutérium $[D/(D+H)]$ ou tritium $[T/(T+H)]$ de la phase gazeuse

y_0 : teneur initiale d'un mélange traité

x : teneur en deutérium ou tritium de la phase adsorbée supposée homogène et en équilibre avec y (on néglige une diffusion s'accompagnant d'un gradient isotopique)

x_0 : en équilibre avec y_0

L : longueur de la colonne de chromatographie

A : capacité en phase adsorbée de la colonne (cm^3 TPN)

B : volume interstitiel de la colonne (cm^3 TPN)

d : débit (cm^3/TPN/s) d'introduction du mélange et de l'hydrogène déplaçant

$$\alpha = \frac{\frac{D}{H}\text{ phase gazeuse}}{\frac{D}{H}\text{ phase adsorbée}} = \frac{\frac{y}{1-y}}{\frac{x}{1-x}} = \text{coefficient de séparation « globale » [6]}$$

Front d'adsorption : frontière entre le palladium vierge d'adsorbé et celui saturé en un mélange hydrogéné (de composition isotopique quelconque) de vitesse V_a : $V_a = \mathrm{d}L/(A+B)$

Premier profil isotopique : frontière entre D_2 (ou T_2) pur et le palier de mélange introduit (y_0 en phase gazeuse, x_0 en phase adsorbée) dans une frontale directe [6] ou un déplacement de bande « non achevé » [6] (régime stationnaire atteint) de vitesse $V_1 = \mathrm{d}L/B + A\,\alpha(x_0/y_0) = \mathrm{d}L/[B + A\,\alpha/1 + (\alpha - 1)(1 - y_0)]$

Second profil isotopique : frontière entre le palier de mélange (y_0 ou x_0) et l'hydrogène déplaçant ($y = 0$ $x = 0$) dans un déplacement de bande « non achevé [6] régime stationnaire atteint)

de vitesse $V_2 = \mathrm{d}L/B + A\,(x_0/y_0)$

$$= \frac{\mathrm{d}L}{B + A/[1 + (\alpha - 1)(1 - y_0)]}$$

$V_2 \geqslant V_a \geqslant V_1$

$V_2 \to V_a$, $V_1 \to V_a$ $\Big\{$ lorsque le déplacement de bande est « achevé », il n'y a plus qu'un profil isotopique séparant D_2 (ou T_2) de H_2 et avançant à la vitesse V_a

$T = l_a/L = A/[(B+A)\,1/(\alpha - 1) + (1 - y_0)] =$ taux de charge maximal qu'on peut employer pour qu'un déplacement de bande soit « achevé » — l_a en unité de longueur de la colonne est la longueur maximale de colonne sur laquelle on peut fixer une bande.

l_a peut être $> L$, longueur de la colonne si α est élevé, et y_0 grand.

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courant par un débit gazeux G_2 et d'adsorbé F_2. On définit la courbe d'équilibre par l'équation

$$\left(\frac{y}{1-y}\right)_n = \alpha\left(\frac{x}{1-x}\right)_{n-1} \tag{1}$$

en considérant qu'un enrichissement égal à α est réalisé entre phases gazeuse et adsorbée aux bornes n et $n-1$ de la tranche $(n-1, n)$ du profil isotopique. On définit la droite de fonctionnement

$$y_n = (F/G)\,x_n + \text{constante} \tag{2}$$

au moyen d'un bilan matière entre les débits F et G en négligeant la diffusion longitudinale. Ces deux courbes ou équations permettent de déterminer le nombre de plateaux théoriques, comptés ici par rapport à un enrichissement donné, enrichissement en phase gazeuse, soit graphiquement (par un diagramme de McCabe et Thiele), soit analytiquement. Un changement de variables permet d'étendre la détermination analytique au cas des frontales grâce à une relation de forme $\left(\frac{Y}{1-Y}\right)_{z+n} = \beta^n\left(\frac{Y}{1-Y}\right)_z$

Le tableau 2 rappelle le principe de la détermination graphique et analytique du nombre de plateaux théoriques; et dans le deuxième cas illustre une méthode de dépouillement du chromatogramme simple et nouvelle. Le rapport des longueurs caractéristiques r/R donne immédiatement $Y/1 - Y)$, d'où le nombre n de plateaux théoriques relatifs à une tranche $\mathscr{L}$ du profil isotopique.

En multipliant n par le facteur $\mathscr{L}_c/l\ V_1$ (ou V_2)$/V_a$, on obtient le nombre N de plateaux théoriques de la colonne de chromatographie. $\mathscr{L}_c$ caractérise la capacité de la colonne par le temps écoulé entre l'introduction du mélange et l'apparition du front d'adsorption.

$l\,(V_a/V_1)$ (ou $l\ V_a/V_2$) caractérise la tranche de colonne de chromatographie concernée, le rapport V_a/V_1 (ou V_a/V_2) tenant compte des différences de vitesse d'avancement du front d'adsorption et du profil isotopique dans le cas d'une frontale directe ou inverse; dans le cas du déplacement de bande ce rapport de vitesses est égal à l'unité.

Résultats

a) Nous avons établi avec précision la variation de α en fonction de la température pour des mélanges HD-H_2 et obtenons : $\log_{10}\alpha = 82/T + 0{,}025$ en désaccord avec [4] et [9].

b) Compte tenu de l'influence de divers paramètres [6] sur la hauteur équivalente à un plateau théorique (HEPT), nous donnons dans le tableau 3 la comparaison de l'efficacité de diverses masses palladiées, établie à l'aide de mélanges H_2, D_2.

c) Le tableau 4 compare les performances obtenues sur la masse d'alumine palladiée (*E*, tableau 3) et avec le prototype d'appareil préparatif pour la séparation des mélanges H_2-D_2 et H_2-T_2. La séparation chromatographique elle-même d'un litre de mélange dure une dizaine de minutes.

L'efficacité de la colonne est sensiblement la même pour les deux séparations : environ 1 200 plateaux théoriques pour 1 colonne de 1 m contenant 23 g de palladium. Ceci est conforme aux prédictions théoriques [6] basées sur le modèle et le mode de dépouillement adoptés.

La pureté isotopique du deutérium et du tritium séparés a été respectivement de 99,5 % et 97,1 %, et les rendements respectivement de 80 % et 84 % dans les conditions opératoires du tableau 4.

Avec une colonne de même garnissage mais de capacité supérieure, les rendements augmenteraient, ainsi qu'avec le titre en isotope lourd du mélange traité. Ainsi une colonne de capacité 80 l traitant un mélange initial à 10 % de D_2 ou de T_2 permettrait d'obtenir des rendements de 98,5 % et 99,3 %, sans

Tableau 2. Calcul du nombre de plateaux théoriques

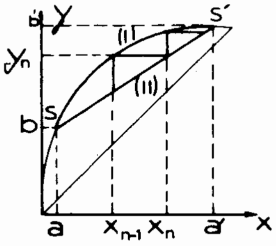
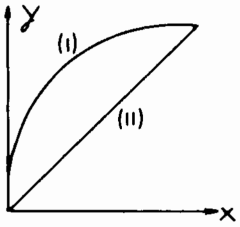
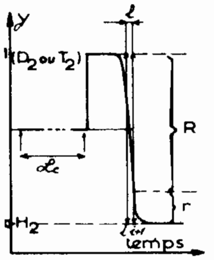
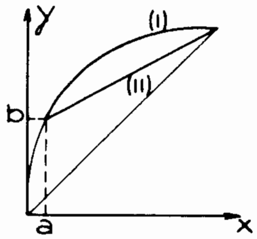
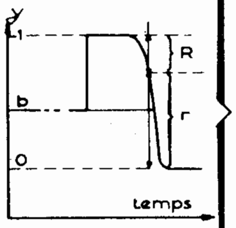
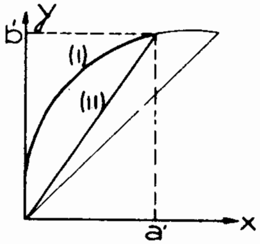
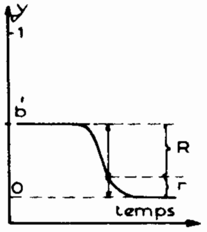
Détermination graphique (Mac Cabe et Thiele) du nombre de plateaux théoriques	Divers cas expérimentaux possibles. Définition (cas général et cas particuliers) des variables y et x et du paramètre β	Détermination analytique du nombre de plateaux théoriques		
		Équations des courbes opératoires (II) et d'équilibre (I) écrites avec les variables :		Méthode de dépouillement des chromatogrammes pour le calcul du nombre N de plateaux théoriques d'une colonne. Définition des longueurs r et R sur le chromatogramme représentant la variation de teneur isotopique de la phase gazeuse.
		y et x	Y et X	
	Frontale, cas général On opère entre une teneur « tête » : $y = b'$, $x = a'$ et une teneur « queue » $y = b$, $x = a$ $\beta = \frac{a-(\alpha-1)b}{a-(\alpha-1)b'} = \frac{b}{a}\cdot\frac{a'}{b'}$ $Y = \frac{y-b}{b'-b}$ $X = \frac{x-a}{a'-a}$	(I) $\left(\frac{y}{1-y}\right)_n = a\left(\frac{x}{1-x}\right)_{n-1}$ (II) $y_n = \frac{b'-b}{a'-a}x_n + \frac{a'b-ab'}{a'-a}$	(I) $\left(\frac{Y}{1-Y}\right)_n = \beta\left(\frac{Y}{1-Y}\right)_{n-1}$ (II) $Y_n = X_n$ $\left.\right\} \left(\frac{Y}{1-Y}\right)_{z+n} = \beta^n\left(\frac{Y}{1-Y}\right)_z$	
	Déplacement de bande $a' = b' = 1$ $a = b = 0$ $Y = y$ $X = x$ $\beta = a$	(I) Idem (II) $y_n = x_n$ $\left.\right\} \left(\frac{y}{1-y}\right)_{z+n} = a^n\left(\frac{y}{1-y}\right)_z$	Idem	 $\frac{r}{R} = \frac{Y}{1-Y}$ $\left(\frac{r}{R}\right)_i = \beta^n\left(\frac{r}{R}\right)_{i+1}$ $N = n\,\frac{\ell}{\mathscr{L}_c}\,\frac{V_1\,(\text{ou } V_2)}{V_a}$
	Frontale directe $a' = b' = 1$ $Y = \frac{y-b}{1-b}$ $X = \frac{x-a}{1-a}$ $\beta = \frac{b}{a}$	(I) Idem (II) $y_n = \frac{b}{a}x_n + \frac{b-a}{1-a}$	Idem	
	Frontale inverse $a = b = 0$ $Y = \frac{y}{b'}$ $X = \frac{x}{a'}$ $\beta = \frac{a'}{b'}a$	(I) Idem (II) $y_n = \frac{b'}{a'}x_n$	Idem	

Tableau 3. Chromatographie gazeuse

Colonnes		Quantité de		Quantité de support pour 1 g de Pd	Géométrie de la colonne		Capacité A (cm³) en phase adsorbée	Volume interstitiel B cm³	B/A
Nature support	Paramètres ayant varié	Pd (g)	support (cm³ ou g)		L (cm)	∅ int. (cm)			
Pd/amiante :	Géométrie	20	40 cm³	2 cm³/1 g Pd	36	1,28	1 350 ± 10 %	40	0,029
A									
B			ou 6 g		92	0,8	—	—	—
Pd/charbon :	Granulométrie du support								
A		1,13	15 cm³	11,45 cm³	23	0,9	108	10,11	$0,093_6$
B		1,19	11 cm³	12,60 cm³	23	0,9	99,6	12,1	0,12
C		1,18	11 cm³	12,71 cm³	23	0,9	99,6	10,94	$0,11^2$
Pd/ponce :	Géométrie								
A		21,35	71,5 g	3,35 g	85,7	0,99	1 118	55	0,049
B		19,6	65,8 g	3,35 g	89,2	0,93	1 028	48,8	0,047
C		9,8	37,9 g	3,85 g	55,0	0,90	514	21,2	0,041
D.		9,8	37,9 g	3,85 g	55,0	0,90	514	21,2	0,041
Pd/Pyrex fritté :		5,73	33 cm³	5,6 cm³	50,0	0,90	529	18,4	0,034
Pd/Al_2O_3 :	Poids de Pd								
A		1,73	20 cm³	11,56 cm³	55,0	0,68	128,4	14,6	0,114
B		3,36	20 cm³	5,88 cm³	55,0	0,68	318,6	14,4	0,045
C		5,46	20 cm³	3,66 cm³.	55,0	0,68	424,4	14,6	0,034
D.		7,18	20 cm³	2,78 cm³	55,0	0,68	639,4	14,6	0,023
E		23,15	76 cm³	3,28 cm³	98,0	1	1 844,7	55,3	0,03

Colonnes		A/1g Pd	HEPT (mm)	Nombre de plateaux par cm de colonne	Nombre de plateaux par g de P_d	Poids de P_d pour 1 plateau (mg)	Nombre de plateaux de la colonne N	Remarques
Nature support	Paramètres ayant varié							
Pd/amiante :	Géométrie	67,5 ± 7,5 %	⩾ 6	—	⩽ 10	⩾100	—	Détermination de N par déplacement
A								
B		—	—	—	—	—	—	
Pd/charbon :	Granulométrie du support							
A		83,5 ± 8,5 %	14,1	0,7	13	—	17	Détermination de N par déplacement
B		83,5 ± 8,5 %	—	—	—	—	15,5	
C		83,5 ± 8,5 %	—	—	—	—	15,3	
Pd/ponce :	Géométrie							
A		57,6 ± 12 %	6,6	1,5	7,1	—	151	Détermination de N par déplacement
B		—	6,6	1,5	7,1	—	151	
C		52,45 ± 10 %	3,7	2,7	12,13	—	119	
D.		—	2,9	3,42	19,5	—	190	
Pd/Pyrex fritté :		92,5	2,82	3,55	31	—	178	Détermination de N par déplacement
Pd/Al_2O_3 :	Poids de Pd							
A		74,8	0,91	10,9	347	2,88	600	Détermination par frontale $b = 0{,}75$ $b' = 1$
B		95,8	0,81	12,26	202	2,88	674	
C		77,6	0,77	13,8	140	2,88	764	
D.		89,0	0,67	14,9	117	2,88	818	
E		79,7	0,817	12,2	104	9,65	1 200	Déplacement et frontales

Efficacités déterminées à 20 °C et pour le débit optimal

Tableau 4. Séparation des isotopes de l'hydrogène par chromatographie gazeuse.

Titre isotopique du mélange initial [en D/(D + H) ou T/(T + H)]	Bande fixée sur la colonne de capacité (A = ≈ 2 000 cm³)	D_2 ou T_2 séparés en tête; quantité et titre isotopique	D_2 ou T_2 dans « mixte » à ≈ 50 % de H_2	D_2 ou T_2 restant chimisorbé sur la colonne	D_2 ou T_2 dans l'hydrogène déplaçant de « queue », en fonction du volume écoulé de H_2	Rendement en $\frac{D_2 \text{ pur}}{D_2 \text{ traité}}$ ou $\frac{T_2 \text{ pur}}{T_2 \text{ traité}}$ sans retraitement des récupérations
Deutérium :					[a]	
≈ 10 % . .	≈ 1 000 cm³ à ~ 10 % soit 100 cm³ de D_2	80 cm³ à 99,5 % en D/D + H	15 cm³ D_2	≈ 1 cm³	1 430 ppm après 75 cm³ 960 ppm après 250 cm³ 730 ppm après 430 cm³ 635 ppm après 860 cm³ au total : 1 cm³ D_2	$\frac{80 \times 99{,}5}{100}$ # 80 %
Tritium :	[b]					
17,8 % . .	960 cm³ à ≈ 18,3 % soit 177,1 cm³ de T_2	153,5 cm³ (dont ^3He) à ≈ 97,1 %	20 cm³ T_2	≈ 0,45 cm³ sous forme de 1 800 cm³ à 235 ppm	515 ppm/238 cm³ 337 ppm/633 cm³ 200 ppm/837 cm³ au total ~ 0,5 cm³ de T_2	$\frac{153{,}5 \times 0{,}971}{177{,}5}$ # 84 %

[a] Partie par million D/(D+H) ou T/(T+H).

[b] Un premier enrichissement s'est fait lors du transfert du mélange par une pompe à Pd [8].

tenir compte du retraitement des fractions mixtes.

Pour la préparation de D_2 ou T_2 de bonne pureté isotopique, la chromatographie de déplacement de bande sur masse palladiée est donc une méthode de rendement élevé, (quoique inférieur à celui de la méthode par diffusion thermique), rapide et simple.

ENRICHISSEMENT DU XÉNON EN ISOTOPE 124 PAR DIFFUSION THERMIQUE [10,11] (P. Molinari)

L'accroissement des besoins médicaux en iode 125 et la nécessité de réduire les volumes de xénon soumis à l'irradiation ont conduit à enrichir ce gaz en xénon 124. Le facteur d'enrichissement désiré est de 4 à 5. Un tel résultat peut être obtenu à l'aide de la cascade de diffusion thermique décrite dans la figure 2, où sont aussi rassemblées les conditions opératoires.

Le groupement des colonnes de diffusion dans un seul tube de refroidissement donne au montage l'allure d'un faisceau tubulaire d'échangeur de chaleur. C'est une originalité de l'installation. Les colonnes sont reliées entre elles par tubes capillaires et le déplacement du gaz s'effectuera au moyen d'un oscillateur thermique.

La production est de l'ordre de 100 à 200 cm³ de xénon enrichi par quinzaine.

SÉPARATION DES ISOTOPES DU LITHIUM

Par échange chimique (E. Saito)

Des essais préliminaires ont montré l'existence d'une séparation isotopique liée à l'échange entre le lithium sous forme de sel dans un solvant et le métal dissous dans le mercure. Nous avons effectué une étude de l'influence de divers paramètres sur les facteurs de séparation.

La réaction d'équilibre peut s'écrire :

$$^6\mathrm{Li}^+_{\mathrm{Sol}} + {}^7\mathrm{Li}^+_{\mathrm{Hg}} \rightleftharpoons {}^7\mathrm{Li}^+_{\mathrm{Sol}} + {}^6\mathrm{Li}^+_{\mathrm{Hg}}$$

le facteur de séparation α est défini par :

$$\alpha = R_{\mathrm{Sol}}/R_{\mathrm{Hg}} \text{ [}R \text{ étant le rapport } {}^7\mathrm{Li}/{}^6\mathrm{Li}]$$

Influence du solvant

Il n'y a pas un grand choix car la plupart des solvants sont attaqués par le lithium de l'amalgame.

Nous avons fait quelques essais avec la *diméthylamine*, la *diéthylamine* et la *pyridine*. Avec ces solvants, la valeur de α variait entre 1,03 et 1,055. Mais l'étude de la réaction pour ces amines est perturbée par la formation d'une boue constituée d'amalgame dispersé dans le solvant. La boue se forme aussi avec le *tétrahydrofurane* (THF) mais presque pas avec la *diméthylformamide* (DMF).

C'est avec ces deux derniers solvants que nous avons poursuivi l'étude de l'influence d'autres facteurs.

Influence de la température

Le tableau 5 montre que le facteur de séparation baisse de 1,060 à 1,035 entre — 10 et 85 °C. Cet abaissement est parallèle pour le BrLi dans le THF et la DMF. Dans la DMF, la valeur de α est légèrement plus faible avec le chlorure qu'avec le bromure.

Influence de la concentration

La concentration de l'amalgame en lithium ou du sel dans le solvant organique n'a aucune influence sur la valeur du facteur de séparation.

Tableau 5. Facteurs de séparation des isotopes du lithium dans divers échanges chimiques

$\alpha = [^7\text{Li}/^6\text{Li}]_{\text{Sol}}/[^7\text{Li}/^6\text{Li}]_{\text{Hg}}$

Solvant	Sel	T (°C)						
		— 10	4	15	25	50	70	85
THF .	BrLi	—	1,056	—	1,053	1,046	—	—
DMF .	BrLi	1,060	1,056	1,052	1,051	1,041	1,041	1,035
DMF .	ClLi	—	—	1,048	1,044	1,038	1,035	—

Par résines échangeuses d'ions
(S. Grunspan — F. Botter)

Les travaux récents [14, 15] infirmant nos résultats sur la séparation des isotopes du lithium sur échangeurs d'ions et solutions aqueuses de sels ou de bases [16], nous avons refait [17] de nouvelles déterminations de $\alpha = \left[\frac{^6\text{Li}}{^7\text{Li}}\right]_R \Big/ \left[\frac{^6\text{Li}}{^7\text{Li}}\right]_S$ sur des systèmes analogues à ceux cités :

a) Par équilibres uniques. Mais les valeurs $\varepsilon = \alpha - 1$ obtenues étant à la limite du seuil de mesure des spectromètres de masse, des méthodes de cumul furent envisagées ;

b) Par équilibres successifs en reprenant les travaux cités en [18, 19] ;

c) Par chromatographie frontale directe et inverse. Cette dernière technique donne les résultats les plus précis. Ils sont résumés dans le tableau 6. Ils confirment l'ordre de grandeur de nos premières mesures. Nous pensons qu'une grande partie des différences entre les résultats des autres auteurs et les nôtres sont d'origine analytique ou d'exploitation des résultats expérimentaux.

ENRICHISSEMENT DU CALCIUM 46 PAR ÉLECTROMIGRATION A CONTRE-COURANT EN SELS FONDUS
(F. Menes — D. Maire)

A. — Nous avons étudié, d'abord dans le cadre d'un contrat avec l'AIEA, la séparation des isotopes du calcium, dans le but d'enrichir cet élément en calcium 46, à partir duquel on obtient, par irradiation, le calcium 47, dont on connaît l'intérêt pour les recherches biologiques.

a) Parmi les méthodes d'enrichissement, celle qui a donné les meilleurs résultats est la séparation par électromigration à contre-courant en sels fondus.

Le milieu utilisé est le bromure de calcium à 750-800 °C. La première cellule d'électrolyse est du type tube en U et l'appareillage, dans son ensemble, a déjà été précédemment décrit [20]. Rappelons, pour mémoire, qu'on utilise une cellule où les deux électrodes de graphite fonctionnent en « électrode à brome réversible ».

b) Cet appareil de laboratoire est capable de produire

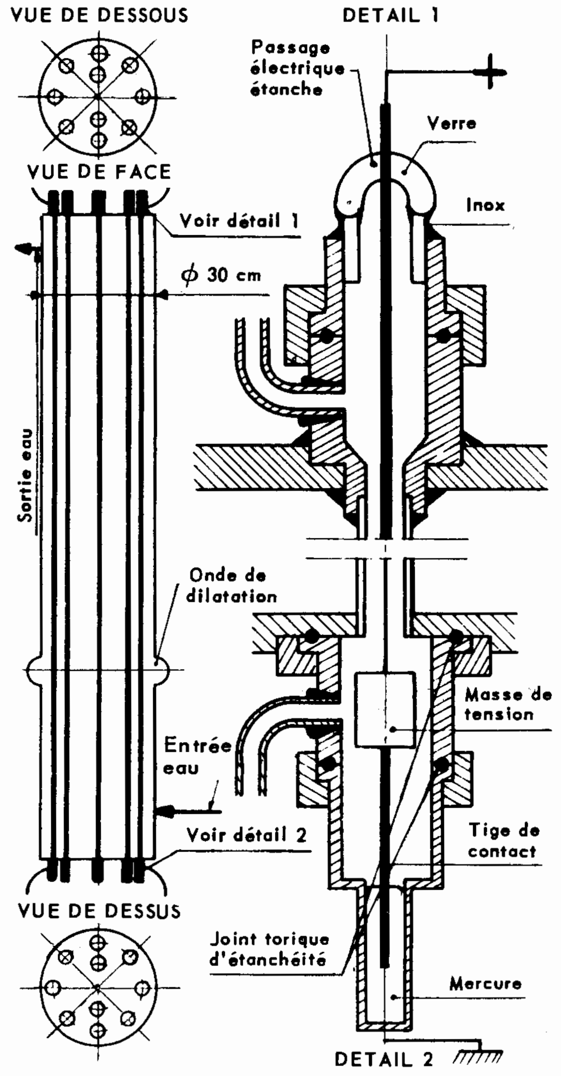


Figure 2. Enrichissement du xénon en isotope 124

Nombre de colonnes en série	4
Assemblage en faisceau tubulaire d'échangeur de chaleur	
Circulation du gaz assurée par oscillateur	
Longueur :	
D'une colonne	300 cm
De la cascade	1 200 cm
Fil chaud :	
Diamètre	0,05 cm
Température	1 500 °K
Matière	Tungstène
Tube froid :	
Diamètre	1 cm
Température	288-300 °K
Matière	Acier inox
Électricité (courant redressé)	
Intensité	13,5 A
Voltage	30 V/m
Pression de fonctionnement	0,4 atm
Enrichissement en ^{124}Xe	4 à 5

Tableau 6. Facteurs de séparation des isotopes du lithium sur résines échangeuses d'ions

Résine	Soluté	Solvant	$\alpha = \left[\frac{^6\text{Li}}{^7\text{Li}}\right]_R \Big/ \left[\frac{^6\text{Li}}{^7\text{Li}}\right]_S$
Dowex 50 × 12			
200 — 400 Mesh . .	LiOH = 0,0886 *N*	eau 20 % acétone	1,0020 ± 0,0002
200 — 400 Mesh . .	LiOH = 0,303 *N*	eau 20 % acétone	1,0017 ± 0,0002
200 — 400 Mesh . .	LiOH = 0,335 *N*	eau 20 % acétone	1,0020 ± 0,0002
200 — 400 Mesh . .	LiOH = 0,300 *N*	eau 20 % acétone	1,0018 ± 0,0002
Dowex W 50 × 12			
200 — 400 Mesh . .	LiOH = 0,306 *N*	eau	1,0017 ± 0,0002
200 — 400 Mesh . .	ClLi = 0,4 *N*	eau	1,0016 ± 0,0002
200 — 400 Mesh . .	ClLi = 1 *N*	eau	1,0016 ± 0,0002

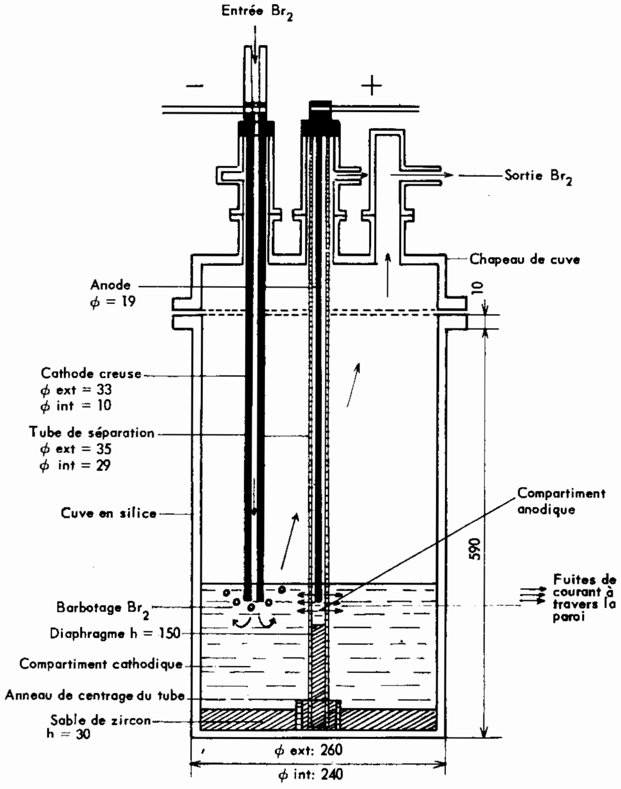


Figure 3. Cellule électrolytique « à tube immergé ». Schéma de principe

en un mois quelques grammes de calcium dont la teneur en calcium 46 a été multipliée par un facteur voisin de 2. Nous avons même pu atteindre, dans de récentes expériences, un facteur d'environ 5.

c) La principale difficulté de mise au point d'une petite cellule de laboratoire est liée à la présence d'eau dans le bromure de calcium à 750-800 °C, ce qui inhibe le fonctionnement de la cathode en électrode à brome et limite l'intensité admissible, dont l'enrichissement, si on cherche à le pousser au maximum.

On évite cette difficulté en séchant soigneusement le sel par passage de gaz inerte sec dans le bain fondu.

B. — En ce qui concerne la production à plus grande échelle, l'appareil classique de laboratoire, en silice, ne peut être utilisé pour des raisons de facilité d'extrapolation et de prix de revient.

a) Un type de cellule d'électromigration de grande capacité a donc été étudié. Il s'agit d'un appareil à « tube immergé » (fig. 3). Le tube de séparation est immergé à l'intérieur du compartiment réservoir. Mais, dans ce montage, il y a un risque de passage des ions à travers la paroi du tube de séparation. Il existe alors une « fuite » non soumise au contre-courant, qui contrecarre d'autant plus l'enrichissement que l'effet élémentaire de séparation est plus faible et peut même l'annihiler totalement.

b) De ce fait peut-être, parmi les tubes de séparation en silice et en alumine, seuls certains types d'alumine ont permis d'obtenir des enrichissements.

c) Les premiers essais ont permis d'obtenir des facteurs d'enrichissement d'environ 1,5 en calcium 46 sur des quantités de l'ordre de 100 g de calcium métallique.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/90 France

Physico-chemical separation of stable isotopes: theory and practice of small-scale production

by F. Botter *et al.*

Chromatography

Pure deuterium has been separated from gaseous mixtures of hydrogen and deuterium by band-displacement chromatography, using columns of palladium on a support.

The best results were obtained with columns of palladium on sintered α-alumina. With a column of this type having a total capacity of about 2 litres, a preparative apparatus of low dead volume has been built which produces 1 litre of pure D_2 from a 50% D_2, 50% H_2 mixture in about 12 minutes.

As a first approximation, chromatography can be likened theoretically to counter-current fractionation, neglecting superficial resistance to the exchange and longitudinal and lateral diffusion. The number of theoretical plates required for a given enrichment of the gas phase is determined graphically or by calculation, enabling comparisons to be made between the efficiencies of columns containing different amounts of palladium.

Thermal diffusion

For the separation of hydrogen isotopes a thermal diffusion apparatus, made of stainless steel and entirely remote-controlled, has been constructed. The separation cascade is made up of two identical pairs of hot-wire columns. Each pair can operate independently, or they can be connected by a thermosyphon.

The temperature of the hot wire is kept at around 1 000 °C; heating is by direct current.

With this apparatus, hydrogen samples with a deuterium content lower than 0.5 ppm were obtained from gas originally containing 32 ppm. It was thus possible to prepare tritium of 99.3% concentration from gas with an initial content of 6%.

For the quantitative separation of xenon enriched five times in ^{124}Xe by thermal diffusion, two identical cascades were built, each consisting of 5 columns, working in parallel but connected by a thermosyphon or a capillary tube linked to a thermal gas oscillator. The central tungsten wire is heated to 1 200 °C.

The columns are grouped like a cluster of a heat exchanger, in a shell 30 cm in diameter through which cooling water is circulated.

Studies are continuing to increase the separation factor of the cascade by using an auxiliary gas.

Isotopic exchange

A series of experiments was carried out to determine the isotopic separation factor between a lithium amalgam and an organic solvent containing a salt of lithium. The various parameters which may enter into the exchange were studied : the influence of the type of solvent (the two solvents used were dimethylformamide and tetrahydrofurane), of the temperature, and of the concentration and nature of the associated halogen.

Solutions of Li metal and liquid NH_3 also were studied. A number of tests were carried out to see whether there was a difference between the isotopic compositions of the Li present in the two liquid layers obtained by the dissolution of Li metal in ammonia;

no difference was observed. This was true also in the case of a layer of Li in liquid NH_3 and a layer of LiI in a similar solvent.

Electromigration

Counter-current electromigration in fused salts is a powerful method of isotopic enrichment. It can be used successfully to separate the isotopes of elements of a strongly metallic nature.

In the case of alkalies, small quantities of isotopically pure ^{7}Li were obtained, while the enrichment factors for potassium were of the order of 10.

In the case of the alkaline earths, it proved possible to produce small quantities of calcium enriched 5 times in ^{46}Ca.

However, considerable technological difficulties are encountered in working this process on the semi-industrial scale.

A/90 Франция

Разделение стабильных изотопов

Ф. Ботье *et al.*

Хроматографическое разделение

Описывается способ выделения чистого дейтерия из газовых смесей водорода и дейтерия методом элюэнтной хроматографии на колонках с палладиевой насадкой.

Наилучшие результаты были получены с помощью колонок из палладия на спеченной α-окиси алюминия. Производительность колонки такого типа общей емкостью приблизительно 2 *л* составляет 1 *л* чистого дейтерия из смеси $50\% D_2 - 50\% H_2$ в течение приблизительно 12 *мин*.

При теоретическом описании хроматография в первом приближении рассматривается как противоточное разделение, при этом пренебрегают поверхностным сопротивлением обмену, а также продольной и поперечной диффузией. Требуемое число теоретических тарелок, необходимых для заданного обогащения газовой фазы, устанавливается графически или путем расчета, что позволяет сравнить эффективность колонок, различающихся по количеству палладия.

Термодиффузия

Для разделения изотопов водорода из нержавеющей стали была сконструирована полностью телеуправляемая термодиффузионная установка. Каскад разделения состоит из двух одинаковых пар колонок с накаливаемой центральной нитью. Колонки соединяются с помощью термосифона, кроме того, каждая пара может работать изолированно. Температура накала нити около 1000° C поддерживается с помощью постоянного тока. С помощью этой установки были получены пробы водорода с содержанием дейтерия менее $5 \cdot 10^{-5}$ % из исходного газа, содержащего $32 \cdot 10^{-4}$ % дейтерия. Оказалось также возможным получать тритий с изотопным содержанием 99,3% из газа с исходным содержанием 6%.

Для количественного разделения ксенона, пятикратно обогащенного Xe^{124}, методом термодиффузии были сконструированы два идентичных каскада по пять колонок, функционирующих параллельно, соединенных с помощью термосифона или с помощью капиллярной трубки, присоединенной к газовому термоосциллятору. Вольфрамовая нить накала имеет температуру 1200° C. Эти колонки сгруппированы подобно пучку труб теплообменника в кольце диаметром 30 *см*, где циркулирует охлаждающая вода. В настоящее время проводятся исследования с целью увеличить коэффициент разделения этого каскада с помощью дополнительной подачи газа.

Изотопный обмен

Проведен ряд опытов для определения коэффициента разделения изотопов при обмене между литиевой амальгамой и органическим растворителем, содержащим соль лития. Изучены различные параметры, которые могут влиять на этот обмен: природа растворителя (были использованы два растворителя — диметилформамид и тетрагидрофуран), температура, влияние концентрации, ассоциированного галогена.

Проведены также исследования с растворами металлический Li — жидкий NH_3 и опыты по установлению различий в изотопном составе лития в двух жидких фазах, полученных растворением металлического лития в аммиаке. Никакого различия в изотопном составе лития в двух фазах не обнаружено. То же самое наблюдалось в случае слоя лития в жидком аммиаке и слоя Li — J в том же самом растворителе.

Электромиграция

Метод противоточной электромиграции в расплавленных слоях является очень распространенным способом изотопного обогащения. Этот метод с успехом применяется при разделении изотопов элементов с ярко выраженными металлическими свойствами. В случае щелочных металлов можно получить небольшие количества чистого Li^7. Для калия коэффициенты обогащения составляют около 10. Что касается щелочноземельных элементов, то этот метод позволил получить небольшие количества калия, пятикратно обогащенного Ca^{46}. Но применение его в полупромышленном масштабе связано со значительными технологическими трудностями.

A/90 Francia

Separación de isótopos estables : realizaciones y estudios de producción en pequeña escala

por F. Botter *et al.*

Cromatografía

Aplicando la cromatografía de desplazamiento de banda sobre columnas de paladio, con soporte, se ha efectuado la separación de deuterio puro, a partir de mezclas gaseosas de hidrógeno y de deuterio.

Los mejores rendimientos se obtuvieron trabajando con columnas de Pd sobre alúmina α sinterizada. Con una columna de este tipo, de unos 2 l de capacidad total, se construyó un aparato de ensayo, de reducido volumen muerto, que permite producir 1 l de D_2 puro en unos 12 min, partiendo de una mezcla de 50 % de D_2 y 50 % de H_2.

Para el estudio teórico, los autores asimilan en primera aproximación la cromatografía a un fraccionamiento en contracorriente y desprecian la resistencia superficial opuesta al intercambio así como la difusión longitudinal y lateral. Gráficamente o mediante cálculos, se determina el número de platos teóricos necesario para obtener un enriquecimiento dado de la fase gaseosa, lo que permite comparar la eficacia de las columnas caracterizadas por diferentes masas de paladio.

Difusión térmica

Con el propósito de asegurar la separación de los isótopos del hidrógeno, los autores proyectaron una instalación de difusión térmica de acero inoxidable, enteramente accionada a distancia. La cascada de separación se compone de dos pares idénticos de columnas provistas de un alambre central calentado. Cada uno de los pares puede funcionar aisladamente o bien pueden conectarse mediante un termosifón. El alambre se mantiene a una temperatura del orden de los 1 000 °C mediante una corriente eléctrica rectificada.

Partiendo de un gas inicial conteniendo 32 ppm se obtuvieron con esta instalación muestras de hidrógeno con un contenido isotópico de deuterio inferior a 0,5 ppm. Asimismo se pudo preparar tritio de 99,3 % partiendo de un gas con 6 % de tritio.

Para la separación cuantitativa del xenón enriquecido cinco veces en ^{124}Xe por difusión térmica se han construido dos cascadas idénticas de cinco columnas que funcionan en paralelo y están comunicadas por termosifón o bien por un tubo capilar unido a un oscilador térmico de gas. El alambre central de volframio trabaja a 1 200 °C.

Las columnas están agrupadas de la misma manera que el haz tubular de un intercambiador de calor, en una vaina de 30 cm de diámetro por la que circula el agua de refrigeración. Se está estudiando la posibilidad de aumentar el factor de separación de la cascada recurriendo a un gas auxiliar.

Intercambio isotópico

Se ha realizado una serie de experimentos a fin de determinar el factor de separación isotópica entre una amalgama de litio y un solvente orgánico que contiene una sal de litio. Los autores estudiaron la influencia de los diversos parámetros que pueden intervenir en este intercambio, a saber : la naturaleza del solvente (se ha ensayado la dimetilformamida y el tetrahidrofurano), la temperatura, la concentración y la índole del halógeno asociado.

Se han estudiado asimismo las soluciones Li metálico - NH_3 líquido, realizándose cierto número de ensayos a fin de comprobar si existe una diferencia entre la composición isotópica del Li presente en las dos capas líquidas que se obtienen al disolver el Li metálico en amoníaco. No se observó ninguna diferencia entre esas razones isotópicas del Li. Lo mismo ocurrió con una capa de Li en NH_3 líquido y una capa de LiI en el mismo disolvente.

Electromigración

La electromigración en contracorriente en sales fundidas constituye una técnica de enriquecimiento isotópico sumamente eficaz. Se aplica con éxito para separar isótopos de elementos de carácter metálico muy pronunciado. En el caso de los metales alcalinos, se han podido obtener pequeñas cantidades de ^{7}Li istotópicamente pura. Para el potasio, los factores de enriquecimiento alcanzados son del orden de 10. En lo que respecta a los metales alcalinotérreos, con el mismo método se han obtenido pequeñas cantidades de calcio enriquecido cinco veces en ^{46}Ca. Sin embargo, la aplicación de este procedimiento en escala semiindustrial, tropieza con considerables dificultades tecnológicas.

Опытное производство стабильных изотопов

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ВВЕДЕНИЕ

Для развития работ с использованием стабильных изотопов в г. Тбилиси организована экспериментальная площадка по производству изотопов бора, азота, кислорода, углерода, неона, аргона, криптона и др. Разделение изотопов осуществляется методами дистилляции, химического обмена и масс-диффузии. Технологический цикл экспериментального производства включает также получение исходных продуктов для питания установок по разделению изотопов и синтез ряда соединений на основе изотопов бора, азота, кислорода и др.

Рис. 1. Общий вид производственного корпуса с башенной частью

Основным сооружением опытного производства является пятнадцатиэтажная башня высотой 63 *м*. В ней по вертикали размещаются разделительные установки колонного типа, а на этажах — масс-диффузионные каскады, вспомогательная и контрольная аппаратура. Значительная высота башни позволяет располагать отдельные колонны каскада друг над другом и таким образом осуществлять массообмен между колоннами через дозирующие устройства. Такая система регулирования потоков является простой и значительно повышает эксплуатационную надежность разделительных установок.

К башенной части здания примыкает четырехэтажный корпус. В корпусе размещены: центральная пультовая, в которой сосредоточены системы автоматического управления разделительными процессами; установки по получению исходных продуктов; установки по переработке обогащенного сырья, а также лаборатории контроля изотопного состава и химического анализа.

Общий вид производственного корпуса с башенной частью показан на рис. 1.

ПРОИЗВОДСТВЕННЫЙ ЦИКЛ ПО ПОЛУЧЕНИЮ ИЗОТОПОВ B^{10} И B^{11}

Общая схема технологического процесса, на которой показана взаимосвязь между отдельными циклами, представлена на рис. 2. Технологический процесс включает:

1) получение трехфтористого бора BF_3 и его комплекса с диметиловым эфиром $(CH_3)_2O \cdot BF_3$;

2) разделение изотопов бора методами обменной дистилляции $(CH_3)_2O \cdot BF_3$ и дистилляции BF_3;

3) переработку обогащенного продукта в элементарный бор, борную кислоту и другие соединения.

Трехфтористый бор получается кислотным методом (установка *1*) по реакции

$$6KBF_4 + B_2O_3 + 6H_2SO_4 = 8BF_3 + 6KHSO_4 + 3H_2O$$

Содержание BF_3 в продукте 99%. Основные примеси — SO_2, SO_3, SiF_4. Часть BF_3 по-

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ступает на питание колонны по разделению изотопов бора низкотемпературной дистилляцией BF_3 (установка *4*), оставшееся количество BF_3 подается в установку *2*, где синтезируется его комплекс с диметиловым эфиром. Отходы процесса получения BF_3 нейтрализуются в аппарате *3* и сбрасываются.

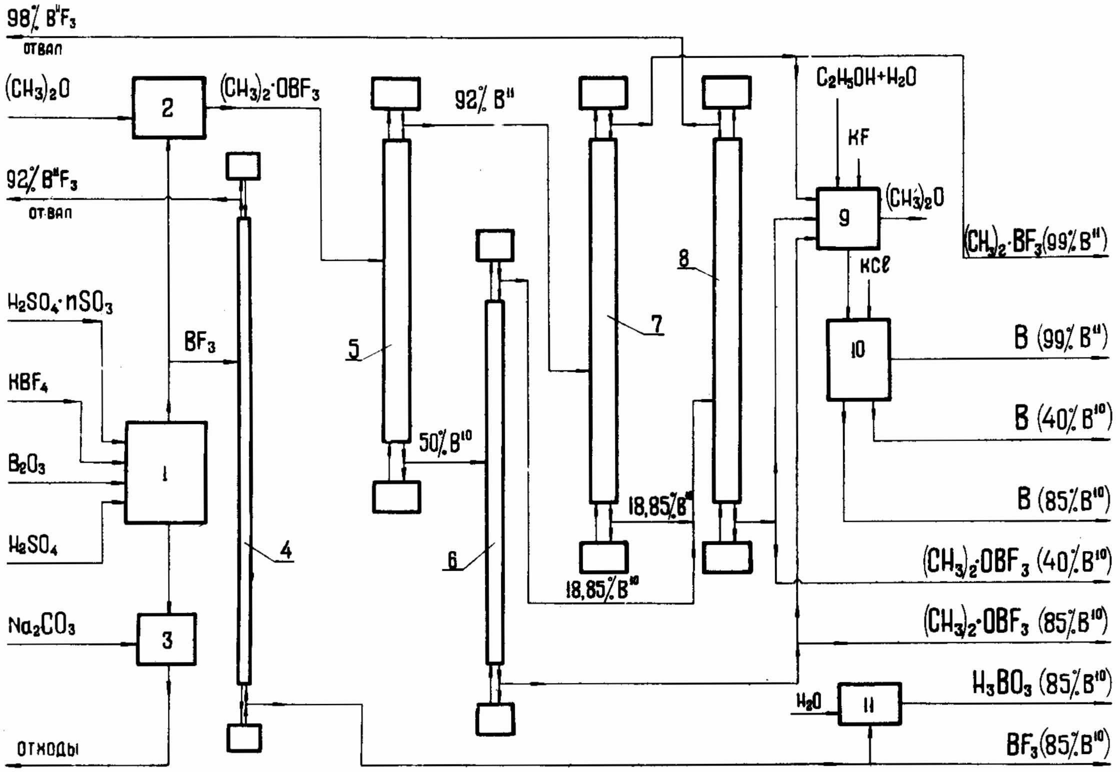

Рис. 2. Схема производственного цикла по получению соединений на основе B^{10} и B^{11}:

1 — установка для получения трехфтористого бора; *2* — установка для получения комплекса трехфтористого бора с диметиловым эфиром; *3* — нейтрализатор отходов; *4* — установка для получения 85% B^{10} дистилляцией трехфтористого бора; *5*, *6* — первая и вторая колонны каскада для получения 85% B^{10} обменной дистилляцией комплекса; *7* — колонна для получения 99% B^{11} обменной дистилляцией комплекса; *8* — колонна для получения 40% B^{10} обменной дистилляцией комплекса; *9* — аппарат для получения тетрафторбората калия; *10* — электролизер; *11* — аппарат для получения борной кислоты

Для получения изотопов бора (B^{10} и B^{11}) сооружена группа установок, состоящая из трех разделительных каскадов *5*, *7*, *8* по получению бора методом обменной дистилляции комплекса $(CH_3)_2O \cdot BF_3$ [1, 2] и колонны *4* по разделению изотопов бора методом дистилляции BF_3 [3–5].

Питанием колонны *7* служит поток отвала с колонны *5*, а потоки отвала из колонн *6* и *7* поступают на питание колонны *8*. Основные расчетные параметры установок представлены в таблице.

Отличительной особенностью установок дистилляции комплекса по сравнению с установками дистилляции BF_3 является малая величина допустимой плотности орошения жидкости, обусловленная ограничением величины перепада давления в колоннах из-за термической нестабильности комплекса при повышенных температурах. С этим же связана и необходимость проведения дистилляции комплекса при пониженном давлении — давление в конденсаторах колонн поддерживается равным 150 *мм рт. ст.* В дальнейшем на одной из колонн путем термической стабилизации комплекса фтористым метилом будет повышено рабочее давление, а соответственно и плотность орошения. Производительность установки повысится приблизительно на 70%.

Представляется целесообразным в дальнейшем повышать плотность орошения и соответственно производительность на установках по дистилляции BF_3 путем увеличения давления в колоннах. В этом случае предельная плотность орошения ограничена лишь точкой захлебывания, величина которой с повышением давления возрастает. Возможное увеличение производительности при этом определится характером за-

Параметры установок для получения изстопов бора

Метод разделения	Установка		Насадка	Диаметр колонн, *мм*	ВЭТС	Длина колонны, *м*		Плотность орошения потока жидкости в *см³/мин* на 1 *см²* сечения колонны	Плотность орошения в *г* B на 1 *см²* сечения колонны в 1 *мин*	Концентрация B^{10}, %		Перепад давления, *мм рт. ст.*	Потоки, *моль/сутки*			Производительность по B *кг/год*
						секция обогащения	секция извлечения			секция обогащения	секция извлечения		отбор	отвал	питание	
Обменная дистилляция $(CH_3)_2O\cdot BF_3$	Каскад для получения 85% B^{10}	Первая колонна	Треугольные спирали 3,5×3,0 *мм*	128	7,2	11,88	9,72	1,27	0,140	50	8	140	16,2	49,8	66	25
		Вторая колонна	Треугольные спирали 3,2×2,8 *мм*	70	5,5	11,94	10,18	1,30	0,143	85	18,85	160	6,85	18,15	15	
	Колонна для получения 99% B^{11}		Треугольные спирали 3,5×3,0 *мм*	128	7,2	15	8	1,27	0,140	1	18,85	150	21,52	13,89	35,41	86
	Колонна для получения 40% B^{10}		Треугольные спирали 3,5×3,0 *мм*	128	7,2	6,34	16,42	1,18	0,130	40	2	148	13,8	12,5	26,3	50
Дистилляция BF_3	Колонна для получения 85% B^{10}		Колпачковая	57	3,5	22,33	9,33	8	1,92	85	8	350	10,23	62,36	72,59	35

висимости коэффициента обогащения от температуры. Эта зависимость [6] приведена на рис. 3. Как было установлено, ε слабо зависит от температуры, в связи с чем целесообразно осуществить процесс дистилляции BF_3 при давлении 3—5 *ат*. Это обстоятельство может привести к увеличению производительности установки на 40—60%. В таблице приведены основные данные установки по дистилляции BF_3 в условиях рабочего давления 1 *ат*.

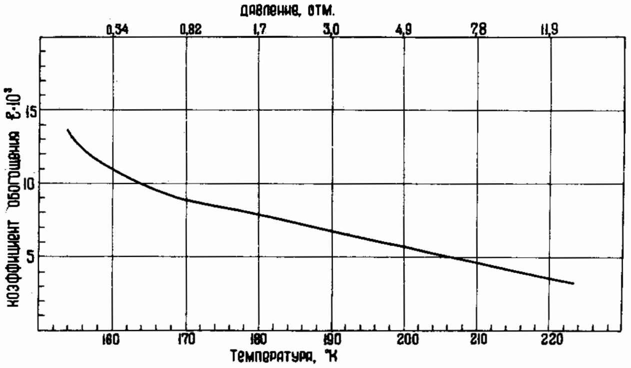

Рис. 3. Зависимость коэффициента обогащения изотопов бора при дистилляции BF_3 от температуры

При разработке разделительных установок значительное внимание было уделено не только исследованию эффективности существующих насадочных систем, но и созданию новых. Учитывая, что на установках колонного типа большого диаметра (более 30 *мм*) практически невозможно произвести предварительное смачивание насадки, были созданы новые насадочные системы относительно высокой эффективности, которые не требуют предварительного смачивания.

В колоннах дистилляции комплекса насадочная система состоит из слоев треугольных спиралей с высотой каждого слоя около 1 *см* и капиллярных прокладок, представляющих собой полосы перегнутой вдвое сетки [7]. Сверху каждого слоя спиралей располагается ряд прокладок. Эффективность этой насадочной системы определена при дистилляции комплекса на колоннах диаметром 47, 74 и 128 *мм*. Полученные величины ВЭТС приведены на рис. 4.

В колоннах дистилляции BF_3 применена колпачковая насадка [8], изготовленная из двойной сетки. Элементы этой насадки имеют вид колпачков с четырьмя острыми зубцами. Насадка изготовляется путем продавливания кусков перегнутой пополам сетки через круглое отверстие. Насадка не требует предварительного смачивания. На рис. 5 представлена зависимость эффективности от плотности орошения при работе без предварительного смачивания для колпачковой и треугольной насадки с прокладками и без прокладок. Определение ВЭТС проведено на колонне диаметром 94 *мм*. Рабочим веществом являлась смесь бензол — четыреххлористый углерод. Как видно на рис. 5, минимальные значения ВЭТС и перепада давления на единицу высоты достигаются для колпачковой насадки. В основу расчета параметров установки дистил-

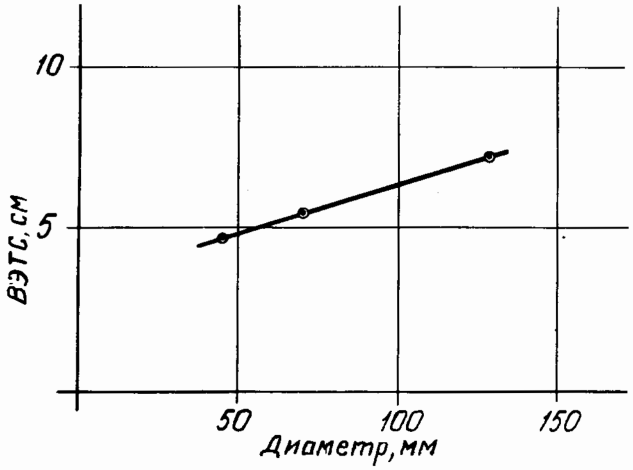

Рис. 4. Зависимость высоты эквивалентной теоретической ступени от диаметра колонны для насадочной системы из отрезков треугольной спирали и капиллярных прокладок

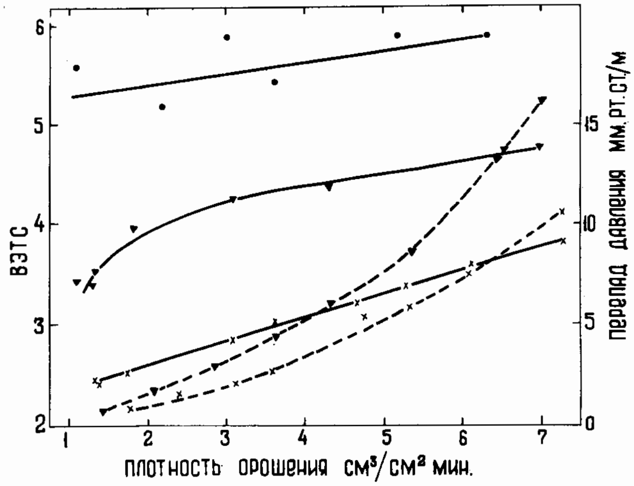

Рис. 5. Эффективиость различных насадок при работе без предварительного смачивания:

● — отрезки треугольной спирали 3,0 × 2,4; ▲ — та же насадка с капиллярными прокладками; x — колпачковая насадка 4,5/2,8 из двойной сетки (пунктирные кривые относятся к перепаду давления) ляции BF_3 (см. таблицу) положены характеристики колпачковой насадки, представленные на рис. 5.

Полученные на установках обогащенные продукты $(CH_3)_2O \cdot B^{10}F_3$ и $(CH_3)_2O \cdot B^{11}F_3$ перерабатываются в элементарный бор (аппараты *9*, *10* на рис. 2) электролизом расплава [1] смеси KCl и KBF_4. Выход продукта 80%. Содержание бора в продукте 92—98%. Кроме широкого использования $B^{10}F_3$ в нейтроннофизических исследованиях, а также в приборах для регистрации нейтронов, он является сырьем для получения борной кислоты, меченной изотопом. Борная кислота получается гидролизом BF_3 (аппарат *11* на рис. 2) по реакции

$$4BF_3 + 3H_2O = 3HBF_4 + H_3BO_3$$

и последующим разложением борфтористоводородной кислоты

$$HBF_4 + 2CaCO_3 + H_2O = 2CaF_2 + H_3BO_3 + 2CO_2$$

ПРОИЗВОДСТВЕННЫЙ ЦИКЛ ПОЛУЧЕНИЯ N^{15} И O^{18}

Общая схема цикла представлена на рис. 6.

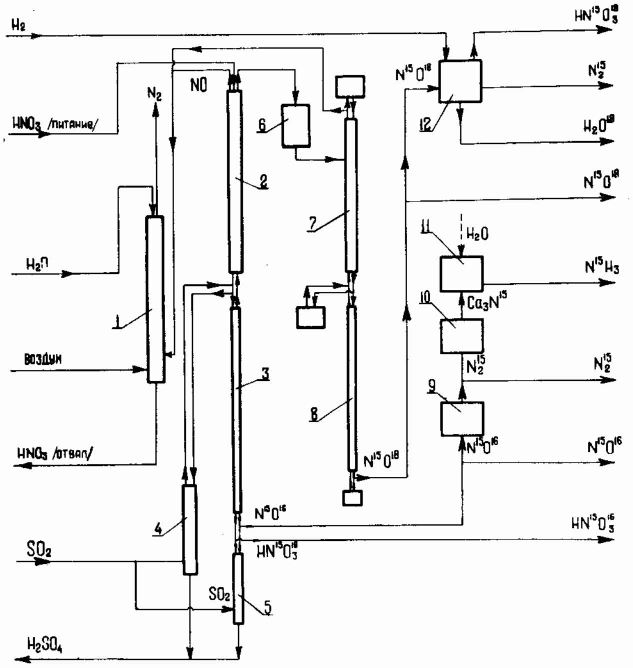

Рис. 6. Схема производственного цикла по получению соединений, меченных N^{15}:

1 — абсорбер окислов азота; *2*, *3* — первая и вторая колонны каскада для получения N^{15} методом химического обмена; *4*, *5* — система возврата фазы; *6* — аппарат для очистки окиси азота; *7*, *8* — первая и вторая колонны каскада для получения N^{15} и O^{18} методом дистилляции; *9* — аппарат для восстановления окиси азота; *10*, *11* — аппарат для синтеза и гидролиза нитрида кальция; *12* — система для получения воды и азотной кислоты из окиси азота

Цикл включает:

1) разделительные установки;
2) установки по переработке обогащенного продукта.

Для получения тяжелого изотопа азота используются два процесса: химический обмен в системе окись азота — азотная кислота [9–12] и низкотемпературная дистилляция окиси азота [13–15].

Как известно, при дистилляции одновременно с тяжелым изотопом азота можно получить также тяжелый изотоп кислорода O^{18} и частично концентрированный изотоп O^{17}.

Несмотря на то что процесс получения N^{15} методом химического обмена является достаточно простым и легко осуществляется в промышленном масштабе, он обладает и рядом существенных недостатков, основными из которых являются: большая величина расхода сернистого ангидрида и соответственно образование большого количества серной кислоты в системе возврата фазы установки. Затраты на обращение фазы составляют большую часть общих затрат процесса.

В связи с тем что процесс низкотемпературной дистилляции технологически несколько сложнее процесса химического обмена, первоначально сооружена химобменная установка. В последующем основная часть производства N^{15} будет осуществляться методом дистилляции окиси азота. Схема химобменной каскадной установки по получению N^{15} представлена на рис. 6.

Диаметры первой *2* и второй *3* колонн каскада 120 и 26 *мм*, длины насадочной части колонн 17,0 и 17,8 *м*. Насадочная система первой колонны — треугольные спирали с размером элемента 2,5 × 2,5 *мм*, через каждый сантиметр расположены слои сетчатых прокладок; насадка второй колонны — треугольные спирали с размером элемента 2,3 × 2,3 *мм*. Потоки орошения первой и второй колонн 400 и 16 $см^3/мин$ 10 *М* азотной кислоты соответственно.

Концентрация в точке перехода от первой ко второй колонне каскада $C_{к1}$, а следовательно, и длины колонн определены из условия минимума времени установления стационарного состояния каскада. Результаты расчета в виде зависимости времени достижения концентрации $C_{к2} = 98\%$ N^{15} на конце второй колонны от величины концентрации $C_{к1}$ на конце первой колонны приведены на рис. 7. Расчет выполнен для двух значений высоты эквивалентной теоретической ступени первой колонны $h_1 = 12$ и 20 *см*.

Как видно из рис. 7, кривая, характеризующая эту зависимость, имеет пологий минимум в области значений $C_{к1} = 10 \div 30\%$. При уменьшении $C_{к1}$ ниже 5% время установления резко возрастает. Изотоп N^{15} получается в виде окиси азота, азотной кислоты, свободного азота и аммиака. Процесс получения аммиака состоит из трех стадий (см. рис. 6):

1) восстановления окиси азота до свободного азота (аппарат *9*);
2) синтеза нитрида кальция (аппарат *10*);
3) гидролиза нитрида кальция (аппарат *11*).

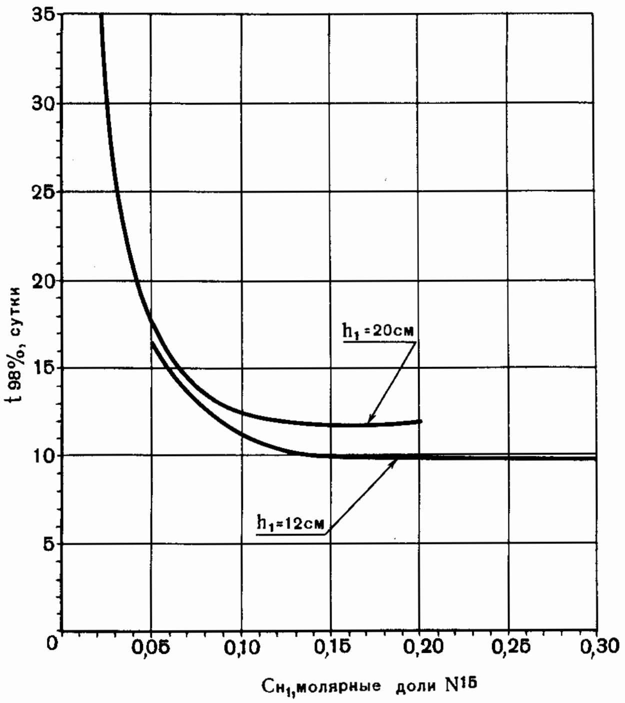

Рис. 7. Зависимость времени достижения концентрации $C_{к2}$ 98% N^{15} на конце второй колонны от величины концентрации в точке перехода $C_к$ при высоте ступени первой колонны h_1 = 20 и 12 см

Содержание аммиака в продукте 99,9%. Основные примеси N_2, H_2, H_2O, выход 95%. На основе окиси азота, обогащенной изотопами N^{15} и O^{18}, предусматривается выпуск тяжелокислородной воды H_2O^{18} и азотной кислоты $HN^{15}O_3{}^{18}$.

МАСС-ДИФФУЗИЯ

Для получения целого ряда высокообогащенных изотопов, требующихся в небольших количествах, предполагается сооружение двух каскадов, одного из 120 масс-диффузионных элементов и второго — из 30 масс-диффузионных колонок. Аналогичные установки при длительной их эксплуатации и в лабораторных условиях показали высокую надежность и стабильность работы[16, 17]. Основными видами изотопной продукции, получаемой на масс-диффузионных установках, будут изотопы неона Ne^{21}, Ne^{22}, Ne^{20}, углерода C^{13}, аргона Ar^{36}, Ar^{38}, криптона Kr^{86} и др. В качестве исходного сырья будет использоваться природная смесь изотопов. На масс-диффузионных каскадах также будет производиться дообогащение изотопов, полученных методом химического обмена и дистилляции до сверхвысоких концентраций. Производительность каждой из установок, рассчитанная по Ne^{22} с концентрацией 95—99%, примерно 200 *г/год*.

КОНТРОЛЬ ИЗОТОПНОГО И ХИМИЧЕСКОГО СОСТАВА

Изотопный состав соединений на основе изотопов бора измеряется двумя методами: ядерно-магнитным резонансом и масс-спектрометрическим. При этом пробы с установок обменной дистилляции комплекса в виде $(CH_3)_2O \cdot BF_3$ измеряются методом ядерно-магнитного резонанса, а с установки дистилляции трехфтористого бора в виде BF_3 масс-спектрометрическим методом.

Изотопный состав соединений на основе N^{15} измеряется масс-спектрометрическим методом[18] в виде соединений NO и N_2.

Химическими методами систематически контролируется чистота исходных и конечных продуктов.

СИСТЕМА АВТОМАТИЧЕСКОГО УПРАВЛЕНИЯ ТЕХНОЛОГИЧЕСКИМИ ПРОЦЕССАМИ

Система автоматического управления предприятием должна осуществлять оптимальное регулирование всех технологических процессов. Оптимизация должна происходить по таким параметрам, как концентрация ценного изотопа в конечном продукте разделительных установок, максимальная производительность, экономичность и др. Эти функции должна выполнять управляющая электронно-вычислительная машина, работающая совместно с автоматическим оптимизатором и электронной моделью разделительных колонн. Функциональная схема системы автоматического управления предприятием приведена на рис. 8.

Автоматическое регулирование установок разделения и установок получения исходных и конечных продуктов осуществляется соответствующими пультами управления при помощи датчиков Д, контролирующих технологический процесс, и исполнительных механизмов ИМ.

Общее управление осуществляет электронно-вычислительная машина. Она производит «опрос» датчиков, после чего данные поступают в автоматический оптимизатор, и совместно с управляющей машиной и электронной моделью вырабатывается программа регулирования. Реализация этой программы происходит посредством командного устройства, которое посылает необходимые команды соответствующим пультам автоматического регулирования.

Для контроля технологических процессов и работы системы автоматического регулирования служит диспетчерский пульт. Кроме того, при помощи диспетчерского пульта осуществляется ввод дополнительных данных и изменение режима установок.

Полная система автоматического управления предприятием реализуется в два этапа. Первый этап — создание пультов автоматического управления отдельными установками — включает разработку специальных датчиков, регуляторов и исполнительных механизмов. Второй этап — создание автоматического оптимизатора, электронной модели и командного устройства, которые совместно с управляющей электронно-вычислительной машиной осуществят полную автоматизацию предприятия.

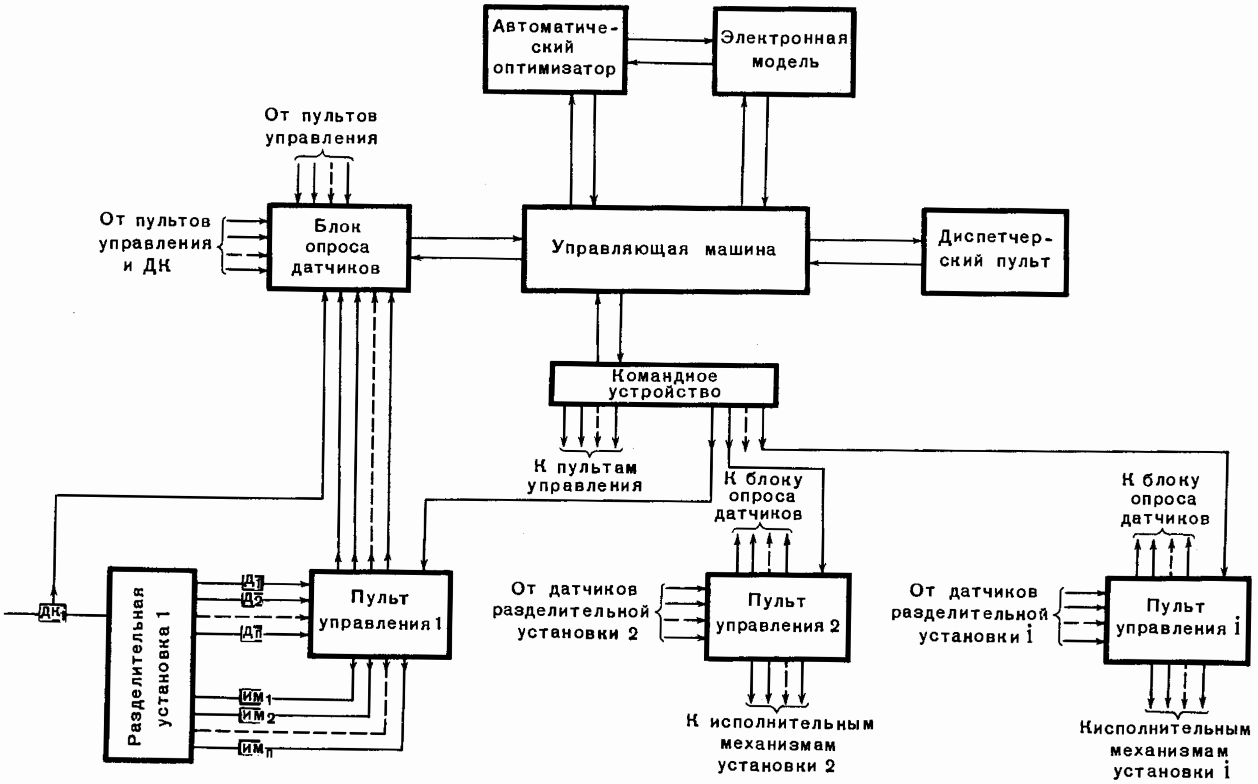

Рис. 8. Функциональная схема системы автоматического управления предприятием.

В настоящее время осуществлен первый этап автоматизации — созданы пульты автоматического управления процессов разделения изотопов. Регулирование этих процессов ведется по гидродинамическим параметрам установок. Это потребовало решения ряда вопросов, связанных с измерением и регулированием малых потоков агрессивных жидкостей, относительно малых потоков газа, регулирования положения зон реакции в установках, работающих по методу химического обмена, и пр. Разработаны расходомеры малых потоков жидкостей и газов, специальные исполнительные механизмы для прецизионного регулирования потоков, устройство для регулирования потоков жидкостей, насыщенных растворенными в них газами, и другие устройства. Особое внимание уделено надежности и точности регулирования. Электронные регуляторы полностью бесконтактны и собраны на транзисторах и магнитных элементах.

Регуляторы потоков жидкостей, а также регуляторы потоков газов обеспечивают регулирование с погрешностью, не превышающей ± 1,5%, причем основная часть ошибки приходится на расходомеры (погрешность самих регуляторов не более ± 0,4%).

Регулирование положения зон реакции в реакторах осуществляют самонастраивающиеся регуляторы, которые автоматически выбирают необходимый режим работы. Регуляторы циркуляции в дистилляционных колоннах обеспечивают ее поддержание в зависимости от уровня жидкости в испарителе. Регуляторы других параметров обеспечивают их регулирование[19] с погрешностью, не превышающей ± 1%. Система автоматического регулирования разделительных процессов включает аварийную и предупредительную сигнализацию. Учитывая особую важность надежности сигнализационных устройств, разработана система с полной самопроверкой.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/388 USSR

Experimental production of stable isotopes

By I. G. Gverdtsiteli *et al.*

With a view to developing work on the use of stable isotopes, a pilot plant for the production of isotopes of boron, nitrogen, oxygen, carbon, neon, argon, krypton and other elements has been built in Tiflis.

The basic experimental data and general technological flowsheet for the plant are presented in the paper.

Operations began with the production of the boron isotopes ^{10}B and ^{11}B and the heavy isotope of nitrogen ^{15}N.

Two methods are used to separate the boron isotopes: low-temperature distillation of boron trifluoride and exchange distillation of its dimethyl ether complex. Flowsheets and parameters of columns designed to produce 25 kg/year of ^{10}B are described.

The nitric oxide-nitric acid exchange process is used to separate the nitrogen isotopes. Flowsheets and parameters of columns designed to produce 4.5 kg/year of ^{15}N are described.

The automatic control system is also described; this includes a number of special sensing elements, actuating mechanisms and governors.

Next, the production of the isotopes ^{18}O and ^{15}N is envisaged by the low-temperature distillation of nitric oxide, and that of ^{22}Ne, ^{36}Ar, ^{13}C and ^{86}Kr by diffusion through a current of steam.

Finally, an account is given of the results obtained experimentally and by theoretical calculations.

A/388 URSS

Production expérimentale d'isotopes stables

par I. G. Gverdtsiteli *et al.*

En vue de développer l'utilisation d'isotopes stables, on a construit à Tbilissi une installation pour la préparation d'isotopes du bore, de l'azote, de l'oxygène, du carbone, du néon, de l'argon, du krypton et d'autres éléments.

Le mémoire présente les principales données expérimentales et le schéma de principe général de l'installation.

L'exploitation a commencé avec la production des isotopes ^{10}B et ^{11}B du bore et de l'isotope lourd de l'azote ^{15}N.

La séparation des isotopes du bore est faite par deux méthodes : distillation à basse température du trifluorure de bore et distillation d'échange du complexe du trifluorure de bore avec le diméthyléther. On donne le schéma de principe et les paramètres des colonnes permettant de produire 25 kg de bore 10 par an.

La séparation des isotopes de l'azote est réalisée par la méthode de l'échange chimique dans le système oxyde d'azote-acide nitrique. On donne le schéma de principe et les paramètres d'une installation dont la capacité de production est de 4,5 kg d'azote 15 par an.

On décrit le système de régulation automatique comprenant une série de sondes spéciales, de mécanismes de commande et de régulateurs.

On envisage de produire ensuite ^{18}O et ^{15}N par une méthode de distillation à basse température d'oxyde

d'azote, et les isotopes ^{22}Ne, ^{36}Ar, ^{13}C, ^{86}Kr et d'autres par la méthode de diffusion à contre-courant de vapeur.

On décrit les résultats des travaux expérimentaux et des calculs théoriques.

A/388 URSS

Producción experimental de isótopos estables

por I. G. Gverdtsiteli *et al.*

Con objeto de fomentar la utilización de isótopos estables se ha construido en Tiflis, una planta piloto para producir los isótopos del boro, nitrógeno, oxígeno, carbono, neón, argón, criptón y otros elementos.

En la memoria se exponen los datos básicos experimentales y los diagramas de circulación generales de la instalación.

Las operaciones comenzaron con la producción de los isótopos del boro, ^{10}B y ^{11}B, y del isótopo pesado del nitrógeno, ^{15}N.

La separación de los isótopos del boro se realiza por dos procedimientos : destilación a baja temperatura del trifluoruro de boro y destilación de intercambio del complejo de trifluoruro de boro con eter dimetílico. Se dan los diagramas de circulación y los parámetros de las instalaciones destinadas a producir 25 kg de boro-10 al año.

La separación de los isótopos del nitrógeno se realiza por el método de intercambio químico en el sistema óxido de nitrógeno-ácido nítrico. Se dan los diagramas de circulación y los parámetros de las instalaciones destinadas a producir 4,5 kg de nitrógeno-15 al año.

Se describe un sistema de control automático que contiene una serie de transductores especiales, mecanismos de acción y reguladores.

Se considera la producción de los isótopos ^{18}O y ^{15}N por el método de destilación a baja temperatura del óxido nítrico, y de los isótopos ^{22}Ne, ^{36}A, ^{13}C, ^{86}Kr y otros, por el método de difusión en contracorriente de vapor.

Se presentan los resultados de los trabajos experimentales y de los cálculos teóricos.

La producción de isótopos estables en España

por M. M. Urgell *, J. Iglesias *, J. Casas **, J. M. Savirón ** y M. Quintanilla ***

La producción de isótopos estables ha adquirido gran interés en los últimos años, y España, a través de la JEN, ha desarrollado un programa de trabajo para la separación de diversos isótopos estables por cromatografía de intercambio iónico y por difusión térmica. El primer método se está aplicando en el Centro de Energía Nuclear « Juán Vigón » de Madrid y el segundo en el Departamento de Física de la Facultad de Ciencias de la Universidad de Zaragoza.

Dentro del primer grupo se ha estudiado la separación de los isótopos ^{14}N y ^{15}N, ^{10}B y ^{11}B, describiéndose las experiencias llevadas a cabo para la determinación del factor de separación por el método del punto de ruptura. Los valores hallados para el factor de separación $(^{15}N/^{14}N)_R/(^{15}N/^{14}N)_S$ utilizando soluciones de hidróxido amónico oscilan entre 1,028 y 1,002 según las condiciones experimentales; por el contrario, el cloruro y el acetato amónico dan valores muy próximos a la unidad.

En el caso del boro y usando soluciones de ácido bórico se ha obtenido un factor de separación $(^{11}B/^{10}B)_R/(^{11}B/^{10}B)_S$ igual a 1,035–1,027 (según la concentración), siendo del mismo orden los obtenidos con los complejos de manita (1,024) y glicerina (1,027). Utilizando borato sódico el factor de separación difiere muy poco de la unidad.

Queda confirmado que, tanto en el caso del nitrógeno como del boro, para obtener factores de separación elevados es necesario emplear compuestos de estos elementos que estén poco ionizados en solución. Aplicando la técnica cromatográfica de desarrollo por desplazamiento se ha conseguido obtener nitrógeno-15 enriquecido del 24,3 % y boro-10 del 61,0 % partiendo siempre de la composición normal (0,365 % y 20,0 % respectivamente). Se ha diseñado y construido una planta piloto de control automático y de funcionamiento continuo con la que se espera alcanzar enriquecimientos más elevados.

En relación con los estudios de difusión térmica se investiga la separación de los distintos isótopos de los gases nobles y del oxígeno, nitrógeno y carbono-13, a través de los siguientes aspectos: *a*) correlación entre las predicciones teóricas y los resultados experimentales en diversos tipos de columnas, en relación con el diseño de plantas de separación en condiciones óptimas de rendimiento; *b*) determinación en columna cilíndrica de factores de difusión térmica de mezclas isotópicas y binarias con objeto de determinar si un gas puede actuar como « gas filtro » en una mezcla isotópica; *c*) distribución, en columnas de difusión térmica, de mezclas multicomponentes, para la separación de isótopos de masas intermedias, utilizando en cada caso gases que actúen como « filtros ».

INTERCAMBIO IÓNICO

Factores de separación

Nitrógeno

Las experiencias se han llevado a cabo en columna utilizando resina Dowex 50W, X-12, 100-200 mallas y soluciones de hidróxido, cloruro y acetato amónico. El factor de separación se ha calculado a partir de los datos experimentales por aplicación de la fórmula simplificada (1) según el método del punto de ruptura [1]:

$$\varepsilon = \sum_{i=1}^{i=m} \frac{V_i C_i (R_0 - R_i)}{Q R_0} \qquad (1)$$

siendo el factor de separación $K = 1 + \varepsilon$; y en donde V_i = volumen recogido en la fracción *i* (ml); C_i = concentración de ión amonio en la fracción *i* (meq/ml); R_0 = relación $^{15}N/^{14}N$ normal; R_i = relación $^{15}N/^{14}N$ en la fracción *i*; Q = capacidad total de cambio de la columna de resina.

En la tabla 1 se dan los valores hallados para el factor de separación $K = (^{15}N/^{14}N)_R/(^{15}N/^{14}N)_S$, empleando solución de hidróxido amónico de diferentes concentraciones y a velocidades de flujo distintas.

La variación de la relación isotópica del nitrógeno

Tabla 1. Factor de separación de los isótopos de nitrógeno

Compuesto en solución	Concentración (equiv./litro)	Velocidad (ml/cm² min)	Factor de separación
NH_4OH	1	0,98	1,0281
NH_4OH	0,1	1,16	1,0256
NH_4OH	1	4,74	1,0272
NH_4OH	0,1	5,22	1,0223

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($^{15}N/^{14}N$) en función de la concentración de ión amonio

$$\sum_{i=1}^{i=m} V_i C_i / Q$$

en el efluyente de la columna está representada en la figura 1 para una solución alimentadora de hidróxido amónico $1N$ y $0{,}1N$ a diferentes velocidades de flujo. La relación isotópica de la primera fracción recogida disminuye con la velocidad de flujo, o sea, el enriquecimiento frontal en ^{14}N es más elevado a velocidades de flujo lentas. Igual ocurre al considerar la concentración de la solución alimentadora; para una concentración más baja, el enriquecimiento en ^{14}N de la primera fracción recogida es superior. En estas experiencias con hidróxido amónico el volumen de las primeras fracciones efluyentes recogidas fué de 25 ml tanto en el caso de la solución $1N$ como en el de $0{,}1N$. Aparte de otras posibles consideraciones, es lógico que el enriquecimiento en ^{14}N sea superior en el caso de la solución $0{,}1N$ pues existe un gradiente en la relación isotópica y el número de miliequivalentes recogidos en el mismo volumen de efluyentes es muy superior en el caso de la solución concentrada.

Se realizaron también varias experiencias utilizando soluciones $1N$ y $0{,}1N$ de cloruro amónico y acetato amónico, pero la composición isotópica frontal de la primera fracción recogida era casi igual a la composición normal de los isótopos de nitrógeno a diferencia de lo que ocurría en el caso del hidróxido. Mayor información sobre este particular y sobre los factores de separación se encuentran en otro trabajo [2] de los autores. El anión hidroxilo, para una separación de los isótopos de nitrógeno por intercambio iónico es muy superior al cloruro y acetato, de tal manera que estos dos últimos deben ser desechados para este objeto.

Boro

Con objeto de encontrar las condiciones experimentales más convenientes, para llevar a cabo la separación de los isótopos ^{10}B y ^{11}B por cambio iónico, se ha realizado la determinación de factores de separación para diversos sistemas. En particular, se ha estudiado el comportamiento de las disoluciones de ácido bórico frente a las resinas aniónicas « Dowex-1 » y « Dowex-2 ». En disoluciones concentradas de este ácido aparecen aniones complejos con varios átomos de boro [3]. Para poner de manifiesto la influencia de éstos sobre el factor de separación, se han realizado determinaciones del mismo a diversas concentraciones. Los restantes sistemas estudiados fueron: disoluciones de ácidos glicero-bórico y manito-bórico, de ácido fluobórico y, por último, de borato sódico; en todos los casos, frente a resinas aniónicas fuertemente básicas.

El método de determinación fué análogo al seguido en el caso del nitrógeno, y se describe con detalle en [4].

En las figuras 2 y 3 se representa, para algunas de las experiencias realizadas, la variación de la composición isotópica con la cantidad de boro recogida en el efluyente a partir del punto de ruptura.

Los valores del factor de separación obtenidos se resumen en la tabla 2. En la misma se indican las condiciones de cada experiencia, así como la relación entre la cantidad total del boro fijado y la capacidad de la columna. Este valor, que representa el número medio de átomos de boro retenidos por cada punto activo de resina, es función de la concentración de la disolución correspondiente. Como en el cálculo del factor de separación interviene directamente la capacidad de cambio de la resina, se ha tomado ésta referida al ión cloruro, con objeto de tener una base firme de referencia.

Examinando los resultados de la tabla 2, se observa que hay una disminución apreciable en el factor de separación, al pasar del ácido bórico a sus complejos con polialcoholes; disminución que parece estar en relación inversa con la establilidad del complejo.

El factor de separación para borato sódico es prácticamente igual a la unidad y despreciable frente a los obtenidos en los demás casos. De esto se deduce

Tabla 2. Factor de separación de los isotopos de boro

Resina	Disolución	Concentración (equiv./litro)	$\frac{\text{Cap. boro}}{\text{Cap. cloruro}}$	$K = \frac{(^{11}B/^{10}B)_S}{(^{11}B/^{10}B)_R}$
Dowex 1-X-8	BO_3H_3	0,1	2,40	1,0272
Dowex 1-X-8	BO_3H_3	0,03	1,72	1,0262
Dowex 1-X-8	BO_3H_3	0,015	1,51	1,0269
Dowex 1-X-8	BO_3H_3 + FH (1: 1)	0,1	—	1,0296
Dowex 1-X-2	BO_3H_3 + Manita (1: 1,5)	0,1	1,05	1,0224
Dowex 2-X-8	BO_3H_3	0,1	2,24	1,0285
Dowex 2-X-8	BO_3H_3	0,5	3,60	1,0354
Dowex 2-X-8	BO_3H_3 + Glicerina (1: 3).	0,1	1,82	1,0269
Dowex 2-X-8	BO_3H_3 + Manita (1: 1,2).	0,1	0,98	1,0245
Dowex 1-X-8	$B(OH)_4Na$	0,1	—	0,99995 ± 0,00004

que, para el ácido bórico, el enriquecimiento isotópico se debe a la reacción de intercambio:

$$^{10}BO_3H_3 + {}^{11}B(OH)_4^- \rightleftharpoons {}^{11}BO_3H_3 + {}^{10}B(OH)_4^-$$

Dada la semejanza formal de esta reacción con las de intercambio entre BF_3 y sus complejos, utilizadas en la separación de los isótopos de boro por intercambio químico [5], no es de extrañar la semejanza entre los factores de separación correspondientes. En ambos casos el ^{10}B tiende a concentrarse en el compuesto con boro tetracoordinado.

Experiencias de separación en columna

Nitrógeno

Se montaron en serie 10 columnas de vidrio Pyrex de 150 cm de altura y 5 cm de diámetro interno llenas con resina Dowex 50 W, X-12, 100-200 mallas forma hidrógeno. Se fijó una banda de 210 cm de ión amonio mediante el paso de hidróxido amónico 0,5N a través de dos columnas conectadas en serie a una velocidad de flujo de 30-32 ml/min.

Es un poco difícil distinguir visualmente el frente de la banda de ión amonio, pero es fácil de detectar por la elevación de la temperatura en la zona de transición. La elución con hidróxido sódico 0,6N provoca un desplazamiento de la banda de ión amonio y la separación en ella de los isótopos de nitrógeno, enriqueciéndose en cabeza el nitrógeno-14 y en cola el nitrógeno-15.

En la figura 4 se representa la composición isotópica de una banda de ión amonio después de haber recorrido 24 y 81 metros de columna, lo que equivale a tomar las muestras a la salida de la columna 16 y 54, considerando una longitud nominal de 150 cm. Sin embargo, hay que tener presente la contracción de volumen que experimenta la resina al pasar de forma hidrógeno a forma amonio, que se puede cifrar en 6,5 % y la manera de depositarse la resina forma hidrógeno en la columna después de un lavado en contracorriente que puede ocasionar pequeñas variaciones iniciales en la altura de la resina.

La curva correspondiente a 24 metros tiene una gran zona plana correspondiente a la concentración normal (0,365 %) y se alcanzó un enriquecimiento de nitrógeno-15 de 1,506 %. La curva de 81 metros no presenta ya zona plana y se logró obtener una concentración de nitrógeno-15 de 24,336 %. Se observó que, a medida que la banda de ión amonio se desplaza a lo largo de las columnas, disminuía ligeramente su longitud; en parte, debido a la toma de muestras y en parte, a una pequeña cantidad residual de ión amonio que permanecía en cola en la zona del ión sodio.

El frente en cabeza (H^+/NH_4^+) es fácil de identificar por el cambio a pH alcalino que experimenta el efluyente en el momento de transición, pero es conveniente tomar dos muestras, ya que la primera a veces no contiene suficiente cantidad de nitrógeno-15 para verificar el análisis isotópico. El frente de cola es fácil de identificar por el cambio de color de la resina pero es preciso tomar varias muestras sucesivas a pequeños intervalos para evitar pase desapercibido el máximo enriquecimiento.

Como la composición isotópica normal del nitrógeno es baja respecto al nitrógeno-15, es del mayor interés que no se pierda nada del mismo en la cola y, por ello, fué necesario comprobar la interacción entre la banda de ión amonio y la de hidróxido sódico eluyente. Para ello se procedió a valorar la concentración de ión amonio en la banda de hidróxido sódico a distintas longitudes y tomando como origen el punto de transición de una banda a otra. Las muestras se tomaron por el extremo inferior de una columna y se midió el avance de la zona de transición ión amonio – ión sodio en la columna siguiente. La experiencia se realizó en las columnas de vidrio descritas anteriormente, utilizando solución de hidróxido sódico 0,93N a una velocidad de flujo de 16 ml/min.

En la figura 5 se representa la concentración de ión amonio expresada en meq/litro en función de la distancia recorrida por la zona de separación NH_4^+/Na^+. Según se deduce de la gráfica, para conseguir una concentración inferior a 0,1 meq. HN_4^+/litro es necesario conservar en cola una banda de ión sodio superior a 75 cm. Teniendo en cuenta que la altura de las columnas es de 150 cm y que no es recomendable conectar más de tres columnas en serie en el desplazamiento de la banda, por la elevada pérdida de carga que se produciría, queda determinada una banda de ión amonio de 225 cm de longitud en la que se realizará la separación de los isótopos de nitrógeno. La longitud de la banda de ión sodio variará a lo largo de las columnas desde un valor máximo de 225 cm en el momento antes de entrar en circuito una nueva columna en estado hidrógeno, a un valor mínimo de 75 cm momentos después de entrar en circuito dicha cuarta columna y eliminar del sistema la primera que pasará a regeneración.

Después de la elución con hidróxido sódico, las columnas de resina en forma sodio deben ser regeneradas a la forma hidrógeno para poder entrar de nuevo en circuito. El ácido sulfúrico es el ácido más conveniente para este objeto desde un punto de vista económico por tener el precio equivalente más bajo.

Se hicieron una serie de experiencias empleando ácido sulfúrico 1N y 2N a velocidades de flujo de 1,2 y 4 ml/cm^2 min en columnas de 5 cm de diámetro interno [6].

El número total de equivalentes de ácido sulfúrico que se gastan en la regeneración varía poco en las condiciones equivalentes ensayadas y es ligeramente inferior a velocidades lentas.

Disponiendo tres columnas de 150 cm de altura en serie, se aprovecha prácticamente todo en ácido

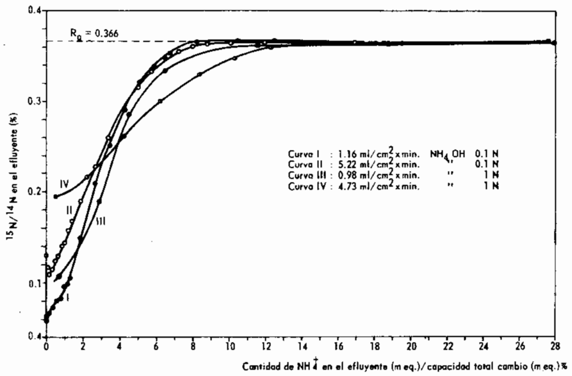

Figura 1. Composición isotópica $^{15}N/^{14}N$ en el efluyente frente a cantidad de NH_4^+ en el efluyente

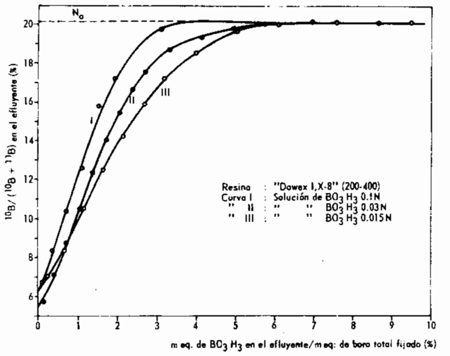

Figura 2. Cambio en la composición isotópica (% ^{10}B), en función de la cantidad de boro en el efluyente

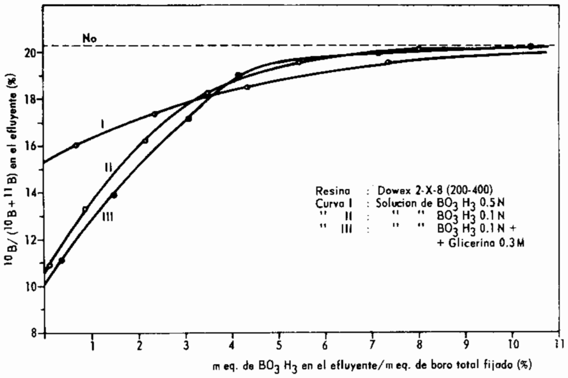

Figura 3. Cambio en la composición isotópica (% ^{10}B), en función de la cantidad de boro en el efluyente

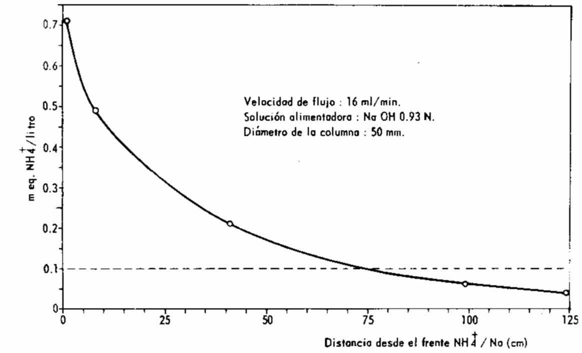

Figura 5. Concentración de NH_4^+ en la cola de la banda

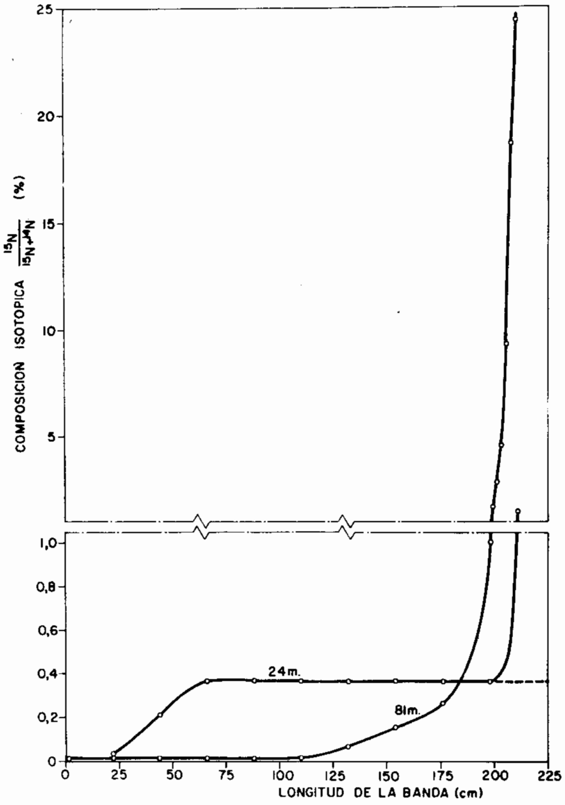

Figura 4. Composición isotópica de una banda de NH_4^+, después de haber recorrido 24 y 81 m

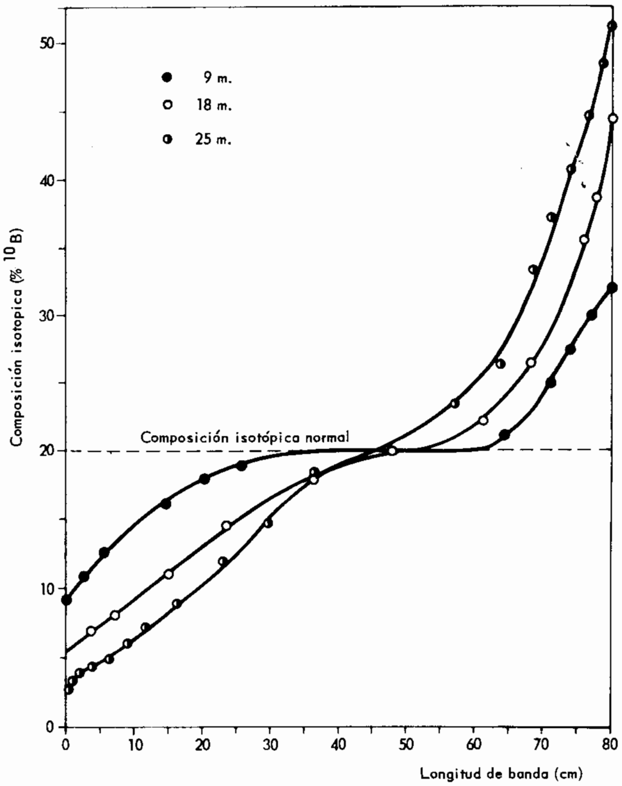

Figura 6. Composición isotópica de una banda de BO_3H_3 después de haber recorrido 9, 18 y 25 m

sulfúrico, con tal de ir eliminando del sistema las columnas regeneradas completamente y añadiendo otras nuevas columnas a regenerar conservando siempre tres en serie.

Boro

Para realizar las experiencias de separación isotópica de boro se ha construído un sistema de seis columnas de « plexiglás », de 19 mm de diámetro interno y 1 500 mm de longitud. Estas columnas se llenaron con resina aniónica « Dowex 2 X-8 » de 200 a 400 mallas.

Con la resina en forma básica se fija en la primera columna una banda de ácido bórico conteniendo 0,85 moles de este compuesto. La banda se desplaza con disolución 0,1*N* de ácido acético. Se mantienen en circuito dos columnas conectadas en serie. Cuando el frente de banda llega al final de la segunda, se conecta la tercera y se aisla la primera, la cual se encuentra ya totalmente en forma acetato. La longitud de banda, después de dos metros de desplazamiento, se establiza en 80 cm. Esta longitud depende de la concentración del acético, ya que ésta influye en el grado de asociación del ácido bórico. Con disolución de ácido acético 0,1*N*, el ácido bórico efluyente alcanza una concentración de 0,28*N*. Para el desplazamiento de la banda podría utilizarse cualquier ácido con constante de disociación mayor que la del bórico ($K_a = 6{,}5 \times 10^{-10}$), siempre que no reaccione con este compuesto. La elección del acético se basa en que el ión acetato presenta poca afinidad por la resina, lo que facilita la regeneración de la misma y, además, en que el cambio de volumen de la resina, al pasar de forma borato a acetato, es muy pequeño.

Se mantiene una velocidad de flujo de 1 ml/cm^2 min, con lo que se logra un desplazamiento de banda de aproximadamente un metro cada 24 horas. Se efectúan pequeñas tomas de muestra en diversos puntos de la banda, después de haber recorrido ésta 9, 18 y 25 m. Se toma un volumen de muestra de 1 ml, con lo que no se afecta prácticamente la distribución isotópica en el seno de la banda. La localización de los puntos de toma de muestra se realiza por medida del volumen de efluyente, recogido entre cada dos muestras. Los resultados obtenidos vienen representados en la figura 6. Se observa que existe un aumento progresivo de la concentración de ^{10}B en cola, mientras que el ^{11}B tiende a concentrarse en la cabeza de la banda.

El mayor inconveniente de este sistema se debe a la formación de burbujas de un gas poco soluble en la zona de cola de la banda. Este gas está constituido por anhidrido carbónico, procedente de contaminación del hidróxido sódico, utilizado en la regeneración a ciclo OH$^-$. El efecto es acumulativo, pues el carbónico no se elimina, porque su primera constante de disociación es intermedia entre las del bórico y acético. La formación de burbujas tiene como consecuencia el que disminuya la eficacia de la separación en la zona de concentración en ^{10}B. Esto se pone de manifiesto si comparamos el enriquecimiento global que tiene lugar en cabeza y en cola, como puede verse en la tabla 3.

Tabla 3

Longitud desplaz.	% ^{10}B (cabeza)	% ^{10}B (cola)	R/R_0 (cabeza)	R_0/R (cola)
9 . .	9,03	31,8	2,52	1,86
18 . .	5,60	44,3	4,21	3,18
25 . .	2,69	51,1	9,05	4,17

La aparición de burbujas puede evitarse por aplicación de una sobrepresión al sistema, hasta obtener una solubilidad suficiente del gas. Un método más sencillo consiste en la adición de un agente complejante para el bórico, de manera que forme un ácido más fuerte que el carbónico.

Para comprobar la eficacia de este procedimiento se ha fijado una banda de complejo manito-bórico, que se ha desplazado con ácido fórmico 0,1*N*. Se ha utilizado el mismo sistema de la experiencia anterior. La velocidad de flujo fué de 0,7 ml/min cm^2. La banda tenía una longitud de 150 cm. La distribución isotópica dentro de esta banda, después de 18 y 27 m de desplazamiento, está reflejada en la figura 7. Se obtiene en este caso una mayor similitud entre los valores de enrique-

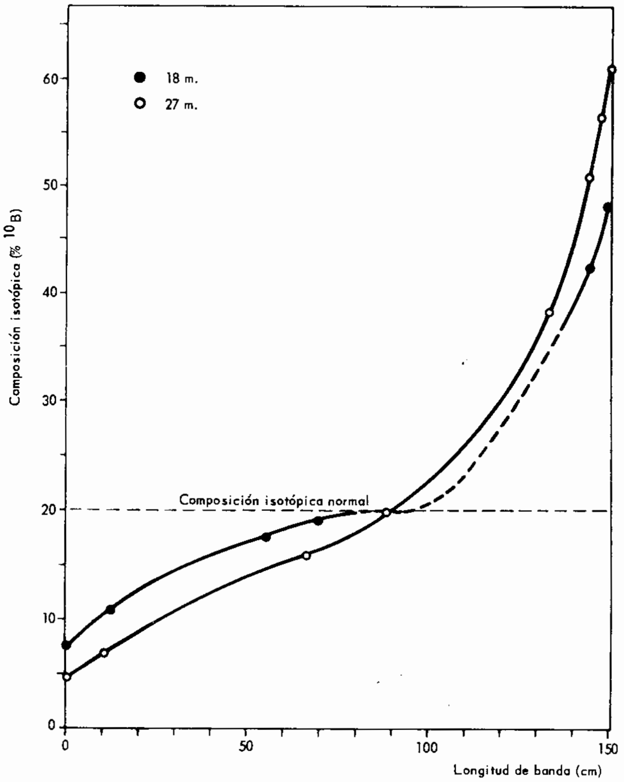

Figura 7. Composición isotópica en el seno de una banda de BO$_3$H$_3$-manita después de haber recorrido 18 y 27 m

cimiento global logrados en cabeza y en cola, que al cabo de 27 m de desplazamiento fueron de 5,14 y 6,26, respectivamente.

Análisis isotópico

Las determinaciones de composición isotópica de nitrógeno y boro se realizaron con un espectrómetro de masas « Consolidated Electrodynamics Corporation » modelo 21-103 C.

Para el nitrógeno se utilizó el nitrógeno elemental, que se obtiene por oxidación de amoníaco de la muestra con hipobromito sódico.

En la determinación del boro se utilizó borato de metilo, obtenido por reacción directa del ácido bórico de la muestra correspondiente con metanol.

Unidad automática para la producción de isótopos estables

Se ha llevado a cabo el diseño y la construcción de una unidad automática para la producción de isótopos estables enriquecidos por cromatografía de intercambio iónico [7]. Actualmente se procede al montaje de la misma que se utilizará en primer lugar para la separación de los isótopos de nitrógeno y en una segunda fase para la separación de los isótopos de boro. La única variación importante será el cambio de resina catiónica a aniónica y el uso de reactivos diferentes.

Consta de 10 columnas de vidrio Pyrex de 1 500 mm de altura y 150 mm de diámetro interno terminadas con un ensanchamiento cónico en su parte externa, qué permite suspenderlas mediante bridas metálicas de forma adecuada. Estas bridas se han diseñado especialmente para descansar sobre tres tornillos graduables sujetos a un armazón metálico. La presión de operación máxima permisible, según el diámetro de las columnas, es de 1,6 kg/cm², suficiente para la pérdida de carga que se origina al disponer en serie tres columnas de resina Dowex 50 W, X-12, 100-200 mallas. Las partes de la instalación que están en contacto con líquidos corrosivos se han construido con cloruro de polivinilo y plexiglás o bien de acero inoxidable y monel. A la tapa superior de las columnas se le puede acoplar un depósito de PVC que sirve

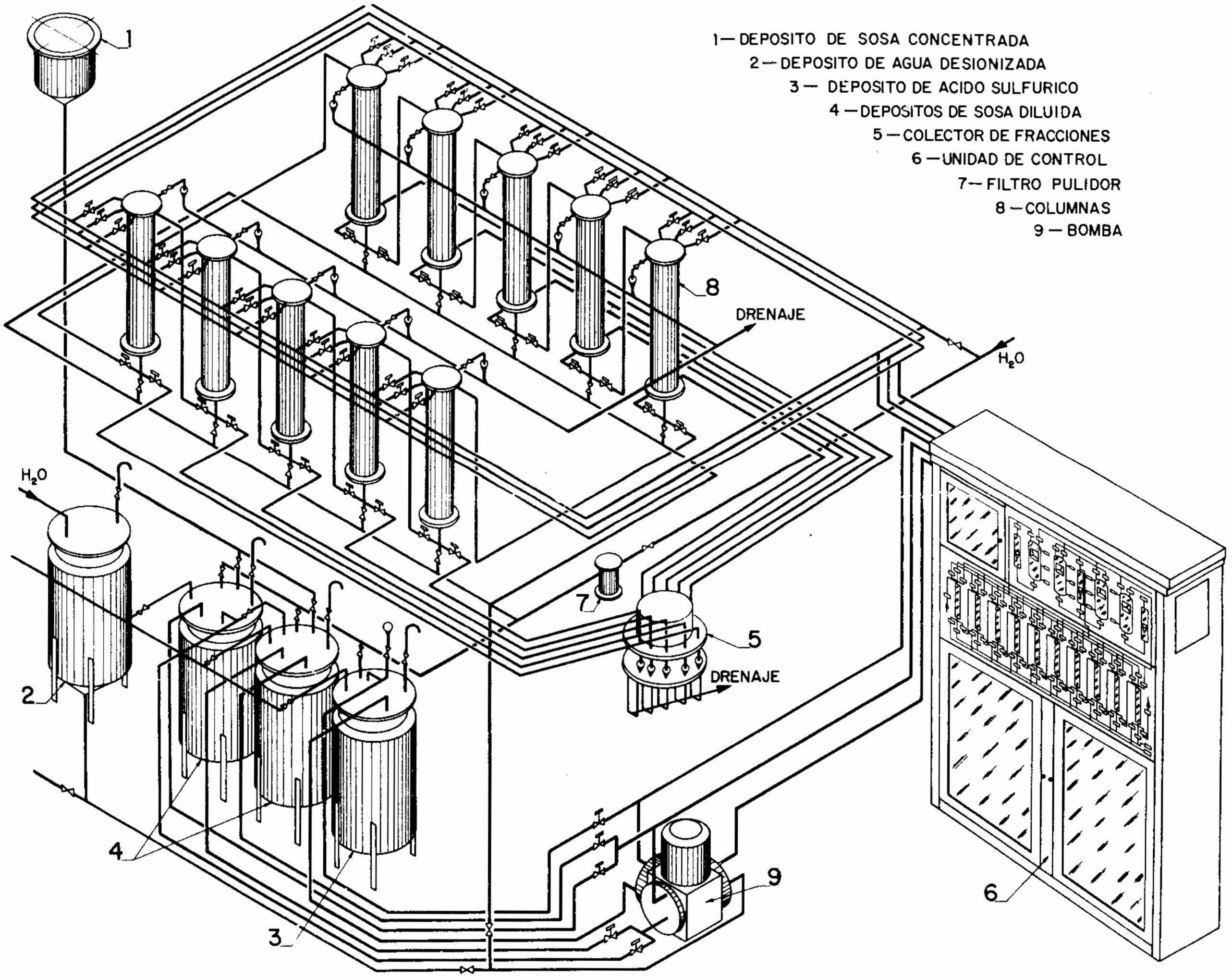

Figura 8. Unidad de producción de isotopos estables por intercambio iónico (nitrógeno)

de receptáculo en el lavado en contracorriente de la resina. La tapa inferior lleva una tela filtrante tipo Dralon o Dynel que tiene la ventaja sobre la tela poliamídica de una mayor resistencia a los ácidos.

En la figura 8 se representa un esquema de la unidad. Cada columna lleva en su parte superior cinco conducciones de las que tres son para entrada de agua desionizada, hidróxido sódico y ácido sulfúrico y van gobernadas por válvulas de solenoide. Otra enlaza con la columna anterior y la quinta actúa como purga. En la parte inferior, dos válvulas de solenoide permiten la salida de líquido hacia la columna siguiente o hacia el drenaje de acuerdo con las señales que transmite un programador electrónico. Otra válvula situada en la parte inferior de las columnas permite lavar la resina en contracorriente.

La unidad puede marchar en forma continua y con la planificación siguiente: tres columnas en serie con una banda de ión amonio de 225 cm de longitud fijada en la resina (verificándose el enriquecimiento del nitrógeno-15 en cola y del nitrógeno-14 en cabeza). Inmediatamente antes de esas tres columnas, otras tres en serie en fase de regeneración con ácido sulfúrico con salida de la última al drenaje. La columna anterior a esas, que, según la planificación, estará recien regenerada, se conectará automáticamente a la línea de agua desionizada para su lavado. Las tres columnas procedentes, que han sido lavadas con agua desionizada en contracorriente, están dispuestas para recibir la banda de ión amonio cuando progrese a lo largo de la serie.

En la figura 8 no está representado el sistema de filtración de la sosa concentrada, constituido por un depósito de monel refrigerado exteriormente con agua, una bomba y un filtro de acero inoxidable con cuatro cartuchos filtrantes de monel de un tamaño de poro de 14 μ y una superficie filtrante total de 3 600 cm^2. La disolución de sosa concentrada pasa a continuación al depósito de almacenaje *1* construido también de monel. El depósito de agua desionizada *2* alimenta la bomba dosificadora de membrana *9* que está situada a una altura superior al depósito para evitar el paso directo del agua cuando la bomba está parada.

Los depósitos de sosa diluida *4* tienen situada la toma de líquido a unos 20 cm del fondo y está constituida por una bujía filtrante de monel de un tamaño de poro de 3 μ. Tanto estos depósitos como el ácido sulfúrico diluido *3* tienen los correspondientes retornos constituidos por válvulas de solenoide.

El colector de fracciones *5* está destinado a recibir las soluciones efluyentes de las columnas de resina con la particularidad de que las soluciones que proceden de la banda de ión amonio son enviadas a un recipiente conteniendo los electrodos de un pH–metro, mientras que las procedentes de la regeneración con ácido sulfúrico y lavado con agua desionizada van directamente al drenaje. Esto es posible mediante un embudo móvil que recoge solamente el efluyente de una columna determinada y que lo envía al recipiente donde están los electrodos del pH–metro (no dibujado en la figura). Cada vez que el pH de esta solución pasa de neutro a alcalino (o sea cuando aparecen las primeras trazas de hidróxido amónico, el aparato manda una señal al colector de fracciones trasladando el embudo móvil al efluyente de la columna siguiente, mientras que un sistema de microinterruptores cambian el estado de las válvulas de solenoide para adecuarlas al nuevo estado del sistema de columnas.

En el panel de control *6* se centralizan todos los mandos de la instalación y en él se tiene indicación visual del estado de cada columna de resina, de los depósitos de almacenaje de reactivos, de las válvulas de solenoide, de la velocidad de flujo de las soluciones, etc.

DIFUSIÓN TÉRMICA

Factores de forma para la operación de las columnas

La teoría de las columnas del tipo Clusius-Dickel para la separación de isotopos por difusión térmica ha sido objeto, en los últimos años, de una considerable extensión a partir de los trabajos de W. Furry y R. C. Jones [8]. Varios autores han obtenido soluciones de las ecuaciones de transporte adaptadas a diversos modelos de interacción y adecuadas a los dos tipos de columnas, de hilo caliente y de tubos concéntricos, usados en la práctica. En nuestro departamento se ha trabajado en este aspecto y dos de los autores [9] han extendido la teoría de la columna y calculado los « factores de forma » para columnas de tubos concéntricos en el caso de un gas cuyo comportamiento pueda ser descrito por el modelo RES de interacción. La confrontación de nuestros cálculos con la experiencia aplicada a los casos $^{20}Ne/^{22}Ne$, $^{20}Ne/CH_4$ y $^{20}Ne/NH_3$, da resultados más concluyentes en la previsión de la presión óptima de separación que en la de los factores de separación máximos en el equilibrio.

Predicciones cualitativas de la teoría : aplicación para el diseño

El análisis de los procedimientos de diseño de columnas dado por distintos autores y los resultados obtenidos experimentalmente, permiten llegar a la conclusión de que el conocimiento de los parámetros moleculares y los que definen el funcionamiento de las columnas en función de los anteriores, no son suficientes para el diseño de las mismas en condiciones prefijadas, puesto que no se ha encontrado un acuerdo cuantitativo entre las predicciones teóricas y los resultados experimentales registrados en la bibliografía.

Sin embargo, hay algunas particularidades en la operación de una columna para las cuales son buenas desde el punto de vista cualitativo las predicciones teóricas. Una de ellas es la dependencia del factor de separación con la presión; hemos comprobado [9-12] su absoluta validez para todas nuestras medidas, efectuadas en sistemas muy distintos, tanto en el caso de isótopos con Ne, O_2, Kr, CH_4, como para mezclas binarias no isotópicas en neon/metano y derivados deuterados en operaciones en columnas diferentes de pequeña longitud.

Un estudio de la influencia de la temperatura en las constantes de separación [12] ha llevado a conclusiones muy útiles para nuestro programa de trabajo. Utilizando Kr natural en una columna de hilo caliente de modelo análogo al utilizado por K. Clusius, se han obtenido para las presiones óptimas de separación y para los factores de separación en el equilibrio los resultados que se muestran en las figuras 9 y 10. La simple inspección de las mismas permite observar la concordancia existente entre las predicciones de las teorías de la columna basadas en el modelo Lennard-Jones (12-6) y en el modelo de interacción potencial para la previsión de la presión óptima.

Tal consistencia no se observa en las predicciones de ambas teorías para el valor del factor de separación máximo; esto era de esperar dado que los puntos de partida en la elección de la dependencia del factor de termodifusión α_0 con la temperatura son distintos en ambas. No obstante, esta discordancia se soslaya tomando en el caso del modelo de interacción potencial no el valor de α_0 a la temperatura de la pared fría, sino su valor a una temperatura media entre la de la pared fría y la caliente, tomada ésta apropiadamente, como hemos comprobado en nuestros trabajos sobre Kr y Ar realizados en columnas de tubos concéntricos.

Puede observarse también la estrecha coincidencia existente entre los resultados de una cuidadosa serie de medidas experimentales de la presión óptima y las predicciones teóricas obtenidas para la misma usando un modelo molecular potencial correspondiente a un índice de viscosidad $n = 0{,}70$. Conclusiones menos claras se obtienen para el máximo factor de separación de la citada columna. Quizá la imprecisión en el conocimiento de la constante de difusión térmica para el citado gas sea la causa de la inesperada magnitud de la separación, bastante superior a las predicciones teóricas.

Utilizando posteriormente otra columna con distintos parámetros de construcción y operando con el mismo gas en el mismo rango de temperaturas se han obtenido resultados consistentes con los anteriormente citados [13]. Estas previsiones cualitativas de la teoría han sido particularmente útiles en el diseño de una planta de separación apropiada para obtener en alto grado de pureza los isótopos extremos del Kr y enriquecer los de masas intermedias.

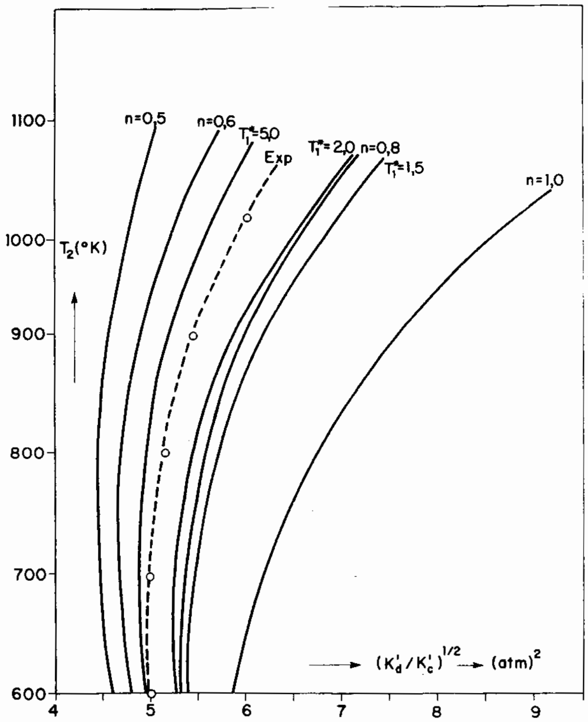

Figura 9. Variación con la temperatura del hilo caliente de la magnitud $(k_d'/k_c')^{\frac{1}{2}}$, proporcional a la presión óptima

Las líneas llenas representan las predicciones teóricas con los modelos RES y L-J (12-6); los puntos experimentales (línea rayada) están situados sobre la línea teórica correspondiente a $n = 0{,}70$

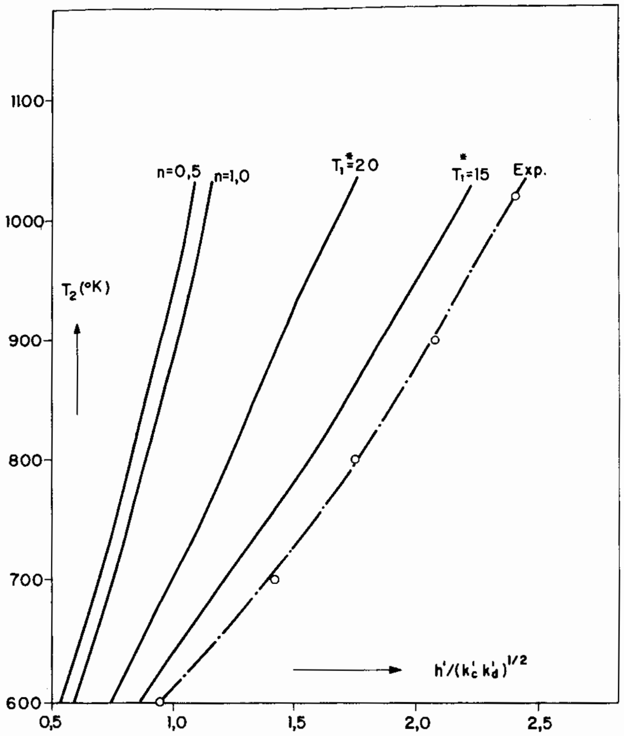

Figura 10. La magnitud $h'/(k_c'k_d')^{\frac{1}{2}}$ es proporcional a ln Q_{max}.

En la figura se muestran comparativamente los resultados teóricos y los experimentales, obtenidos con una columna de especificaciones $r_1/r_2 = 24{,}5$ y $T_1 = 292$ °K; utilizando Kr natural

Medida de factores de difusión térmica

Utilizando una columna de tubos concéntricos de corta longitud, uno de los autores [11, 14] ha realizado la medida de constantes de difusión térmica en diversos sistemas de isótopos de neon, metano y mezclas binarias de ellos.

El método seguido se reveló de una particular eficiencia, puesto que permite obtener la separación suficiente para efectuar medidas de precisión de factores de difusión térmica. La columna de tubos concéntricos opera con una reducida diferencia de temperaturas entre sus dos paredes y por ello permite obtener los valores medios de los factores de un pequeño rango de temperaturas. Los resultados obtenidos para el factor de difusión térmica en diferentes sistemas Ne/CH_4, se muestran en la figura 11. Un adelanto de los mismos fué dado en el Congreso de Paris [15]. Es de interés destacar el diferente comportamiento que presentan las moléculas $^{13}CH_4$ y $^{12}CH_3D$, cuyo factor de difusión térmica es distinto de cero [11] a pesar de ser isotópico-isobáricas.

En una instalación similar montada en nuestros laboratorios, se miden los factores de difusión térmica a diferentes temperaturas en los gases nobles y en mezclas binarias de ellos. En la actualidad están en curso medidas en el sistema $^{86}Kr/^{40}Ar$, utilizando la columna de difusión térmica y un aparato de dos bulbos, con el fin de esclarecer la validez del primer método para los sistemas más dispares.

Simultáneamente se lleva a cabo una investigación, usando las técnicas expuestas para una columna de hilo caliente, sobre el comportamiento de las mezclas HBr/DBr/Kr y la posible utilización de éstas moléculas como « gas filtro » en la separación de los isótopos intermedios de Kr.

Estudio de las distribuciones isotópicas en mezclas multicomponentes

Son bien conocidas las dificultades con que se tropieza en la separación por difusión térmica de los isótopos de masas intermedias en una mezcla multicomponente. Aun en el caso de una mezcla ternaria esta dificultad se acentúa cuando el isótopo medio es muy escaso en la mezcla; ésta es la situación para la separación de $^{17}O_2$, ^{21}Ne, ^{38}Ar, etc.

En determinados casos estas dificultades pueden obviarse con el empleo adecuado de un « gas filtro ». La utilización de $^{12}CD_4$ para la separación de ^{21}Ne y la de ^{37}ClH en la de ^{38}Ar son ejemplos patentes. El papel del « gas filtro » en la separación tiene dos aspectos igualmente interesantes; por una parte la presencia de una nueva especie molecular hace a veces aumentar el valor del factor de difusión térmica relativa a dos de los isótopos presentes. Por otra parte, y esto es importante, origina una « redistribución » de concentraciones dentro de la instalación, en general más favorable para la obtención de resultados satisfactorios que el propio aumento del referido factor.

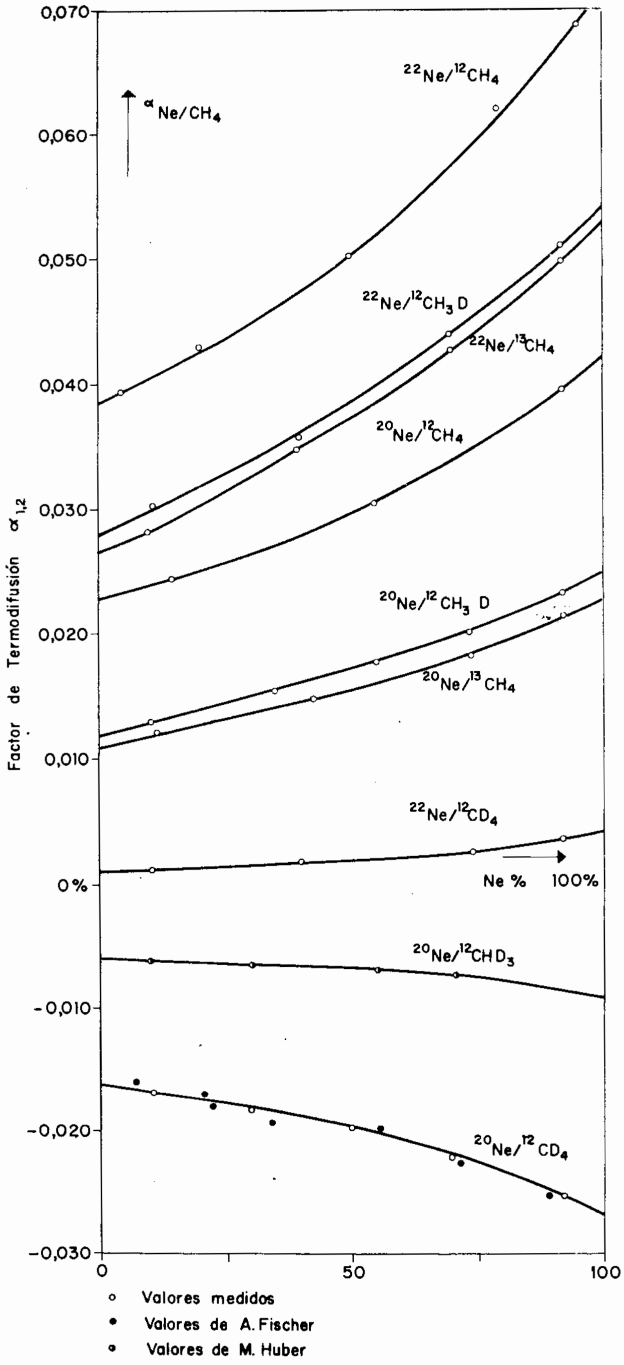

Figura 11. Medidas del factor de difusión térmica en una columna de tubos concéntricos

Se comprende pues que sea igualmente interesante para poder predecir el comportamiento de una mezcla isotópica con « gas filtro » en una columna de separación el conocimiento del valor de las constantes de difusión térmica como el disponer de una información adecuada sobre el comportamiento y distribución de la citada mezcla en la columna.

Actualmente en nuestro laboratorio se está poniendo a punto [12, 16] una técnica de estudio del comportamiento de las mezclas multicomponentes en los sistemas ya citados Kr/HBr/DBr. Extendiendo los estudios existentes de K. Clusius y E. Varde, para la distribución de concentraciones isotópicas de mezclas multicomponentes en una instalación cerrada, al caso en que exista un « gas filtro » en la mezcla de partida. Utilizando para ello un ordenador IBM 7070 se ha puesto a punto una técnica de optimación para la obtención de isótopos intermedios de la mezcla natural de Kr.

Nuestro programa de trabajo provee una extensión de este proceso, una vez suficientemente comprobado experimentalmente, a la separación de ^{13}C.

Espectrómetro de masas

Para llevar a cabo los análisis de abundancia hemos diseñado y construido en nuestros laboratorios un espectrómetro de masas de sector magnético de 90° con sistema electrónico de alimentación y registro gráfico.

El rango de medida llega hasta 400 uma con un poder de resolución 1/200 y una precisión mejor que 0,1 %.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/491 Spain

Production of stable isotopes in Spain

By M. M. Urgell *et al.*

The paper describes work carried out under the stable isotope production programme on the separation of stable isotopes by ion-exchange chromatography and thermal diffusion. With the former technique, a study was made of the separation, of ^{14}N, ^{15}N, ^{10}B and ^{11}B. This work included laboratory scale experiments carried out with a view to determining the separation factor by means of the breaking-through technique.

For nitrogen, use was made of ammonium hydroxide, chloride and acetate; only the first of these proved suitable for obtaining a good separation. Experimental conditions, e.g., flux velocity and concentration, were varied so as to ascertain their influence on the separation factor. Use was made of the strongly acidic cationic resin Dowex 50W (100-200 mesh). In the favourable case of ammonium hydroxide, the values for the separation factor varied between 1.028 and 1.022, depending upon experimental conditions.

In the case of boron, the strongly basic resins Dowex 1 and Dowex 2 (100-200 mesh and 200-400 mesh) were used to study boric acid and sodium borate compounds and complexes of boric acid with mannite and glycerine. The highest separation factor was obtained with boric acid (1.035-1.027, depending upon concentration); reasonable values were also found with mannite (1.024) and glycerine (1.027) complexes. With sodium borate, the separation factor varied only slightly from unity.

In the case of both nitrogen and boron, these experiments confirm the need for employing complexes of these substances that are slightly ionized in solution to obtain separation factors appreciably different from unity.

Laboratory experiments were carried out to study the separation of nitrogen and boron isotopes by means of displacement development chromatography. In the case of nitrogen, a band of ammonium hydroxide was fixed on a cationic resin in the hydrogen form and was displaced by sodium hydroxide. For boron, a boric acid band was fixed on an anionic resin in the OH form and displacement carried out by means of acetic acid.

A pilot plant for the separation of stable isotopes by

means of ion-exchange chromatography has been built; this installation is automatically controlled and is designed for continuous operation.

In the course of the thermal diffusion investigations, a study was made of the separation of the various isotopes of the noble gases, oxygen, nitrogen and carbon-13. The object of this work was to: (*a*) correlate theoretical and experimental data in different types of column; (*b*) determine the thermal diffusion coefficients of isotopic mixtures in cylindrical columns and study the distribution of multi-component mixtures with a view to discovering gases capable of acting as *filters*.

A 90° sector mass spectrometer has been built for measuring isotope abundance ratios between 1 and 400 atomic mass units.

A/491 Espagne

La production d'isotopes stables en Espagne

par M. M. Urgell *et al.*

Dans le programme de production d'isotopes stables, on a abordé la séparation de ces substances par chromatographie d'échange ionique et par diffusion thermique. Dans le premier groupe, on a étudié la séparation des isotopes ^{14}N, ^{15}N, ^{10}B et ^{11}B; on décrit les expériences réalisées en laboratoire pour déterminer le facteur de séparation par la méthode du point de rupture.

Dans le cas de l'azote, on a utilisé l'hydroxyde, le chlorure et l'acétate d'ammonium, le premier composé étant le seul qui donne une bonne séparation. On a travaillé en faisant varier les conditions expérimentales, comme le débit et la concentration, pour connaître leur influence sur le facteur de séparation, et en utilisant la résine cationique fortement acide Dowex 50 W, 100-200 mesh. Les valeurs trouvées pour le facteur de séparation, dans le cas favorable de l'hydroxyde d'ammonium, oscillent entre 1,028 et 1,022 selon les conditions expérimentales.

Dans le cas du bore, on a étudié les composés acide borique, borate de soude et les complexes de l'acide borique avec la mannite et la glycérine en utilisant les résines fortement basiques Dowex 1 et Dowex 2, 100-200 mesh et 200-400 mesh. Avec l'acide borique on a obtenu le facteur de séparation le plus élevé (1,035-1,027, selon la concentration) mais ceux qui ont été obtenus avec les complexes de mannite (1,024) et glycérine (1,027) sont acceptables. Au contraire, avec le borate de soude, le facteur de séparation diffère très peu de l'unité.

On a confirmé qu'aussi bien dans le cas de l'azote que dans celui du bore, si l'on veut obtenir des facteurs de séparation qui diffèrent suffisamment de l'unité, il est nécessaire d'employer des composés de ces éléments, qui sont faiblement ionisés en solution.

On a réalisé des expériences de laboratoire pour la séparation des isotopes de l'azote et du bore au moyen de la technique chromatographique d'évolution par déplacement. Pour l'azote, on fixe une bande d'hydroxyde d'ammonium sur une résine cationique H et on le déplace par l'hydroxyde de sodium. Pour le bore, une bande d'acide borique est fixée sur résine anionique OH et le déplacement se réalise au moyen d'acide acétique.

On a construit une installation pilote automatique devant fonctionner en continu, destinée à la séparation d'isotopes stables par chromatographie d'échange d'ions.

En relation avec les études de diffusion thermique, on examine la séparation des différents isotopes des gaz inertes, de l'oxygène, de l'azote du carbone 13, sous les aspects suivants : *a*) corrélation entre les prévisions de la théorie et les résultats expérimentaux pour différents types de colonnes; *b*) détermination en colonne cylindrique de facteurs de diffusion thermique de mélanges isotopiques et études sur la distribution de mélanges à plusieurs constituants, en essayant de trouver des gaz agissant comme « filtres ».

On a élaboré et construit un spectromètre de masse de secteur 90°, pour la mesure des relations d'abondance isotopique entre 1 et 400 u.m.a.

A/491 Испания

Производство стабильных изотопов в Испании

М. Ургел *et al.*

В докладе приводится обзор производства стабильных изотопов ионообменной хроматографией и термодиффузией. Методом ионообменной хроматографии изучалось разделение изотопов N^{14}, N^{15}, B^{10}, B^{11}. Это исследование включало проведение лабораторных опытов по определению коэффициента разделения по методу точки проскока.

Для разделения изотопов азота использовались гидроокись, хлорид и ацетат аммония, причем гидроокись оказалась единственно пригодной для хорошего разделения. При исследовании производилось изменение таких условий эксперимента, как скорость потока и концентрация, с тем чтобы выяснить их влияние на коэффициент разделения. При этом использовался сильно кислый катионит дауэкс-50*W* (100—200 меш). Полученные значения коэффициента разделения в случае гидрата окиси аммония находятся в пределах между 1,028 и 1,022 в зависимости от экспериментальных условий.

Для разделения изотопов бора использовались борная кислота и борат натрия, а также комплексные соединения борной кислоты с маннитом и глицерином. При этом применялись сильноосновные смолы дауэкс-1 (100—200 меш) и дауэкс-2 (200—400 меш). С борной кислотой был получен наибольший коэффициент разделения (1,035—1,027 в зависимости от концентрации), высокие величины коэффициента разделения были получены и в случае комплексов с маннитом (1,024) и глицерином(1,027). В случае бората натрия коэффициент разделения мало отличается от единицы.

Показано, что при разделении изотопов азота и бора для получения коэффициентов разделения, заметно отличающихся от единицы, необходимо использовать комплексные соединения, слабоионизированные в растворе.

В лабораторных условиях были проведены опыты по разделению изотопов азота и бора методом элюентной хроматографии. В случае изотопов азота осуществлялась фиксация полосы гидрата окиси аммония на катионной смоле в Н-форме и ее перемещение осуществлялось с помощью гидрата окиси натрия. В случае изотопов бора полоса борной кислоты фиксировалась на анионной смоле в ОН-форме, а ее перемещение осуществлялось с помощью уксусной кислоты.

Построена опытная установка непрерывного действия с автоматическим управлением, которая предназначалась для разделения стабильных изотопов ионообменной хроматографией.

В связи с изучением термодиффузии исследовалось разделение различных изотопов инертных газов, кислорода, азота и углерода-13 с целью: а) определения соотношения между теоретическими и экспериментальными данными по различным типам колонн; b) определения коэффициентов термодиффузии изотопных смесей в цилиндрической колонке и изучения распределения многокомпонентных смесей с учетом выяснения роли газов в качестве «фильтров».

Для измерения концентраций изотопов сконструирован и построен масс-спектрометр с сектором в 90°.

P/557 Italy

A new distillation technique for isotope concentration

By M. Silvestri, G. C. Angelino and B. Grigoli *

In CISE's laboratory, the application of concurrent two-phase flow as a contacting medium for the separation of the components of a mixture has been studied since 1957.

At the Second International Conference on the Peaceful Uses of Atomic Energy held in Geneva (1958), a paper concerning the construction of a plant for $H_2{}^{18}O$ enrichment was presented [1]. The aim of the present paper is to illustrate the main results of further experiments carried out in this field during the last four years.

The separating element, schematically represented in Fig. 1, consists of a vertical tube into the bottom of which the liquid and gas phases are fed.

If the gas velocity is sufficiently high, the liquid phase is spread on the tube wall in the form of a thin film and is raised upward by friction with the gas phase. In this way, a good contact between the two phases is ensured. It has to be noted that the internal surface of the tube is completely wet at a distance of less than one diameter from the liquid injection point. At the top end of the contact tube the phases are separated. For correct operation, the type of motion must be always viscous in the liquid phase and turbulent in the gas phase, as defined by Martinelli [2].

Hydrodynamic conditions are such that the liquid flows entirely on the tube wall as an annular film, and at the outlet of the tube the liquid separates from gas phase without spraying. In this type of flow pattern, assuming that the flow of liquid is perfectly viscous and neglecting the effect of pressure drop, the relationship between the liquid flow rate A per unit periphery of tube and the liquid film thickness y is

$$A = ay^2 - by^3, \qquad (1)$$

where the coefficient a takes into account the vapour flow conditions and b represents the contribution of liquid weight.

The coefficients are :

$$a = \frac{f_g G_g^2}{4 \mu_L \varrho_g} \quad \text{and} \quad b = \frac{g \varrho_L}{3 \mu_L}.$$

The concurrent two phase flow in the separating element allows a high specific flow rate, while the value of the pressure drop is comparable with the one found in the majority of conventional distillation devices.

DISTILLATION IN A GAS STREAM

As an application of this working principle, a laboratory plant was designed and assembled to evaluate the efficiency of mass transfer in the fractional distillation of water. The plant was operated with a gas carrier at room temperature and the main purpose was to produce water enriched in oxygen-18 [3]. Due to the presence of the gas carrier, the operating temperature of the plant was independent of pressure drop in the elements. Room temperature was chosen in order to have high separation factors of $H_2{}^{18}O/H_2{}^{16}O$. The enrichment cascade was composed of 100 pyrex glass tubes 2.1 cm id and 140 cm in length. The contact elements were connected in series and the countercurrent arrangement of the cascade was obtained by external connections.

Since the plant was operated in non-output conditions, the first element of the cascade was fed with a quantity of natural water equal to that which left the plant as water vapour; the last element was fed with dry air and operated as a saturator. In hydrodynamic tests, it was found that 6.5 kg/h of liquid water and 40 kg/h of air represented satisfactory values for the

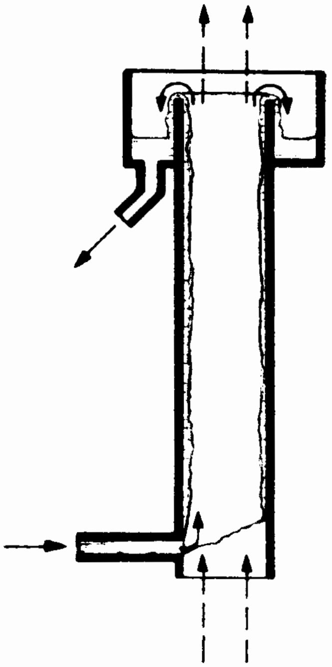

Figure 1. Schematic drawing of a separating element

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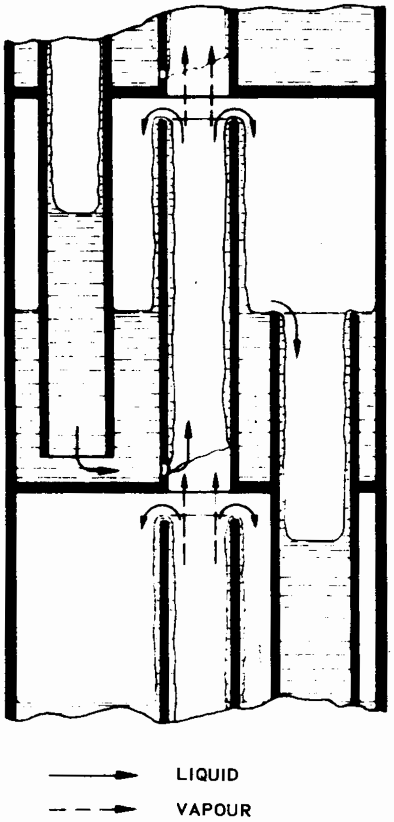

Figure 2. Schematic assembly of a contact tube showing the countercurrent arrangement

flow rates; under these conditions the pressure drop in the whole cascade was found to be 1.5 atm. The hold-up of each element was found to be about 20 ml, the hundredth element had a 200 ml reservoir.

After 365 hours of operation, at an average temperature of 27 °C and an air flow rate of 40 kg/h, water samples were taken from stages Nos. 1, 25, 50, 75 and 100. Deuterium and oxygen-18 content were determined at the Saclay laboratories of the French Commissariat à l'énergie atomique by means of a mass spectrometer, the results are collected in Table 1. The single stage efficiency was found to lie between 0.8 and 0.9.

The plant, now dismantled, has been operated continuously for about 2 000 hours.

Table 1. Oxygen-18 and deuterium contents and enrichment ratios throughout the plant

Stage No.	Oxygen-18		Deuterium	
	Content ppm	Enrichment	Content ppm	Enrichment
1	1 988	—	159.2	—
25	2 174	1.094	278.3	1.75
50	2 274	1.144	460.2	2.89
75	2 301	1.158	693.0	4.35
100	2 370	1.192	1 176.0	7.38

CONCURRENT DISTILLATION

The applicability of the concurrent distillation principle to conventional distillation in the steam-water system was the aim of a further development stage. For this purpose, the hydrodynamic and preliminary isotopic behaviour of a concurrent plate was investigated [4].

The plate is schematically represented in Fig. 2, where, for simplification, just one contact pipe is drawn.

The liquid enters the contact tube through a small bore tube, and at the top end of the contact pipe liquid overflows down the external walls and recirculates. Liquid feed flow rate is provided by a constant head. Plates are arranged for countercurrent flow, in the distillation column, by means of weirs which also provide liquid seals between two consecutive plates.

The geometric characteristics of the plate are as follows :

Dimensions of contact pipe: 4.2 mm id, 5 mm od, 10 cm length
Diameter of feed tube: 0.6 mm
Number of contact pipes: 32
Diameter of the plate: 4.8 cm
Geometrical liquid head : adjustable from 4 to 6 cm.

Hydrodynamic tests on the plate were carried out to determine the proper operating conditions. Pressure drops and entrainment were measured at temperatures ranging from 77 to 110 °C as a function of the specific mass flow rate of the vapour whilst keeping the geometrical liquid head at 4, 5 and 6 cm. The liquid flow rate inside the contact tubes was also measured as a function of vapour flow rate, in a properly designed test section. Tests were carried out at 89, 100 and 110 °C and at a geometrical liquid head of 4, 5 and 6 cm.

Preliminary tests on mass transfer efficiency were performed by feeding the test section with natural liquid water and different amounts of deuterated water vapour under the above mentioned conditions of temperature and geometrical liquid head. During these experiments the molar ratio between the liquid and vapour feed flow rates was kept as close as possible to unity.

The results of hydrodynamic and mass transfer experiments were encouraging, so it was decided to pursue experiments on a laboratory scale distillation column.

PLATE AND COLUMN PERFORMANCE AND CALCULATION

Under the same conditions of geometrical liquid head and feed tube diameter, the liquid flow rate which passes through each tube is a function of vapour flow rate. The geometrical liquid head can be ideally divided into two fractions : the first overcomes the difference in pressure between the injection point of the water and the free surface of liquid, while the second represents the liquid head necessary to ensure the liquid flow rate into each contact tube.

In effect, as the value of vapour flow rate increases, the pressure drop of the plate increases and, consequently, the useful liquid head and the liquid flow rate inside the contact tubes decrease. In particular, when the pressure drop of the plate is greater than the geometrical liquid head, the liquid flow stops. On the other hand, below a certain value of the vapour flow rate, there is a change in the flow pattern and the entrainment of liquid droplets is observed. It was found that by gradually lowering the vapour flow rate the transition from annular two-phase flow to slug flow occurs over a relatively large range of vapour flow rate.

To determine the parameters which characterize the operating conditions of the transfer column, a simple analytical expression was derived, by assuming the operation of the column in steady state conditions at constant temperature and pressure. For this purpose, two distinct liquid flow rates must be distinguished. The first one is the liquid flow rate which feeds the contact pipes and, after mass exchange, is recirculated, while the second is the actual liquid flow rate which passes through the column, i.e., the flow rate which passes through the weirs of the plate. Therefore the generic plates of the column can be represented as composed of two sections: a feeding section and a contact section. The block scheme of the plate is shown in Fig. 3.

In this plate, countercurrent is obtained between the water flow rate L and the vapour flow rate V, and their molar ratio is indicated by ψ. The water flow rate L' circulating inside the contact section and the ratio L'/V is indicated by ξ.

From the isotopic balance of the two sections of the plate, the transport equation and the definition of efficiency ε of the contact section, the following relationship between the molar fraction N_{s-1}, N_s of the heavy isotope in the liquid coming from two successive plates is

$$N_{s-1} = \frac{q\xi\psi(1-\varepsilon) + \xi\varepsilon + \psi}{\psi(q\xi + 1)} N_s + \frac{q\xi\varepsilon\tau}{\psi(q\xi+1)}, \quad (2)$$

where q is the distillation separation factor and τ is the isotope transport of the column per unit of vapour molar flow rate.

This equation, integrated with the boundary conditions, gives the output molar fraction N_S as a function of the feed flow concentrations N_0 of the liquid and n_S of the vapour:

$$N_S = fqn_S + (1-f)\,N_0, \quad (3)$$

where

$$f = \frac{B^S - 1}{B^S - q\psi} \quad \text{and} \quad B = \frac{q\xi\psi(1-\varepsilon) + \xi\varepsilon + \psi}{\psi(q\xi+1)}.$$

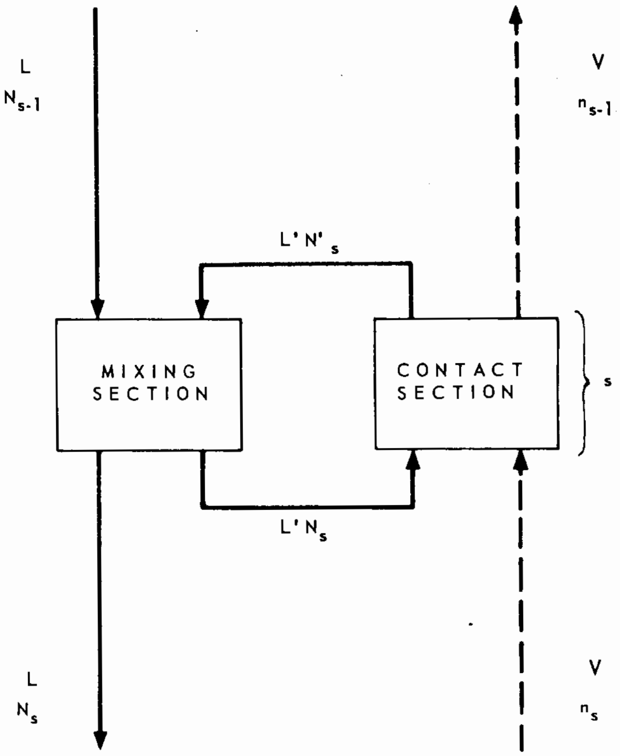

Figure 3. Block diagram of a distillation plate

As the global Murphree's efficiency β of a plate must account for the behaviour of both sections, it is possible to express this parameter as a function of ψ, ξ and ε, as follows:

$$\beta = \frac{\xi\varepsilon(q\psi + 1)}{\psi(q\xi + 1) + \xi\varepsilon}. \quad (4)$$

DESCRIPTION OF THE LABORATORY COLUMN

The column consists of 24 AISI 304 stainless steel plates assembled in a pyrex glass shell of 6 cm id and

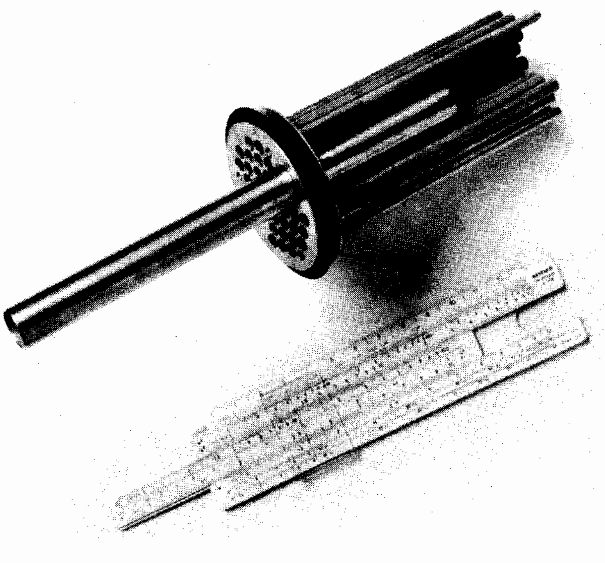

Figure 4. View of a plate

285 cm length. Heat losses were greatly reduced by surrounding the column with a perspex shell fitted with baffles every 22 cm. Each plate (Fig. 4) consists of 30 contact pipes, 0.42 cm id and 11 cm in length, fitted in a baseplate; three spacer rods ensure a constant distance between two consecutive plates. A 1.2 cm id tube acts as a weir and delivery tube to the next plate. The height of the weir was fixed at 6 cm.

A 4 mm diameter orifice was inserted at the outlet of each delivery tube. These orifices ensure the damping of the liquid level oscillations found in a first set of experiments. It should be pointed out that these oscillations (about ± 1 cm with a period of 2-3 cycles/s) did not appreciably influence the efficiency of mass transfer of the plates. The liquid is fed through a 0.6 mm diameter tube. In Fig. 4, the rubber seal between the shell and the plate base is visible.

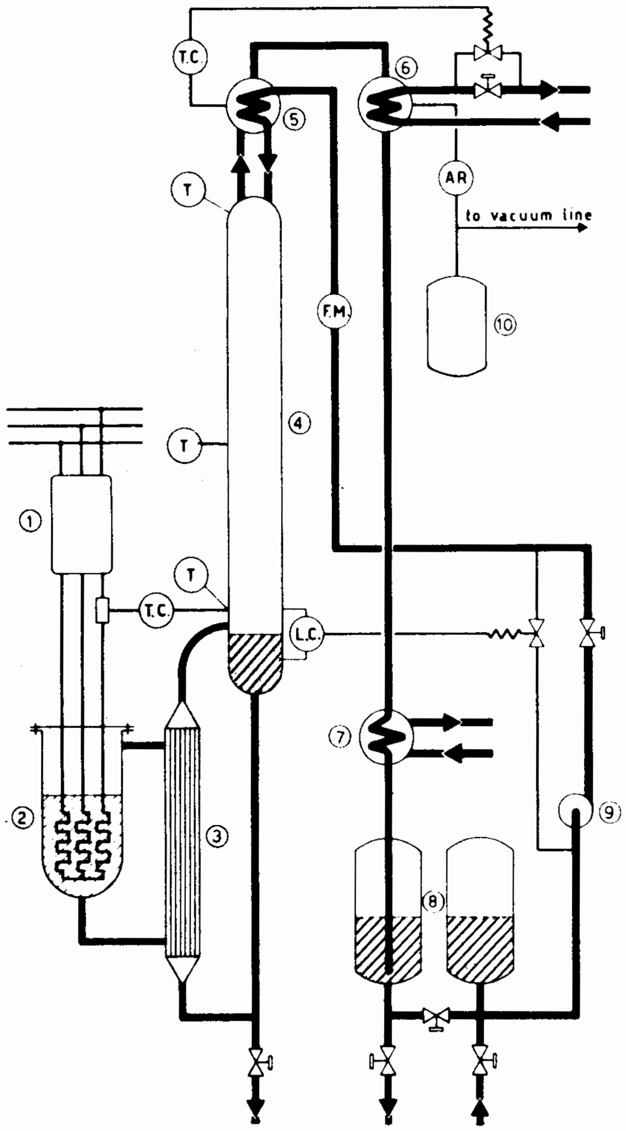

Figure 5. Schematic flow sheet of the plant

T: Thermometer; T.C.: Temperature control;
L.C.: Level control; F.M.: Flowmeter;
A.R.: Air removal system; 1: Electric power meter;
2 : Boiler; 3: Reboiler; 4: Column; 5: Feed water preheater;
6: Condenser; 7: Cooler;
8: Condensate and feed water storage tanks;
9: Feed water pump; 10: Vacuum tank

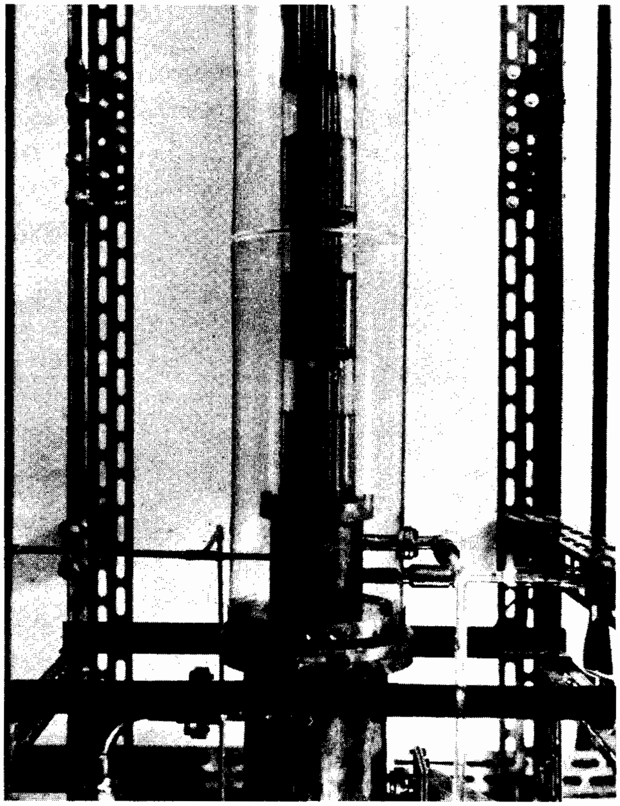

Figure 6. View of the bottom of the column

A schematic flow sheet of the plant is given in Fig. 5 and a view of the column in Fig. 6. The reboiler consists of a long vertical evaporator tube followed by a cyclone separator. This evaporator uses natural circulation of the vater throught ubes which are surrounded by a steam jacket. 30 copper tubes, 4 mm id, 1 m length, were used, the other parts of the reboiler were made from brass. A floating head condenser condensed the vapour leaving the column. A contact thermometer inserted on the steam side, kept the condensation temperature constant through a regulating system. Condensed steam drained into a well provided with a barometric column.

The control system (Fig. 5) has been designed in order to keep the following three parameters constant: (*a*) the temperature at the top of the column, (*b*) the vapour flow-rate and (*c*) the level in the reboiler. Since the temperature of the column head is constant, the vapour flow rate is determined by the temperature of the bottom of the column itself, the vapour flow rate regulation is based on this assumption. The level control corrects the integral differences between the liquid and vapour mass flow rate. No details are entered into here, A more detailed description will appear in a paper now in preparation.

The deuterium content in the water samples was determined by using the float method of density analysis [5].

Experimental procedure

Preliminary experiments to measure the operating characteristics of the reboiler, the heat losses in the whole apparatus and the hold-up of the column and the reboiler, were carried out. The main features of the plant are summarized in Table 2 for a typical run.

Table 2

Power of steam generator	15 kW
Column heat losses	1.61 kW
Reboiler mean temperature	99.1 °C
Mean temperature at the top of column	96.3 °C
Mean pressure drop of a plate	3.99 cm H_2O
Feeding flow rate of liquid	6 g/s
Reboiler hold-up	1 535 ml
Column hold-up	3 075 ml
Plate hold-up	128 ml

Tests on the apparatus were devoted to the determination of the plate efficiency and equilibrium time of the column operated in total reflux conditions. All experiments were performed using a D_2O-H_2O mixture containing 0.4 moles % of D/(D + H). From the concentration and operating data, the Murphree's efficiency of a single plate was calculated.

As is well known, in total reflux conditions the enrichment factor *a* as a function of the number of theoretical plates *S*, can be calculated from the relationship:

$$a = q^S \tag{5}$$

q being the separation factor of the process considered.

Besides, if β is the Murphree's efficiency of a plate and S_r is the number of real plates which constitutes the column, it is:

$$S_r = S\frac{2-\beta}{\beta}, \tag{6}$$

and, from Eqs. (5) and (6)

$$\beta = \frac{2}{1 + S_r \cdot \dfrac{\ln q}{\ln a}}. \tag{7}$$

The equilibrium time determinations were performed with a similar procedure, but samples were taken about every 5 minutes from the bottom of column, to follow the increase of deuterium content as a funtion of time. The total hold-up of the apparatus was reduced to the minimum permissible value (10.75 liters).

Experimental results

Murphree's efficiency and pressure drops of the plate were measured as a function of vapour flow rate in about 70 experimental runs. These tests were carried out a temperatures of 91, 95 and 101 °C and with mass flow rate of vapour ranging between 15 and 23 kg/h. The results are shown in Fig. 7 where the specific vapour mass flow rate G_v refers to the free cross section of the plate (4.16 cm²). On the left hand side of the curves in Fig. 7, the efficiency drop is due to entrainment, while the drop on the other side is essentially due to the decrease of liquid flow rate in the contact tubes.

In Fig. 8 the pressure drop of a theoretical plate is shown as a function of specific vapour mass flow rate under the same operating conditions. The values of Murphree's efficiency and the pressure drop of the plate, found in the experiments described here, are in good agreement with those found in the experiments carried out on one plate [4] as far as non-entrainment conditions are concerned.

The determination of plant equilibrium time was performed under the best operating conditions obtained from the plate efficiency tests, therefore the temperature was kept at 95 °C and the specific mass

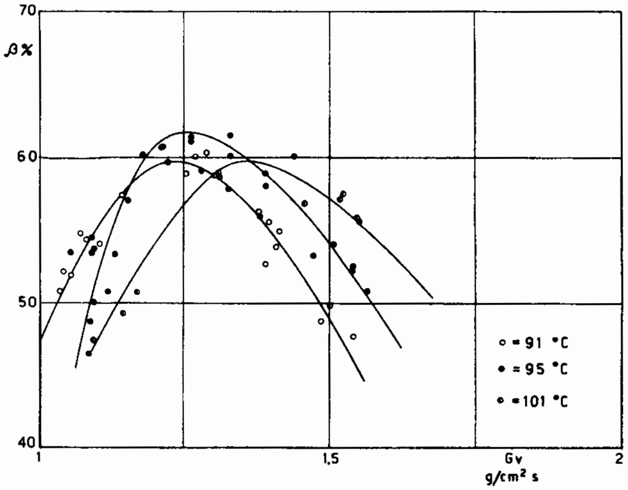

Figure 7. Plate efficiency β as a function of specific vapour mass flow rate

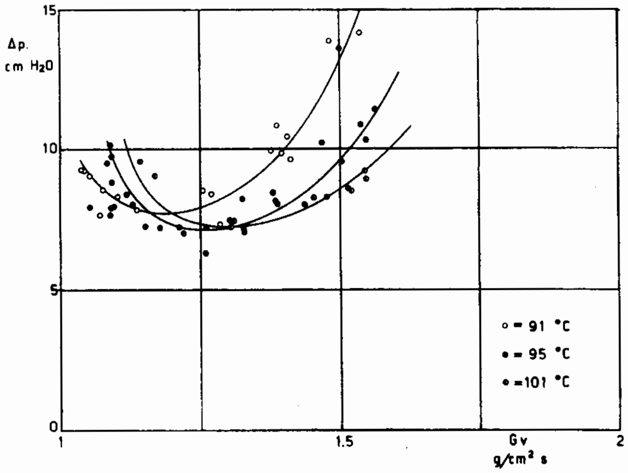

Figure 8. Pressure drop of a theoretical plate as a function of specific vapour mass flow rate

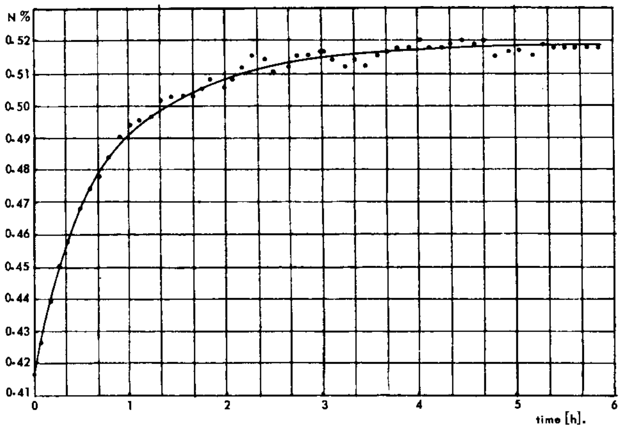

Figure 9. Deuterium concentration rise in an equilibrium time determination

flow rate of vapour was adjusted to 1.2 g/cm² s (equivalent to about 20 kg/h). One of the eight determinations of equilibrium time is shown in Fig. 9. The results of these determinations show that the plant reaches the steady state conditions of concentration in about 4 hours.

CONCLUSIONS

From the results of operation for 350 hours, some important conclusions can be drawn as to the behaviour of the plant.

The column shows a good flexibility, a variation of the specific mass flow rate of vapour between 1.2 and 1.4 g/cm² s does not appreciably change the performance of the column. Also entrainment does not constitute a serious problem provided that the operating conditions are not too far from the optimum. Last but not least, the control of the column is easy because of the low transit time for the liquid and vapour phases and the low hold-up involved.

The experiments described on a laboratory column show that the method is capable of development on a larger scale.

It is worthwhile pointing out that the distillation technique developed can be applied to a number of processes other than heavy-water separation.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/577 Italie

Une nouvelle technique de distillation pour la concentration isotopique

par M. Silvestri *et al.*

Il est bien connu qu'un liquide peut être contraint de s'élever sur une surface verticale sous forme d'un film liquide mince par l'action d'un courant de gaz suffisamment rapide.

Dans ces conditions, le transfert de masse a lieu en écoulement isotherme. Depuis 1957, aux laboratoires du CISE, on étudie l'application de l'écoulement annulaire à deux phases circulant dans le même sens comme mécanisme de contact pour la séparation des constituants d'un mélange isotopique. La séparation de l'oxygène 18 et du deutérium par distillation de l'eau à température ambiante en présence d'un gaz inerte a été la première application étudiée.

Une installation de distillation à cent étages a été projetée et construite pour vérifier les possibilités de réalisation et les meilleures conditions pour obtenir un contact satisfaisant entre les deux phases. Le gaz d'entraînement choisi était l'air. Le comportement de l'installation du point de vue du transfert de masse et de l'hydrodynamique a été étudié durant un fonctionnement de 2 000 heures.

Une nouvelle application de cette technique de contact a été faite dans le cas d'une colonne de distillation classique pour un système eau-vapeur; dans ce but, on a établi le projet d'un type convenable de plateau. Le comportement hydrodynamique d'un plateau et le transfert de masse ont été étudiés avec un système eau-vapeur à des températures comprises entre 90 et 110 °C.

A de nombreux points de vue, ce type de plateau s'est révélé plus avantageux que les plateaux classiques des colonnes de distillation de sorte que les recherches ont été poursuivies à l'échelle du laboratoire sur une colonne de 24 plateaux. Le rendement, les pertes de charge et le délai nécessaire pour atteindre les conditions de régime ont été mesurés. La colonne a été conçue pour la séparation de l'eau lourde par distillation fractionnée à des températures comprises entre 90 et 101 °C. On montre que la colonne composée de plateaux avec circulation des phases dans le même sens

permet une réduction considérable des dimensions par rapport à la colonne classique à plateaux à bulles; ces colonnes d'un type nouveau sont faciles à contrôler, elles ont un délai de mise en régime court et un faible contenu de liquide.

A/557 Италия

Новый метод дистилляции для концентрирования изотопов

М. Сильвестри *et al.*

Хорошо известно, что можно заставить жидкость подниматься в виде тонкой пленки по вертикальной поверхности, если для этого использовать газ с достаточно большой скоростью.

При этих условиях в изотермальном потоке имеет место перемещение массы. В лабораториях CISE вопросы применения совместного двухфазного кольцевого потока в качестве контактирующего механизма для разделения компонентов смеси изотопов изучаются с 1957 года. Вначале изучалось разделение O^{18} и дейтерия путем дистилляции воды при комнатной температуре в присутствии инертного газа.

Сконструирована и смонтирована 100-секционная дистилляционная установка для определения возможности и наилучших условий создания хорошего контакта фаз. В качестве газаносителя был выбран воздух. Массообмен и гидродинамика установки изучались в течение 2000 *ч* эксплуатации.

Дальнейшей стадией совершенствования контактного метода явилось применение этого принципа к обычной дистилляционной колонке в системе пар — вода. Для этой цели была сконструирована пластина соответствующего типа. Массообмен и гидродинамика пластины исследовались в ходе осуществления экспериментов в диапазоне температур 90—110° C в системе пар — вода.

Во многих отношениях такая пластина оказалась более удобной по сравнению с обычными дистилляционными тарелками, так что исследование проводилось на лабораторной колонке, собранной из 24 пластин. Изучались эффективность, перепад давления и время установления равновесия в колонке. Колонка предназначалась для разделения тяжелой воды методом фракционной перегонки при температуре 90—101° C. Показано, что пластиночные колонки с противотоком позволяют добиться значительного уменьшения размера колонки по сравнению с обычными колонками с колпачковыми тарелками. Они, по-видимому, более удобны в управлении, в них равновесие устанавливается за более короткое время и характеризуются малым удержанием материала.

A/557 Italia

Nueva técnica de destilación para la concentración de isótopos

por M. Silvestri *et al.*

Como es bien sabido, se puede hacer que un líquido ascienda a lo largo de una superficie vertical en forma de película fina por acción de una corriente gaseosa suficientemente rápida.

En tales condiciones, la transferencia de masa se produce en régimen isotérmico. En los laboratorios CISE se viene estudiando desde 1957 el escurrimiento anular de dos fases que circulan en el mismo sentido como mecanismo de contacto para la separación de los componentes de una mezcla isotópica. Como primera aplicación, se ha estudiado la separación de oxígeno-18 y de deuterio por destilación de agua a temperatura ambiente, en presencia de un gas inerte.

Se ha proyectado y montado una instalación de destilación de cien etapas para comprobar las posibilidades de realización del procedimiento y las condiciones en que el contacto entre las dos fases es óptimo. El gas de arrastre utilizado fue el aire. Se ha estudiado, durante 2 000 h de funcionamiento, la transferencia de masa y el comportamiento hidrodinámico de la instalación.

Otra aplicación de la técnica de contacto ha consistido en el perfeccionamiento de una columna de destilación para el sistema agua-vapor; a tal efecto se ha diseñado un tipo adecuado de plato. La transferencia de masa y el comportamiento hidrodinámico del mismo se han estudiado en experimentos efectuados a temperaturas comprendidas entre 90 y 110 °C en un sistema de agua-vapor.

En muchos aspectos, este tipo de plato ha resultado ser más práctico que los platos clásicos de destilación, de modo que las investigaciones prosiguieron en laboratorio con una columna provista de 24 platos. Se estudiaron el rendimiento, las pérdidas de presión y el tiempo necesario para alcanzar un régimen estacionario en la columna. Esta se proyectó para la separación de agua pesada por destilación fraccionada, a temperaturas comprendidas entre 90 y 101 °C. Se demuestra que las columnas de platos con circulación de las fases en el mismo sentido permiten una considerable reducción de las dimensiones, en comparación con las columnas clásicas de platos de burbujeo; su control parece sencillo, su tiempo de equilibrio es corto y la retención de material, reducida.

The economic separation of stable isotopes on a commercial scale

By A. O. Edmunds, E. Blancke and E. Rogers *

Separations of the isotopes of boron and carbon have been carried out for some time in the United Kingdom [1, 2, 3]. The demand for these materials although showing a steady increase has been found extremely difficult to forecast. The original demand for boron-10 in the United Kingdom was for highly enriched boron trifluoride gas for proportional counters used to measure thermal neutron flux. The number of applications has now increased and covers, in addition, a wide variety of compounds of boron-10. Typical applications include: control and safety rods, burnable poisons in fuel elements, flux fuses and incorporation in materials such as stainless steel, aluminium and plastics to produce neutron shields of minimum weight and thickness.

Considerable reductions in the price of boron-10 in the United Kingdom have been achieved during the last five years as a result of the increasing number of applications. The demand for carbon-13, whilst on a much smaller scale than that of boron-10, has also shown a steady increase which has now outstripped the original production facility.

THE BORON PLANT

Design considerations

The direct distillation of boron trifluoride gas at low temperatures has been well established as a method for continuous production of boron-10 at a fixed rate [4]. To lay the basis for an annual increase in demand a design study was carried out for a plant with a production rate of 100 grams per day of boron with enrichments up to 95 at. % boron-10. It was necessary that the plant should operate economically for high and low production rates and, in addition, the capital cost should be low. These requirements led to the choice of a chemical exchange distillation process and our previous extensive experience of boron trifluoride dimethyl ether led to its adoption as the working material. The main factors governing the design are: scale of production, product enrichment, theoretical plate height obtainable, the stripping efficiency required and the available building height. With the high natural isotopic abundance of boron-10 (18.8 at. %) it was reasonable to consider a single column unit capable of producing the maximum enrichment required. With the building height available it was found possible to construct a unit with a production rate of 10 grams per day at 92 at. % boron-10, or 5 grams per day at 95 at. %. Consideration was then given to the choice between ten such units and a cascade system similar in concept (but of smaller scale) to the American plant [5]. This detailed consideration led to the adoption of a multiplicity of single columns for the following reasons:

(*a*) The short equilibrium time of such a unit due to the negligible static hold up of the intermediate boiler;

(*b*) The transfer of material from one column to another using liquid pumps was not required;

(*c*) The capital cost of the units was low owing to their comparative simplicity and the short equilibrium time meant that new units could be brought quickly into production.

Furthermore, although the original design estimate had been for 100 grams per day to meet an anticipated increase in demand, adoption of single units allowed actual demand to be met at any time without stockpiling the product.

The column height and packing

At least 300 plates were known to be needed to obtain the necessary separation, 240 in the rectifying section and 60 in the stripper. Plate height experiments were carried out using 3 in internal diameter tubing as this was considered to be the largest size likely to yield a plate height of under 2 in. The tests were carried out using packing of our own design and it was found that plate heights of between 1.8 in and 2 in could be obtained at the boil-up rates and partial pressure envisaged in the rectifier section. The packing used, a 1/4 in by 1/4 in 60 mesh stainless steel gauze ring has an excellent pressure drop characteristic, a very important property in this application where charring can occur even at moderate boiler temperatures.

Although a substantial increase in boil-up was anticipated in the stripper due to the extra electrical

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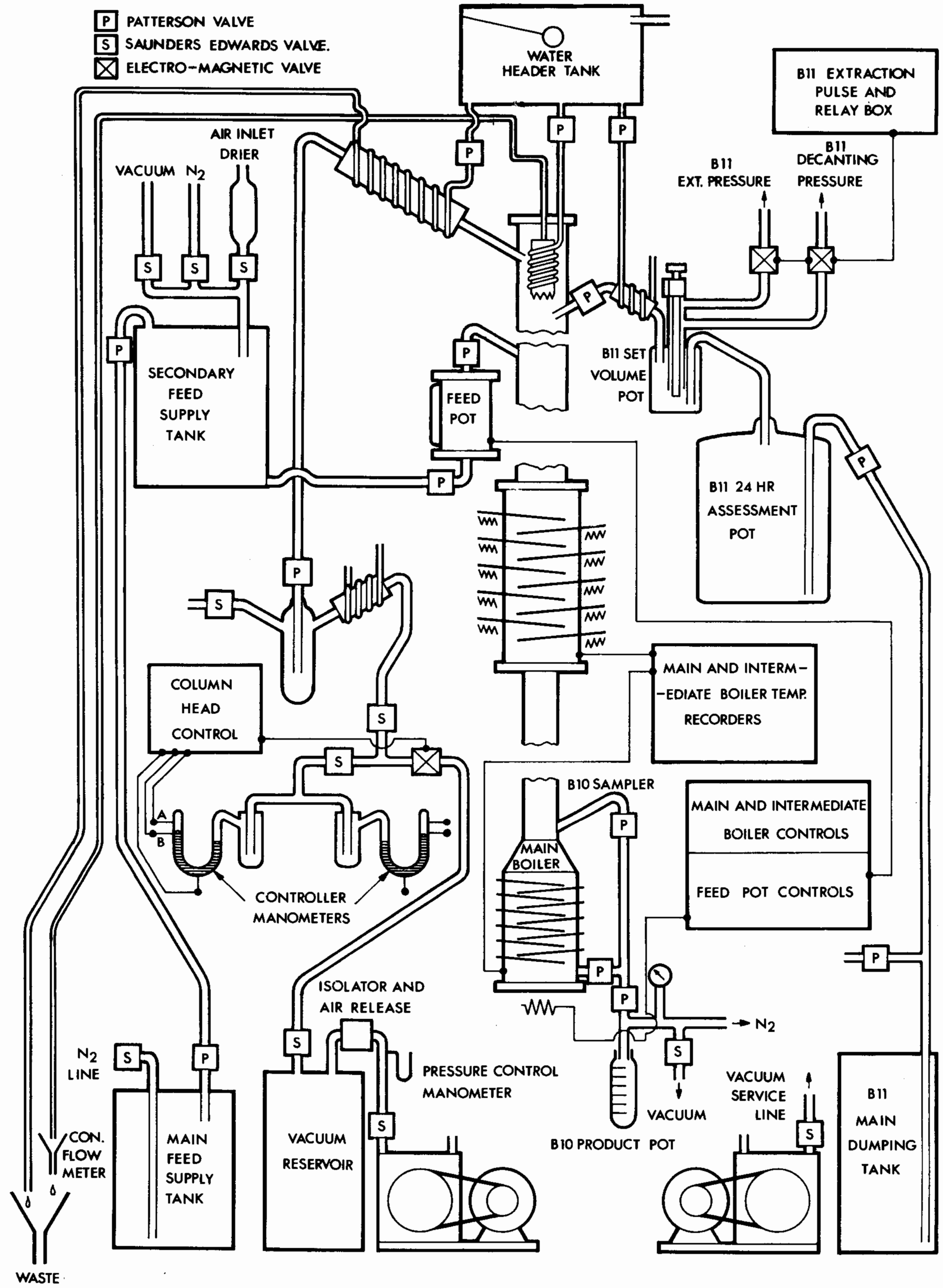

Figure 1. General arrangement of a unit column

power applied at the intermediate boiler, it was considered that plate heights of under 4 in could be expected in the upper 4 in diameter section if suitable redistributors were incorporated.

The unit column

Columns were constructed to confirm the experimental results and were of the following form : A rectifying section, 46 ft long, was surmounted by a stripper, 18ft long, with a main boiler at the base and an intermediate boiler mounted at the junction of the 4 in and 3 in section, 6 ft below the feed point. The general arrangement is shown in Fig. 1. Lagging and trace heating have been omitted for the sake of clarity. The main column sections and all pipework have been fabricated in copper.

Basic controls such as feed arrangements and boiler hold-up are identical to those described in a previous paper [3]. Transfer of feed material between the various containers is accomplished by pressure difference using dry nitrogen. Final transfer from the feed pot into the column is carried out by vaporizing the boron trifluoride dimethyl ether using suitably controlled heating elements.

The condenser and associated equipment

The column is designed to operate with a condenser pressure of 30 mm. A constant condenser pressure which is very desirable in plant of this type has been found extremely difficult to maintain in columns of this size. Considerable development has therefore taken place in the associated controlling equipment to minimise column head pressure changes and their effect on the plant as a whole. The most serious difficulties occur due to over-pumping which lowers the column head pressure below the correct level. This can produce surges of vapour which the condenser is unable to absorb, particularly if it is set critically for maximum column efficiency. These surges then carry over large quantities of vapour into the pumping equipment where condensation occurs. Apart from the difficulty of handling this liquid in the pipe lines and control gear, the balance of the column is seriously upset and thermal control of the boiler is often lost. The column head arrangement shown in Fig. 1 has been designed to overcome this difficulty in the following way: the pumping lines controlling the column head pressure pass through two condensers. The water flow in the main condenser is adjusted to absorb the normal boil-up under steady conditions. The secondary condenser has a cooling capacity at least ten times that of the main condenser thus ensuring that no surges of vapour are allowed past it into the pumping and control pipe-work. The condensers are continually monitored with a thermo-couple system giving both instantaneous readings and audible alarm.

In a plant of this type it is implicit, for economical operation, that the maintenance be kept to a minimum and reliability extremely high. These considerations govern every part of our column design and are well illustrated in the column head controller. The sensing element consists of a small sealed mercury manometer with electrical contacts positioned to operate at the correct partial pressures. Relay contacts proved unreliable in service so solid state switching is now employed to control the pressure regulating valves. This arrangement reduces the switching current in the control element appreciably which adds further to the reliability of the whole system.

Boiler design

One of the aims in operating plant using boron trifluoride dimethyl ether is that of minimising charring of the working fluid in the boiler. Apart from the serious loss of product which can occur from this cause, the related clogging and coking in the lower part of the boiler leads to extraction difficulties and serious inconsistencies in the boiler temperature/content characteristic. Since this is used for controlling the boiler hold-up it is imperative that serious charring be avoided [3].

To obtain a good control using the constant boiler power input system the region A B of Fig. 2 should be flattened as much as possible. The points from zero content to the turnover point at 250-300 cc. content should not be too steep. Further, after the turnover point is reached temperature rise at the

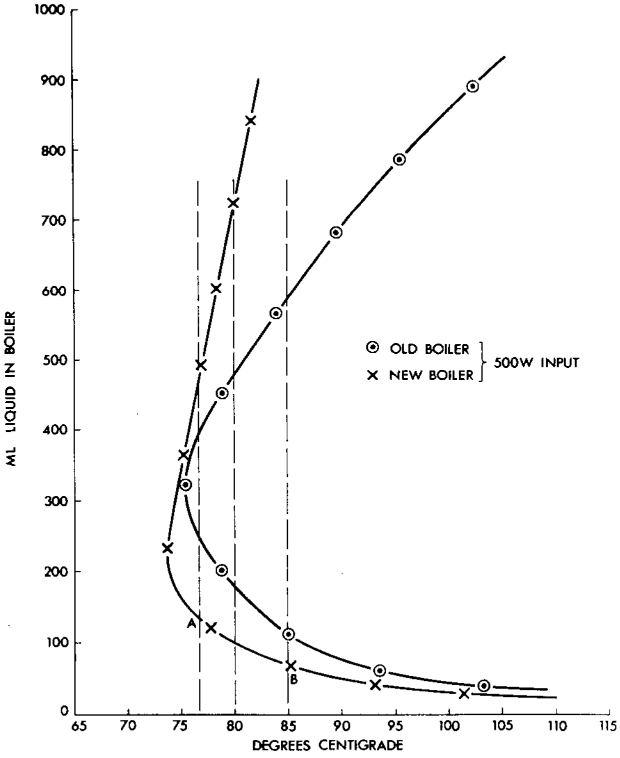

Figure 2. Bottom boiler characteristics

higher content levels should be as small as possible to minimise charring and decomposition from superheat effects when the boiler is flooded. These cause losses which have a direct bearing on the economics of the plant. The equilibrium time is directly affected by the hold-up in the boiler and this also must be borne in mind when considering a design. The final main boiler design is shown in Fig. 3. It consists of a 4 in inner diameter tube slotted as indicated and into which are brazed shaped copper evaporation plates angled and cross-grooved to obtain good reboiling characteristics. Ten grooves, approximately 0.01 in deep are cut across the plate having a pitch of approximately 0.4 in (see fin detail in Fig. 3). The semi-circular cutouts are to allow free passage to the rising vapour being generated below. Using heavy gauge tubing for the body of the boiler made it possible to keep the temperature difference between the boiler heater at the base and the top evaporator plate small (approximately 5 °C) at bottom boiler powers of 550-600 watts.

The intermediate boiler uses the same evaporator plate design and angle of slot but has no base. Heat is therefore injected into each individual plate by a smaller heater mounted on an extension to the plate as shown in Fig. 3 b. It has been found possible to operate these boilers with input powers up to 1 kW without producing temperature differences of more than 10 °C between the evaporator plates and the refluxing liquid. It can now be said that with the dimensions of column now in use boiler input power is no longer a limiting factor. Loss of column efficiency at the higher boil-up rates makes it necessary to run well within the ratings of the boilers.

Boron-11 extraction system

The extraction of boron-11 from the top of the column must be maintained at a very constant mean rate. It was therefore essential that some automatic metering of the extraction be arranged and this took the form shown in Figs. 1 and 4. The flow from the column is controlled by a pressure difference maintained by local vacuum service lines between the column and the extraction system. The metered volume consists of a small glass container of special shape (Fig. 4). This has a thermally sensitive finger mounted inside it which is set to a critical height in the container. Two partial pressure lines are used, one adjusted to be slightly below the column pressure at the extraction point and the other slightly above. An electromechanical timer is used which can be adjusted to the required number of cycles per hour, and the complete system works in the following way. In the extraction phase solenoid valve EMV2 is open and EMV1 is shut. The glass container slowly fills until the liquid touches the sensing element which closes EMV2. As a result of this change the pressure in the extraction system rises to that of the column and no further extraction occurs. After a time interval determined by the electromechanical timer, valve EMV1 opens discharging the contents of the metered volume into the boron-11 assessment container (normally kept at column pressure). Immediately after this operation

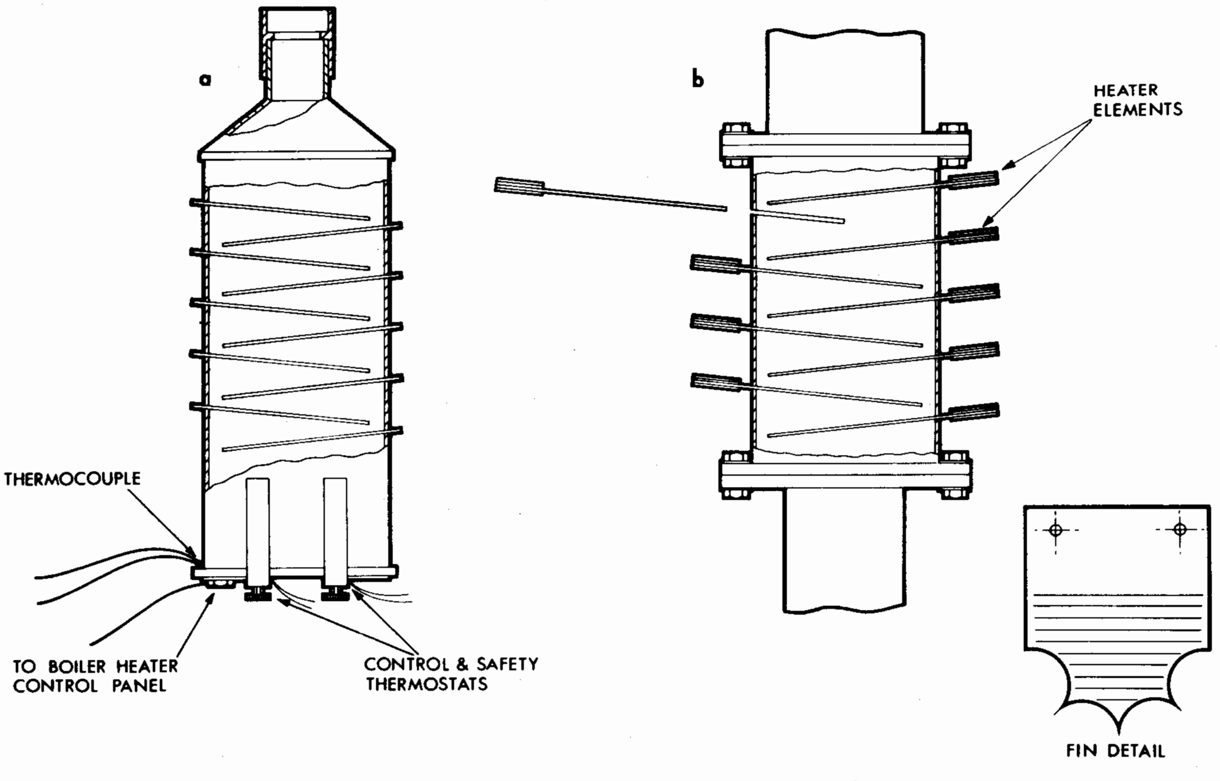

Figure 3. (*a*) Bottom boiler; (*b*) Intermediate boiler

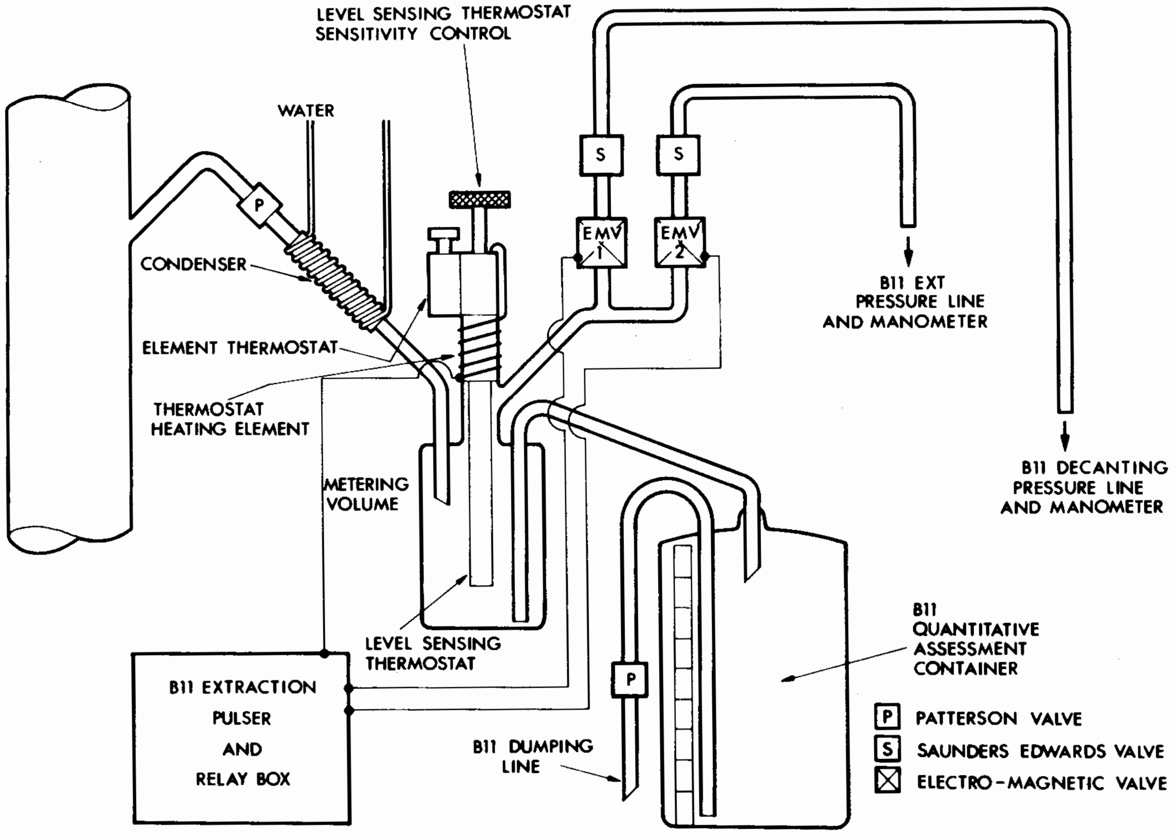

Figure 4. Boron-11 extraction

the timer resets to zero time, valve EMV1 is closed, valve EMV2 and a new cycle commences.

CARBON-13 PLANT

A carbon-13 plant based on one designed in 1949 (H. London and T. Johns [2]) has been operating in the United Kingdom for some years. The process is one of fractional distillation of carbon monoxide at a temperature of 70 °K using a pumped liquid nitrogen condenser. This was quite close to the triple point of CO (68 °K) as experiments indicated that the separation factor rose steadily from 77 °K down to the triple point at 68 °K [5]. Although there is no doubt that this is the case, the measurements were carried out using a vapour pressure apparatus, not distillation equipment. Subsequent experiments at a later date using a packed column and an atmospheric nitrogen condenser (77.4 °K) produced results indicating that little change of apparent separation factor occurred when operating at a higher temperature. This has been attributed to a competing effect due to the change of operating pressure from approximately 300 mm to 720 mm at the higher temperature [7].

Since substantial simplification results from running the condenser at atmospheric pressure the new plant recently constructed has been designed to operate at this pressure. When the plant is run under these conditions neither nitrogen pumps nor partial pressure control equipment are needed. Consideration was given to operating without a column head/liquid nitrogen reservoir but it was thought advisable to maintain this arrangement so that supplies could be taken from it to new units when required. To make absolutely certain that no loss of enrichment occurred as a result of these changes the packed height was increased from 32 ft to 38 ft. This raised the number of plates in the rectifier from 600 to approximately 730. A condenser vessel of much greater capacity has been used and the feed is arranged via a syphon vapour pump from a 70 litre container at ground level (Fig. 5). The large volume allows well spaced replenishing cycles of the order of 30 minutes which avoids continual cooling of the syphon tube and reduces coolant losses. The fact that the main container at ground level can be vented to the atmosphere via EMV3 between feed periods ensures that the liquid nitrogen remains in equilibrium at atmospheric pressure and does not boil violently when it is fed into the condenser.

The electromagnetic valve EMV1 (Fig. 6) meters liquid nitrogen into the condenser and is operated by the controlling vapour pressure thermometer (VPT). The level in the reservoir is maintained by the sensing element in that container operating EMV2. Interlocks link EMV2 with EMV3 and 4 (Fig. 5) so that in the feed condition EMV4 and 2 are open and EMV3 is

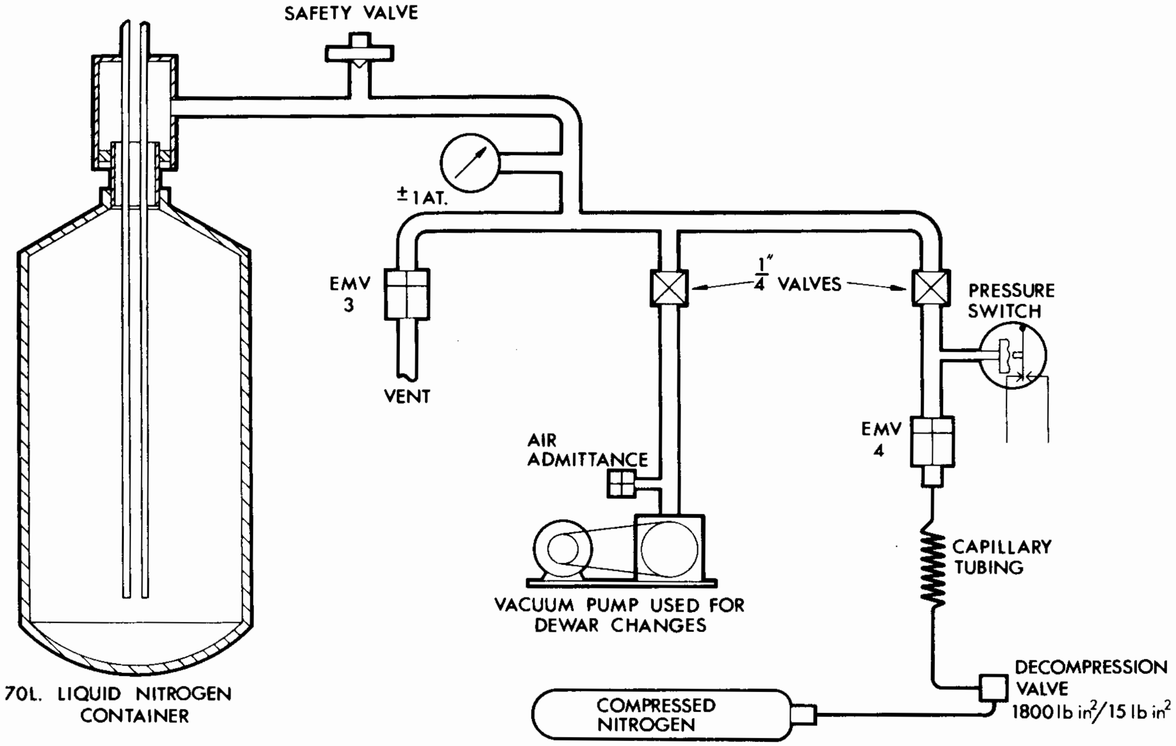

Figure 5. Ground level N_2 container, carbon-13 plant

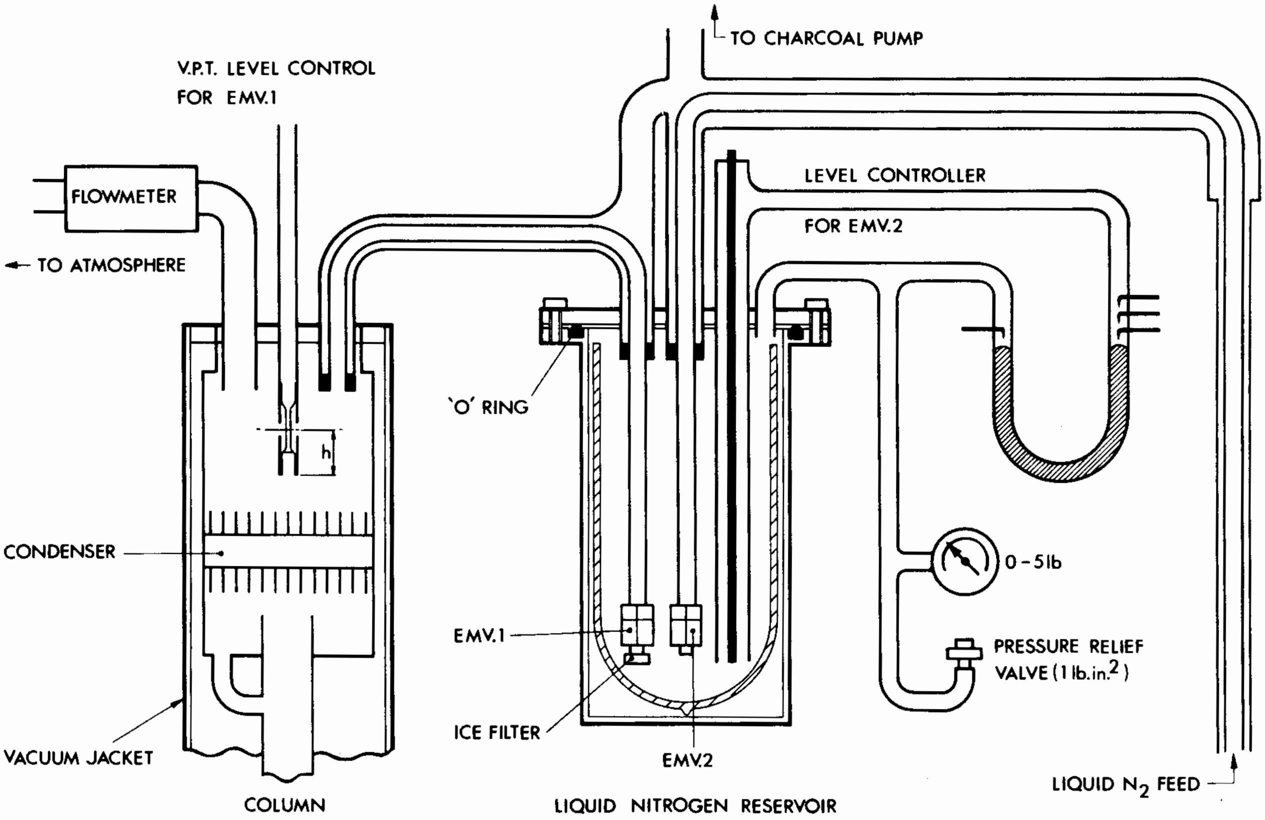

Figure 6. Reservoir container, carbon-13 plant

shut. Furthermore, an over-ride control ensures that EMV2 is held shut whilst EMV1 is open and no liquid nitrogen enters the reservoir whilst the condenser is taking in feed. It has been found that the condenser temperature remains more stable under these conditions and there is less possibility of the condenser feed cycle upsetting the column.

A small positive pressure (1-2 pounds/in^2) is required to transfer coolant from the reservoir to the condenser and this is obtained by using a sealed reservoir vented to the atmosphere with a safety valve set at the required level.

CONCLUSION

Requirements for boron-10 range in quantity from a few grams to many kilograms, in enrichment from 50 to 95 at. % and a plant consisting of a multiplicity of the units herein described is capable of meeting these various requirements at a minimum cost and optimum efficiency. For most requirements parallel operation has proved satisfactory and variations in product enrichment can be controlled by altering the flow rates. A unit column produces 10 grams per day when running at an enrichment level of 92 at. %, and 5 grams per day at 95 at. %. For higher enrichments a booster column is used. Maintenance and operation of this plant has proved straightforward and does not require skilled labour.

The efficiency of carbon-13 production has been improved by a significant saving in nitrogen coolant. The new condenser functions well and the atmospheric arrangement, eliminating as it does three backing pumps and their associated valves and switches has improved the reliability of this section of the plant.

Multi-kilogram quantities of boron-10 and boron-11 are now being handled, the main forms being elemental boric acid and boron trifluoride gas. A wide range of compounds of both boron-10 and boron-11 and carbon-13 is now available.

ACKNOWLEDGEMENTS

The authors wish to thank Mr. R. W. McIlroy of AERE Harwell for many useful discussions relating to the design and operation of the boron plant and Mr. T. F. Johns and Mr. J. Hill of AERE Harwell for their advice in connection with problems on the carbon-13 plant.

Our thanks are also due to our colleagues in the isotope section whose responsibility it was to erect and commission the plant and to the Directors of 20th Century Electronics Limited for permission to publish this work.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/567 Royaume-Uni

Séparation économique des isotopes stables à l'échelle industrielle

par A. O. Edmunds *et al.*

Depuis quelque temps déjà, on effectue, au Royaume-Uni, la séparation des isotopes de bore et de carbone. En 1953, on a commencé le travail sur la séparation du bore 10; à cette époque on était spécialement intéressé à obtenir du gaz BF$_3$ hautement enrichi pour le remplissage de compteurs. Contrastant avec ceux des États-Unis, où il existait une demande appréciable, les besoins initiaux européens étaient faibles et sporadiques. Cette fluctuation de la demande exigeait une conception spéciale de l'installation afin d'obtenir une unité de production économique. Le développement a pris la forme d'une multiplicité d'ensembles indépendants à la base, car on a trouvé que de tels ensembles offrent le maximum de flexibilité du point de vue de la production, de la gamme des enrichissements et de l'utilisation des matières premières.

Les problèmes techniques relatifs à l'utilisation de diméthyléthérate de trifluorure de bore dans les installations de distillation et d'échange chimique proviennent presque entièrement de deux de ses propriétés : sa nature hautement corrosive, particulièrement en présence de faibles quantités d'humidité, et sa tendance à se décomposer à des températures assez modérées. Les travaux de mise au point mentionnés

ci-après ont été faits en ayant bien présentes à l'esprit ces propriétés limitatives.

La conception des chaudières, le garnissage des colonnes, le contrôle partiel de la pression et les méthodes d'extraction sont autant de facteurs affectant la température de fonctionnement d'une manière directe ou indirecte. Un garnissage de haute efficacité avec faible chute de pression a été mis au point, de nouvelles chaudières ont été conçues et la tête de la colonne et les commandes d'extraction ont été améliorées. Les qualités des appareils à cascades et à une phase (effectuant l'enrichissement depuis l'abondance naturelle jusqu'à 90 % de bore 10 en une seule phase) font l'objet d'une discussion et on expose la toute dernière conception de l'appareil à une seule phase. L'installation actuelle se compose de huit appareils de ce genre, produisant de 25 à 30 kg par an. Les considérations économiques jouent également un rôle important en ce qui concerne la conception et des aspects tels que la simplicité de fonctionnement et de construction. Le temps d'équilibre est particulièrement important et les appareils décrits peuvent être en pleine production dans les cinq semaines suivant leur mise en marche. Ainsi une décision d'augmenter la production peut être appliquée relativement rapidement.

En 1949 déjà, la séparation de carbone 13 était effectuée par l'Atomic Energy Authority du Royaume-Uni. La demande n'en est encore que de l'ordre de quelques grammes par semaine et dans la nouvelle installation les progrès ont été orientés vers des économies, à la fois dans l'utilisation du réfrigérant (qui constitue le coût principal de la fabrication) et par l'amélioration de la régularité de fonctionnement. La mise en marche de la nouvelle installation a doublé la production de carbone 13 et ces progrès sont exposés en détail.

A/567 Соединенное Королевство

Экономичные методы разделения стабильных изотопов в промышленности

А. О. Эдмундс *et al.*

В течение ряда лет в Соединенном Королевстве ведутся работы по разделению изотопов бора и углерода. В 1953 году приступили к извлечению B^{10}, в то время главной задачей была поставка сильно обогащенного газа BF_3 для заполнения счетчиков. В противоположность США, где существовал большой спрос, первоначальные потребности Европы были незначительны и носили спорадический характер. Эти колебания спроса вызывали необходимость особого подхода к конструкции установок для получения экономичных производственных агрегатов. Разработка приняла форму создания преимущественно независимых устройств, так как было установлено, что они обеспечивают максимальную гибкость с точки зрения мощности, степени обогащения и потребления сырья.

Технические проблемы, связанные с использованием эфирных соединений трехфтористого бора на химической установке, работающей по схеме обменной дистилляции, возникают почти полностью вследствие двух свойств, а именно: их сильного коррозионного характера, в особенности в присутствии небольших количеств влаги, и их тенденции разлагаться при совсем умеренных температурах. Описываемые ниже этапы строительства осуществлялись в значительной мере с учетом этих свойств.

Как конструкция испарителя, так и насадка колонны, контроль парциального давления и методы извлечения отражаются прямым или косвенным образом на рабочей температуре. Найдена насадка, характеризующаяся высокой эффективностью и малым перепадом давления, сконструированы новые испарители и головная часть колонны, усовершенствованы приборы, регулирующие извлечение. Обсуждаются особенности каскадных и некаскадных агрегатов (обогащение от природного содержания до 90% B^{10} в одной ступени), дается краткое описание последней конструкции одноступенчатой установки. Существующая в настоящее время установка состоит из восьми таких агрегатов производительностью 25—30 *кг/год*. Экономические факторы оказывают также сильное влияние на конструкцию, причем приходится учитывать такие аспекты, как простота эксплуатации и сооружения. Особенно важную роль играет время установления равновесия. Описанные агрегаты могут достичь полной мощности пять недель спустя после их запуска. Таким образом, решение об увеличении производительности можно осуществить относительно быстро.

Уже в 1949 году Управление по атомной энергии Соединенного Королевства проводило в небольшом масштабе извлечение C^{13}. Спрос все еще выражается в нескольких граммах в неделю. На новой установке усилия были направлены на осуществление экономии как в использовании охладителя (главная статья расходов по изготовлению), так и на повышение надежности. Введение в строй новой установки удвоило производство C^{13}. В докладе подробно описываются достигнутые преимущества.

A/567 Reino Unido

Separación económica de isótopos estables a escala comercial

por A. O. Edmunds *et al.*

Durante algún tiempo se ha efectuado en el Reino Unido la separación de los isótopos del boro y del carbono. En 1953 comenzó el trabajo de la separación del boro-10, entonces principalmente para el suministro de BF_3 gaseoso altamente enriquecido, destinado al llenado de contadores. Al principio, las necesidades europeas eran pequeñas y esporádicas, a diferencia de los Estados Unidos, donde existía una demanda importante. Esta demanda variable requirío un especial diseño de la instalación con objeto de obtener una unidad de producción económica. Su desarrollo ha tomado la forma de una multiplicidad de unidades básicamente independientes, que dans la máxima flexibilidad desde el punto de vista de la producción, intervalo de enriquecimientos y utilización de materias primas.

Los problemas técnicos relativos al uso del compuesto doble de trifluoruro de boro y éter, en instalaciones de intercambio químico y de destilación, son debidos, casi enteramente, a dos de sus propiedades: su naturaleza corrosiva, particularmente en presencia de pequeñas cantidades de humedad, y su tendencia a descomponerse a temperaturas bastante moderadas. Los desarrollos que siguen se han efectuado teniendo muy presente estas propiedades limitadoras.

La temperatura de operación es afectada de un modo directo o indirecto por el diseño de los calderines, el relleno de la columna, el control de la presión parcial y los métodos de extracción. Se ha desarrollado un relleno de alto rendimiento con baja caída de presión, y se han proyectado nuevos calderines, mejorándose la cabeza de la columna y los controles de extracción. Se discuten las ventajas de las unidades de cascada y de paso único (enriquecimiento desde el natural al 90 % de boro-10, en un paso único), y se indica el último diseño de una unidad de paso único. Nuestra instalación actual consiste en 8 de dichas unidades, produciendo de 25 a 30 kg por año. Las consideraciones económicas han representado también un importante papel en el proyecto, y se deben tener en cuenta aspectos tales como la simplicidad en la operación y en la construcción. El tiempo de equilibrio es particularmente importante, y las unidades descritas pueden estar en plena producción dentro de cinco semanas a partir de la puesta en servicio. Por lo tanto, una decisión de incrementar la producción puede cumplirse de un modo relativamente rápido.

Ya en 1949, la Atomic Energy Authority del Reino Unido efectuó alguna separación del carbono-13. La demanda es todavía del orden de los gramos por semana solamente, y en la nueva fábrica el desarrollo se ha orientado para conseguir economías en el uso del refrigerante (el principal gasto de la fabricación) y en mejorar el funcionamiento. La puesta en marcha de esta nueva instalación ha doblado nuestra producción de carbono-13; en la memoria se discute ampliamente este hecho.

Separation by countercurrent exchange-electrolysis applied to lithium isotopes

By G. J. Arkenbout *

In the field of reactor technology several applications of pure lithium isotopes are possible [1]:

(*a*) The use of lithium-7 as a coolant in a nuclear reactor;

(*b*) The application of 7LiH or 7LiD as a moderator in a high temperature reactor;

(*c*) The use of 7LiF as a solvent for nuclear fuels.

The technical separation of the lithium isotopes still constitutes a problem. According to recent publications, separation by countercurrent exchange-electrolysis is one of the rare methods that might lead to acceptable results.

Hitherto literature on this subject has been rather scarce. Apart from a French patent of the Commissariat à l'énergie atomique, which appeared in 1959 [2], we found only a paper by Lewis and Macdonald dating as far back as 1936 [3]. By letting fine droplets of amalgam descend through an ascending alcoholic solution of lithium chloride, Lewis and Macdonald obtained a noticeable separation in a column 18 m in length and only 4 mm wide. From their paper it appears that the maintenance of the desired zigzag movement of the amalgam droplets is a severe problem.

The information which may be derived from the French patent mentioned above is rather poor. No data on the experimental conditions such as the dimensions of the columns, flow rates of the phases, size of the amalgam droplets and no results on the separations obtained are given. However, the application of dimethyl-formamide as a solvent for the electrolytic phase instead of alcohol is new.

In the present paper, it will be shown that the problem of keeping the amalgam dispersed can be solved by using a finely packed column. Further, a new continuous method (based on exchange) for obtaining an anodic reflux will be presented.

COUNTERCURRENT EXCHANGE-ELECTROLYSIS

Mass transfer between an ionic conducting electrolytic phase and an electronic conducting electrode phase can be realised in several ways. It can be obtained by contacting the two phases, each containing a mixture of the metals A and B in concentrations different from the equilibrium values. When the electrode potential of metal A is higher than that of B, ions of metal A will be reduced and will move into the electrode phase. At the same time, an electrochemically equivalent quantity of metal B will be oxidised and transferred to the electrolytic phase. Such an exchange will be called exchange-electrolysis. The elementary separation effect of this exchange-electrolysis can be accumulated by a countercurrent transport of the two phases in a column. The separation method based on this principle will be called countercurrent exchange-electrolysis (CCEE).

In each cross-section of a CCEE column, an electrochemical balance will be maintained, provided secondary chemical or electrochemical reactions do not interfere. The rate of exchange is proportional to the deviation from equilibrium. The rate also depends on the interface area, the thickness of the liquid layers and a number of electrochemical factors. The equilibrium conditions may be formulated by the Nernst equation. For a mixture of two metals having the same valence, the Nernst equation is

$$K = \frac{x\,(1 - y)}{y\,(1 - x)}$$

K = equilibrium constant.

x, y = gramequivalent fraction of lithium-6 in the amalgam and the electrolytic solution, respectively.

The equilibrium constant K may also be called the elementary separation factor of the system. A mathematical treatment of the multiplication of an elementary effect in a column has been given by Cohen [4].

A complete apparatus for CCEE consists essentially of three parts, *viz.*, the exchange column and two reflux sections. The reflux sections at the top and at the bottom of the column, where the lithium is transported from the electrolytic solution to the amalgam and vice versa, are called the cathodic and anodic reflux sections.

APPLICATION OF A PACKED COLUMN

So far the countercurrent between the electrode and the electrolytic phase has been achieved in unpacked columns. In these columns, both the contact surface

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and the residence time per unit of length are rather small. In view of the difficulties presented by unpacked columns it was considered whether a suitable packed column could be found.

When a countercurrent of an amalgam and an electrolytic solution was started in a packed column without any precautions, it appeared that severe channelling occurred. This channelling resulted in a poor contact interface and could not be decreased by prolonging the process. However, it was found that this difficulty could be overcome if the column was started in a special way.

The required distribution of the two phases was obtained by first filling the free volume completely with mercury and then partly replacing the mercury by the electrolytic solution. This filling treatment may be explained as follows. The interstices in the packing may be considered as capillaries and the filling of a capillary with mercury requires considerable energy due to its high surface tension. Therefore, the mercury will not enter the empty capillaries as long as it can pass down through some channels of the column which are already filled with mercury. Therefore, a homogeneous distribution in the column cannot be obtained without previously filling all the capillaries with mercury.

In the column, neither of the phases seems to be fully dispersed. The mercury flows down in a continuous stream between the packing particles, whereas the electrolytic phase follows the surface of the packing and the wall when ascending.

Sand with a particle size of between 0.35 and 0.5 mm acts very well as a packing material. We have used columns 1 and 2 m in length and 2.5 cm wide (inner diameter). The ratio between the volumes of the electrode and electrolytic phases in the column was about 4 : 3. The flow rates of the both phases were 0.1 or 0.2 ml/min cm^2.

CHOICE OF THE ELECTRODE-ELECTROLYTE SYSTEM

Mercury may be used as a solvent for the electrode phase in the separation of the lithium isotopes by CCEE.

The choice of solvent for the electrolytic phase is more difficult (many solvents react with lithium amalgam or do not dissolve lithium salts to a sufficient extent). The activation polarisation of the applied electrode reactions must be small, so that the rates of exchange will be sufficiently large. Dimethylformamide (DMF), already mentioned in a French patent [2], seemed to be the most promising solvent. DMF does not react with lithium amalgam and dissolves lithium halogenides very well. From polarographic measurements it was deduced that the rates of exchange in DMF will be sufficiently large [5]. Except for the first two experiments with lithium bromide, all other experiments were carried out with lithium chloride.

The elementary separation factor of the system Li(Hg)-LiBr(DMF) was determined by Perret and co-workers [6]. They mixed an amalgam and a DMF solution containing lithium with rather different isotopic ratios and analysed the isotopic ratios in both phases. It follows from their experiments that the elementary separation factor amounts to 1.05 ± 0.025.

We have deduced the elementary separation factor from CCEE experiments without reflux. The elementary separation factor found in this way for lithium chloride as well as for lithium bromide is 1.05 ± 0.02.

THE ANODIC REFLUX

The discontinuous method of refluxing mentioned in the literature [2, 3] is not promising. A continuous procedure for the anodic reflux based on a reaction with acid is not very attractive.

We have developed an anodic refluxing procedure based on exchange electrolysis with DMF solutions containing halogenides of the alkaline or alkaline earth metals. For several reasons, halogenides of other metals appeared to be less suitable. Actually, sodium bromide and strontium chloride have been used because of their appropriate solubility.

A large and constant reflux fraction can only be obtained if the amount of reagent supplied to the refluxing section is exactly equivalent to the amount of lithium entering the refluxing section. This amount of lithium may vary because of changes both in the flow rate and in the concentration of the amalgam. This means that the supply of reagent must be adapted to the lithium flow. This necessary adaption is easily achieved with the refluxing method presented.

The anodic refluxing apparatus developed shown in Fig. 1 consists of three parts: the lower part of the exchange column, the refluxing column and the saturating section. The refluxing column is a sand-filled column 20 cm in length and 2.5 cm wide.

The amount of reagent supplied to the exchange column per unit of time is kept too small to oxidise all the lithium, yet large enough to transfer about 80% of the lithium to the electrolytic phase. By introducing only about 80% of the required reagent into the lower part of the column, any danger of the reagent penetrating too far into the column is prevented. The amalgam leaving the exchange column and entering at the top of the refluxing column still contains 20% of the original amount of lithium metal. At the bottom of the refluxing column, a saturated or at least concentrated DMF solution of sodium bromide or strontium chloride is introduced. In the refluxing column, the lithium left in the amalgam exchanges with some of the sodium or strontium ions. As a result, the amalgam leaving the refluxing column contains no lithium.

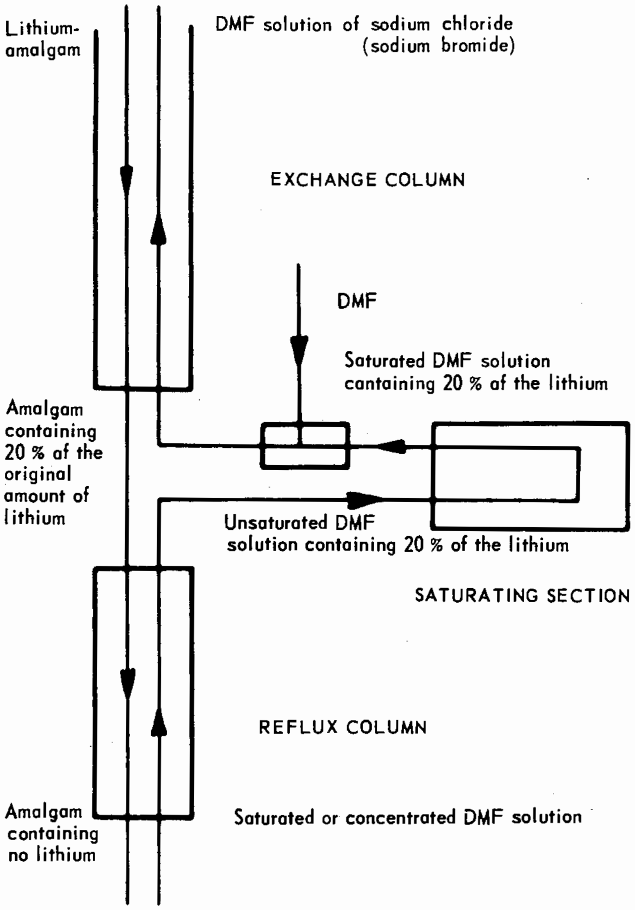

Figure 1. The anodic reflux section

The reagent solution leaving the refluxing column is saturated in the saturating section by mixing the solution vigorously with solid sodium bromide or strontium chloride. The temperature of the saturating section is constant. The solution leaving the saturating section is diluted to the required extent and then pumped into the exchange column. By using this procedure, the concentration of the reagent solution entering the exchange column is kept constant and independent of the amount of lithium exchanged in the refluxing column.

The lithium amalgam is easy to handle, provided that the concentration of the lithium does not exceed $0.5M$. The saturation concentrations of sodium bromide and strontium chloride are $0.95M$ and $0.35M$. Since equal flow rates are required for both phases, the DMF solution leaving the saturating section was diluted to double its volume before entering the exchange column.

THE CATHODIC REFLUX

The cathodic reflux was obtained discontinuously by evaporating the DMF, dissolving the salt residue in water and electrolysing the aqueous solution. Lithium chloride has been chosen as the salt, as the gaseous chlorine, liberated at the anode, can be removed very simply due to its limited solubility. The electrolysis of an aqueous solution of an alkaline chloride is complicated by many side reactions [7]. The electrolyser finally used and shown in Fig. 2, produced lithium amalgam in small amounts (1 ml/min) with a current efficiency up to 95%. The concentration of the lithium chloride must be larger than $2M$. The volume of the electrolytic solution is 15 ml [8].

The good results obtained with this electrolyser are due to the high current density, the small contact time of the amalgam and electrolytic solution and the continuous and quick removal of the amalgam. The height of the mercury level in the cell is very important. Solid lithium amalgam is formed if the mercury level rises a few millimeters, whereas current fluctuations occur if the mercury level drops.

The DMF was evaporated in a vacuum. At intervals of about one hour, 5 ml of electrolytic solution were removed from the electrolyser and used for dissolving solvent free lithium chloride. The solution obtained was returned again to the cell.

Obviously, this refluxing method has some disadvantages. Improvement of this refluxing method will be the subject of further investigation. The large hold-up of lithium chloride in the refluxing section (equivalent to about 200 ml electrolytic phase) caused by the large concentration in the aqueous solution is an additional drawback, demanding further attention.

THE SEPARATION EXPERIMENTS

Ten separation experiments have been carried out in sand-filled columns 1 or 2 m in length and 2.5 cm wide as follows: four experiments with an anodic reflux only, at the bottom of the column, four experiments with a cathodic reflux only, at the top of the

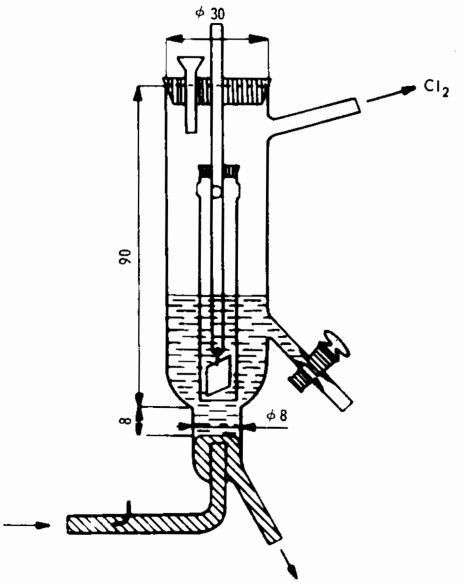

Figure 2. The electrolyser

column, and two experiments with both refluxing sections. In the experiments with an anodic reflux, lithium amalgam prepared by electrolysing an aqueous solution of the starting lithium chloride was supplied to the top of the column. In the experiments with only a cathodic reflux section, a DMF solution of the starting concentration of lithium chloride was introduced at the bottom of the column. The starting lithium chloride contained 7.5% lithium-6. Data on experimental conditions are given in Table 1.

Table 1. Experimental conditions and results of the separation experiments

Experiment No.	Column length m	Flow rates ml/min cm²	System	Time h		Lithium-6 content obtained[a]	Ratio out/in [b]	Q^c	$\frac{\ln Q}{\ln K}$
				Anodic reflux	Cathodic reflux				
1	1	0.1	Li (Hg)-LiBr (DMF)	43	—	12.0	1.60	1.68	10.6
2	1	0.2	Li (Hg)-LiBr (DMF)	23	—	11.0	1.47	1.53	8.7
3	2	0.2	Li (Hg)-LiCl (DMF)	24	17	6.5- 9.5	0.87-1.27	1.51	8.4
4	2	0.2	Li (Hg)-LiCl (DMF)	35	31	6.5-10.8	0.87-1.44	1.74	11.3
5	2	0.2	Li (Hg)-LiCl (DMF)	—	28	5.8	0.77	1.31	5.5
6	2	0.2	Li (Hg)-LiCl (DMF)	—	42	5.3	0.71	1.45	7.6
7	2	0 2	Li (Hg)-LiCl (DMF)	—	42	5.3	0.71	1.45	7.6
8	2	0.2	Li (Hg)-LiCl (DMF)	—	43	5.3	0.71	1 45	7.6
9	2	0.2	Li (Hg)-LiCl (DMF)	27	—	12.0	1.60	1.68	10.6
10	2	0.2	Li (Hg)-LiCl (DMF)	42	—	13.0	1.73	1.84	12.5

[a] The lithium-6 content of the starting material is always equal to 7.5%.

[b] Ratio out/in stands for the ratio between the lithium-6 content of the sample obtained and the lithium content of the starting material.

[c] $Q = \text{separation factor} = \frac{(y\ \text{bottom})}{(y\ \text{top})} \cdot \frac{(1\text{-}y\ \text{top})}{(1\text{-}y\ \text{bottom})}$

During the experiments with a cathodic reflux, the current efficiency in the electrolysis cell decreased initially from 95 to 70% and remained constant afterwards. The amalgam concentration was kept as constant as possible by adjusting the electric current to the current efficiency. The concentration of the amalgam produced was frequently determined by separate analyses.

A number of lithium samples were collected both during and at the end of each experiment. The isotopic ratio of these samples were determined by mass-spectrographic analyses, carried out by the FOM Laboratory for Mass Separation. The ratios of the final samples have been summarized in Table 1.

The isotopic ratio of the samples taken at intervals during the experiments have been plotted in Fig. 3 as a function of time.

DISCUSSION

The results given in Table 1 show, that a sand filled column is an efficient contact apparatus for CCEE. It is shown in Fig. 3 that the concentration gradient in the column is built up in a reproducible way. The sand-filled column appeared to be a very reliable apparatus needing hardly any special attention.

The column requires a rather long start-up time because of its large hold-up in comparison with the applied flow rates. A steady state could not be attained in the exchange column during our experiments, as may be seen in Fig. 3.

The continuous procedure for achieving the anodic reflux proved to be very satisfactory. This method seems to be fit for a technical application.

The separations in the cathodic reflux experiments appear to be less effective than those obtained during the anodic reflux experiments. This must be mainly ascribed to the large hold-up of this refluxing section.

COMMERCIAL POSSIBILITIES OF THE PROCESS

A preliminary estimate of the costs of producing lithium-7 by countercurrent exchange-electrolysis has

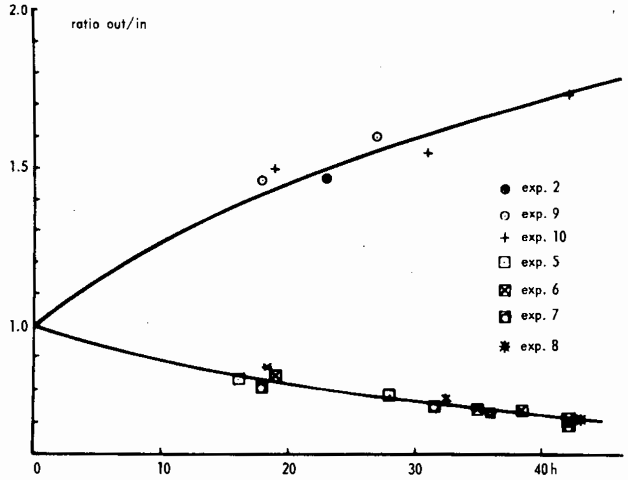

Figure 3. The lithium-6 content as a function of time

Ratio out/in stands for the ratio between the lithium-6 content of the sample obtained and the lithium-6 content of the starting material been made. The cost of manpower appears to be the most important contribution to the price of the product. Automation of the process may reduce the price of lithium-7 to below the present price of $120 per kg of 99.99% lithium hydroxide monohydrate.

A method which might compete with countercurrent exchange-electrolysis is electromigration in molten salts. A complete cost-analysis of electromigration cannot be given because the development of this method is not yet completed. However, it is likely that the costs of electromigration will be higher than those of countercurrent exchange-electrolysis. Moreover, the application of countercurrent exchange-electrolysis will not seriously be hampered by the lack of suitable construction materials which is among the problems met with in electromigration in molten salts.

In the meantime, we have found a new solvent which can be used instead of dimethylformamide. By using this new solvent, the lithium chloride can easily be transported in a continuous way from the electrolytic phase to the electrolysis cell. In this way, the cathodic refluxing procedure at the top of the column has been made continuous and the most important problem involved in the automation of the process has been solved. So it may be expected that further automation will give rise to few difficulties. It may be concluded that a continued investigation of countercurrent exchange-electrolysis for its possible technical application is certainly worthwhile. It is clear that much additional data, e.g., on column properties, should be collected before optimum conditions for a technical apparatus can be chosen.

OTHER POSSIBLE APPLICATIONS OF CCEE

The application of the described method is not restricted to the separation of the lithium isotopes. It also offers possibilities for the separation of the calcium isotopes and for the reprocessing of a liquid metal reactor fuel such as a solution of uranium in molten bismuth. For the latter problem, a packed column seems to be more promising than the disk and doughnut extractor as developed by Josephson and Burkhart [9].

ACKNOWLEDGEMENT

The mass-spectrographic determination of the isotope ratios of about 150 samples was carried out by the FOM Laboratory for Mass Separation, Amsterdam. I wish to thank sincerely Dr. Ir. A. J. H. Boerboom and his co-workers Mrs. R. Reyn-Teyema and Mr. C. Rijkeboer for performing all these analyses. I am much indebted to Dr. W. M. Smit, Director of our Institute, for his stimulating interest, valuable suggestions and critical discussions. Thanks are also due to Mr. C. A. van Deventer and Mr. A. van Kuijk for their enthusiastic and skilful assistance in the experimental work.

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ABSTRACT—RÉSUMÉ—АННОТАЦИЯ—RESUMEN

A/639 Pays-Bas

Séparation par électrolyse d'échange à contre-courant appliquée aux isotopes du lithium

par G. J. Arkenbout

Plusieurs applications des isotopes purs du lithium sont possibles dans le domaine de la technologie des réacteurs, par exemple :

a) L'utilisation du lithium 7 comme fluide de refroidissement dans un réacteur nucléaire;

b) L'application de ^{7}LiH ou ^{7}LiD comme modérateurs dans un réacteur à haute température;

c) L'utilisation de ^{7}LiF comme solvant pour combustibles nucléaires.

La séparation des isotopes du lithium à l'échelle technique pose encore un problème. Selon des publications récentes, la séparation par électrolyse d'échange à contre-courant est une des rares méthodes qui pourraient conduire à des résultats acceptables.

La littérature concernant ce sujet est encore peu abondante. Outre un brevet d'invention français de 1959, nous n'avons trouvé qu'une publication de Lewis et Macdonald remontant à 1936. Ces auteurs faisaient tomber des gouttelettes d'amalgame à contre-courant dans une solution ascendante de chlorure de

lithium et obtenaient ainsi une séparation notable dans une colonne longue de 18 m et ayant un diamètre de 4 mm seulement. Il ressort de ce travail que la nécessité de maintenir un mouvement de zigzag des gouttelettes d'amalgame crée un problème difficile, qui s'oppose à l'application technique de ce mode opératoire.

Des travaux récents utilisant des colonnes à garnissage ont donné des résultats plus prometteurs. Un traitement convenable d'une colonne contenant du sable de granulométrie 0,35-0,5 mm rend possible le transport de l'amalgame de lithium et d'une solution de chlorure de lithium dans de la dimétylphormamide en sens inverse l'un de l'autre.

Le reflux au bas de la colonne, où le lithium est transporté de l'amalgame à la solution électrolytique (reflux anodique), est réalisé à l'aide d'une nouvelle méthode continue fondée sur l'électrolyse d'échange. Le reflux cathodique est obtenu par l'évaporation du solvant diméthylformamide, transfert du chlorure de lithium dans l'eau et électrolyse de la solution aqueuse de chlorure de lithium.

Dans des expériences effectuées durant 20 à 40 heures dans une colonne d'échange de 1 à 2 m de long, on a obtenu un enrichissement en lithium 6 de 7,5 à 13,0 % au bas de la colonne et un appauvrissement en lithium 6 de 7,5 à 5,3 % au haut de la colonne, comme le montrent des analyses par spectrographie de masse (ces chiffres correspondent à des facteurs de séparation de 1,68 et 0,76 alors que le facteur de séparation élémentaire est égal à 1,05).

L'application de la méthode exposée n'est pas limitée à la séparation des isotopes de lithium, elle offre aussi des possibilités pour la séparation des isotopes du calcium et pour la régénération d'un combustible nucléaire constitué par un métal liquide, par exemple une solution d'uranium dans du bismuth fondu.

A/639 Нидерланды

Разделение изотопов лития путем электролиза с обменом в противотоке

Г. И. Аркенбоут

Чистые изотопы лития могут найти несколько способов, применения в технологии реакторов, например:

a) использование Li^7 в качестве теплоносителя в ядерном реакторе;

b) использование Li^7H или Li^7D в качестве замедлителя в высокотемпературном реакторе;

c) использование Li^7F в качестве растворителя ядерного топлива.

Однако разделение изотопов лития в промышленном масштабе связано пока еще с определенными трудностями. Согласно последним публикациям разделение путем электролиза с обменом в противотоке является одним из превосходных методов, который может привести к желаемым результатам.

До сих пор опубликовано очень мало литературы, посвященной этому вопросу. Кроме патента Франции, появившегося в 1959 году, был обнаружен лишь доклад Льюиса и Макдональда, датированный 1936 годом. Закапывая маленькие капельки амальгамы навстречу восходящему раствору хлорида лития, Льюис и Макдональд добились заметного разделения в колонке длиной 18 *м* и диаметром лишь 4 *мм*. Из данного доклада видно, что обеспечение необходимого зигзагообразного движения капелек амальгамы представляет сложную проблему, исключающую техническое применение данного метода.

Последние работы при помощи насадочных колонн, сулят многообещающие результаты. Соответствующая подготовка колонны, содержащей песок с размером частичек порядка 0,35—0,5 *мм*, обеспечивает перенос в противотоке амальгамы лития и раствора хлорида лития в диметилформамиде.

Орошение на дне колонны, где происходит переход лития из амальгамы в электролитический раствор (анодное орошение), было осуществлено непрерывным методом, основанным на электролизе с обменом. Катодное орошение производилось путем выпаривания диметилформамидного растворителя, переноса хлорида лития в воду и электролиза раствора хлорида лития в воде.

Масс-спектрографический анализ результатов экспериментов, проводимых в течение 20—40 *ч* в обменной колонке длиной от 1 до 2 *м*, показал, что содержание лития-6 на дне колонки увеличилось с 7,5 до 13%, а в верхней части колонки уменьшилось с 7,5 до 5,3% (эти данные соответствуют коэффициентам разделения, равным 1,68 и 0,76, тогда как первоначальный коэффициент разделения равнялся 1,05).

Использование описываемого в докладе метода не ограничивается разделением изотопов лития. Он может быть применен также для разделения изотопов кальция и для переработки жидкометаллического реакторного топлива, например раствора урана в расплавленном висмуте.

A/639 Países Bajos

Separación de los isótopos del litio por intercambio electrolítico en contracorriente

por G. J. Arkenbout

Los isótopos puros del litio encuentran diversas aplicaciones en tecnología nuclear, por ejemplo:

a) El litio-7 se usa como refrigerante en los reactores;

b) El $_7$LiH y el $_7$LiD se emplean como moderadores en los reactores de temperatura elevada;

c) El $_7$LiF se utiliza como disolvente para combustibles nucleares.

La separación de los isótopos del litio en escala técnica sigue siendo un problema. Según publicaciones recientes, la separación basada en el intercambio electrolítico en contracorriente constituye uno de los pocos métodos que podrían dar resultados aceptables.

Las publicaciones sobre este tema son bastante escasas. Fuera de una patente francesa, publicada en 1959, el autor sólo encontró una memoria de Lewis y Macdonald, del año 1936. Dejando caer finas gotas de amalgama a través de una solución ascendente de cloruro de litio, esos autores obtuvieron una separación apreciable, en una columna de 18 m de largo y solamente 4 mm de diámetro. Se deduce de la memoria que la conservación del necesario movimiento en zigzag de las gotas de amalgama constituye un problema grave que entorpece la aplicación técnica del procedimiento.

Mejores perspectivas ofrece la labor con columnas rellenas recientemente realizada. Sometiendo a un tratamiento adecuado una columna que contenga arena de tamaño de grano comprendido entre 0,35 y 0,5 mm, es posible establecer un transporte en contracorriente de amalgama de litio y solución de cloruro de litio en dimetilformamida.

Aplicando un nuevo método continuo basado en el intercambio electrolítico, el autor pudo lograr el reflujo en el fondo de la columna, donde el litio pasa de la amalgama a la solución de electrolito (reflujo anódico). En cuanto al reflujo catódico, se obtiene evaporando el disolvente (dimetilformamida) para disolver luego nuevamente el cloruro de litio en auga y someter esta solución a la electrólisis.

En experimentos de 20 a 40 h de duración, llevados a cabo en una columna de intercambio de 1 a 2 m de longitud, se logró aumentar el contenido de litio-6 desde 7,5 hasta 13,0 % en el fondo de la columna, y reducir el contenido de litio-6 desde 7,5 hasta 5,3 % en la parte superior, según se deduce de los análisis por espectrografía de masas (estos datos corresponden a factores de separación de 1,68 y 0,76, mientras que el factor de separación elemental alcanza a 1,05).

La aplicación del método descrito no se limita a la separación de los isótopos del litio. Se presta también para separar los isótopos del caclio y para regenerar combustibles nucleares metálicos líquidos como, por ejemplo, soluciones de uranio en bismuto fundido.

Record of session 2.10

Isotope separation

Chairman : M. Benedict (United States of America)

Paper P/440 (presented by Y. Takashima)

There was no discussion of this paper.

Paper P/89 (presented by C. Fréjacques)

DISCUSSION

C. U. LINDERSTRØM-LANG (Denmark): Can you state the cost of separation work related to a unit quantity of material?

C. FRÉJACQUES (France) : As we do not know the exact size of American plants, it is difficult to quote valid comparative figures. Under normal economic conditions and with the large plants envisaged in this paper, I would estimate the unit cost of separation work to be about 80% higher, and the cost of an additional gram to be about 40% higher, than the official rates in the United States.

[The Chair was taken by C. Fréjacques (France)]

Paper P/29 (presented by J. A. Morrison)

DISCUSSION

W. P. BEBBINGTON (United States of America): Your extremely interesting exposition fully accords with our experience and is well worth the attention of anyone contemplating the operation of a heavy-water reactor. Any organic compounds are certainly to be avoided, since they can seriously upset the control of conductivity and deuterium ion concentration.

Following the Canadian lead, we have adopted the infra-red method for analysis of heavy water, for both the reactors and the production plant. Our chemists believe that their precision in the very high range is even somewhat greater than that quoted in this paper.

Have you any estimate of the amount of light water that is added to the reactor as adsorbed moisture or as the hydrate of alumina on reactor components, and do you make any effort to minimize such contamination? Also, do you use additives for the control of acidity or corrosion?

J. A. MORRISON (Canada): In our NRU reactor the fuel rods are in contact with the D_2O. The quantity of H_2O added to the D_2O system in this way is very small since we dry the rods with hot air before they are inserted into the reactor. I cannot give an absolute figure, but the downgrading is less than 0.005 wt%, since we operated the reactor for several years with only a small decrease in the isotopic concentration.

We do not use additives to control acidity or corrosion. We conducted and extensive experiment with the pH of the D_2O between 5 and 5.5, but did not see any significant decrease in the quantity of gibbsite ($Al_2O_3 \cdot 3D_2O$) that was produced and the experiment was stopped. This work is reported in reference 11.

The precision quoted in the paper was about what we obtained with technicians in a normal laboratory. Since the paper was written, an adaptation of the infra-red method, using glass inserts, has been developed for analyses in the 90-99.5 wt% D_2O range. This has improved the precision of routine analyses. Of course, if greater care is taken, more precision than that quoted can also be obtained with the original method.

E. ROTH (France): Is the downgrading of 0.5 t of heavy water in NRX (or 6 t in NRU) caused by the entry of the 0.2 kg/year of H_2O mentioned, or are these additional quantities of downgraded water?

At what temperature does the electrolytic plant operate?

J. A. MORRISON (Canada): The figure of 0.2 kg/year represents the quantity of H_2O that enters the D_2O system and it causes a very small degradation, < 0.001 wt%, which is of little consequence. Most of the downgraded water is either water that escapes accidentally as a result of equipment failure, or water that is withdrawn deliberately during maintenance or an experiment.

The temperature of the river water varies from 1 °C in winter to 20 °C in summer. The cells are run a few degrees above these temperatures, depending on the time of year.

Paper P/290 (presented by W. P. Bebbington)

DISCUSSION

J. GAUSSENS (France): Referring to Savannah, you mentioned investments of $145/lb/year, operating costs of $13.5/lb and a United States Atomic Energy Commission (USAEC) selling price of $24.5/lb. This corresponds to an annual amortization of approximately 7%, which is very low. Have you used the same rate in your forecasts?

W. P. BEBBINGTON (United States of America): The relationships between operating cost, investment and selling price have been determined somewhat arbitrarily by the USAEC without great regard to commercial standards of profit or return on investment. A more complete discussion of these aspects is included in reference 14. I believe the USA price of heavy water has been kept rather low to encourage the early development of heavy-water reactors.

Paper P/753 (presented by P. G. Deshpande)

DISCUSSION

W. P. BEBBINGTON (United States of America) : I believe that Mr. Deshpande is very conservative in his estimate of 7 500 hours of operation annually. Even in our 12-year-old plant we are able to attain about 8 500 hours and it is not uncommon for one of our units to run continuously for a year without a shutdown. If natural gas were to become available in the Nangal region, it would constitute an ideal energy source, permitting direct firing of heaters and the use of gas turbines, as pointed out by my colleagues Mr. Proctor and Dr. Thayer in reference 14 to the paper. However, the gas might prove too valuable as a chemical raw material to use for this purpose.

P. G. DESHPANDE (India) : The estimate of 7 500 hours of operation annually is based on the operational experience of chemical plants in India. We are not sure about the availability of natural gas in the Nangal regions and therefore have not considered natural gas as a fuel.

Paper P/754 (presented by P. G. Deshpande)

There was no discussion of this paper.

Paper P/91 (presented by B. Lefrançois)

DISCUSSION

U. SCHINDEWOLF (Federal Republic of Germany): In view of the frequent references in the literature to the favourable properties of the NH_3-H_2 system for the production of heavy water, and after we had concluded pilot-plant experiments on heavy-water production by the H_2O-H_2 exchange system in dual-temperature operation, we started experiments with the ammonia system. We began on a laboratory scale and then continued in a small counter current exchange column, using a gas pressure of 200 atm and temperatures of — 30 to + 60 °C.

We are now working with a pilot plant constructed and operated by the firm Friedrich Uhde GmbH at Dortmund, Germany. This dual-temperature pilot plant consists of two exchange columns of length 28 m and 10 m, which are fitted with about 200 sieve plates and can be operated at a pressure of 200 atm and temperatures of —40 and +60 °C respectively. The plant can be run with a maximum throughput of 1 000 m³/hr (STP) of synthesis gas (N_2-H_2 mixture 1 : 3) at a pressure of 200 atm. The optimum liquid flow rate follows from the theory of K. Bier.

In one typical dual-temperature experiment lasting 10 days we obtained an enrichment factor of 3.2, operating the columns at —20 and +37 °C respectively. This result was to be expected on the basis of our earlier experiments in the small single-temperature countercurrent column. By approaching the optimal operating conditions we can expect a considerably higher enrichment factor.

Evaluation of the experiments indicates that the dual-temperature system using ammonia and hydrogen as exchange partners and potassium amide as catalyst is a technically and economically feasible one for the production of heavy water.

I should therefore like to know why Mr. Lefrançois considers that dual-temperature exchange is not economical. Is his conclusion due to the special contact devices needed?

B. LEFRANÇOIS (France): On the basis of experience with various contact systems, we believe that if the temperature of — 50 °C alone is used, the single-temperature system is the most economical. We have tried 14 dispersion systems.

C. U. LINDERSTRØM-LANG (Denmark) : I suppose that the basic need to extract as much as 80% of the deuterium in the feed was one of the main reasons for your adoption of the single-temperature process.

B. Lefrançois (France) : The large output imposed by the ammonia/hydrogen process was indeed one of the reasons for our choice. The *super-stripping* tower increases the number of contacts, and we tried to reduce these by using a single-temperature process.

M. Benedict (United States of America): Are there any plans to construct a commercial plant in France for the production of heavy water by the ammonia/hydrogen exchange process?

B. Lefrançois (France) : Yes, a plant with an annual output of 20 t is under construction.

W. P. Bebbington (United States of America): We have awaited with great interest further information on the French development of ammonia/hydrogen exchange and are pleased to know that it has warranted application in a commercial plant. Could you tell us a little about the unique problems of handling the catalyst and say how successfully these have been solved; that is, how much catalyst is lost or destroyed in the process?

B. Lefrançois (France): We believe that we have in fact successfully dealt with the catalyst problems. We make the catalyst by dissolving potassium in ammonia. All the reactions for destruction of potassium amide are well known. The main substance formed is potash, which we filter out, as it is insoluble in ammonia. About 1 kg of amide is destroyed daily.

(Mr. M. Benedict resumed the Chair)

Paper P/388 (presented by Y. V. Nikolaev)

DISCUSSION

M. Higatsberger (Austria): For about three years the Reactor Centre at Seibersdorf operated by the Österreichische Gesellschaft für Atomenergie has been using an electromagnetic isotope separator which is especially suitable for radioactive and fission product separation work. The machine has a non-uniform 180° magnetic field and an average beam radius of 100 cm. In the case of certain isotopes, as much as 100 mg/day can be separated. The separator is at present used mainly for destructive spent-fuel analysis and nuclear data work.

P. G. Deshpande (India): What materials are employed for the columns and packings of the exchange distillation method using the dimethyl ether complex $[(CH_3)_2OBF_3]$ for the production of B^{10}?

Y. V. Nikolaev (USSR): The columns are of stainless steel and the packings of copper.

F. Viehboeck (Austria): Have the intermediate isotopes of rare gases, such as ^{131}Xe, been separated by mass diffusion methods and, if so, what enrichments have been achieved?

Y. V. Nikolaev (USSR): A device for the separation of intermediate-mass isotopes by mass diffusion is at present under construction.

P. Huber (Switzerland): Are you operating an NO rectification plant and, if so, what is its output? Do you know whether the exchange $^{14}N^{18}O + {}^{15}N{}^{16}O \rightarrow {}^{14}N^{16}O + {}^{15}N^{18}O$ takes place in the rectification column?

Y. V. Nikolaev (USSR): We possess a laboratory installation with which ^{15}N concentrations of 35% and ^{18}O concentrations of 20% have been achieved. Using the data obtained, we are now constructing equipment to produce $\sim$ 4 kg of 99% ^{15}N annually.

As regards the exchange to which you refer, from the kinetics of concentration growth in our laboratory cascade we can conclude that it does take place, because otherwise the kinetics of growth would be considerably slower.

Paper P/465 (read by title only)

DISCUSSION

E. Roth (France): At Saclay we are building a plant which has a hydrogen water exchanger as a means of feeding the tritium to the thermal diffusion equipment.

Compte rendu de la séance 2.10

Séparation des isotopes

Président : M. Benedict (États-Unis d'Amérique)

Mémoire P/440 (présenté par Y. Takashima)

Ce mémoire n'a pas fait l'objet d'une discussion.

Mémoire P/89 (présenté par C. Fréjacques)

DISCUSSION

C. U. LINDERSTRØM-LANG (Danemark) : Pouvez-vous indiquer le coût du travail de séparation par unité de matière?

C. FRÉJACQUES (France) : Les dimensions exactes des usines américaines n'étant pas connues, il est difficile de donner des chiffres de comparaison valables. Avec des conditions économiques normales et pour les grosses usines envisagées dans le mémoire, le prix de l'unité de travail de séparation est supérieur d'environ 80 %, et le prix du gramme supplémentaire d'environ 40 %, à celui déduit du tarif officiel des États-Unis.

[C. Fréjacques (France) prend la présidence]

Mémoire P/29 (présenté par J. A. Morrison)

DISCUSSION

W. P. BEBBINGTON (États-Unis d'Amérique) : Votre très intéressant exposé correspond entièrement à l'expérience que nous avons, et il mérite d'être étudié par tous ceux qui se proposent de faire fonctionner un réacteur à eau lourde. Il faut certainement éviter tous les composés organiques, car ils peuvent perturber gravement le contrôle de la conductivité et de la teneur en ion deutérium.

A la suite des chercheurs canadiens, nous avons adopté la méthode infrarouge pour l'analyse de l'eau lourde, pour les réacteurs comme pour l'usine de production. Nos chimistes pensent que la précision dans le domaine des fortes concentrations est même supérieure à la précision indiquée dans votre texte.

Avez-vous une idée de la quantité d'eau légère ajoutée au réacteur sous forme d'humidité adsorbée ou d'hydrate d'alumine sur les composants du réacteur? Essayez-vous de limiter cette contamination? Enfin, utilisez-vous des additifs pour combattre l'acidité ou la corrosion?

J. A. MORRISON (Canada) : Dans notre réacteur NRU, les éléments de combustible sont en contact avec l'eau lourde. La quantité de H_2O ajoutée au système D_2O de cette façon est très faible car nous séchons les éléments à l'air chaud avant de les insérer dans le réacteur. Je ne peux pas vous donner de valeur absolue, mais la dégradation est inférieure à 0,005 % en poids, car nous avons fait fonctionner le réacteur plusieurs années avec une très faible diminution de la concentration isotopique.

Nous n'utilisons pas d'additifs pour combattre l'acidité ou la corrosion. Nous avons fait un long essai en maintenant le pH de l'eau lourde entre 5 et 5,5, mais n'avons observé aucune diminution notable de la quantité de Gibbsite (Al_2O_3, 3 D_2O) produite, et cet essai a été arrêté. Ce travail est exposé dans la référence 11.

La précision indiquée dans le mémoire est à peu près celle qu'obtiennent des techniciens dans un laboratoire normal. Depuis que ce mémoire a été rédigé, on a mis au point une variante de la méthode infrarouge, avec insertion de verres, pour les analyses dans le domaine 90-99,5 % D_2O en poids. Cette variante a amélioré la précision des analyses courantes. Bien entendu, on peut, en prenant plus de soins, obtenir avec la méthode originale une précision supérieure à celle qui est indiquée.

E. ROTH (France) : La dégradation de 0,5 t d'eau lourde dans NRX (ou de 6 t dans NRU) est-elle causée par l'entrée des 200 g/an de H_2O mentionnée ou s'agit-il de quantités suppémentaires d'eau dégradée? A quelle température fonctionne l'usine électrolytique?

J. A. MORRISON (Canada) : Le chiffre de 200 g/an correspond à la quantité de H_2O qui pénètre dans le système D_2O et provoque une dégradation très petite, inférieure à 0,001 % en poids, de peu d'importance. La plus grande partie de l'eau dégradée est soit de l'eau qui s'échappe accidentellement à la suite d'une avarie de l'équipement, soit de l'eau qui est volontairement soutirée pendant l'entretien ou pendant une expérience.

La température de l'eau de la rivière varie de 1 °C en hiver à 20 °C en été. Les cellules fonctionnent à quelques degrés au-dessus de ces températures, suivant l'époque de l'année.

Mémoire P/290 (présenté par W. P. Bebbington)

DISCUSSION

J. Gaussens (France) : A propos du *Savannah*, vous indiquez un investissement de 145 dollars par livre et par an, un coût de fonctionnement de 13,5 dollars par livre, et le prix de vente de la United States Atomic Energy Commission (USAEC) de 24,5 dollars par livre. Ceci correspond à un amortissement annuel de 7 % environ, ce qui est très faible. Avez-vous fait les mêmes hypothèses pour vos prévisions?

W. P. Bebbington (États-Unis d'Amérique) : Les relations entre les frais de fonctionnement, l'investissement et le prix de vente ont été déterminées assez arbitrairement par la USAEC, sans tenir réellement compte des marges bénéficiaires commerciales ou de l'intérêt sur l'investissement. Ces aspects sont discutés plus complètement dans la référence 14. Je pense que le prix de l'eau lourde aux États-Unis a été maintenu à une valeur assez basse pour encourager le développement rapide des réacteurs à eau lourde.

Mémoire P/753 (présenté par P. G. Deshpande)

DISCUSSION

W. P. Bebbington (États-Unis d'Amérique) : Je pense que les 7 500 heures de fonctionnement annuel envisagées par M. Deshpande constituent une estimation très modérée. Notre usine, qui a déjà douze ans, nous permet encore d'atteindre 8 500 heures, et il n'est pas rare qu'une de nos unités fonctionne pendant un an sans aucun arrêt. Si du gaz naturel devient disponible dans la région de Nangal, il constituera une source d'énergie idéale, permettant le chauffage direct des bouilleurs et l'utilisation de turbines à gaz, comme mes collègues M. Proctor et le D^{r} Thayer l'ont signalé dans la référence 14 du mémoire. Cependant le gaz peut se révéler une matière première trop précieuse pour la chimie pour être ainsi utilisé.

P. G. Deshpande (Inde) : La valeur estimée de 7 500 heures de fonctionnement annuel correspond à l'expérience de fonctionnement des usines chimiques en Inde. Nous ne savons pas si nous pourrons disposer de gaz naturel dans la région de Nangal et n'avons donc pas envisagé le gaz naturel comme combustible.

Mémoire P/754 (présenté par P. G. Deshpande)

Ce mémoire n'a pas fait l'objet d'une discussion.

Mémoire P/91 (présenté par B. Lefrançois)

DISCUSSION

U. Schindewolf (République fédérale d'Allemagne) : En raison des nombreuses références aux propriétés favorables du système NH_3-H_2 pour la production d'eau lourde, et après avoir achevé des expériences à l'échelle pilote sur la production d'eau lourde par le système d'échange H_2O-H_2 en fonctionnement bitherme, nous avons commencé des expériences avec le système à l'ammoniac. Nous avons commencé au laboratoire, et continué avec une petite colonne d'échange à contre-courant, avec une pression de gaz de 200 atm et des températures de —30 et +60 °C.

Nous travaillons maintenant sur une usine pilote construite par la firme Friedrich Uhde GmbH, de Dortmund (Allemagne), qui se charge également du fonctionnement de l'installation. Cette usine pilote à deux températures comprend deux colonnes d'échange longues de 28 et 10 m, équipées de 200 plateaux tamis environ, et peut fonctionner à une pression de 200 atm et à des températures de —40 et +60 °C respectivement. L'installation peut fonctionner à un débit maximal de 1 000 m^3 TPN/h de gaz de synthèse (mélange N_2-H_2 dans la proportion de 1 pour 3), à une pression de 200 atm. Le débit liquide optimal est donné par la théorie de K. Bier.

Dans une expérience type à deux températures, pendant une durée de 10 j, nous avons obtenu un facteur d'enrichissement de 3,2 en faisant fonctionner les colonnes à —20 et +37 °C respectivement. Ce résultat correspondait bien à nos premières expériences avec la petite colonne à contre-courant à une seule température. On peut espérer un facteur d'enrichissement beaucoup plus grand en s'approchant des conditions optimales de fonctionnement.

Nos expériences indiquent que le système à deux températures utilisant l'ammoniac et l'hydrogène comme partenaires d'échange et l'amidure de potassium comme catalyseur constitue un procédé techniquement et économiquement réalisable pour la production d'eau lourde.

Je voudrais donc savoir pourquoi M. Lefrançois considère que l'échange bitherme n'est pas économique. Cette conclusion est-elle due à la nécessité d'utiliser des systèmes de contact spéciaux?

B. Lefrançois (France) : A la suite de nos expériences avec différents systèmes de contact, nous pensons qu'avec une seule température de —50 °C le système monotherme est le plus économique. Nous avons essayé 14 systèmes de dispersion.

C. U. Linderstrøm-Lang (Danemark) : Je pense que le fait de vouloir extraire jusqu'à 80 % du deutérium contenu dans le mélange d'alimentation est l'une des principales raisons ayant conduit au procédé monotherme.

B. Lefrançois (France) : La production importante imposée par le procédé ammoniac-hydrogène a certainement été l'une des raisons de notre choix. La tour d'extraction augmente le nombre de contacts, et nous avons cherché à réduire ce nombre en utilisant un procédé monotherme.

M. Benedict (États-Unis d'Amérique) : Projetez-vous la construction en France d'une usine de production d'eau lourde par le procédé d'échange ammoniac-hydrogène?

B. Lefrançois (France) : Oui, une usine devant produire 20 t/an est en construction.

W. P. Bebbington (États-Unis d'Amérique) : Nous attendions avec intérêt des renseignements sur les travaux français concernant l'échange ammoniac-hydrogène et nous sommes heureux de savoir qu'ils justifient le passage à une usine commerciale. Pourriez-vous nous donner quelques renseignements sur les problèmes particuliers de manipulation du catalyseur, et nous dire s'ils ont été résolus de façon satisfaisante, c'est-à-dire quelle quantité de catalyseur est perdue ou détruite?

B. Lefrançois (France) : Nous croyons avoir résolu les problèmes de catalyseur. Nous produisons le catalyseur par dissolution du potassium dans l'ammoniac. Toutes les réactions de destruction de l'amidure de potassium sont bien connues. La principale substance formée est la potasse, que nous filtrons, car elle est insoluble dans l'ammoniac. Un kilogramme environ d'amidure est détruit journellement.

(M. Benedict reprend la présidence)

Mémoire P/388 (présenté par Y. V. Nikolaev)

DISCUSSION

M. Higatsberger (Autriche) : Le Centre du réacteur de Seibersdorf, géré par l'Oesterreichische Gesellschaft für Atomenergie, utilise depuis trois ans environ un séparateur électromagnétique d'isotopes, particulièrement adapté à la séparation des produits radioactifs et des produits de fission. Cet appareil a un champ magnétique à 180° non uniforme et un rayon moyen du faisceau de 100 cm. Pour certains isotopes, on peut séparer jusqu'à 100 mg/j. La séparation est principalement utilisée en ce moment pour l'analyse destructive du combustible irradié et pour l'obtention de données nucléaires.

P. G. Deshpande (Inde) : Quels matériaux utilisez-vous pour les colonnes et les garnissages dans la méthode d'échange par distillation avec le complexe de l'éther diméthylique $[(CH_3)_2OBF_3]$ pour la production de ^{10}B?

Y. V. Nikolaev (URSS) : Les colonnes sont en acier inoxydable, les garnissages en cuivre.

F. Viehboeck (Autriche) : Avez-vous séparé les isotopes intermédiaires des gaz rares, comme ^{131}Xe, par des méthodes de diffusion de masse et, le cas échéant, quels enrichissements avez-vous obtenu?

Y. V. Nikolaev (URSS) : Un appareil pour la séparation des isotopes de masses intermédiaires par diffusion de masse est en cours de construction.

P. Huber (Suisse) : Avez-vous une installation de rectification de NO et, dans ce cas, quelle est sa production? Savez-vous si l'échange $^{14}N^{18}O + {}^{15}N^{16}O \rightarrow {}^{14}N^{16}O + {}^{15}N^{18}O$ a lieu dans la colonne de rectification?

Y. V. Nikolaev (URSS) : Nous avons une installation de laboratoire avec laquelle nous avons obtenu des concentrations en ^{15}N de 35 % et des concentrations en ^{18}O de 20 %. A partir des résultats obtenus, nous construisons une installation qui produira annuellement environ 4 kg de ^{15}N à 99 %.

En ce qui concerne l'échange que vous avez mentionné, nous pouvons conclure de la cinétique de variation de la concentration dans notre cascade de laboratoire qu'il se produit effectivement, car, dans le cas contraire, cette cinétique serait beaucoup plus lente.

Mémoire P/465 (seul le titre de ce mémoire a été lu)

DISCUSSION

E. Roth (France) : Nous construisons à Saclay une installation qui utilise un échangeur hydrogène-eau pour alimenter en tritium l'appareillage de diffusion thermique.

Протокол заседания 2.10

Разделение изотопов

Председатель: М. Бенедикт (США)

Доклад Р/440 (представил Я. Такашима)

По этому докладу дискуссии не было.

Доклад Р/89 (представил К. Фрежак)

ДИСКУССИЯ

К. У. ЛИНДЕРСТРЁМ-ЛАНГ (Дания): Можете ли Вы сообщить стоимость разделения на единицу произведенного материала?

К. ФРЕЖАК (Франция): Как Вы знаете, нам неизвестны точные мощности американских заводов, но при нормальных экономических условиях, указанных в нашем докладе, по моим расчетам, стоимость разделения почти на 20% выше, чем в США.

Место председателя занимает К. Фрежак (Франция)

Доклад Р/29 (представил Дж. А. Моррисон)

ДИСКУССИЯ

У. П. БЕББИНГТОН (США): Ваше чрезвычайно интересное описание полностью совпадает с нашей практикой, и оно вполне заслуживает внимания всех, кто занимается эксплуатацией тяжеловодных реакторов. Несомненно, следует избегать применения каких-либо органических соединений, так как они могут серьезно помешать регулировать проводимость и концентрацию ионов дейтерия.

Следуя канадскому примеру, для анализа тяжелой воды мы приняли метод инфракрасной спектроскопии как для реакторов, так и для промышленных установок. Наши химики считают, что точность их анализов в очень высоком диапазоне, даже несколько больше, чем указывалось в канадском докладе.

Проводили ли Вы какие-либо расчеты количества обычной воды, которое добавляется в реактор в виде адсорбированной влаги или гидрата алюминия на узлах реактора, и принимаете ли Вы какие-либо меры для сведения к минимуму этого загрязнения? Кроме того, используете ли Вы добавки для регулирования кислотности или коррозии?

Дж. А. МОРРИСОН (Канада): В нашем реакторе NRU топливные стержни находятся в контакте с тяжелой водой. Количество обычной воды, добавляемой в систему с тяжелой водой, таким образом, очень невелико, так как мы сушим стержни в горячем воздухе перед установкой в реакторе. Я не могу привести абсолютную цифру, но разбавление осуществляется до концентрации ниже 0,005 вес. %, так как мы эксплуатируем реактор в течение нескольких лет с очень небольшим понижением концентрации изотопов.

Мы не применяем добавок для регулирования кислотности или коррозии. Мы провели большой эксперимент при pH тяжелой воды от 5 до 5,5, но не наблюдали сколько-нибудь значительного уменьшения количества образующегося гибсита ($Al_2O_3 \cdot 3D_2O$), и эксперимент был прекращен. Этот эксперимент описан в работе[11].

Точность, указанная в докладе, была почти такой же, какую мы получили с техниками обычной лаборатории. С тех пор как был написан доклад, разработан вариант метода инфракрасной спектроскопии с использованием стеклянных вкладышей для анализов концентрации тяжелой воды в диапазоне 90—99,5 вес. %. Это позволило повысить точность серийного анализа. Конечно, при соблюдении большой осторожности можно также получить бо́льшую точность и при первоначальном методе анализа.

Э. РОТ (Франция): Было ли разбавление 0,5 *т* тяжелой воды в реакторе NRX (или 6 *т* в реакторе NRU) вызвано поступлением 0,2 *кг* обычной воды в год, как указано в докладе, или это были дополнительные количества разбавленной воды? При какой температуре работает электролитическая установка?

Дж. А. МОРРИСОН (Канада): Цифра

0,2 *кг/год* соответствует количеству обычной воды, которое попадает в систему с тяжелой водой и вызывает очень небольшое разбавление (менее 0,001 вес. %), что не имеет почти никаких последствий. Основная часть разбавленной воды приходится на ту воду, которая случайно вытекает в результате повреждения оборудования, или на ту воду, которая намеренно удаляется во время ремонта или эксперимента.

Температура речной воды колеблется от 1° С зимой до 20° С летом. Электролизные ванны работают при температуре на несколько градусов выше этих температур в зависимости от времени года.

Доклад Р/290 (представил У. П. Беббингтон)

ДИСКУССИЯ

Ж. ГОССЕН (Франция): Говоря о заводе в Саванна-Ривере, Вы упоминали такие цифры: капиталовложения 145 *долл/фунт·год,* эксплуатационные расходы 13,5 *долл/фунт* и продажная цена КАЭ США 24,5 *долл/фунт.* Это соответствует годовой амортизации около 7%, что является очень низким. В Ваших прогнозах Вы использовали такие данные?

У. П. БЕББИНГТОН (США): Зависимость между стоимостью эксплуатации, капиталовложениями и продажной ценой была определена несколько произвольно КАЭ США без особого учета промышленных норм прибыли или возврата капиталовложений. Более подробное описание этих аспектов дается в работе[14]. Я полагаю, что американская цена на тяжелую воду была установлена довольно низкой, с тем чтобы поощрять быструю разработку тяжеловодных реакторов.

Доклад Р/753 (представил П. С. Дешпанде)

ДИСКУССИЯ

У. П. БЕББИНГТОН (США): Я полагаю, что г-н Дешпанде очень консервативен в своих расчетах относительно 7500 *ч* эксплуатации в год. Даже на нашем заводе, работающем 12 лет, мы смогли достичь почти 8500 *ч*, и нередко некоторые из наших установок работают непрерывно в течение года без остановок. Если природный газ станет доступным в районе Нангала, то он будет идеальным источником энергии, так как обеспечит непосредственный подогрев нагревателей и применение газовых турбин, как указывали мои коллеги г-н Проктор и д-р Тейер в работе[14], приведенной в докладе. Однако газ может оказаться слишком ценным химическим сырьем, чтобы его можно было использовать для этой цели.

П. Г. ДЕШПАНДЕ (Индия): Расчет на 7500 *ч* эксплуатации в год был основан на опыте эксплуатации химических заводов в Индии. Мы еще не уверены в доступности природного газа в районе Нангала и поэтому не рассматривали природный газ в качестве топлива.

Доклад Р/754 (представил П. Г. Дешпанде)

По этому докладу дискуссии не было.

Доклад Р/91 (представил Б. Лефрансуа)

ДИСКУССИЯ

Т. ШИНДЕВОЛЬФ (ФРГ): Ввиду частых ссылок в литературе на благоприятные свойства системы $NH_3 — H_2$ для получения тяжелой воды и после того, как мы закончили эксперименты на опытной установке для производства тяжелой воды в системе, где происходит обмен $H_2O — H_2$ при двух температурах, мы приступили к экспериментам с системой на аммиаке. Мы начали работу в лабораторном масштабе и затем продолжали в небольшой противоточной обменной колонне при давлении газа 200 *ат* и температурах от —30 до +60° С.

Сейчас мы работаем на полузаводской установке, построенной и эксплуатируемой фирмой «Фридрих Юде» в Дортмунде, ФРГ. Эта двухтемпературная полузаводская установка состоит из двух обменных колонн длиной 28 и 10 *м*, которые имеют около 200 сетчатых тарелок и могут работать при давлении 200 *ат* и температурах —40 и +60° С соответственно. Установка может работать с максимальной производительностью 1000 $м^3/ч$ (NTP) синтетического газа ($N_2 — H_2$ в смеси 1 : 3) при давлении 200 *ат*. Оптимальная скорость потока жидкости соответствует теории К. Бира.

В одном типичном эксперименте при двух температурах, продолжавшемся 10 дней, мы получили коэффициент обогащения 3,2, когда колонны работали соответственно при температуре —20 и +37° С. Этот результат можно было ожидать на основании наших более ранних экспериментов на небольшой противоточной колонне, работавшей при одной температуре. При приближении к оптимальным рабочим условиям мы можем ожидать значительно более высокого коэффициента обогащения.

Оценка результатов экспериментов показывает, что двухтемпературная система, в которой в качестве сырья используется аммиак и водород, а в качестве катализатора амид калия, является технически и экономически осуществимой для производства тяжелой воды.

Поэтому я хотел бы знать, почему г-н Лефрансуа считает, что двухтемпературный обмен не экономичен. Основано ли его заключение на том, что необходимы особые контактные устройства?

Б. ЛЕФРАНСУА (Франция): На основе опыта с различными контактными системами мы считаем, что, если использовать лишь температуру —50° С, однотемпературная система является наиболее экономичной. Мы испытывали 14 дисперсионных систем.

К. Л. ЛИНДЕРСТРЕМ-ЛАНГ (Дания): Я предполагаю, что необходимость извлечения до 80% дейтерия из исходного продукта была одной из главных причин Вашего выбора однотемпературного процесса.

Б. ЛЕФРАНСУА (Франция): Большой выход, обеспечиваемый аммиачно-водородным процессом действительно был одной из причин нашего выбора. Башня со «сверхотгонкой» увеличивает число контактов, и мы попытались сократить их путем применения однотемпературного процесса.

М. БЕНЕДИКТ (США): Имеются ли какие-нибудь планы построить промышленную установку во Франции для производства тяжелой воды путем обмена аммиака и водорода?

Б. ЛЕФРАНСУА (Франция): Да, строится установка с годовой производительностью 20 *т*.

У. П. БЕББИНГТОН (США): Мы с большим интересом ожидали дальнейших сообщений о французских работах по аммиачно-водородному обмену и сейчас с удовольствием узнали о том, что этот процесс найдет применение на промышленной установке. Могли бы Вы немного рассказать о специфических проблемах, связанных с катализатором, и сказать о том, как успешно они были разрешены, то есть, как много катализатора теряется или разрушается в процессе?

Б. ЛЕФРАНСУА (Франция): Мы считаем, что мы успешно справились с проблемами катализатора. Мы получаем катализатор путем растворения калия в аммиаке. Все реакции разрушения амида калия хорошо известны. Основным образующимся веществом является поташ, который мы отфильтровывали, так как он не растворяется в аммиаке. Ежедневно разрушается около 1 *кг* амида.

(Г-н М. Бенедикт занимает место председателя)

Доклад Р/388 (представил Ю. В. Николаев).

ДИСКУССИЯ

М. И. ХИГАТСБЕРГЕР (Австрия): Около трех лет в реакторном центре в Зайберсдорфе эксплуатируемом Австрийским обществом по атомной энергии, используется электромагнитный разделитель изотопов, который особенно подходит для работы с радиоактивными изотопами и продуктами деления. Установка имеет неоднородное 180° магнитное поле и средний радиус пучка 100 *см*. В случае некоторых изотопов она может разделять до 100 *мг/день*. В настоящее время разделитель используется главным образом для разрушительного анализа отработанного топлива и для работы по получению ядерных данных.

П. Г. ДЕШПАНДЕ (Индия): Какие материалы используются для изготовления колонн и насадок при обменной дистилляции, когда применяется диметиловый эфир $[(CH_3)_22 \cdot O \cdot BF_3]$ для получения B^{10}?

Ю. В. НИКОЛАЕВ (СССР): Колонны сделаны из нержавеющей стали, а насадки из меди.

Ф. ФИБЁК (Австрия): Разделялись ли промежуточные изотопы редких газов, такие, как Xe^{131}, масс-диффузионным методом и, если да, какое обогащение было достигнуто?

Ю. В. НИКОЛАЕВ (СССР): Установка для разделения промежуточных изотопов методом масс-диффузии сейчас строится.

П. ГУБЕР (Швейцария): Работает ли у Вас установка для ректификации NO и, если да, то какова ее производительность? Знаете ли Вы, что в ректификационной колонне происходит обмен $N^{14}O^{18} + N^{15}O^{16} \rightarrow N^{14}O^{16} + N^{15}O^{18}$.

Ю. В. НИКОЛАЕВ (СССР): У нас есть лабораторная установка, на которой мы получали концентрации N^{15} до 35% и O^{18} до 20%. На основании полученных данных мы сейчас строим установку для производства 4 *кг* 99% N^{15} в год.

Что касается обмена, о котором Вы говорили, то на основе кинетики роста концентрации в нашем лабораторном каскаде мы можем заключить, что обмена не происходит, потому что в противном случае кинетика роста была бы значительно медленнее.

Доклад Р/465 (зачитывается только название).

ДИСКУССИЯ

Э. РОТ (Франция): В Сакле мы строим установку, в которой происходит обмен водорода воды как средство подачи трития в термодиффузионное оборудование.

Acta de la sesión 2.10

Separación de isótopos

Presidente : M. Benedict (Estados Unidos de América)

Documento P/440 (presentado por Y. Takashima)

No hubo discusión de esta memoria.

Documento P/89 (presentado por C. Fréjacques)

DISCUSIÓN

C. U. LINDERSTRØM-LANG (Dinamarca): ¿Puede Vd. establecer el coste del trabajo de separación por unidad de material?

C. FRÉJACQUES (Francia): Como no se conocen las dimensiones exactas de las instalaciones americanas es difícil dar cifras de comparación válidas. En condiciones económicas normales y para las grandes instalaciones previstas en la memoria, el precio de la unidad de trabajo de separación es superior en cerca del 80% y el precio del gramo suplementario en un 40% aproximadamente al que se deduce de la tarifa oficial de los Estados Unidos.

[El Sr. C. Fréjacques (Francia) ocupa la Presidencia]

Documento P/29 (presentado por J. A. Morrison)

DISCUSIÓN

W. P. BEBBINGTON (Estados Unidos de América): Su exposición, extraordinariamente interesante, está por completo de acuerdo con nuestra experiencia y bien merece la atención de cualquiera que se proponga explotar un reactor de agua pesada. Debe, ciertamente, de evitarse cualquier compuesto orgánico, ya que éstos pueden perturbar seriamente el control de la conductividad y de la concentración de iones deuterio.

Siguiendo la iniciativa canadiense, hemos adoptado el método infrarrojo para el análisis del agua pesada, tanto en reactores como en instalaciones de producción. Nuestros químicos opinan que su precisión para concentraciones muy elevadas es aun algo mayor que la indicada en esta memoria.

¿Tiene Vd. alguna estimación de la cantidad de agua ligera que entra en el reactor bien en forma de humedad adsorbida o bien como alúmina hidratada en los componentes del reactor, y han tomado Vds. algunas medidas para reducir a un mínimo tal contaminación? Además, ¿han empleado Vds. aditivos para el control de la acidez o de la corrosión?

J. A. MORRISON (Canadá): En nuestro reactor NRU las barras de combustible están en contacto con el D_2O. La cantidad de H_2O introducida en el sistema del agua pesada, por este concepto, es muy pequeña, ya que nosotros secamos las barras con aire caliente antes de introducirlas en el reactor. Yo no puedo dar una cifra absoluta, pero la degradación es inferior al 0,005 % en peso, ya que tenemos el reactor en funcionamiento desde hace varios años y sólo hemos apreciado una disminución muy pequeña en la concentración isotópica.

No empleamos aditivos para el control de la acidez ni de la corrosión. Hemos llevado a cabo un largo experimento con el pH del D_2O entre 5 y 5,5 pero no notamos una disminución significativa en la cantidad de gibbsita ($Al_2O_3 . 3D_2O$) que se produjo y el experimento se paró. Este trabajo se reseña en la referencia [11].

La precisión indicada en la memoria es, aproximadamente, la que se obtuvo con laborantes trabajando en un laboratorio normal. Desde que se redactó la memoria, se ha desarrollado una adaptación del método de infrarrojo empleando vidrios suplementarios, para los análisis en el intervalo del 90-99,5% de D_2O en peso. Esto ha mejorado la precisión de los análisis de rutina. Desde luego, si se tiene más cuidado, se puede obtener una precisión mayor que la indicada con el método original.

E. ROTH (Francia): La degradación de las 0,5 t de agua pesada en el NRX (ó 6 t en el NRU) ¿es originada por la entrada de los 0,2 kg/año de H_2O mencionados ó se refiere a las cantidades adicionales de agua degradada?

¿A qué temperatura funciona la instalación electrolítica?

J. A. MORRISON (Canadá): La cifra de 0,2 kg/año representa la cantidad de H_2O que entra en el sistema del D_2O originando una degradación muy pequeña, inferior a 0,001 % en peso, lo que tiene poca importancia. La mayor parte del agua degradada es o bien la que escapa accidentalmente como consecuencia de fallos en el equipo, o agua que se extrae deliberadamente durante el entretenimiento o durante un experimento.

La temperatura del agua del río varía desde 1 °C en invierno à 20 °C en verano. Las celdas trabajan a unos pocos grados por encima de estas temperaturas, según la época del año.

Documento P/290 (presentado por W. P. Bebbington)

DISCUSIÓN

J. GAUSSENS (Francia): Con referencia a Savannah, Vd. mencionó inversiones de 145 dólares/lb año, costes de funcionamiento de 13,5 dólares/lb y un precio de venta de la United States Atomic Energy Commission (USAEC) de 24,5 dólares/lb. Esto corresponde a una amortización anual del 7 %, aproximadamente, la cual es muy baja. ¿Ha empleado Vd. el mismo porcentaje en su cálculo?

W. P. BEBBINGTON (Estados Unidos de América): Las relaciones entre costes de funcionamiento, inversión y precio de venta han sido determinadas por la USAEC algo arbitrariamente, sin considerar demasiado las normas comerciales en cuanto a beneficios sobre las inversiones. En la referencia [14] se presenta una discusión más completa sobre estas cuestiones. Yo creo que el precio estadounidense del agua pesada se ha mantenido bastante bajo con objeto de alentar el rápido desarrollo de los reactores de agua pesada.

Documento P/753 (presentado por P. G. Deshpande)

DISCUSIÓN

W. P. BEBBINGTON (Estados Unidos de América): Yo creo que el Sr. Deshpande es muy prudente en su estimación de 7 500 horas anuales de funcionamiento. Incluso en nuestra instalación que lleva en funcionamiento 12 años, somos capaces de llegar aproximadamente a las 8 500 horas y no es raro que alguna de nuestras unidades trabaje continuamente durante un año sin una parada. Si se dispusiera de gas natural en la región de Nangal, ello constituiría una fuente de energía ideal, permitiendo la calefacción directa de los calentadores y el empleo de turbinas de gas, como señalan mis colegas el Sr. Proctor y el Dr. Thayer en la referencia [14] de la memoria. Sin embargo, el gas puede resultar demasiado valioso como materia prima química para emplearlo en estos usos.

P. G. DESHPANDE (India): La estimación de las 7 500 horas anuales de funcionamiento está basada en la experiencia de explotación de instalaciones químicas en la India. No estamos seguros de la disponibilidad de gas natural en las regiones de Nangal y por esta razón no hemos considerado el gas natural como combustible.

Documento P/754 (presentado por P. G. Deshpande)

No hubo discusión de esta memoria.

Documento P/91 (presentado por B. Lefrançois)

DISCUSIÓN

U. SCHINDEWOLF (República Federal de Alemania): En vista de las frecuentes referencias que se hace en las publicaciones científicas a las favorables propiedades del sistema NH_3-H_2 para la producción de agua pesada, después de haber terminado los experimentos en planta polito para la producción de agua pesada por el proceso de intercambio H_2O-H_2 a dos temperaturas, hemos comenzado experimentos con el sistema de amoniaco. Empezamos a escala de laboratorio y continuamos en una pequeña columna de intercambio en contracorriente, utilizando una presión de gas de 200 atm y temperaturas de — 30 a + 60 °C.

Ahora estamos trabajando con una planta piloto construída y explotada por la firma Friedrich Uhde GmbH en Dortmund, Alemania. Esta planta piloto a dos temperaturas consta de dos columnas de intercambio con longitudes de 28 m y 10 m, equipadas con unos 200 platos perforados que pueden funcionar a una presión de 200 atm y temperaturas de — 40 y + 60 °C, respectivamente. La planta puede funcionar con un caudal máximo de 1 000 m^3/h (C.N.) de gas de síntesis (mezcla N_2-H_2 en la proporción 1:3) a una presión de 200 atm. La medida del gasto óptimo de líquido sigue la teoría de K. Bier.

En un experimento típico del proceso a dos temperaturas, de 10 días de duración, obtuvimos un factor de enriquecimiento de 3,2, funcionando las columnas a — 20 y + 37 °C respectivamente. Este resultado se había previsto sobre la base de nuestros experimentos anteriores en la pequeña columna en contracorriente a una sola temperatura. Aproximándonos a las condiciones óptimas de funcionamiento, podemos esperar un factor de enriquecimiento considerablemente superior.

La evaluación de los experimentos indica que el sistema a dos temperaturas empleando amoniaco e hidrógeno como sustancias de intercambio y amida de potasio como catalizador es un sistema factible tanto técnica como económicamente para la producción de agua pesada.

Por esta razón me gustaría saber porqué el Sr. Lefrançois considera que el proceso de intercambio a dos temperaturas no es económico. ¿Se debe su conclusión a la necesidad de sistemas de contacto especiales?

B. LEFRANÇOIS (Francia): Basándanos en la experiencia con diversos sistemas de contacto, creemos que si se emplea únicamente la temperatura de — 50 °C, el proceso a una temperatura única es el más económico. Hemos ensayado 14 sistemas de dispersión.

C. U. LINDERSTRØM-LANG (Dinamarca): Yo supongo que la necesidad fundamental de extraer un 80 % del deuterio del material de alimentación fue una de las principales razones para la adopción del proceso a una temperatura única.

B. LEFRANÇOIS (Francia): La gran capacidad exigida por el proceso amoniaco-hidrógeno fue realmente una de las razones para nuestra elección. La torre de *super-extracción* aumenta el número de contactos y nosotros intentamos reducir éstos empleando un proceso a una temperatura única.

M. BENEDICT (Estados Unidos de América): ¿Existen planes para construir en Francia una instalación comercial para la producción de agua pesada por el proceso de intercambio amoniaco-hidrógeno?

B. LEFRANÇOIS (Francia): Sí; se encuentra en construcción una fábrica con una capacidad anual de 20 t.

W. P. BEBBINGTON (Estados Unidos de América): Hemos esperado con gran interés una posterior información sobre el desarrollo en Francia del intercambio amoniaco-hidrógeno y nos alegra saber que tiene aplicación garantizada en una instalación comercial. ¿Podría Vd. decirnos algo acerca de los problemas de manipulación del catalizador y el éxito con que han sido resueltos?; es decir, ¿cuánto catalizador se pierde o se destruye durante el proceso?

B. LEFRANÇOIS (Francia): Creemos haber resuelto, con éxito, los problemas del catalizador. Preparamos el catalizador disolviendo potasio en amoniaco. Son bien conocidas todas las reacciones de destrucción de la amida de potasio. La principal sustancia formada es el hidróxido potásico, que lo filtramos, dada su insolubilidad en el amoniaco. Aproximadamente se destruye 1 kg de amida diariamente.

(El Sr. M. Benedict vuelve a ocupar la Presidencia)

Documento P/388 (presentado por Y. V. Nikolaev)

DISCUSIÓN

M. HIGATSBERGER (Austria): Durante unos tres años el Centro de Reactores de Seibersdorf, explotado por la Österreichische Gesellschaft für Atomenergie, ha empleado un separador electromagnético de isótopos, especialmente adaptado para trabajos de separación de productos de fisión y radiactivos. La máquina dispone de un campo magnético de 180° no uniforme y un radio medio del haz de 100 cm. En el caso de ciertos isótopos pueden separarse cantidades de hasta 100 mg/día. En el momento actual el separador se está empleando principalmente en trabajos de análisis destructivo de combustible irradiado y en la determinación de datos nucleares.

P. G. DESHPANDE (India): ¿Qué materiales se emplean para las columnas y para el relleno en el método de destilación por intercambio usando el complejo éter dimetilo $[(CH_3)_2OBF_3]$ para la producción de ^{10}B?

Y. V. NIKOLAEV (URSS): Las columnas son de acero inoxidable y el relleno de cobre.

F. VIEHBOECK (Austria): ¿Han separado los isótopos intermedios de gases raros tales como ^{131}Xe, por métodos de difusión de masa? y si es así, ¿qué enriquecimientos han alcanzado?

Y. V. NIKOLAEV (URSS): En los momentos actuales se encuentra en construcción un dispositivo para la separación de isótopos de masas intermedias por difusión de masa.

P. HUBER (Suiza): ¿Tienen Vds. en funcionamiento una instalación de rectificación de NO? y si es así ¿cuál es su capacidad? ¿Saben Vds. si tiene lugar en la columna de rectificación el intercambio $^{14}N^{18}O + {}^{15}N^{16}O \rightarrow {}^{14}N^{18}O + {}^{15}N^{18}O$?

Y. V. NIKOLAEV (URSS): Tenemos una instalación de laboratorio con la cual se han alcanzado concentraciones de ^{15}N del 35 % y concentraciones de ^{18}O del 20 %. Empleando los datos obtenidos, estamos ahora construyendo un equipo para producir aproximadamente unos 4 kg de ^{15}N del 99 % al año.

Con respecto al intercambio al que Vd. se refiere, a partir de la cinética del crecimiento de concentración en nuestra cascada de laboratorio, podemos decir que, en efecto, tiene lugar, debido a que, de otra forma, la cinética del crecimiento sería considerablemente más lenta.

Documento P/465 (se leyó solamente el título)

DISCUSIÓN

E. ROTH (Francia): Estamos construyendo en Saclay una instalación que emplea el intercambio hidrógeno-agua como sistema de alimentación del tritio al equipo de difusión térmica.

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