

UNITED NATIONS
ECONOMIC AND SOCIAL COUNCIL

Distr.
General
E/ESCWA/NR/1993/13
21 October 1993
Original:English

ECONOMIC AND SOCIAL COMMISSION
FOR WESTERN ASIA
Natural Resources Division

Down-Stream Phosphate Industries
and their Prospects in the
ESCWA Region

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- The views expressed in this report are those of the author and do not represent those of the Economic and Social Commission for Western Asia
 - Issued without formal editing

93-0764

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INTRODUCTION

Phosphorus which makes up more than 0.11% of the Earth crust is the eleventh most abundant element, coming far before carbon. About 150 known minerals contain at least 1% P_2O_5 . The natural phosphate minerals are however nearly all of the apatite group represented by the general formula $xCa_3(PO_4)_2 \cdot yCaZ_2$, with Z being either F, Cl, OH or CO_3 . Phosphate deposits are numerous and vary widely in quality and phosphorus contents expressed usually in terms of % P_2O_5 .

Apatite as an accessory mineral of most igneous rocks has attracted interest not so much for phosphorus content as for some other valuable elements which tend to accumulate in such rocks and are associated with the presence of phosphate. The igneous apatite forms only 3-4% of the total world resources of phosphate which are mainly found in the former Soviet Union, Brazil and South Africa.

The basic raw material for phosphate is a sedimentary rock of which the essential mineral component is fluorapatite, which has the formula for the pure mineral $Ca_{10}(PO_4)_6F_2$ and is of marine or continental origin.

The term phosphorite or phosphate rock is usually used where the phosphate mineral forms a major constituent of sedimentary rocks. Some authors limit the term phosphorite to those rocks that contain more than 18-20% P_2O_5 , and others use the term phosphate rock for apatite-bearing rock or a beneficiated apatite concentrate containing enough P_2O_5 to be processed commercially.

In the ESCWA region, the phosphate deposits are typical marine formations, nearly all of which are late Cretaceous to Eocene age as identified for the phosphate fields in Egypt, Iraq, Jordan, Saudi Arabia and the Syrian Arab Republic. These fields form an easterly continuation of the belt of major phosphate fields extending across North Africa from Morocco through Algeria and Tunisia and include the phosphorite basins of Egypt and the Northern Arabian Peninsula where they are found in northern Saudi-Arabia, western Iraq and in Jordan and the Syrian Arab Republic.

It is interesting to note that on global consideration, no relation was found between the age and chemical composition of phosphorite, as shown by comparing the chemical analysis figures given in Table 1-1 for samples of different ages and locations; that for Egypt is typical of other ESCWA countries as may be judged by referring to Table 3-2.

As for the World resources of phosphate rock, shown in Table 1-2, the ESCWA countries account for almost all of the Middle East total resources and form more than 12% of the total for the whole world. It is interesting to note that the combined resources of the Arab countries of the Middle East and North Africa represents

55% of the total world resources, while that of the United States of America, the world largest producer of phosphate rock forms only 23%. Among ESCWA countries, Jordan is the world third largest producer after Morocco and the United States.

Most of the phosphate-rich countries of the ESCWA region, with their extensive phosphate deposits, which are both typical of the phosphrite ores of the world as well as forming a sizeable share of its resources, have established world-scale phosphate industry as in Egypt, Iraq, Jordan and the Syrian Arab Republic. However, Saudi Arabia has not yet exploited its sizeable phosphate reserves but has, like Lebanon, built phosphatics production plants.

It is worth noting that the phosphate industry in the ESCWA region has concentrated on ore production and beneficiation or/and on phosphatic fertilizers, to the almost complete neglect of the very wide-ranging other phosphate-based products with their multitude of uses and applications in industry, the home and services. This situation might have arisen because of the historic fact that all the established phosphate industries in the region were based on the wet-process phosphoric acid production, which product is mainly suitable for making phosphatic fertilizers, and which unless very specially processed and purified is unsuitable for many uses as for example in the food and pharmaceutical industries.

Now, with the wide experience, technical resources and investment capabilities of the local phosphate industry which has been well-established in some countries of the ESCWA region for over four decades, it is considered timely for the industry to look into the down-stream phosphate industries, and alternative products, and their prospects in the region. thus, it is intended here to study the technical aspects of the down-stream phosphate industry as well as to consider the by-products and wastes of the phosphate industry and their possible uses. this is to be done with special consideration being paid to the potentials for such industries and their implication to the regional development of the ESCWA countries.

Table 1-1
Chemical Analysis of Phosphorite *

Country Age	Peru- Chili	U.S.A Florida	Morocco	Egypt* **	India	Australia
%Compos- ition	Holo- cene	Piocene	Lower Eocene	Creta- ceous	Perm- ian	Cambrian
P ₂ O ₅	22.61	32.07	34.26	25.20	22.50	35.00
SiO ₂	22.13	9.31	0.03	12.50	7.05	10.30
Al ₂ O ₃	5.15	1.29	0.37	0.84	0.66	1.59
Fe ₂ O ₃	2.85	1.57	0.26	1.86	2.56	0.14
CaO	33.93	46.98	52.78	40.66	40.55	48.20
MgO	1.07	0.19	0.48	1.75	6.00	0.15
Na ₂ O	0.85	0.21	0.84	0.68	0.18	0.04
K ₂ O	1.30	0.13	0.09	0.10	0.24	0.09
CO ₂	- -	3.07	3.59	5.58	15.10	1.20
SO ₃	- -	0.59	1.59	- -	1.35	0.07
F ⁻	2.22	3.68	3.05	2.57	2.15	3.16
Cl ⁻	- -	0.013	0.03	1.06	0.06	-
H ₂ O**	- -	1.88	2.34	4.30	0.99	1.23
C,org	- -	0.053	- -	1.20	0.76	0.60
CaO/P ₂ O ₅	1.50	1.46	1.54	1.61	1.80	1.37
P ₂ O ₅		0.115	0.089	0.101	0.095	0.090
CO ₂ /P ₂ O ₅	0.098	0.09	0.10	0.22	0.67	0.03
SO ₃ /P ₂ O ₃	- -	0.018	0.04	- -	0.06	0.002
	- -					

* Source: Nathan (1984), (ref.14).

** Total H₂O content.

*** For other ESCWA countries see Table (3-2).

Table 1-2
World Resources of Phosphate Rock *
(Unit 10⁶ tonnes)

Region	Total Resources	Content	P ₂ O ₅		
			%		
			Average	Highest	Lowest
N.America (U.S.A)	34999 (32600)	8288	24	30**	4
S.America	5243	931	18	31**	5
Africa (1)	64016	17419	26	36**	2.5
(N.Africa)	59850				
Middle East	18462	3877	21	28	4
(ESCWA region)	17561				
Europe	1168	77	7	17	5
Asia	13947	3289	14	38	5
Oceania	3955	712	18	39***	17
World Total	141790				
%USA	23%				
% ESCWA region	12%				
% Arab countries	55%				

(1) Except Egypt resources of 3000 million tonnes added to M.E.

* Source: Notholt, Sheldon and Davidson (1989) (ref.15).

** Phosphate concentrate.

*** Guano-derived Phosphate

THE WORLD PHOSPHATE INDUSTRY

2.1 Phosphate Rock

The World phosphate industry is based mainly on the processing of phosphate rock which is aimed at the production of the following major primary products:

- 1- Beneficiated phosphate rock.
- 2- Phosphoric acid by the wet-process.
- 3- Elemental phosphorus by the electric-furnace process.
- 4- Calcium phosphates by acidulation of phosphate rock.
- 5- Defluorinated phosphate rock by calcination, fluorine compounds.

Of-course in each of these processes the primary basic product may be itself the final salable product or is aimed at manufacturing many other chemicals whether as final products or as intermediates for further products. Table 2-1 outlines the main important processes currently in use in the phosphate industry and their main products and immediate derivatives and by-products.

The beneficiation of phosphate rock is aimed at freeing the phosphate deposits from unwanted contaminants and to enhance their economic value. It involves usually such operations as washing, froth flotation, screening, scrubbing, grinding, drying, and calcining, not necessarily in that order, and not always all these operations are needed. It depends very much on the quality of the ore. For example grinding and calcining are important to remove organic matter to avoid the production of "black" phosphoric acid in the wet process. The beneficiation process enhances the P_2O_5 content of the phosphate rock which may be marketed as such. Even when used directly for phosphoric acid production the higher P_2O_5 content and the diminished amount of impurities cut considerably in material and energy cost.

The beneficiation process is becoming increasingly important as poor-quality ores are being mined.

The most important single basic product in the phosphate industry is phosphoric acid followed by elemental phosphorus. For the acid, beside being used as primary chemical for the production of wide variety of products, is itself a final chemical that enters as such in many product formulation. On the other hand, elemental phosphorus is essentially used for the production of other chemicals, among them phosphoric acid itself. The advantage of producing phosphoric acid from elemental phosphorus, rather than directly by the wet process from phosphate rock, is that the so-called thermal acid contains very little impurities as compared with the wet process acid and therefore is suitable for human and animal consumption as well as for many other applications where purity of the acid is a premium.

Acidulation of phosphate rock is used to produce calcium superphosphates which are sold as fertilizers under either the name of normal superphosphate (NSP), when the rock is treated with sulphuric acid to give monocalcium monohydrate, or under the name of triple superphosphate (TSP), when the rock is treated with phosphoric acid to give the more concentrated product, containing 45-47% P_2O_5 compared to 20% P_2O_5 in NSP. Another advantage for TSP production is the poorer quality phosphate rock that can be used in the process.

Phosphate rock cannot be used as direct stock-food supplement because it contains fluorapatite with fluorine content from 2-4% which makes it unsuitable for animals. Also the increased value of fluorine makes its removal desirable both economically as well as for the better operation of the wet process, beside the benefit of reducing environmental pollution by fluorine compounds. Various defluorinating processes are used, but the ones that directly defluorinate phosphate rock involve the heating of finely ground material to 1200-1400°C in the presence of water vapor with added phosphoric acid and silica. The fluorine is evolved as the volatile silicon tetrafluoride, hydrogen fluoride and fluorosilicic acid, which mixture when passed through water yields fluorosilicic acid that can be concentrated to commercial strengths (generally 30-35%). The defluorinated phosphate rock with fluorine content of less than 1 part in 10000 for every 1% of phosphorus in the product is suitable as animal nutrient supplement (content 18.5% P).

Table 2-2 shows the relative importance of the various uses of phosphate rock as used by producers in the United States for the year 1981 for which detailed figures are available. U.S.A. being the World major producer and consumer of phosphate rock, the percentages for the different uses may serve as indication of their relative importance.

The World natural phosphate production is given by regions for the years 1981-1990 both in terms of gross weight (Table 2-3) and in terms of P_2O_5 content (Table 2-4). The figures of Table 2-3 show that the world production of natural phosphate has grown at an average annual rate of just under 1% over the period 1981-1990, while that for the United States, the World number one producer, has fallen at an annual rate of 1.5%.

2.2 Phosphoric Acid (ortho phosphoric acid)

Orthophosphoric acid or simply phosphoric acid (H_3PO_4) is, in terms of volume, the single most important product of the phosphate industry. Its consumption per se although commercially insignificant, but its greatest use is in the manufacturing of phosphate salts, of which the phosphate fertilizers have the greatest share. Table 2-5 gives the World production of phosphoric acid in terms of P_2O_5 from which it could be deduced that the production of this commodity has enjoyed an average annual growth of 6% for the period 1985-1990.

Although the Wet-process phosphoric acid has established itself as the major source of the World acid production, thermal acid still has an important position, being the only source of "pure" acid suitable for such applications as food additives, catalysts, water treatment and such other uses that require higher quality acid than can be provide by the wet-process even when purified. Table 2-6 shows typical analysis of phosphoric acids from wet-process (both commercial and purified) and thermal acid, from which the superiority of the latter is quite evident.

Several methods have been developed and some are commercialized for the purification of wet-process phosphoric acid. They are mainly based on chemical precipitation and solvent extraction. The cost differential between the sulphur used in wet-process phosphoric acid and the electricity needed for the thermal acid is the reason behind the development of purification methods for the former. However, where relatively cheap electricity is available, as from hydroelectric power, then the thermal acid, with its superior purity, is preferred and used in all applications other than fertilizer production and where trace elements are needed to be extracted.

2.3 Phosphatic Fertilizers

As mentioned in (2.1) both normal superphosphate (NSP) and triple superphosphate (TSP) are made by direct acidulation of phosphate rock. Other fertilizers such as monoammonium phosphate (MAP) and diammonium phosphate (DAP) are made by mixing ammonia with phosphoric acid in the required proportions.

During the seventies the share of ammonium fertilizers was on the increase in terms of the World P_2O_5 fertilizer production and reached about 60% of World production. while the share of normal superphosphate had declined from the high level of over 60% in the mid-fifties to just over 20% in the mid-seventies that for triple superphosphate maintained a level share just under 20%. However, the situation seems to have steadied in the eighties with the superphosphates steady at around 50% of the World production.

Tables 2-7 and 2-8 give the relevant statistics for World phosphate fertilizers production. The annual growth rate for the period 1981-1990 is just under 2% for the total fertilizers industries, as compared with over 2.8% for the superphosphates, which trend points to the resurgence of the superphosphate fertilizers.

Table 2-1
The Basic Processes of the Phosphate Industry

Process	Raw material & reagents	Main products	By-products
Beneficiation	Phosphate ore, water, energy	Phosphate rock	
Calcination/Defluorination	Phosphate rock, silica, water, fuel	Defluorinated phosphate	Fluorine compounds.
Acidulation	Phosphate rock, sulphuric acid, phosphoric acid, hydrochloric acid	Superphosphate triple superphosphate	Fluorine compounds, vanadium
Wet-Process	Phosphate rock, sulphuric acid, hydrochloric acid	Phosphoric acid	Fluorine compounds, vanadium, uranium, phosphogypsum.
Electric furnace reduction	Phosphate rock, siliceous flux, coke, electric energy	Phosphorus, Phosphoric acid	Fluorine compounds, carbon monoxide, slag, ferrophosphor vanadium

Table 2-2
The Relative Importance of the Various Uses
of Phosphate Rock (The percentages are from consumption
figures by U.S.A. production , 1981)

Use	Quantity (1000 tonnes)	%
Wet-process phosphoric	29085	83
Elemental phosphorus	4055	12
Superphosphates	1382	4
Defluorinated rock	492	1
Ferrophosphorus	89	0.2
Direct applications	27	< 0.1
Total	35130	

*Source : Minerals Yearbook 1982, (ref.13).

Table 2-3
World Production of Natural Phosphate
1981-1990*

unit 1000 tonnes

Region	1981	1985	1986	1987	1988	1989	1990
N.America	53955	51500	41000	41603	46082	49551	46981
S.America	2687	4199	4744	4981	4921	3958	3187
Africa	33602	37800	40694	39435	37527	36592	38036
Asia	20511	18808	19165	22405	30679	33627	33416
Europe	339	713	733	788	739	649	567
Former USSR	30700	33750	33900	34100	34400	34400	33500
Oceania	2938	2728	2408	2229	2327	1879	1539
Total	144732	149498	142644	145541	156675	160656	157226

* Source : Industrial Statistic Yearbook, 1990 (ref.9).

Table 2-4
World Production of Natural Phosphate(P₂O₅ Content),
1981 - 1990*

unit 1000 tonnes

Region	1981	1985	1986	1987	1988	1989	1990
N.America	16515	<u>15870</u>	12081	12698	14034	15090	14294
S.America	1091	<u>1221</u>	1535	1722	1676	1308	1061
Africa	10020	<u>10965</u>	11739	11944	13811	11575	12234
Asia	5489	<u>6344</u>	6234	7597	8959	11125	9104
Europe	121	<u>264</u>	268	278	259	228	203
Former USSR	9700	<u>10650</u>	10700	10750	10850	10850	10200
Oceania	1075	<u>1006</u>	892	827	870	699	569
Total	44011	46320	43449	45816	50459	50875	47665

* Source : Industrial Statistic Yearbook, 1990 (ref.9)

Table 2-5
World Production of Phosphoric Acid (P₂O₅ Content)
1981 - 1990*

unit 1000 tonnes

Region	1981	1985	1986	1987	1988	1989	1990
N.America	10171	10574	9625	10085	11068	11124	11352
S.America	430	707	708	688	780	768	851
Africa	971	1508	2225	2481	1490	1510	3223
Asia	452	308	288	306	296	382	412
Europe	4722	5189	5334	5128	5100	5110	4515
Former USSR	611	653	4657	4926	5048	5128	5043
Oceania	112	72	53	44	34	25	15
Total	17468	19110	22891	23657	23806	24044	25410

* Source : Industrial Statistic Yearbook, 1990 (ref.9)

Table 2-6
Typical Analysis of Phosphoric acids*

Assay	Wet-Process acid merchant grade	Purified Wet-Process acid tech grade	Thermal acid Tech grade
P ₂ O ₅	53.1	54	54.32
CaO	0.06	0.005	0.001
F	0.8	0.08	< 0.0001
Al ₂ O ₃	1.7	0.01	0.0003
Fe ₂ O ₃	1.23	0.007	0.0004
MgO	0.58	0.003	0.0002
K ₂ O	0.01		0.0007
Na ₂ O	0.12		0.0025
SiO ₂	0.07	0.1	0.0015
SO ₄	2.2	0.2	< 0.002

* Kirck-Othmer Encyclopedia of Chemical technology, (ref.10).

Table 2-7
World Phosphate Fertilizers Production (P₂O₅ Content)
1981 - 1990 *

unit 1000 tonnes

Region	1981	1985	1986	1987	1988	1989	1990
N.America	10488	14031	10961	12058	10107	10484	10739
S.America	1183	1331	1505	1511	1439	1575	1647
Africa	1910	2363	2338	2443	2865	2917	3118
Asia	5821	7241	8473	9235	9270	9696	9904
Europe	9594	10003	9606	9267	9616	9147	7463
Former USSR	6836	8596	9279	9693	10013	9657	9434
Oceanic	1176	892	821	809	913	964	739
Total	37008	44457	42984	45016	44223	44440	43043

Source: Industrial Statistics Yearbook, 1990 (ref.9).

Table 2-8
World Superphosphates Production (P₂O₅ Content)
1981-1990*

unit 1000 tonnes

Region	1981	1985	1986	1987	1988	1989	1990
N.America	2039	1316	1096	1998	1984	2035	2156
S.Africa	620	717	747	806	822	881	926
Africa	1679	1809	1806	1822	1809	1882	1925
Asia	2493	3079	3770	4736	5277	5356	5622
Europe	3119	2840	2891	2955	3045	2739	2285
Former USSR	6836	8596	9279	9693	10013	9657	9434
Oceanic	1176	892	821	809	913	964	739
Total	17961	19249	20409	22819	23862	23515	23087

* Sources: Industrial Statistics Yearbook, 1990 (ref.9)

THE PHOSPHATE INDUSTRY OF THE ESCWA REGION

3.1 Phosphate Rock

The phosphate ore of the ESCWA region, like that of North Africa, is of sedimentary phosphate type, and is mainly made up of fluorapatite, with, in some cases, structural chlorine and carbonate.

The countries with major phosphate ore reserves are Egypt, Iraq, Jordan, Saudi Arabia and Syria. The region total reserve is recently estimated at more than 5 billion metric tonne, and is expected to rise to almost twice that figure by the end of the decade. Table 3-1 gives details of the latest estimated reserves for the countries of the region and those of the North African countries for comparison. With the exception of Saudi Arabia, all the other ESCWA countries with sizeable reserves have built extensive phosphate ore utilization facilities.

Phosphate ores resources in the region vary slightly from one deposit to another, and are mainly of the low grade phosphate rock with P_2O_5 content in the 20-25% range, with the exception of some deposits in Jordan where the quality of the ore is significantly higher.

One of the major problems, that affect the quality of sedimentary phosphate deposits, is their contamination with such materials as clay, calcium carbonate, silica, oxides of iron and aluminium, and the relatively high content of such contaminants ions as sodium, potassium, chloride, as well as in some cases organic matters. Being surface and near surface deposits these contaminants could vary considerably from one location to another. This situation necessitates careful processing to up-grade the ores and produce phosphate rock quality product suitable for phosphatic fertilizers and phosphoric acid production.

The deposit location and the associated kind of contaminants dictates the type of beneficiation processes used. But, in general, they are mostly mechanical, involving crushing, washing, scrubbing, grinding and flotation. In some cases where organic matters are present, calcining is also used to avoid "black" phosphoric acid when the ore is destined for wet-process production.

Because of its relevance to the present study the specifications of the phosphate rock as produced by the countries of the region, with the exception of Saudi Arabia, are given in Table 3-2. The specifications in the case of Saudi Arabia because their deposits have not been commercially utilized, are those of field samples and not from mining processing plants.

Uses of phosphate rock produced in the region are distributed between fertilizers and phosphoric acid production on the one hand, and for export on the other hand.

Phosphate rock production in the ESCWA region and North Africa is given in Table 3-3 from which it could be seen that production has fluctuated for the ESCWA countries between 6 to 8% of the world production over the period 1985-1990; the figures for the ESCWA and North African regions are 24 to 28%.

A point of special interest is to examine capacity utilization in the region which has declined from 74% in 1985 down to 64% in 1991 reaching a high of 85% in 1987. However, the trend is not uniform in terms of the individual countries. Thus, for Egypt the corresponding figures are 60% and 76% (i.e. actual increase) and highest of 78% in 1989; for Iraq which maintained a higher utilization than given capacity of 118% over the years 1985-1987, the figure declined to 64% in 1991 as consequence of the effect of the Gulf War; for Jordan with highest production capacity of 57% of the region, capacity utilization has declined from 76% in 1985 to under 61% in 1991 with highest of 87% in 1989; for Syria the figures are 51% in 1985 rising to 94% in 1988 then declining to 70% in 1991. These figures may reflect the effect of the world supply-demand for phosphate rock specially for countries, like Jordan, with sizeable fraction of their phosphate rock is ear-marked for export.

Another point worth mentioning is the ESCWA region share in the world production of natural phosphate which has declined from 7% in 1985 to 6% in 1990 (c.f. for the Arab countries of the Middle East and North Africa the corresponding figures are 25 and 24%; for the United States its share has declined even more sharply from 34% in 1985 to 29% in 1990). The modest increase in world production of just over 5% in the period from 1985 to 1990 is mainly accounted for by the increase in the Asian region (except ESCWA countries) with some but only minor contribution from the African region (except North Africa).

3.2 Phosphoric Acid:

The industrial facilities for the production of phosphoric acid in the ESCWA region all use the wet process technology which involves the treatment of up-graded phosphate rock with sulphuric acid. This is in spite of the low-grade phosphate ore common to most deposits in the region, and thus beneficiation processing of the ore is needed. The adoption of the wet-process may be due to the lower energy needs of the process and the availability of relatively cheap sulphur in the region. The alternative thermal process is based on elemental phosphorus which is produced by electric furnace reduction of phosphate rock of lower grade than that required by the wet-process.

The annual production capacities of the wet-process plants installed in the region vary considerably from small size plant of 65 thousands tonne in Egypt to medium size plants of 400 thousand tonne in Iraq and Jordan. the figures are given in Table 3-4 together with the annual production for the period 1985-1991. the production figures show serious under capacity utilization. Thus of the available total production capacity for the region of 1156 thousand tonnes, the actual production reached only a maximum of 57% in 1990 falling to 43% in 1991. The figures for the North African countries show a healthy trend with overall capacity utilization of about 77% in 1990 rising to 83% in 1991.

3-3 Superphosphates:

Both normal superphosphate (NSP) and triple superphosphate (TSP) are produced by several countries in the region, but with TSP installed capacity exceeding that for NSP by a factor of 1.5. the figure for North African countries is much higher with TSP capacity over 11 times that for NSP. This trends may reflect the fact that low-grade rock can be used in the production of TSP and obtaining product with higher P_2O_5 content.

Production capacity utilization has been in the range 73-80% over the years 1988-1990 but has dropped to 61% in 1991, again possibly due mainly to the drastic fall in the Iraqi production. The world production of superphosphate has shown an average annual growth of about 4% for the period 1985-1990 while the corresponding figure for the ESCWA region is about 2%.

3-4 Ammonium Phosphates:

Most of the fertilizer producers in the region have geared most of their production to diammonium phosphate (DAP), and some of them like Iraq and Jordan have stopped production of monoammonium phosphate (MAP) possibly because of the higher N content of the former 18% as compared to 11% for MAP.

Table 3-6 gives details of production capacities and actual production for both ammonium phosphates taken together. Although the reported production capacity in Saudi Arabia is 200 thousand tonnes, the figures for its production for 1991 far exceeds twice that amount which may indicate an unreported new added capacities.

The Basic Chemicals of the Phosphate Industry: Phosphoric Acid and Elemental Phosphorus

The present survey has shown that the phosphate industry is based primarily upon the two basic chemicals: phosphoric acid and elemental phosphorus, which represent the starting materials for the industrial production of phosphates and organophosphorus compounds used in varieties of applications. It has also been demonstrated that for some of these, phosphoric acid of high level of purity is required as for example, in the food industry, water-treatment, catalysts, metal treatment, electroplating.

For these and other important applications special procedures are employed to purify wet-process phosphoric acid to bring it to the level of purity that makes it acceptable for most, though not all, such applications.

As shown previously, even specially purified wet-process phosphoric acid is inferior to the highly pure thermal phosphoric acid produced from phosphorus obtained by the electric-furnace reduction of phosphate rock. This makes the provision of thermal phosphoric acid imperative for such applications for which the high purity standards are demanded.

Also, elemental phosphorus forms the basic material in the production of wide range of products of important commercial uses, such as pesticides, plastic stabilizers and plasticizers, flame retardants, chelates and metal extractants, and other organophosphorus-based products.

For these reasons it is considered useful to review here the available processes for the purification of wet-process phosphoric acid and the production of elemental phosphorus and its subsequent use to make thermal phosphoric acid.

Of-course, the decision as to purify wet-process phosphoric acid or to manufacture thermal acid from elemental phosphorus depends not only on the cost differential between these two alternatives but also on the ultimate uses for which the respective product is intended.

7.1. Purification of wet-process phosphoric acid.

On aging phosphoric acid produced by the wet-process specially from relatively low-quality phosphate rock, many complex compounds, called sludge, precipitate. Sludge composition varies only slightly, but in general the precipitate is formed mainly by compounds of iron, aluminium, copper, sodium, potassium, calcium, magnesium, as phosphates, sulphate, fluorosilicate and others. These and others more persistently soluble compounds represent the type of impurities usually present in wet-process acid and, therefore are the object for the purification process. The use of

Table 6-1

**Production of Aluminum Fluoride and Cryolite
in the ESCWA Region and in North Africa**

unit 1000 tonnes

Country	Production capacity	
	aluminum fluoride	cryolite
ESCWA region		
Iraq	11	6.4
Jordan	20	--
Syria	3.5	--
subtotal	34.5	6.4
North Africa		
Morocco	n.a.	n.a.
Tunisia	20	--
subtotal	20	--
Total	54.5	6.4

n.a. : not available.

Source: Chemical Fertilizer Industry and its Raw Materials in the Arab Region till the Year 2000, (ref.3).

Table 3-3
Phosphate Mine Production in the ESCWA Region
and in North Africa

units 1000 tonnes

Country	Production Capacity	Production**						
		1985	1986	1987	1988	1989	1990	1991
ESCWA REGION								
Egypt	1800	1074	1272	1103	1348	1397	1143	1367
Iraq	1700	2000	2000	2000		1143	1200	1080
Jordan	8000	6067	6249	6800	5620	6930	6080	4850
Syria	2500	1270	1606	1986	2342	2250	1670	1750
Subtotal	14000	10411	11127	11889	9310	11720	10093	9047
NORTH AFRICA								
Algeria	2000	1207	1203	1073	1329	1224	1100	1150
Morocco	25000	20737	21178	20955	24783	17988	20055	17818
Tunisia	7000	4505	5800	6215	6103	6500	6258	6175
Subtotal	34000	26449	28181	28243	32215	25712	27413	25143
Total	48000	36860	39308	40132	41525	37432	37506	34190

Source: * Annual Statistical Report 1990-1991, (ref.1).
** Arab Mining Co., (ref.4).

Table 3-4
Phosphoric Acid Production in the ESCWA Region
and in North Africa

unit 1000 tonnes P₂O₅

Country	Prod- uction Capaci ty*	Production						
		1985	1986	1987	1988	1989	1990	1991
ESCWA REGION								
Egypt	65	--	50	--	--	--	33	33
Iraq	416	200	200	--	--	--	275	139
Jordan	410	259	282	282	303	303	297	271
Lebanon	100	--	--	--	--	--	45	40
Syria	165	56	67	--	--	--	17	18
Subtotal	1156	515	599	282	303	303	667	501
NORTH AFRICA								
Algeria	115	--	--	--	--	--	62	57
Morocco	2772	1033	1653	1888	634	675	2406	2650
Tunisia	1452	475	572	593	856	834	862	912
Subtotal	4339	1508	2225	2481	1490	1509	3330	3619
Total	5495	2023	2824	2763	1793	1812	3997	4120

Source: * Annual Statistical Report 1990-1991, (ref.1).
 ** Arab Mining Co., (ref.4).
 and Industrial Statistic Yearbook,
 1990, (ref.9).

Table 3-5
Superphosphates Production in the ESCWA Region
and in North Africa

unit 1000 tonnes

Country	Production Capacity*	Production						
		1985	1986	1987	1988	1989	1990	1991
ESCWA Region								
Egypt	1070	930	934	957	986	1021	1170	1018
Iraq	600	270	160	- -	165	344	300	62
Jordan	20	- -	- -	- -	- -	- -	- -	2
Lebanon	420	610	600	- -	773	600	662	520
Saudi Arabia	200	- -	- -	- -	- -	w- - 55	- -	10
Syria	450	197	229	- -	195		72	71
Subtotal	2760 ⁽¹⁾	2007	1923	957	2119	2020	2204	1683
North Africa								
Algeria	290	39	- -	7	43	- -	- -	23
Morocco	1190	- -	700	- -	- -	- -	682	560
Tunisia	1050	368	435	154	419	- -	822	739
Subtotal	2530 ⁽²⁾	407	1135	161	462	- -	1504	1322
Total	5290	2414	3058	1118	2581	2020	3708	3012

Source; * Annual Statistical Report 1990-1991 (ref.1)
 ** Arab Mining Co.(ref.4)

(1) Production capacity for NSP 1090 ton.
 and for TSP 1670 ton.

(2) Production capacity for NSP 200 ton.
 and for TSP 2330 ton.

Table 3-6
Ammonium Phosphates Production in the ESCWA Region
and in North Africa

unit 1000 tonnes

Country	Production* Capacity	Production**	
		1990	1991
ESCWA Region			
Iraq	250	220	142
Jordan	740	596	599
Saudi Arabia	200	116	512
Subtotal	1190	932	1253
North Africa			
Algeria	230	--	--
Morocco	1974	1749	1790
Tunisia	900	549	576
Subtotal	3140	2298	2366
Total	4294	3230	3619

Source: * Annual Statistical Report 1990-1991, (ref.1).
 ** Arab Mining Co.(ref.4).

THE PRODUCTS OF THE PHOSPHATE INDUSTRY

The basic chemical for the phosphate industry is the mineral apatite and in particular the form occurring in sedimentary formation of marine or continental origin, viz., fluorapatite, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, from which the whole products of the phosphate industry originate either directly in what could be termed primary chemicals which may serve as basis for further products or they may themselves enter directly into some final products either as ingredients or as processing chemicals. these phosphorus primary chemicals which are obtained directly from fluorapatite are elemental phosphorus, P_4 , and orthophosphoric acid, H_3PO_4 . Each one of these primary chemicals may be used to produce secondary chemicals or chemical intermediates that could themselves be the desired final products, or once again a reagent for further reaction leading finally to some such products as may be called consumer products.

I. Chemicals from Elemental Phosphorus

The chemical intermediates that could be obtained from elemental phosphorus directly or indirectly are mainly:

4.1 Phosphorus oxide is made commercially by burning phosphorus in stream of dry air, which may then be reacted immediately to produce phosphoric acid by what is known the furnace process. The resulting highly pure acid is called thermal acid of superior quality to wet-process acid obtained directly from phosphate rock (see Table 2-6). When phosphorus pentoxide is manufactured as a reagent or an intermediate chemical, of its several uses are the following: the manufacture of POCl_3 , making acrylate esters, in surfactant manufacture, as catalyst in air-blowing of asphalt, and in making organic phosphates, e.g., triethyl phosphate.

4.2 Phosphorus sulphides are manufactured by direct reaction of phosphorus with sulphur. Of the four different sulphides known, the one termed tetraphosphorus decasulphide P_4S_{10} , or simply phosphorus pentasulphide, is the second largest-volume phosphorus compound produced in the United States other than phosphoric acid and its derivatives. Among the various uses of phosphorus pentasulphide are the following: the manufacture of isecticides, lubricating-oil additives, plasticizers, flame retardants, flotation agent for mineral processing, and as catalyst in the manufacture of blown asphalt which is used to line irrigation canals, ponds and reservoirs.

4.3 Phosphorus halides, of the many halides of the general formula PX_3 , PX_5 , the commercially important ones are phosphorus trichloride, PCl_3 , phosphorus pentachloride, PCl_5 , phosphorus oxychloride, POCl_3 , and phosphorus sulphochloride, PSCl_3 .

1. Phosphorus trichloride is manufactured by direct reaction of the elements chlorine and phosphorus in the presence of phosphorus trichloride. In one process the higher halide, i.e., phosphorus pentachloride PCl_5 , may be made in the same plant by reacting the product from the trichloride reactor with chlorine in a separate reactor. Highly pure halides are obtained.

Because it readily reacts with oxygen, sulphur, chlorine, and water, phosphorus trichloride is widely used as intermediate in the production of many phosphorus compounds of wide applications.

E.g., the phosphorate esters of alkylated phenols are used as lubricating-oil additives to control bearing corrosion and oxidation, and give good antirust property; and also used as stabilizers and flame retardants in plastics, beside being specialty solvents and intermediates. Other phosphite esters are used as textile-treating agents, antiscaling additives and transition metal extractants.

2. Phosphorus pentachloride is made from phosphorus trichloride and chlorine; It has limited uses as catalyst and chlorinating agent.

4.4 Phosphorus Oxychloride is manufactured by bubbling oxygen through liquid phosphorus trichloride. Alternatively, it is also made by using a mixture of phosphorus trichloride and chlorine with phosphorus pentoxide. Phosphorus oxychloride is an important intermediate for the manufacture of alkyl and aryl orthophosphate triesters by reacting the respective alcohol or phenol with POCl_3 . The pure triesters are recovered by a multistep refining process.

Most of the phosphate esters are used in the production of hydraulic fluids, plastic and elastomer additives, oil stabilizer, surfactants and sequestrants, pesticides, and medicinal intermediates.

Some trialkyl phosphates are outstanding solvents for nitrates and are therefore important in uranium processing where it is used to extract uranyl nitrate.

4.5 Phosphorus Sulphochloride is made by direct addition of sulphur to phosphorus trichloride in the presence of alkali or alkaline-earth sulphides, or aluminium chloride as catalysts. It is mainly used in the manufacture of insecticides, e.g., parathion.

4.6 Acids, aside from orthophosphoric acid, two other acids deserve mentioning, viz., phosphinic acid (also known as hypophosphorous acid) and phosphonic acid (also known as phosphorous acid). The former is manufactured by treatment of white phosphorus with boiling slurry of lime and is used as its calcium salt in electroless plating process in which nickel salts

are chemically reduced to form smooth adherent surface plate. The process is used to protect the interior of large vessels, e.g. tank cars. the coating is highly impervious and can be hardened by heat treatment. The other acid is commercially made by the hydrolysis of phosphorus trichloride, and its most important use is as an intermediate in the manufacturing of starting materials for the production of herbicides and water-treatment agent.

4.7 Phosphides are compounds of metals with phosphorus and may of them are prepared by direct reaction of the elements. some of the metallic phosphides have found interesting applications. the reactive phosphides, such as calcium phosphide, are made commercially in small quantities as source of phosphine, PH_3 . Others, like magnesium phosphide and aluminium phosphide which are stable in dry air used with an igniting agent as sea flares. Aluminium phosphide is widely used as grain fumigant.

Phosphide of transition metals are very resistant to chemical attack and can only be decomposed by alkali fusion. Diiridium phosphide has been used in tips of fountain pens.

Ferrophosphorus is a by-product of the manufacture of elemental phosphorus from phosphate rock, silica and coke. It is formed from the reduction of iron compounds present as impurity in the reaction materials. Additional iron-bearing materials may be added to the furnace charge to increase production of ferrophosphorus. this does not affect the purity of the elemental phosphorus produced by this method. An important application of ferrophosphorus is in the production of high strength low alloy steel which is used in large structural members and plates. Ferrophosphorus obtained from furnaces fed with phosphate rock containing vanadium will help in the extraction of this metal.

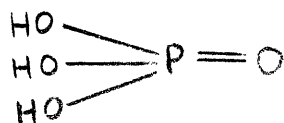
Other commercially important metal phosphides are phosphor copper used for the deoxidation of copper and its alloys; phosphor tin for the deoxidation of bronzes and German Silver.

Zinc phosphide has been made in small quantities and used as rodenticide.

II. Chemicals from Phosphoric Acid

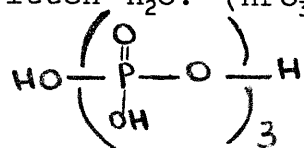
The chemicals that could be obtained from phosphoric acid, of either thermal or wet-process origin, whether directly or indirectly, are mainly phosphate salts which may be described as salts of one of the different forms of phosphoric acid. These forms are referred to as follows:

1. Orthophosphoric acid is simply H_3PO_4 , i.e.,



and may be referred to as $3\text{H}_2\text{O} \cdot \text{P}_2\text{O}_5$, a hydrate of phosphorus pentoxide, which is a common way of expressing phosphoric acids composition.

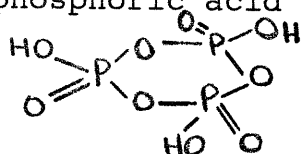
2. Pyrophosphoric acid $\text{H}_4\text{P}_2\text{O}_7$ which is a condensed form of the acid and may be written as $2\text{H}_2\text{O} \cdot \text{P}_2\text{O}_5$.
3. Polyphosphoric acid which may be written $\text{H}_2\text{O} \cdot (\text{HPO}_3)_n$, such as tripolyphosphoric acid, $n = 3$:



tetrapoly phosphoric acid, $n = 4$ and soon.

4. Metaphosphoric acid $\text{H}_2\text{O} \cdot \text{P}_2\text{O}_5$ or simply HPO_3 , i.e., $\text{HO} - \text{P} \begin{array}{l} \text{O} \\ \parallel \\ \text{O} \end{array}$

5. trimetaphosphoric acid which has a cyclic structure.



The term superphosphoric acid is a loose chemical term referring to the low solidification-temperature phosphoric acid of concentration of 75.0 - 76.0% P_4O_{10} (equivalent to 105% H_3PO_4). Because the solidification temperature of superphosphoric acid is 18.3°C , it can be handled as liquid above this temperature. Superphosphoric acid is in fact a mixture of ortho-phosphoric acid and pyrophosphoric acid with some tripolyphosphoric acid. The latter will revert to orthophosphoric acid upon the addition of water and heating. Thus superphosphoric acid is a very convenient form for transporting and handling phosphoric acid, hence cutting on the expense of transporting about 15-25% water which represents the water content of commercially sold phosphoric acids.

The most important difference between thermal acid and wet-process acid is in the higher purity of the former and is reflected in its suitability for such applications where purity is demanded. Therefore, the applications to which the various phosphoric acid and its derivatives will be referred to in this section shall indicate the source of the acid whenever the higher purity is required. In what follows phosphoric acid will be referred to as either wet-process acid, purified wet-process acid, or thermal acid (see Table 2-6).

The manufacturing of phosphate salts follows the general scheme shown in Figure 4-1. This scheme shows the common basis of the various salts which are all made from orthophosphoric acid with the required base, e.g., carbonate, hydroxide, oxide. The salts are obtained by crystallization or dry evaporation. Thermal dehydration (calcination) is used to obtain polyphosphates.

The commercially important salts with largest production volume and wide range of applications are those of sodium, potassium, ammonia and calcium. Their types, manufacturing and major uses will be reviewed in the following paragraphs.

4.8 Sodium Phosphates include one of the most widely used single phosphate salt, viz, sodium tripolyphosphate (STP), which accounts for over half the United State consumption of phosphate salts. figure 4-2 illustrates the relationship of the various sodium phosphates. The figure also shows that they are made by carefully proportioning the amount of Na_2O to P_2O_5 contents of the reacting raw materials orthophosphoric acid and the bases, sodium carbonate and sodium hydroxide with careful control of temperature of solution to realize the formation and crystallization of the required salt, as shown in figure 4-3.

1. Monsodium Phosphate, NaH_2PO_4 , is used primarily as acid-type cleaner in formulations containing orthophosphoric acid. It is also used in boiler-water treatment and in caustic bottle-washing. It has been used as an animal-feed supplement.

2. Disodium Phosphate, Na_2HPO_4 , is widely used as emulsifier for pasteurized processed cheese. A combination with insoluble sodium metaphosphate (IMP) in mixture containing 40-70% IMP is also used as emulsifier. Other food related uses are in meat curing, starch processing and as ingredient in instant cereals and evaporated milk. for all of these applications food-quality orthophosphoric acid is used.

Disodium phosphate is used in a number of industries, e.g., preparations of ceramic glazes and enamels, leather tanning, textile dying, pigment manufacturing, detergents, and water treatment.

Mixtures of mono-and dusodium phosphates are used to control PH of solutions at 4-9 in textile processing and food manufacture.

3. Trisodium phosphate has found many applications due to its strongly alkaline property, as, for example, in heavy-duty cleaning compositions. It is commercially marketed as cleaning compound and paint remover, and as water softener. Its single most important application, fertilizers exempted, which accounts for it being the second largest volume phosphate salt after sodium tripolyphosphate, is in the double salt of trisodium phosphate with sodium hypochlorite $\text{NaCl} \cdot 4(\text{Na}_3\text{PO}_4 \cdot 11\text{H}_2\text{O})$ which is referred to as chlorinated trisodium phosphate (Cl-TSP). Its solution has PH-12 and contains active chlorine. It is used in variety of applications where these properties are useful, e.g. in disinfectant cleaners, scouring powders, and automatic dishwashing formulations.

4. Disodium pyrophosphate, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$, which is commercially referred to as sodium acid phosphate is made to exacting specifications for its most important use as leavening agent. Its other uses are in food industry to eliminate darkening of cut vegetables such as potatoes. It is a good chelating agent for iron and is used as colour remover for materials containing coloured iron compounds impurities. Other important applications are in acid-cleaning formulations, and in electroplating.

5. Tetrasodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$ is used as a detergent builder and in cleaning formations. It is widely used as an effective deflocculant in kaolin clays, drilling muds, dyes and inks. Its other applications are in food industry as consistency control agent. It is also used as stabilizer of hydrogen peroxide.

6. Sodium tripolyphosphate, (STP) $\text{Na}_5\text{P}_3\text{O}_{10}$, is a large volume product that occupies the top of the list for sodium phosphates. It is manufactured by drying and subsequent calcination of a solution or slurry having $\text{Na}_2\text{O}/\text{P}_2\text{O}_5$ ratio of 5/3. Sodium tripolyphosphate can be produced with an assay as high as 98-99% if special care is taken in the drying and calcination processes, in order to obtain the stable hexahydrate form, $\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$. This directly affects its product properties as a builder for synthetic detergents, which is its number one use. STP cleaning formulations include both household and industrial products. Its cleansing action includes sequestering water hardness ions, buffered alkalinity, deflocculation of dirt particles and prevention redeposition of soil.

Food-grade STP is used to cure meat and in the treatment of seafood products. Technical grade STP finds applications in clay processing, water softening, textile processing, drilling muds, paper pulping, rubber and paint manufacturing and ore flotation.

7. Metaphosphates are high molecular weight polyphosphates of the general formula $(\text{MPO}_3)_n$. Some of them like Graham's salt is a water-soluble polyphosphate glass with composition approximating $(\text{NaPO}_3)_{50}$. It is manufactured by heating monosodium phosphate to above 620°C and quenching rapidly. Other polyphosphates are obtained from monosodium phosphate using different heating regimes. The glassy products have limited range of application but some are important, e.g., in water treatment to sequester hardness ions (Ca, Mg, Fe), as threshold agent since ppm levels inhibit scale formations in water systems, as dispersants in clay processing, oil-well drilling and pigment manufacture.

Madrell's salt, which is obtained by careful heating of disodium pyrophosphate to $260-300^\circ\text{C}$, is used as dental abrasive in toothpaste formulation containing soluble fluoride. It is also used as cheese emulsifier.

4.9. Potassium Phosphates are similar to the corresponding sodium salts both in their preparation and most of their uses but of higher cost, which is compensated by utilizing their specific

properties for some applications in which they show superior performance. Examples are: the use of monopotassium phosphate in liquid fertilizers, as mineral nutrient for fermentation broths, in some electronic applications as in sonar systems. It is also used in paper processing and in various buffering systems.

Dipotassium phosphate is used mainly as corrosion inhibitor system in ethylene glycol antifreeze formulations.

Its other uses are in the food industry as anticoagulant, and in paper processing.

Tripotassium phosphate is utilized in the polymerization of styrene-butadiene rubber, in the rejuvenation of scrap rubber, in hydrogen-sulphide scrubbing as well as in liquid cleaners formulation. Terapotassium pyrophosphate also finds wide application in liquid detergent systems to give high degree of stability of several years.

Potassium polyphosphate is obtained by thermal dehydration of monopotassium phosphate. It has molecular weight approaching several millions. It has limited commercial use as potassium Kurrol's salt in sausage processing.

4.10. Calcium Phosphates known by their common names of mono-, di-, and tricalcium phosphate corresponding to the old formulas $\text{CaO} \cdot 2\text{H}_2\text{O} \cdot \text{P}_2\text{O}_5$, $2\text{CaO} \cdot \text{H}_2\text{O} \cdot \text{P}_2\text{O}_5$ and $3\text{CaO} \cdot \text{P}_2\text{O}_5$, respectively.

The main use of monocalcium phosphate $\text{Ca}(\text{H}_2\text{PO}_4)_2$ which depends on its acidic property is as a leavening agent in bread, cake mixes and self-rising flour. It is also used to control acidity in powdered drink mixes, as an ingredient in effervescent tablets, as plastic stabilizer, and in ceramics.

Dicalcium Phosphate, CaHPO_4 , is a large volume product for animal feed supplement. For this application it is produced from defluorinated wet-process phosphoric acid. food-grade dicalcium phosphate is used as a dental polishing agent in toothpastes. Its other uses are as leavening agent, plastic stabilizer and in the manufacture of glass, medicines and phosphors.

Tricalcium Phosphate, $\text{Ca}_3(\text{PO}_4)_2$, has commercial applications as dry-flow conditioner for food products such as sugar and salt, as whitening agent in the manufacture of ceramics, as a mordant in dyeing and as a polishing agent.

Calcium Pyrophosphate, $\text{Ca}_2\text{P}_2\text{O}_7$, is obtained by dehydration of monocalcium phosphate. It is utilized mainly as dental abrasive in fluoride containing toothpastes which achieves a balance of abrasivity and fluoride compatibility.

4.11 Ammonium Phosphates, both monoammonium phosphate (MAP), $\text{NH}_4\text{H}_2\text{PO}_4$, and diammonium phosphate (DAP), $(\text{NH}_4)_2\text{HPO}_4$ are well known fertilizers. their other uses are as flame retarding and fire extinguishing agents, and to prevent afterglow in matches and to control forest fires. Diammonium Phosphate is also used to control the precipitation of alkali-soluble/acid-insoluble colloidal dyes on wool.

Ammonium polyphosphate can be produced by careful thermal dehydration of MAP, or alternatively by a simpler method by heating a mixture of MAP and urea in an atmosphere of NH_3 . It has limited commercial use as water-insoluble fire retardant in paints and mastics.

4.12 Polyvalent metal phosphates, of special interest are the orthophosphates of trivalent ions of the general formula MPO_4 with $\text{M}=\text{B}, \text{Al}, \text{Fe}$. These phosphates are of limited though important applications.

1. Aluminium acid phosphates readily form complex polymers and are used as binders in cements and in high temperature bonding of refractories. Monoaluminium phosphate $\text{Al}(\text{H}_2\text{PO}_4)_3$ in phosphoric solution is employed to surface-treat the steel plates in electrical transformers.

Aluminium phosphate, AlPO_4 , is a highly insoluble, hard, unreactive material with high melting point (greater than 1800°C). It is used as a refractory material.

2. Boron Phosphate, BPO_4 , is obtained by heating boric acid and phosphoric acid. It is used as catalyst support, also, in ceramics and refractories.

3. Iron phosphates are used as catalysts, mineral supplements and in speciality glass manufacture.

4. Heavy metal phosphates are extremely water-insoluble. Few are of commercial interest, e.g., zinc phosphate $\text{Zn}_3(\text{PO}_4)_2$ forms the basis of a group of dental cements; chromium phosphate and zinc phosphate are utilized in metal treating to provide corrosion protection and improved paint adhesion. Cobalt phosphate has bioactivity and is used as insecticides and fungicides. Lead and silver Phosphates are utilized in the production of special glasses.

5. Of special interest are the mixed sodium-aluminium phosphates which are used in some food applications. they are made by reacting phosphoric acid with the proper amount of Na_2O and Al_2O_3 . they are used as leavening agent in conjunction with monocalcium phosphate in flavour-sensitive systems. Another mixed phosphate is prepared from phosphoric acid, alumina and sodium hydroxide. It has alkaline properties and is used as food emulsifier, particularly for processed cheese.

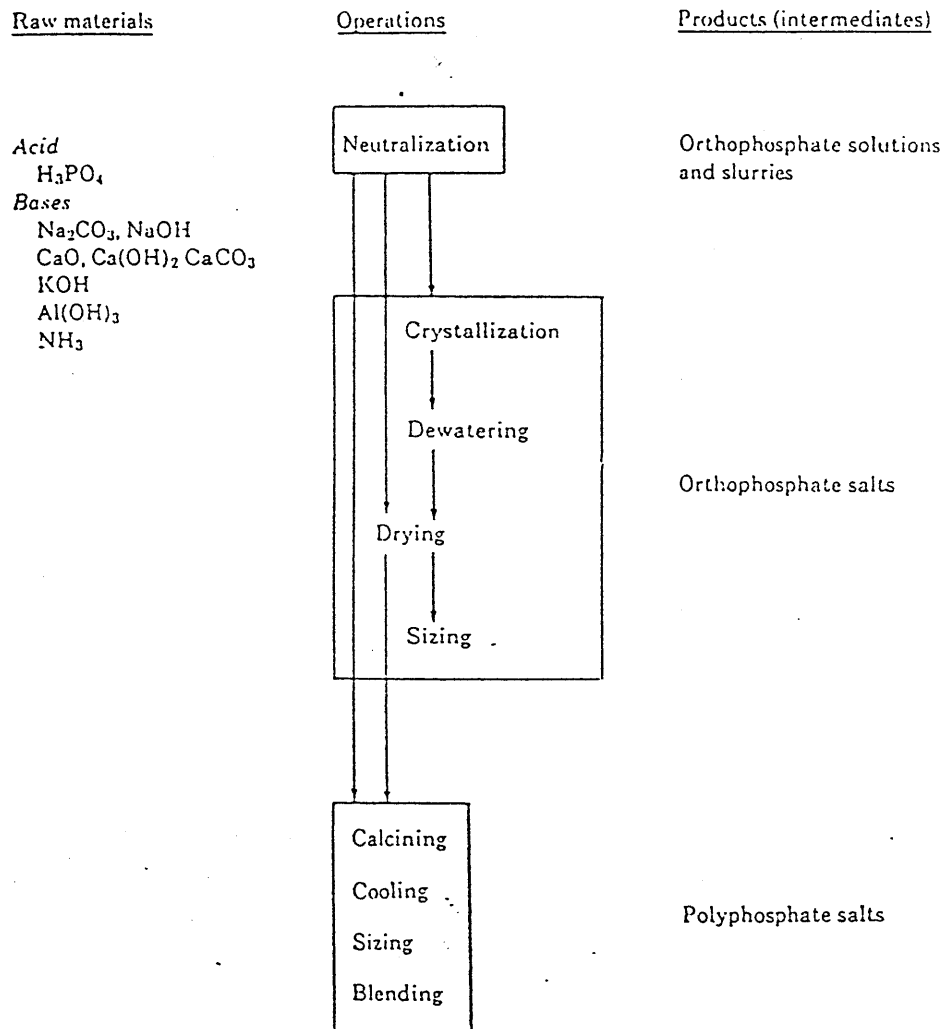


Figure 4-1. General manufacturing scheme for phosphate salts.(ref.10)

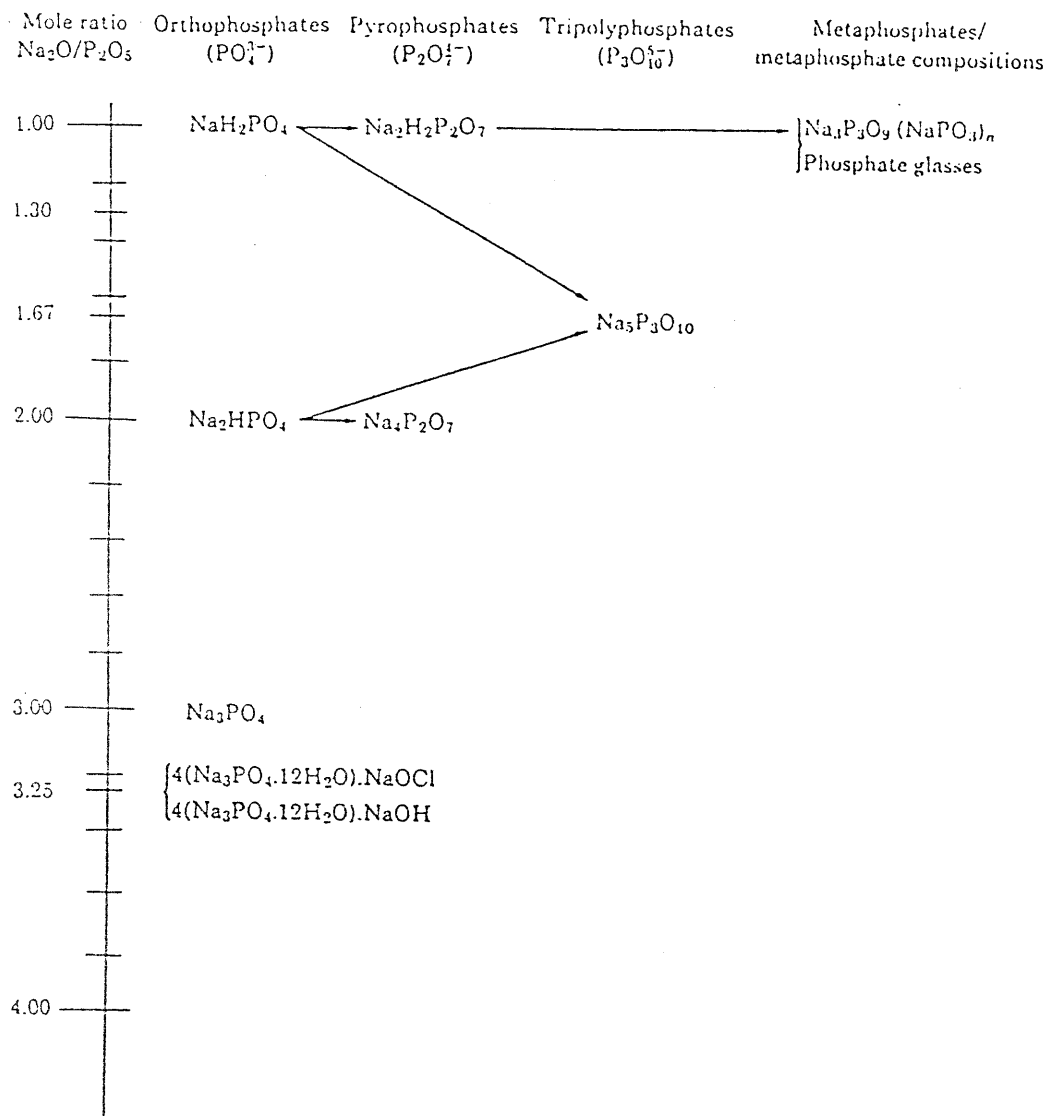


Figure 4-2. Sodium phosphates (ref.10)

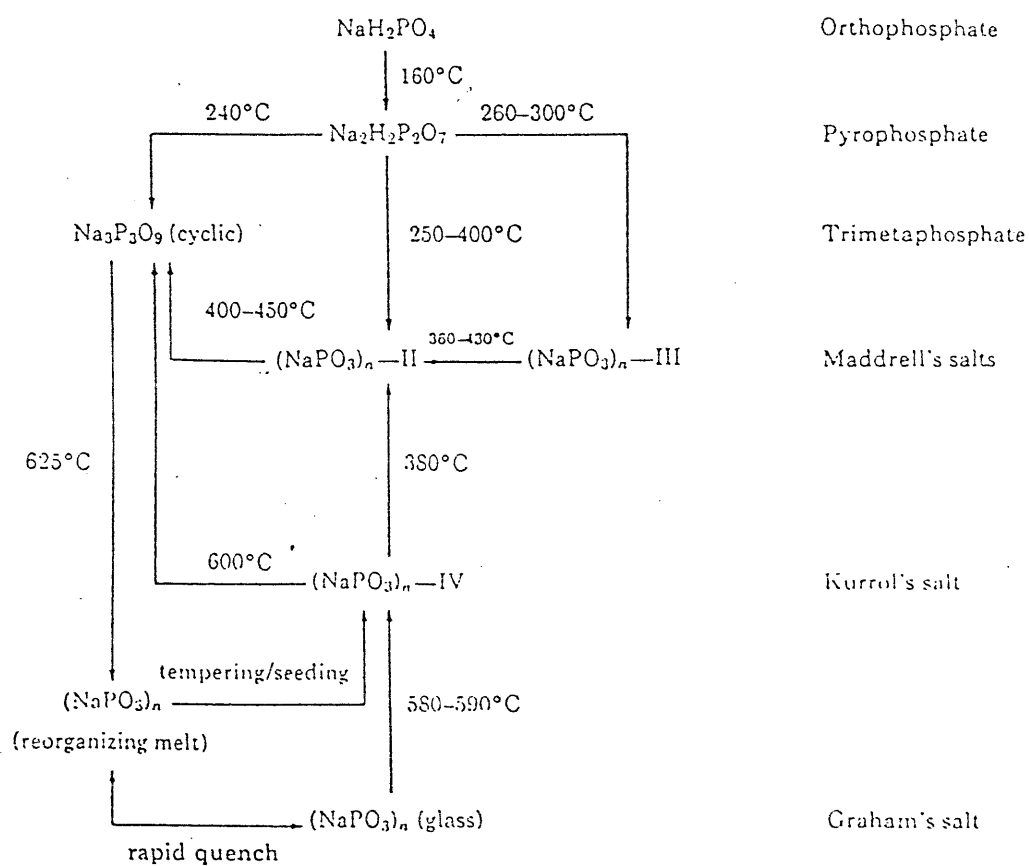


Figure 4-3. Sodium polyphosphate conversions .(ref.10)

Down-Stream Phosphate Industries

"Down-Stream" Industries is a loose term which in the present study is to be taken to refer to those industries that rely on phosphate-rock based chemicals for their ultimate manufacture into market products related closely to the consumer needs.

Within that broad definition one may include a wide spectrum of products extending from fertilizers to genetically-engineered materials. However, on a more modest grounds, it is proposed to limit the presentation to those products, with the exception of fertilizers, that are considered to represent the main uses of the phosphate chemicals. To arrive at such a reasonable decision, one needs world statistics on the volume of the various major products, which, alas, are not available. But, the figures most frequently quoted are those of the United States of America. This is not a dispairing situation, for after all the U.S.A. represents the single largest producer and consumer of the phosphate products. It, also, has the largest reserve of phosphate rock, the world largest producer of phosphoric acid and phosphate fertilizers. Therefore, its uses of the basic chemicals, phosphoric acid, elemental phosphorus, phosphates and other products could be taken to approximate to the relative importance of these uses.

Notwithstanding, in considering the relevance of such considerations to the ESCWA region, it is important to state from the outset that the Arab phosphate market is grossly underdeveloped; and, therefore, the decision as to the relevance or otherwise of the United States, or, for that matter, even world statistics is a matter of relative judgement. It is not the absolute figures, but the relative importance to be attached to various product which is needed.

This being a technical study, its most important contribution will be to lay in front of the reader interested in industrial development of the Arab region most of what the phosphate industry can offer. The final decision will definitely depend on in-depth techno-economic evaluation of the potential and impact of the various phosphate products.

In this chapter a review is undertaken of the wide range of down-stream phosphate industries products that are considered relevant to the needs of the local market, and which may have the potential of promoting intra-regional trade as well as Arab export trade. The rationale for this view is of-course to make use of the relative advantage of abundant phosphate rock resources and a relatively well developed phosphoric acid and phosphate fertilizers industry in a number of ESCWA countries, as well as, in some cases, the availability of most of the needed associated materials and utilities.

5.1. Phosphates in Fertilizers.

The large volume fertilizer industry is well developed, and phosphate salts play a dominant role in many respects whether on their own or in combination with nitrogen and potassium fertilizers.

The most widely used phosphate fertilizers are calcium superphosphates, both normal superphosphate (NSP) and triple superphosphate (TSP), and ammonium phosphates, both monoammonium and diammonium phosphate, (MAP) and (DAP).

Specially treated phosphate rock has also been marketed for fertilizer use.

The fertilizer industry in the ESCWA region has concentrated mainly on production of superphosphates and ammonium phosphates as well as on their use in NPK fertilizers formulation.

However of special interest are the potassium phosphates for their various industrial uses. As a world market commodity potassium phosphates command special position, not because of their volume of sales, but, for their highly specialized uses. One important compound as a fertilizer is monopotassium phosphate KH_2PO_4 , which is combined with ammonium phosphate to give a special commercial fertilizer, $\text{KH}_2\text{PO}_4 \cdot (\text{NH}_4)\text{HPO}_4$, which contain 10.5% N, 52.0% P_2O_{10} , and 17.5% K_2O and is rated as 10-52-17. This potassium-ammonium phosphate mixture is very soluble in water and extremely effective in minimizing the shock when seedlings such as tomatoes, tobacco, peppers, and cabbages are transplanted. The shock from transplanting usually causes the plants to wilt and sometimes die.

Wet-process phosphoric acid is the basic chemical for the manufacture of fertilizer-grade phosphates. Other raw materials are sodium carbonate, sodium hydroxide, ammonia, and potassium hydroxide. These materials are widely available in the ESCWA region which should command a leading role in the fertilizers market, not only of the conventional but also of the proprietary products.

5.2 Phosphates for the Food Industry.

Phosphoric acid (food-grade) and a wide variety of alkali and alkaline-earth, as well as ammonium, phosphates contribute importantly to the food industry. However, because of the purity requirement, technical-grade phosphoric acid from the wet-process, and salts made from it, are unsuitable for food applications. Either, rather expensive and involved purification procedure for wet-process acid has to be undertaken to obtain "acceptable" acid, or use is made of the pure thermal acid obtained from electric-furnace grade elemental phosphorus.

The major uses of phosphates in the food industry are outlined in the following paragraphs.

1. Beverage additive.

Phosphoric acid in amount ranging from 0.013% to 0.084% of the 75% acid is added to cola drinks and similar soft drinks. The soft-drink market is a large volume world market with progressive rate of growth, and the purity requirement for the acid used in their manufacture is the most stringent. The Arab market forms an important part of the World soft-drink consumption with many local producers.

2. Nutrient supplements

Calcium phosphates suitable for human consumption in foods are made by adding lime to very pure phosphoric acid solution. The correct proportions of lime-to-acid must be used in order to obtain the required compound in highest purity.

Calcium phosphates for animal feed, so-called stock-food-grade calcium phosphate, is made by hydrating hot lime with water followed by neutralizing with phosphoric acid of 75-80% concentration. The phosphorus content of this product is almost 21%, close to that for anhydrous dicalcium phosphate, CaHPO_4 . The actual assay of the product is a mixture of monocalcium phosphate $\text{Ca}(\text{H}_2\text{PO}_4)_2$, tricalcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, unreacted lime and anhydrous dicalcium phosphate as the main components.

Other manufacturing methods for stock-feed dicalcium phosphate is to use hydrated lime or finely ground limestone with phosphoric acid.

Commercially, feed formulators prefer a product with phosphorus content of 18.5%. To meet this requirement, enough ground limestone is added to the original products as needed to lower the phosphorus content to the desired level.

While calcium phosphate for human food supplement must be made from the very pure thermal acid, that for animal feed could be made from wet-process acid.

Defluorinated phosphate rock has also been used for animal feed. The fluoride content must be less than 1 part in 1000 of fluoride for every 1% of phosphorus in the product. The phosphorus content is adjusted to 18.5% by adding phosphoric acid during the defluorination process.

Phosphoric acid is also used as a nutrient supplement in animal feeds in combination with molasses. It also helps reduce the thickness and viscosity of the molasses to facilitate storage and handling.

3. Leavening agents.

Chemical leavening agents are preferred to yeast in the bakery industry and in the production of self-rising flour and cake mixes.

There are several synthetic chemical leavening agents based on phosphate salts. They are mostly calcium phosphates and some sodium and mixed sodium-aluminum salts.

Monocalcium phosphate monohydrate, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, is made industrially by adding hot lime to 75% phosphoric acid in a controlled volume of water with good temperature control to avoid the formation of the anhydrous salt. The product is about 90% pure, the contaminant is mainly dicalcium phosphate, CaHPO_4 . Its most important use is a leavening agent in baking. It is also used in the formulation of effervescent tablets.

A typical combination of baking powder is 28% sodium bicarbonate, 10.7% monocalcium phosphate monohydrate, 21.4% sodium aluminium sulphate, $\text{NaAl}(\text{SO}_4)_2$ and 39.9% starch.

All-purpose self-rising flour contains around 1.375kg of sodium bicarbonate, 1.75kg of monocalcium phosphate monohydrate and 2.25kg of common salt per 100kg of flour.

Monocalcium phosphate monohydrate is also used as bread improver in yeast leavened dough, to stimulate yeast growth. A typical composition for this purpose is 7.5% ammonium sulphate, 50.0% monocalcium phosphate monohydrate, 0.3% potassium bromate, 20.0% salt and 22.0% starch. About 0.50-0.75% of the composition is added to flour.

Anhydrous monocalcium phosphate protected by thin coat of glassy calcium phosphate to prevent attack by atmospheric moisture, has found wide use in the baking industry specially in the preparation of ready mixes.

Dicalcium phosphate dihydrate (DPD), $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ is also used as leavening agent for slow rising cakes.

Sodium acid pyrophosphate (SAPP), $\text{Na}_2\text{H}_2\text{P}_2\text{O}_4$, has acidic property which makes it useful as a baking acid, and its pyrophosphate ion enables it to sequester many metal ions such as iron, magnesium and calcium, which properties are used to make tender bakery products and to keep boiled potatoes white.

Sodium aluminum phosphates form a new family of baking acids. The phosphates that are known industrially have the formula $\text{NaH}_{14}\text{Al}_3(\text{PO}_4)_8 \cdot 4\text{H}_2\text{O}$, known, as 1-3-8 SALP, and $\text{Na}_3\text{H}_{15}\text{Al}_2(\text{PO}_4)_8$, known as 3-2-8 SALP. The former has found wide use in household and commercial baking powders, in self-rising flour and preparing biscuit and cake mixes. A typical formula contains 3 parts of 1-3-8 SALP to 1 part of coated anhydrous monocalcium phosphate.

4. In dairy products.

Phosphates are widely used in dairy products as emulsifiers and additives. In the former role, disodium phosphate dihydrate, $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$, is used in processing pasteurized cheese to evenly distribute the butterfat throughout the cheese.

Disodium phosphate dihydrate (DSP) is made commercially by reacting sodium carbonate with phosphoric acid followed by careful addition of the required amount of sodium hydroxide and good temperature control. As much as 0.5% of tetrasodium pyrophosphate in the product renders it useless as cheese emulsifier.

DSP may also be used in combination with insoluble sodium metaphosphate (IMP) in commercial mixture containing 40-70% IMP and 30-60% DSP. A total of 3% of the mixture may be used in process cheese.

Another emulsifier of commercial importance is a sodium aluminium phosphate of the empirical formula $\text{Na}_{15}\text{Al}_3(\text{PO}_4)_8$, known as "Kasal", which is claimed to give superior product to that obtained with DSP.

DSP also finds use as evaporated-milk additive. Up-to about 0.1% of anhydrous salt is added to milk before heating in order to prevent gelation and keep the milk liquid.

Tetrasodium pyrophosphate (TSPP), $\text{Na}_4\text{P}_2\text{O}_7$, is used in butter milk, chocolate milk and puddings as solid dispersant and to give smooth consistency.

5. In meat products

Sodium phosphate and sodium tripolyphosphate are used to cure meat. Tetrapotassium pyrophosphate is used for pickling meat. Commercial mixture of the phosphates is used with good results.

Potassium polymetaphosphate is made by heating monopotassium phosphate to $330-400^\circ\text{C}$. For very high molecular weight polymetaphosphate the temperature is raised to about 500°C . When dispersed in water a clear viscous gel is formed which is used in sausage manufacture.

6. In seafood products.

To improve the quality of frozen fish filets, they are dipped in solution of 12.5% sodium tripolyphosphate and 4% ordinary salt. In canned seafood, like lobsters, shrimps, crabmeat, haddock, cod and salmon, addition of 0.25-1.5% of sodium acid pyrophosphate or sodium polyphosphate, based on total moisture content of the canned seafood, sequesters magnesium and prevents from forming the objectionable crystals of MgNH_4PO_4 .

7. In cereal and potato products.

Disodium phosphate alone, or in combination with monosodium phosphate, is used to make cold water gel starch, which is sold to make starch for instant puddings and pie fillings. Commercially this is made by adding a solution of mono- and disodium phosphate at pH 6.1 - 6.5 to a starch slurry and after filtration, the starch is heated in a vacuum oven at approximately 60° for few hours. This treated starch will now form gel when cold water is added. Besides its use in deserts, this cold-water gel is also used for industrial sizing of textiles and papers.

Cyclic sodium trimetaphosphate is used to phosphorylate starch and produce cold-water gel similar to the one obtained by treatment with sodium phosphates, and it has the characteristic to resist degradation. This makes it very useful as sizing agent in paper making. It is also used as thickening agent in cooked foods. Cyclic sodium trimetaphosphate is made by heating monosodium phosphate to about 530-600°C. It can also be made by heating glassy sodium polymetaphosphate at 520°C.

Instant cooking cereals contain about 1% of disodium phosphate which acts by bringing the pH slightly above 7.

Commercial potato products have either been dipped or blanched with 1-2% solution of sodium acid pyrophosphate to prevent them from blackening. The pyrophosphate ion sequesters the free ferric ion.

8. Anticaking agent.

Tricalcium phosphate is made industrially by adding phosphoric acid to a slurry of hydrated lime.

The product corresponds to hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, which is extremely insoluble and precipitates as fine particles which after separation and drying is milled as very fine powder, particles of 1-2mm in diameter. The addition of about 1% is sufficient to impart free-flowing properties to other powders, for example, granulated sugar, baking powders, salt and also fertilizers.

5.3 Phosphates in the detergent and allied industries.

Cleaners, detergents, dispersants and chelants are some of the widest uses to which sodium phosphates are put. Twelve different forms of sodium phosphate are known and each possesses distinctive property that makes it best suited for different duties. Some examples of the most important applications of these salts are presented in this section.

1. Cleaning paint surfaces.

Alkaline trisodium phosphate TSP, of the general formula $[(Na_3PO_4 \cdot 12H_2O)_5 \cdot NaOH]$ is made commercially by neutralizing phosphoric acid with sodium carbonate followed by addition of sodium hydroxide. This preparation gives strongly alkaline product which in 10% solution will remove all the paint coating from wooden or metal surfaces. A more dilute solution is used for cleaning painted walls.

2. Cleaning, bleaching and sanitizing.

Chlorinated trisodium phosphate, Cl-TSP, of the composition $[(Na_3PO_4 \cdot 11H_2O)_4 \cdot NaOCl]$ is made by the addition of a sodium hydroxide solution of sodium hypochlorite to a concentrated solution of disodium phosphate. Cl-TSP contains 3.4-3.6% available chlorine. Addition of about 2% of sodium silicate during the manufacture of Cl-TSP increases the available chlorine to 4.0-4.2%, which is closer to the theoretical value.

When mixed with an abrasive, such as silica, and a detergent, such as sodium alkyl benzenesulphonate, Cl-TSP is a very effective cleaner for hard surfaces such as kitchen sinks and bathtubs.

For automatic dishwashing machines, Cl-TSP is formulated with 40-55% sodium tripolyphosphate (STPP) and a surfactant, along with sodium metasilicate.

3. Detergent builders.

The best known detergent builder is sodium tripolyphosphate, (STPP), $Na_5P_3O_{10}$, and is also the largest volume phosphate product on the market, second only to fertilizers. STTP is manufactured by heating a mixture of disodium phosphate and monosodium phosphate in the right proportion.

In synthetic detergent production, a water slurry of solid STPP is mixed with sodium alkylbenzen sulphonate. Alternatively, STPP-built detergents may be made by the reaction of a solution of cyclic sodium trimetaphosphate (STMP) in water with sodium hydroxide to form STPP, in the process best known as the batch fluff process.

The main action of STPP as a builder is its chelating action to sequester ions such as Ca^{2+} and Mg^{2+} which are responsible for water hardening. Its other functions are to increase the efficiency of the surfactant, to furnish the proper alkalinity for cleaning, to keep the dirt in suspension, and to provide resistance to change in alkalinity.

In a very effective automatic dishwashing formulation, STPP 60% is mixed with sodium metasilicate as a corrosion inhibitor and Cl-TSP or other chlorine-generating agent such as potassium dichlorocyanurate (bleaching agent or stain removal). This general

phosphate-containing formulation is quite effective and has found very wide commercial acceptance.

4. Liquid detergents.

Tetrapotassium pyrophosphate is extremely water soluble and very resistant to hydrolysis. These properties make it ideal as a builder for liquid detergents. Tetrapotassium pyrophosphate, $K_4P_2O_7$, is made by heating a solution of dipotassium phosphate to dryness and the heating is continued to about 400°C when a white powder is obtained.

A typical liquid detergent is about 11-20% organic surfactant, about 20% the builder, and 7-10% a coupling agent such as sodium or potassium toluenesulphonate, the remainder, about 50%, is water.

An important use of tetrapotassium pyrophosphate is as a component in catalyst systems containing ferrous iron for the production of butadiene-styrene rubber of superior quality which is called "cold rubber" because the polymerization can take place at low temperature.

5. Chelation.

Chelation agents find extensive use in laundering, metal cleaning, bottle washing and alkaline cleaners. They are also extensively used in textile processing (to prevent iron contamination and discoloration), dyeing, aluminum etching, photography, and as micronutrient in agriculture and in some food products.

Some phosphates are known as good chelating agents, for example, sodium tripolyphosphate and sodium hexametaphosphate. They function mainly by sequestering metal ions and dispersing agent for soils. An important application is their use as "threshold" effect agent, whereby a small quantity can inhibit the formation of precipitates on surfaces, such as in boilers.

5.4 Phosphates in water treatment.

A number of phosphate salts can act as water softener by removing water hardening ions Ca^{2+} and Mg^{2+} .

1. Trisodium phosphate reacts with calcium and magnesium ions in water to form insoluble tricalcium and trimagnesium phosphates. When used in conjunction with the soda-lime process, to precipitate residual calcium and magnesium ions as the very insoluble hydroxyapatite and trimagnesium phosphate. The precipitate is dispersed and does not form a hard scale.

2. Sodium metaphosphates exist in three forms that are commercially known as glassy sodium polyphosphate, cyclic sodium trimetaphosphate, and insoluble sodium metaphosphate. They are all

made from monosodium phosphate by careful heating. Thus when the starting material is heated to 800-900°C and the molten liquid is rapidly cooled, the glassy sodium polymetaphosphate is formed. It is known as Graham's salt. If monosodium phosphate is heated to about 530-600°C it will not go into molten form but cyclic sodium trimetaphosphate is formed. Finally, if the starting material is heated at about 475-500°C, insoluble sodium metaphosphate (IMP) is obtained.

The important compound for water softening is the glassy sodium polymetaphosphate, known commercially as Calgon. It forms a soluble complex with calcium and magnesium ions of hard water and renders them unable to react with soap to form an insoluble scum.

Another important use for this compound is in the so-called "threshold" treatment by preventing scale formation by interference with crystal growth of the precipitates of calcium sulphate and calcium and magnesium carbonates. Threshold treatment prevents the precipitation of scale in boilers. It also prevents metal corrosion by forming a submicroscopic protective film. In cold water 2ppm of Calgon and in hot water 40-60 ppm of Calgon will control corrosion.

Another benefit of Calgon threshold treatment is in preventing iron and manganese compounds from precipitating when water is exposed to air or chlorine.

3. Tetrasodium pyrophosphate (TSPP) is used to sequester heavy metal ions such as iron and vanadium. It is widely used in the textile industry, because hydrogen peroxide suffers decomposition by heavy metal ions. Therefore, they are first removed by the addition of TSPP and sodium silicate.

5.5 Phosphates in dentifrices and pharmaceutical tableting.

1. Dicalcium phosphate finds wide application in dentifrices. Dicalcium phosphate dihydrate DPD, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, is used as polishing agent in toothpaste. To prevent the dihydrate form dehydrating, 2-3% trimagnesium phosphate is added.

However DPD could not be used in the presence of fluoride ions, because the latter will be precipitated as the extremely insoluble CaF_2 . The fluoride containing toothpaste use calcium pyrophosphate, sodium metaphosphate or silica as polishing agents; all of these compounds do not react with fluoride.

A come back of DPD took place when sodium monofluorophosphate ($\text{Na}_2\text{PO}_3\text{F}$) was used as fluoridating agent. MFP is compatible with DPD when the latter is made according to a well controlled procedure.

A typical formulation containing MFP is polishing agent - DPD, 48.76%; humectant-glycerin (95%), 22%; organic surfactant-sodium lauryl sulphate, 1.50%; binder-carboxy methylcellulose, 1.00%;

sweetener-sodium saccharin, 0.20%, stabilizer-tetrasodium pyrophosphate, 0.25% ; flavoring-peppermint, 1.00% ; anticaries agent - sodium monofluorophosphate, 0.76% and distilled water, 24.53%.

Anhydrous dicalcium phosphate, CaHPO_4 , is used in combination with DPD to remove stains in speciality items such as "smoker's toothpaste".

Calcium pyrophosphate, $\text{Ca}_2\text{P}_2\text{O}_7$, is made by thermal dehydration of DPD. It is used as polishing agent compatible with fluoride toothpaste. Also insoluble sodium metaphosphate (IMP) was used in such toothpastes as polishing agent.

2. Dicalcium phosphate dihydrate and tricalcium phosphate are found to be useful as diluents or excipients in preparing tablets by dry compression. Their advantages are low cost, insolubility in water, flowability, compressibility, inertness to most ingredients, stability in storage, food-grade quality and safety.

Pharmaceutical tableting involves not only the active ingredient and the diluent or excipient but a number of other components as lubricants, disintegrators, binders and colors and flavors. The diluent or excipient must be inert to all these materials. The amount of such diluent or excipient may vary from 2-35% by weight of the tablet formulation.

5.6 Metal treatment.

Phosphatizing, metal cleaning and plating are common operations for the protection of metal surfaces especially against corrossions.

1. Phosphatizing entails treating the metal surface to provide it with compact, adherent coating of insoluble metal salts of phosphoric acid. Commercial phosphitizing solution are made from water insoluble metal salts but soluble in mineral acid such as phosphoric acid. Pickling of the metal surface may take place which may result in "conversion coating" when an integrally bonded coating of the surface metal salt is formed.

There are three types of phosphate conversion coating processes classified in accordance with the metal ion in the phosphate salt that precipitates on the surface. These types are:

- Manganese phosphate coating, which gives a thick coating, is produced by immersion in a bath containing a solution of 6-10% manganese phosphate at temperature 60-90°C. It gives a coarse and porous surface which has high retention for lubricating and rust-proofing oil.
- Zinc phosphate coating gives a coating of medium thickness,

and is produced by immersion in a dilute solution of zinc phosphate in phosphoric acid at temperature varies from 38-82°C dependent on the thickness of the deposited layer required. The coatings provide good paint adhesion and good corrosion resistance, and act as binders for lubricants

- Iron phosphate coating produces extremely thin coating. The phosphatizing layer is made from porous monosodium phosphate on which a surfactant is absorbed. It is applied either by spraying or dipping of surfaces which are not expected to be exposed to severe corrosion and weathering conditions.

Several phosphatizing systems have been developed. Some are proprietary formulations, of these of interest is the low-temperature solvent phosphatizing formula which uses organic solvent in place of water, for example trichloroethylene.

2. Metal cleaning.

Phosphorus compounds find their main use in metal cleaning in commercial acid and alkaline cleaners which may be applied by spray or immersion.

Acid cleaning with phosphoric acid involves also the use of surfactant and perhaps an organic solvent such as alcohol, some solutions also contain sodium acid pyrophosphate.

For alkaline cleaners, use is made of alkaline salts of phosphoric acid such as trisodium phosphate, tetrasodium pyrophosphate, sodium tripolyphosphate. The mixture is usually blended with sodium hydroxide, sodium carbonate, sodium silicate or sodium bicarbonate.

For boilers cleaning both phosphorus-based acid and alkaline cleaners are used. The acid cleaner is usually phosphoric acid blended with hydrochloric acid with inhibitor such as an organic amine. Before acid treatment, the boiler is heated with an alkaline cleaning solution of trisodium phosphate dodecahydrate $[(Na_3PO_4 \cdot 12H_2O)_5 \cdot NaOH]$ along with sodium sulphite. After acid cleaning, the boiler is treated with 0.1% phosphoric acid and then conditioned with a solution of tetrapotassium pyrophosphate ($K_4P_2O_7$) and potassium hydroxide along with some potassium sulphite.

3. Metal polishing

Chemical polishing, or "bright dip", of aluminum and its alloys involves the immersion in a hot solution (91-99°C) made from about 95 parts of 85% phosphoric acid and 4-5 parts of 68% nitric acid, along with 0.01-0.04% copper nitrate, and traces of nickel and a little wetting agent, such as fluorocarbon-based surfactant, are also added.

In the case of chemical polishing of copper a bath of 55% phosphoric acid, 20% nitric acid and 25% acetic acid is sometimes

used with small amount (0.5%) of hydrochloric acid or chromic acid are added. For stainless steel a blend of nitric, hydrochloric and phosphoric acids is used.

Electropolishing is specially suited for stainless steel articles with regular or irregular shapes. The electrolytic bath contains either a solution of 75% phosphoric acid or a mixture of phosphoric acid with small amount of sulphuric acid.

Aluminum may undergo alkaline electropolishing by the Brytal process using solution containing 5% trisodium phosphate and 15% sodium carbonate. Alternatively, the Battelle process uses acid electropolishing bath containing 75% phosphoric acid, 4.7% sulphuric acid and 6.5% chromic acid.

A useful bath for stripping metallic coating from aluminum or steel is made up from 3 parts by volume phosphoric acid and 1 part of triethanolamine.

4. Electroplating.

Most electroplating baths contain little if any phosphates. However, one bath, the copper pyrophosphate bath, has gained prominence in the electronic industry for copper-plating printed - circuit boards. A typical copper pyrophosphate bath contains 30g/liter of copper ion, 200g/liter pyrophosphate ion and small amounts of nitrate ion and ammonia. The pyrophosphate is usually in the form of potassium pyrophosphate, the copper as the soluble copper pyrophosphate, $\text{Cu}_2\text{P}_2\text{O}_7$, when mixed the resulting compound is the complex salt $\text{K}_6\text{Cu}(\text{P}_2\text{O}_7)_2$. Some brighteners are usually added such as organic sulphur or organic nitrogen compounds. The advantage this bath has over the conventional cyanide bath is its good throwing power which is important for "through-hole" plating of printed-circuit boards. Another advantage is of-course the disposal problem that arises from using copper cyanide baths.

A similar bath for zinc pyrophosphate electroplating is based on an alkaline solution of the potassium zinc pyrophosphate complex, $\text{K}_6\text{Zn}(\text{P}_2\text{O}_7)_2$. This plating bath results in bright zinc finishes, and has also the further advantage over zinc cyanide bath of relatively harmless waste-disposal problem.

5-7 Phosphates in ceramics, cements, glasses and zeolites:

There are various applications for which phosphoric acid and a number of its salts are unique or superior to other materials in the ceramic, cement and glass industries. Some of the most important ones are outlined in the following paragraphs.

1. Ceramic binders include phosphoric acid and some of its salts are used for bonding various ceramic powdered materials such as alumina, silica or magnesia to form refractory products for such industries as the steel industry and molds for metal casting .

Binders may be made in situ by addition of phosphoric acid to a blend of the filler and hydrated alumina. A number of commercial aluminium acid phosphate solutions are available. These solutions in phosphoric acid have mole ratios of aluminium to phosphorus ranging from 1:2.3 to 1:4.1. The excess phosphoric acid is necessary for obtaining the highest binding strength. Other commercially available products are solids containing aluminium acid phosphates. These binders are effective for wide range of materials.

Other useful binders are made from acid phosphate salts of magnesium, iron, and chromium, also those which are made from mixtures of these metals.

Glassy Sodium Polyphosphates were found to lead to increased strength of refractory bricks made from magnesium oxide for furnace lining to withstand temperatures as high as 1565°C by incorporating lime with the glassy polyphosphate. The refractory material based on $\text{Ca}_3(\text{PO}_4)_2$, whitlockite, has melting point of 1775°C.

2. Phosphate-based cements are of wide applications. Dental cements based on zinc oxide and phosphoric acid are relatively fast setting in which the main component is dibasic zinc phosphate, $\text{ZnHPO}_4 \cdot 3\text{H}_2\text{O}$. A typical formulation is mixing a blend of calcined zinc oxide and magnesium oxide with a phosphoric acid solution of monoaluminium phosphate. It is used for cavity linings and for temporary fillings.

Industrial cements based on phosphorus compounds usually magnesium phosphate or aluminium phosphate are used as anchoring or patching materials. Their advantage derives from their ability to remain workable for sufficient time to apply and then set quickly.

3. Phosphate glasses are non-crystalline solids based on random network structure of PO_4 tetrahedrons. The classical example is bone china made from calcined cattle bones, which consist mainly of calcium phosphate.

Many speciality phosphate glasses are made, examples, heat-absorbing glass made from iron oxide in phosphate glass. Glasses with minimum chromatic aberration suitable for making camera lenses are made from composition containing $[\text{LiF} \cdot \text{Al}(\text{PO}_3)_3]$. A lead-iron-phosphate glass is found to be very effective in encapsulating radioactive wastes.

Other phosphate-based glasses of special interest are: semiconducting glasses based on vanadium phosphate, laser glasses made by embedding rare earth oxides phosphate matrix, e.g., $\text{La}_2\text{O}_3 \cdot \text{BaOPO}_4 \cdot \text{Nd}_2\text{O}_3$.

4. Aluminium phosphate zeolites have several important features different from natural aluminium silicate zeolites. They are strongly hydrophilic and mildly acidic. Applications include desiccants for drying gas and liquid streams, separator of gases

and organic molecules by size and shape, catalysts and catalyst supports.

Aluminium phosphate zeolites are prepared by the hydrothermal reaction of aluminium and phosphate ions in the presence of amines or quaternary ammonium ions at temperatures ranging from 100 to 250°C. The structure of the zeolite is determined by the choice of amine or quaternary ammonium ion used. After crystallization, the zeolites are dried at 600-1000°C to destroy and remove the amines and form the characteristic void spaces.

Modified aluminium phosphate zeolites have been made to provide ion-exchange properties and improve catalytic activity. These products are made by including silicate in the hydrothermal process. Some of these silicoaluminophosphates have some interesting properties that distinct them from the aluminum phosphate and the natural zeolites.

Industrial Organophosphorus Compounds

Although organophosphorone chemistry is a relatively recent field of chemistry when compared to the chemistry of inorganic phosphorus compounds, its rapid development has resulted in a wide variety of chemicals of great industrial importance ranging from purely industrial chemicals for processing and formulation to chemicals for everyday life, such as insecticides and pesticides. In this section some of the most important organophosphorus industries will be reviewed.

However, it must be said from the outset, that organophosphorus industry primarily based on elemental phosphorus as the basic chemical from which are made the building blocks starting chemicals, phosphorus trichloride, PCl_3 , phosphorus oxide, P_4O_{10} , phosphorus sulphide, phosphine, PH_3 , and their immediate derivatives phosphorus pentachloride, PCl_5 , phosphorus oxychloride, POCl_3 , and phosphorus sulphochloride PSCl_3 .

Notwithstanding, their importance is not reflected in their share of the phosphorus industry which is dominated by the large volume fertilizer products. However in terms of their numerous uses and applications they far exceed those of the phosphate-based chemicals. Indeed, for some of these applications the organophosphorus compounds are unique and for which no alternatives are known.

5-8 Insecticides:

No one can doubt the economic and everyday importance of insecticides. However their development is marred by the high level of alertness that must be exercised because of their potent toxicity. Nevertheless, with proper industrial safety measures, they can be handled with relative security. The problem of toxicity and safety is carried over even in the field and home and therefore special care must be exercised in their use.

Insecticides such as malathion, Thimet, and Trithion are made from phosphorus pentasulphide, P_4S_{10} .

Malathion is prepared by reacting phosphorus pentasulphide with methyl alcohol followed by dimethyl maleate. This insecticide has little toxicity to mammals, therefore it is widely used to control garden and agricultural pests. It has the second highest consumption. Among its most important applications is in the control of citrus-fruit fly.

Thimet is made by the reaction of phosphorus pentasulphide with ethyl alcohol followed by reaction with formaldehyde and ethyl mercaptan. This compound is extremely effective systematic insecticide, but is quite toxic to warm-blooded animals.

Trithion is made by reacting phosphorus pentasulphide with ethyl alcohol, followed by reacting the intermediate diethyl phosphorodithioic acid with (para-chlorophenyl thio) methyl chloride.

The most widely used contact insecticide, methyl parathion is made from dimethyl phosphoro-chloridothioate and sodium p-nitrophenolate. Its ethyl analogue is made similarly. The parathions are used extensively to control cotton pests. It is used also to control rice stem borers.

O-Ethyl O-p-nitrophenyl phenyl-phosphonothioate, or EPN a close structural relative to parathion, is less toxic than parathion and is also used for cotton and rice pest control.

Sumithion is structurally close to methyl parathion but has low toxicity to warmblooded animals. Because it is more expensive to make than parathion it has not gained wide market penetration. It uses p-nitrocresol as intermediate which is more expensive than p-nitrophenol used in making methyl parathion.

A requirement for good insecticides, beside non-toxicity to warmblooded animals, is their rapid hydrolysis to harmless products. For example Phosdrin can be applied to a field of lettuce to kill worms the night before harvest.

One interesting insecticide which found use as alternative to the bad smelling malathion is Dipterex which has as decomposition product dimethy(dichlorovinyl) phosphate (DDVP) which is also a good insecticide on its own. It is made by the Perkow reaction from trimethyl phosphite and chloral.

A technique has been developed to allow the use of relatively toxic insecticides as household insecticide. When plastic strips impregnated with such insecticide as DDVP are hung indoors, minute quantities of the insecticide are released into the atmosphere. The vapor kills pests such as flies and mosquitoes.

Some insecticide is a direct derivative of another. For example addition of bromine to DDVP gives the milder insecticide Dibrom. Also acetylating Monitor to form Orthene greatly reduces the toxicity.

Except for Thimet, all the above are what is usually termed contact insecticides. Another class of insecticides called systematic insecticides acts by being absorbed through the roots or leaves of plants to render the sap toxic to sucking insects without harming the plant. Mention is made already of one such insecticide, Thimet, which has the highest consumption in the United States for this class of compounds. Tables 5-1 and 5-2 show some contact and systematic insecticides. Here the term insecticide is used broadly to include acaricides and nematicides.

It is of interest to note here that organophosphorus insecticides have only limited persistence in the environment as compared to the organic chlorine insecticides. Also, insects have been slow in developing resistance to them. Furthermore, insecticides such as methyl and ethyl parathion have been in commercial use for over half a century although not at a large scale now as they used to. One reason for their continued use is they are quite economical to produce.

5.9 Flame retardants

Safety and prevention of accidents and injuries are common everyday instincts. Efforts in this direction have found in phosphorus compounds some effective answers to the provision of flame retardants and fire extinguishers. Although some such compounds are not strictly organophosphorus, viz., ammonium phosphates, the others are. The ammonium salts will be reviewed first.

1. Ammonium phosphates which act as fire retardants are those that can readily decompose into an acid upon heating, and then the acid, so produced, can act to extinguish the fire by decomposition of the combustible material such as cellulose. Both MAP and DAP are known to possess such property. They are used to flameproof such items as theatrical scenery, building materials made of wood or cellulose. They are applied as water solutions. However because of their water solubility they are of little use for flameproofing clothes. However it is precisely for this reason, that match sticks are treated with ammonium phosphates to prevent after glow.

Unlike ammonium orthophosphate and pyrophosphates, ammonium polyphosphate is practically insoluble in cold water. It is used as flame retardant in paint coatings and in nonwoven fabrics where it can be bonded permanently by polymeric binders.

A related industrially available flame retardant is urea phosphate which is made by reacting urea with phosphoric acid. Although it can flameproof cotton fabrics but the treated fabrics suffer by loss of its tensile strength and tear strength.

Another interesting flame retardant is obtained by the high-temperature reaction of P_4O_{10} with gaseous ammonia. The resulting substance is of uncertain structure. However it is known, in one form, under the trade-name Victamide. It dissolves very slowly in water and does not wash off quickly in water. It is used to flameproof paper, fabrics and backings of plastic sheets.

2. Phosphines flame retardants are truly organophosphorus derivatives of phosphine, PH_3 .

Tetrakis(hydroxymethyl)phosphonium chloride (THPC), $(HOCH_2)_4PCl$, is used in what is known as modified THPC process to flameproof specially treated fabric which has been cured by ammonia

at room temperature.

Another phosphine derivative known as tetrakis (hydroxymethyl) phosphonium hydroxide, THPOH, $(\text{HOCH}_2)_4\text{POH}$, is obtained by reacting THPC with sodium hydroxide. More recently THPC has been replaced by the corresponding sulphate, $[(\text{HOCH}_2)_4\text{P}^+]_2 \text{SO}_4^{2-}$, to avoid the use of THPC which may convert to a rather potent carcinogenic compound under reaction conditions.

The new process which has found wide commercial acceptance is claimed to give flame-resistant cloth that retains its original strength and is about as soft as the untreated fabric.

The older THPC process is still used for fireproofing industrial and military garments.

3. Organic Phosphonates, $(\text{RO})_2\text{P}(\text{O})\text{H}$, compositions are known to have good flameproofing properties. Among them are three known by their proprietary names: Pyrovatex CP, an organophosphonic acid dimethyl ester, Fyrol 76 which contains vinyl phosphorus group, and Fyrol 6 which is an aminomethyl phosphorate. The first two give good laundering property for the treated fabrics provided they are laundered with phosphate detergents.

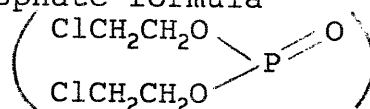
Fyrol 6 is of special interest because it is found to give good flameproofing results for rigid polyurethane foams, which are used extensively for packaging and insulation particularly for house hold appliances and wall boards.

4. Organic phosphates, $(\text{RO})_3\text{PO}$, of various compositions have been developed for their flameproofing properties when applied to plastics. Among those that have gained commercial acceptance is Fyrol CEF and Union Carbide 3CF, based on tris(β -chloroethyl) phosphate, $(\text{ClCH}_2\text{CH}_2\text{O})_3\text{PO}$, which is obtained by reacting phosphorus oxychloride with ethylene oxide in the presence of titanium tetrachloride catalyst. It is used as a versatile flame retardant for flexible as well as for rigid polyurethane foams, for paints and lacquers, epoxy resins, phenolic resins, melamine resins, cast acrylic sheets, and polyester resins. Furthermore, it is used as a secondary plasticizer in polyvinyl chloride.

Another product known as Fyrol PCF is made from phosphorus oxychloride and propylene oxide with titanium tetrachloride as catalyst. It has similar properties to Fyrol CEF, but is less reactive towards water and bases. It covers the same uses as Fyrol CEF with the added advantage of better storage stability.

Fyrol FR-2 tris (dichloroisopropyl)phosphate, is another important flame retardant for flexible polyurethane foam. It has the advantage of having less tendency to volatilize and is also of lower water solubility than either Fyrol CEF or PCF. It is widely used in flexible polyurethane foam for automotive seatings.

A number of related group of phosphates is produced by reacting phosphorus trichloride with ethylene oxide to obtain Thermolin 101, or with pentaerythritol to obtain Phosgard 2Xe20. They both have the general diphosphate formula



Another product based on oligomeric phosphate goes by the trade name Fyrol 99. It enjoys low volatility and is resistance to water and solvents. It is used industrially to impart flame retardancy to resin-impregnated paper for use in automotive air filters. It is also used in polyurethane foams and in structural foams.

A flame retardant which is compatible with thermosetting resins is Fyrol 51 based on oligomeric phosphate and phosphorate, which when formulated with small amount of alcohol, is used in the treatment of resin-impregnated automobile air filters.

Triaryl phosphates, and in particular tricresyl phosphate, $(\text{CH}_3\text{C}_6\text{H}_4\text{O})_3\text{PO}$, have found wide acceptance as plasticizers for polyvinyl chloride which also impart good flame retardancy and provide faster processing and gelation. Other desirable properties are good oil and gasoline extraction resistance, good microbial resistance and good high frequency heating characteristics. They are also used as gasoline and lubricating oil additives, and as hydraulic fluids for machineries operating under severe conditions.

5-10 Chelates, Sequesterants and Flotation Agents:

Many organophosphorus chelating agents have been made, but two of them have become the most prominent in industrial applications. The first to be mentioned is nitrilotris (methylene phosphoric acid), NMPA, which is made commercially by the reaction of phosphorous acid with formaldehyde and ammonium chloride in the presence of hydrochloric acid. The other compound is 1-hydroxyethylidene-1,1-diphosphonic acid, HEDPA, which is made by reacting phosphorus trichloride with acetic acid.

In the field of cleaning agents these organophosphorus chelating agents have gained wide acceptance in applications such as caustic bottle washing formulation, liquid detergents, toilet cleaners, industrial and institutional hard-surface cleaners, and stabilizer in bleaching solutions.

In textile processing and paper making, they are used to control heavy metal ion concentration, reduce water hardness, prevent or remove iron stains and prevent deposition of soils.

NMPA and HEDPA function in many ways like sodium tripolyphosphate (STPP) with the added advantage of pH and hydrolytic stability. This property allows them to be used under conditions where STPP would be hydrolyzed, as for example in metal finishing, boiler-scale removal and oil-well drilling muds.

In the mid-eighties NMPA and HZEDPA have become the market dominant organophosphorus chelants for aqueous systems. These products are sold as aqueous solution 40-60% either in the form of free acid or as sodium salt.

As metal extractants a number of organophosphorus compounds have been developed especially for heavy metals. These include bis (2-ethylhexyl) phosphate, mono-acid dioctyl phenyl phosphoric acids, and the reaction product of 2-ethyl hexyl alcohol with phosphoric anhydride, P_4O_{10} which is named dioctyl pyrophosphoric acid. The most widely used metal extractant is trioctyl phosphine oxide which is made by the reaction of phosphorus oxychloride with octyl-magnesium bromide.

In a related application in the field of ore flotation, the sodium or ammonium salts of dialkyl phosphoro-dithioate (called collectors) have found wide application in this field. These substances are generally made from the corresponding alcohol reaction with phosphorus pentasulphide, P_4S_{10} .

Table 5-1
Organophosphorus Contact Insecticides,
Acaricides and Nematocides

Common and Trade Name	Chemical Name	LD ₅₀ (mg/kg)
methy parathion	0,0-dimethyl 0-p-nitrophenyl phosphorthioate	300 - 400
parathion	0,0-diethyl 0-p-nitrophenyl phosphorothioate	55
EPN	O-ethyl O-p-nitrophenyl phenylphosponothioate	420
chloryrifos, Dursban	0,0 - diethyl 0-(3,5,6 - trichloro - 2 - pyridyl)phosphorothioate	2000
Diazinon	0,0 - diethyl 0-(2 - isopropyl - 6 - methyl - 4 - pryrimidinyl) phosphorothioate	600
trichlorofon, Dipterex	0,0 - dimethyl (2, 2, 2, - trichloro - 1 - hydroxyethyl) phosphonate	> 500
DDVP	2,2 - dichlorovinyl dimethyl phosphate	107
naled, Dibrom	1,2, dibromo - 2,2 - dichloro - ethyl dimethyl phosphate	1100
ethoprop, Mocap	0, ethyl S,S - dipropyl phosphorodithioate	61.5
malathion	diethyl mercaptosuccinate, S-ester with 0,0 - dimethyl phosphorodithioate	4100
terbufos, Counter	S - [1,1 - dimethylethyl - thio] methyl] 0,0 - diethyl phophorodithioate	1.1

Table 5 - 2
Organophosphorus Systematic Insecticides,
Acaricides and Nematocides

Common and Trade Name	Chemical Name	LD ₅₀ (mg/kg)
phorate, Thimet	0,0 - diethyl S - ethyl - thiomethyl phosphorodithioate	20 - 30
disulfoton, Disystem	0,0 - diethyl S - [2 - (ethylthio) ethyl] phosphorodithioate	6 - 25
dimethoate, Cygon	0,0 - dimethyl S - (methyl - carbamoylmethyl) phosphorodithioate	> 1000
monocrotophos, Azodrin	0,0 - dimethyl 0 - [2-(methyl - carbamoyl) - 1- methyvinyl] phosphate	450

Source : Toy and Walsh, 1987, (ref.18).

Common and Trade Name	Chemical Name	LD ₅₀ (mg/kg)
azinphosmethyl Guthion	0,0 - dimethyl S - 4 - oxo - 1, 2, 3- benzotriazin - 3 (4H) - ylmethyl phosphorodithioate .	220
methamidophos, Monitor	O, S - dimethyl phosphoramidothioate	118
acephate, Orthene	O, S-dimethyl acetyl - phosphoramidothioate	> 10250
isofenphos Amaze	1, methylethyl 2 - [[ethoxy [(1 - methylethyl) amino] phos- phinothioyl] oxy] benzoate	162 - 315

Source : Toy and Walsh , 1987, (ref.18).

By-Products and Wastes of the Phosphate Industry

The main by-products of the phosphate industry are based on the presence of fluorine as a constituent of fluorapatite, as well as on the minor components of the phosphate ore of such elements as uranium and vanadium and others of sufficient concentration to make their extraction feasible. Others such as gypsum and other wastes face the phosphate industry with major disposal problem.

6.1. Fluorine.

Fluorine in most phosphate of the ESCWA region, is present at the level of 3-4% and is partly liberated during ore thermal processing (calcining) and acidulation. Also, in both the wet-process and the electric furnace process the remaining fluorine present in phosphate rock is volatilized.

In the wet-process, fluorine as hydrogen fluoride, HF, is first formed. In the presence of silica impurities, this is converted into silicon tetrafluoride, SiF_4 , and fluorosilicic acid, H_2SiF_6 . The mixture is passed through water-absorption tower and the liquor is concentrated to commercial strength of fluorosilicic acid by recycling or distillation.

The fluorosilicic acid can be used in water fluoridation, in the brewing industry as disinfectant for copper and brass vessels, in electroplating, and as preservative.

A number of useful compounds of commercial value, may also be produced, such as:

- Aluminum fluoride, AlF_3 , is used in the aluminum industry.
- Sodium fluoride, NaF , finds application as wood preservative, water fluoridation agent, and as insecticide.
- Sodium fluorosilicate, Na_2SiF_6 is used as an insecticide, laundry sour, fluxing and opacifying agent and protective agent in casting light metals.
- Cryolite, Na_3AlF_6 , finds application in the aluminum industry.

Of these compounds, production facilities in the ESCWA region exist only for aluminum fluoride and cryolite as shown in Table 6-1.

Fluorine removal, in the fertilizers industry and in phosphoric acid produced by the wet-process, is a major environmental issue which has to be seriously addressed by the industry. Defluorination, and proper disposal of fluorine by the economic utilization of its compounds, may be an added incentive for the manufacturers, who would also benefit from the enhanced value of their main products, viz., superphosphates and phosphoric acid which with their lowered fluorine content could find a number

of valuable applications, as discussed earlier.

6.2. Uranium

Uranium extraction from phosphoric acid made by the wet-process has received wide attention. Two main procedures are known for the extraction of uranium, either by solvent extraction or by precipitation.

Uranium may be obtained by solvent extraction either in the U^{4+} form or U^{6+} form. The uranium in wet-process phosphoric acid is first brought to the proper oxidation state. A multistage extraction is then followed. In one process U^{4+} is extracted by using a mixture of mono-acid dioctylphenyl phosphate, (OPAP). In the competing process, the solvents are trioctyl phosphine oxide (TOPO) and bis (2-ethylhexyl) phosphate (DEPA) in which uranium in U^{6+} state is extracted into kerosene solution. The uranium is then adjusted to the U^{4+} state by using a reducing agent, in which form it is then stripped from the DEPA-TOPO-kerosene solution. However, a high-grade uranium oxide is obtained with U_3O_8 purity of greater than 98% by a combined process in which both types of solvents are used.

The alternative, precipitation process known as Blockson Process is based on partial neutralization of the phosphoric acid (pH 4-5), to produce monosodium or monoammonium phosphate. Most impurities are here precipitated. The slurry is mainly phosphates and silicates of aluminum, calcium, magnesium and iron (ferrous) together with calcium fluoride and calcium sulphate. In order to keep the uranium in solution during the precipitation stage, a strong oxidant, such as chlorine, nitric acid, hydrogen peroxide, is added prior to neutralization. After the filtration of the slurry, uranium is precipitated from the filtrate by adding a reducing agent, e.g., sodium thiosulfate, sulphur dioxide, and using a filter aid, such as diatomaceous earth.

Although, the efficiency of the Blockson Process is lower than that of the solvent extraction process, it has the advantage of simpler equipment, and cheaper chemical consumption. Furthermore, with the increasing production of ammonium phosphates, as fertilizers, from wet-process phosphoric acid an improved precipitation process has been developed in conjunction with the manufacturing of the ammonium fertilizers.

When crude phosphate ore is destined for export, as is the case in several countries of the region, it may be economically interesting to consider the possible extraction of uranium, and other valuable metals, such as vanadium, chromium and manganese, by a modified Blockson process, known as heap leaching

It may be of interest to note here, that beside using phosphorus-based compounds for the solvent extraction of uranium, they are also used in purifying uranium. This is done by treating the extracted uranium with nitric acid to obtain uranyl nitrate,

which is then further extracted with tributyl phosphate in kerosene solution. A highly pure uranium salt could then be extracted from the kerosene solution with 10% solution of sodium carbonate.

Tributyl phosphate is a powerful metal extractant with very high selectivity.

6.3. Vanadium and other metals.

Vanadium, as well as other industrially useful metals that may be present in phosphate ore, could be extracted commercially if present at such a level of concentration that makes their extraction feasible. Such other metals of interest are for example chromium, manganese, and titanium.

They may be obtained by modifications of either Blockson process or by solvent extraction.

Some of these metals have important industrial applications for example in alloying and as catalysts, as well as in many manufacturing industries and products.

6.4. Gypsum.

Also known as phosphogypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, is formed as coproduct in the production of phosphoric acid by the wet-process. Under ideal operation, for every tonne of wet-process phosphoric acid 3 tonnes of gypsum are produced, in practice this ratio may exceed 4 tonnes of gypsum to 1 tonne of acid. The so-called phosphogypsum is usually disposed off in gypsum ponds. It is estimated that "for each daily metric ton of P_2O_5 produced, the land required for gypsum stacks is 1357m^3 --- (and) 27.14 million m^3 for a 20-yr life of 1000 t/d (P_2O_5) plant". The environmental issues raised by such waste disposal problem is accentuated by the fact that the phosphogypsum, in most of the technologies employed in the wet-process production of phosphoric acid, contains a number of serious contaminants such as radioactivity, fluoride, heavy metals besides sulphuric and phosphoric acids and their salts. The problem is further worsened by the large volume of gypsum pond water which is used in most plants for scrubbing pollutants. Control of gypsum pond water, therefore, becomes a problem of prime importance.

An associated problem is the production of sludge produced in the neutralization of gypsum pond water by liming. The sludge produced is another solid waste which is a mixture of complex compounds of phosphates and fluorides and is disposed of on the gypsum stacks.

Some of the technologies attempted at minimizing the pollutants in the phosphogypsum and thus allow for its use in such products as plaster boards. Other possibilities exist, but as yet not considered economical, as for example, the production of sulphuric acid and cement clinker.

6.5. Slimes.

Slimes are produced in the ore beneficiation process. They usually contain 30-35% solids and are disposed of into 160-240 hm² ponds where the solids are left to settle. It is estimated that the slime wastes occupy about 32 times the initial volume of the rock. To the impounded slime, tailings, from the matrix concentration procedures, are usually added.

The only known procedure to handle this problem at the present is to use the waste in reclaiming mined out land. But the level of radioactivity present in reclaimed phosphate lands was found in some areas to exceed the level of exposure allowed by radiological protection guidelines, though only slightly.

Table 3-2

Specification of Phosphate rock Produced by
Countries in the ESCWA
Region and in North Africa

Component	% Content						
	Egypt ¹	Iraq ²	Jordan	Syria	Algeria ²	Morocco	Tunisia
P ₂ O ₅	30.0	33.5	33.9	32.4	34.6	33.9	29.8
CaO	49.0	58.0	52.2	51.2	54.2	52.4	49.4
SO ₃	2.7	3.0	1.3	1.8	1.6	1.47	2.85
CO ₂	6.5	3.0	4.2	5.6	1.2	4.29	6.55
SiO ₂	3.5	2.5	3.15	3.6	2.2	2.65	3.26
Fe ₂ O ₃	} 1.7	} 1.2	0.17	0.25	0.4	0.23	0.43
Al ₂ O ₃			0.20	0.40	0.5	0.52	0.77
SrO			0.25	0.15		0.04	
MnO ₂			0.01	0.02		0.01	
MgO	2.4	2.6	0.23	0.35	0.8	0.32	0.77
TiO ₂			0.04	0.04		0.02	
Na ₂ O	0.1		0.54	0.45	0.6	0.65	1.21
K ₂ O			0.02	0.03	0.01		0.57
F ⁻		4.2	3.99	3.45	4.0	3.57	3.27
Cl ⁻		0.15	0.03	0.18	0.01	0.01	0.04
H ₂ O Org.	2.5		} 1.45	} 1.52		} 1.44	

Source : Chemical Fertilizer Industry and its Materials in the Arab Region till
the Year 2000, 1983, (ref.3) .

1. Red Sea Coast.

2. Calcined Samples.

Table 3-1
Phosphate Ore Reserves in the ESCWA Region
and in North Africa^{*}

unit 10⁶ tonnes. () P₂O₅%

Country	Proved	Probable	Possible	Total	Resources **
ESCWA region					
Egypt	1887 (25)	40 (25)	- -	1927	3000 (22)
Iraq	432 (20)	- - -	- -	432	4050 (22)
Jordan	1031 (26)	58 (28)	234 (17)	1323	1574 (28)
Saudi Arabia	- - -	500 (23)	- -	500	7880 (20)
Syria	624 (30)	235 (26)	- -	859	1057***
Subtotal	3974	833	234	5041	17561
North Africa	25 (26)	- - -	480 (26)	505	500 (24)
Algeria	- -	136 (19)	500 (19)	636	100 (20)
Mauritania					56250 (28)
Morocco	95612 (32)	- - -	- - -	95612	3000 (16)
Tunisia	795 (27)	- - -	- - -	795	
Subtotal	96432	136	980	97548	59850
Total	100406	969	1214	102589	77411

Source: * Arab Mining Co. (ref.4)
 ** Notholt, Sheldon and Davidson (1989), (ref.15).
 *** 414 million tonne 4% P₂O₅ and 643 million tonne 25% P₂O₅.

low-grade phosphate rock containing organic matters, causes the production of so-called black-acid. These impurities necessitate a pretreatment of the acid by an oxidation agent to remove the organic matter.

Although the amount of impurities present in wet-process phosphoric acid depends both on the quality of ore and the beneficiation process used for the production of phosphate rock, as well as on the technology of the process used for the production of acid, the products themselves suffer in general from the presence of similar types of impurities.

Two main procedures used for the purification of wet-process phosphoric acid, viz., chemical precipitation and solvent extraction. Crystallization and ion exchange methods have also been used, but on a limited scale.

Color-forming organic matter may be removed from wet-process acid by using oxidizing agents such as nitric acid or ammonium nitrate. But more effective method for producing clear acid is calcination of the phosphate ore before acidulation.

In the chemical precipitation method, all wet-process acid impurities may be induced to precipitate as the acid is neutralized with sodium carbonate followed by sodium hydroxide. The main exception, sulphate may be precipitated as calcium or barium sulphate. Most fluorine and silica can be removed with the sulphate filter cake as sodium fluorosilicate by the addition of sodium ion.

In the solvent extraction method, a number of alternative solvents systems are available. They are based on organic solvents with low solubility in water, e.g., short-chain alcohols, ether, ketones, amines and phosphate esters. Crude wet-process acid is firstly concentrated and clarified prior to extraction to remove the sludge-forming components and improve partitioning process. Chemical precipitation of sulphate, silicate and fluoride is affected as a prepurification step preceding solvent extraction. Figure 7-1 sketches the main steps in solvent extraction of the wet-process acid. In general back-extraction with water recovers the purified acid and after filtration of the precipitated impurities, the solvents are recovered by distillation.

7.2. Electric furnace phosphorus and thermal phosphoric acid.

The electric furnace reduction of phosphate rock affords the only commercial method for the production of pure elemental phosphorus, suitable for the production of highly pure phosphoric acid by burning the element in excess air followed by hydrating the resulting phosphorus pentoxide.

Electric furnaces for producing phosphorus are usually located near phosphate mines and a source of cheap electric power. The phosphate rock needed for the process is of lower grade than that

usually required for the wet-process production of phosphoric acid. The rock, after washing to remove most of the clay impurities, is then dried and fused in high temperature kiln into granular lumps which are crushed to produce nodules of suitable size in order to avoid the formulation of fine phosphate dust in the furnace. The coreactants silica and coke of matched sizes are introduced inside the furnace which is then operated to reach temperature of 1200-1450°C.

The major coproducts are reacted with silica to produce calcium silicate and silicon tetrafluoride. The former is withdrawn at the bottom as a melt, while the latter is removed from the furnace vapors by scrubbing with lime solution.

The iron impurity, as iron oxide, is reduced to iron which reacts with phosphorus to produce ferrophosphorus which may be drained away at the bottom. Ferrophosphorus finds many uses such as in the manufacture of low alloy steels, a filler in high density concrete, and additive for zinc-based anticorrosion paints.

Dependent on the composition of the phosphate rock, ferrophosphorus could also be used as raw material for the production of vanadium.

The carbon monoxide by-produced is usually used as fuel to supplement the heat required to fuse the phosphate rock into nodules as needed for the furnace reaction. It may also be used as source of raw materials for organic synthesis.

The furnace slag of mainly calcium silicate contains most of the impurities originally present in the phosphate rock, and it is weakly radioactive.

Elemental phosphorus from the electric furnace reduction process is a distilled product of high purity, when burned in excess air in specially constructed wetted combustion chambers, phosphoric acid is formed of purity high enough for industrial uses without further purification. The main impurity, however, is about 20-100 ppm arsenic present in the phosphorus as the element and in the phosphoric acid as arsenious acid. To remove this arsenic, phosphoric acid is treated with excess hydrogen sulphide, filtered and blown with air to strip out excess H_2S . This treatment reduces arsenic content in phosphoric acid to less than 0.5ppm. The resulting highly pure acid suitable to be used for food, pharmaceutical and other applications for which such purity demands.

Electric furnaces phosphorus production plants vary widely in annual capacity. Small 3-5 thousand tonnes annual capacity plants are quite common in America, Europe and Asia. The average world plant capacity is about 50 thousand tonnes. It is interesting to compare this with the average plant capacity for wet-process phosphoric acid plants in the Arab countries which comes to about 230 thousand tonnes. The smallest capacity of 60 thousand t/y is

found in Egypt. The largest wet-process world capacity plant is 600 thousand t/y as compared to 200 t/y for elemental phosphorus plants.

The smaller capacity plants for elemental phosphorus together with the lower grade phosphate rock which can be used, as well as the wide range of elemental phosphorus and thermal-acid based products, all of these factors make it attractive to consider the feasibility of such facilities to operate on their own or as very useful supplementary units attached to existing wet-process phosphoric acid and fertilizers plants.

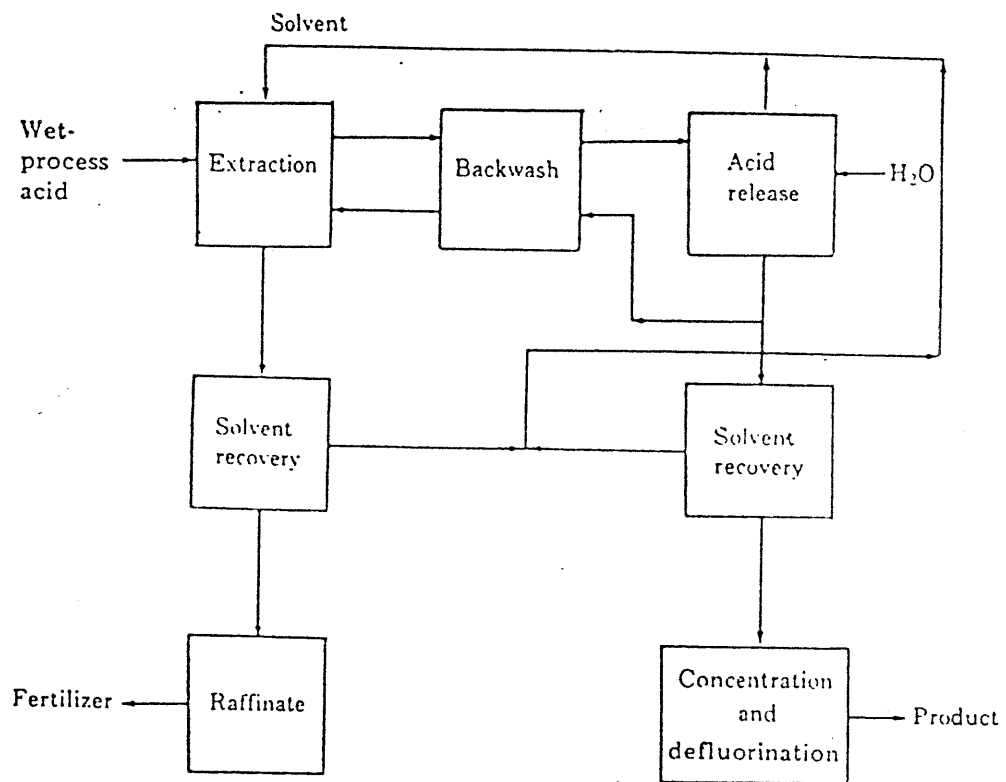


Figure 7-1. Solvent extraction purification of wet-process phosphoric acid (ref.10).

The Prospects for Down-Stream Phosphate Industry in the ESCWA Region

There can be no doubt about the diversity of products that the down-stream phosphate industry could make available in an active market like that of the ESCWA region and of North Africa, with great potentials for rapid development in the near future. These wide-ranging products cover varieties of needs extending from those of other industries to consumer goods for both domestic use and services.

In this section, the question of the prospects for developing the down-stream phosphate industry in the region will be discussed. The relevant issues which will be considered are the availability of materials and the presence of the industrial base and technical know-how, the immediate needs of the market, and the future development of the industry.

8.1. The availability of materials for down-stream phosphate industry

As has been fully demonstrated in earlier parts of this study, the quantity and quality of the phosphate ores available in the ESCWA region make it one of the richest areas in the world in phosphate rock, the primary material for the phosphate industry. The accessibility of the phosphate deposits, although they are mostly classified as low-grade phosphate, and the amount of reserves concentrated in any one location, have made their utilization, both mining and beneficiation, highly economical. This is witnessed by the rapid growth of the phosphate mining industry not only for the provision of phosphate rock for local production of phosphoric acid and fertilizers, but also for export. Table 8-1 shows the sizeable proportion of phosphate rock destined for export.

These facts point to the availability of the basic raw material needed for any future expansion of the phosphate industry whether along existing lines of products or any other that is deemed necessary.

The primary materials for the phosphate industry are phosphoric acid and elemental phosphorus as has been shown previously. Of these at the present only phosphoric acid is manufactured in the region. Most of it is captive for the production of phosphatic fertilizers. It is interesting to note here that, although the rate of consumption of these fertilizers in the Arab countries is among the lowest in the world, yet most phosphatic fertilizer producers in the region carry out an active export trade in these commodities. This fact shows that there is phosphoric acid production capacity in excess of local needs for fertilizer production. In fact most of the phosphoric acid plants are producing under capacity as shown in Table 8-2. This means

that there is excess capacity of phosphoric acid that can be made available for the manufacturing of materials or products other than phosphatic fertilizers.

Of the various materials needed for establishing a viable down-stream phosphate industries, those that are made in the region, at the present, and could be used as starting intermediate chemicals for non-fertilizer products are very limited. In fact one can say, there is only phosphoric acid and possibly also monoammonium phosphate, diammonium phosphate and a certain grade of superphosphate that can be considered for non-fertilizer uses. The existing utilization of by-product fluorine is very limited and at an insignificant level. The production of sodium tripolyphosphate (STPP) is still on a very limited scale.

Notwithstanding, the available wet-process phosphoric acid has only limited uses for many of the down-stream phosphate products, and, therefore, purified of the acid has to be undertaken in order to bring it to the specifications required for most non-fertilizer uses. Even then, purification of wet-process acid is still not accepted for some uses in the food and pharmaceutical industries. For these and for many other applications thermal phosphoric acid produced from electric-furnace elemental phosphorus must be used.

The availability of low-grade phosphate rock, and, in some ESCWA countries, the low cost of electric power, together, make the proposition of making elemental phosphorus highly feasible, especially if it is considered in the light of the small capacity electric furnaces that could be used. The product, elemental phosphorus can serve dual role, both as basic material for the production of the intermediate chemicals (the building blocks) for organophosphorus and organophosphate products, and for the production of highly pure food-grade phosphoric acid.

The "building block" chemicals for organophosphorus compounds are phosphorus chlorides, PCl_3 and PCl_5 , phosphorus pentoxide, P_2O_5 , phosphorus sulphide, P_4S_{10} , phosphorus oxychloride, POCl_3 , and phosphorus thiophosphate, PSCl_3 . These intermediates can all be made by simple reactions of the elements.

Hence, beside phosphorus, to be made by the electric furnace reduction of phosphate rock, all the others, specially chlorine and sulphur, are, or could easily be made, available.

In summary, the primary chemicals and the intermediate chemicals needed for the down-stream phosphate industry are:

- elemental phosphorus, by the electric-furnace reduction of phosphate rock.
- Orthophosphoric acid, either by purification of wet-process acid, or from elemental phosphorus (food-grade quality acid).
- Phosphoric acids, from orthophosphoric acid.

- Phosphates, from phosphoric acids and corresponding bases.
- Phosphorus chloride, oxides, sulphides and their direct derivatives oxychloride and thiochloride, from elemental phosphorus and the corresponding elements. Phosphine, from phosphides.
- Organophosphates and organophosphorus compounds, from phosphorus compounds with hydrocarbon reagents (alkyl or aryl derivatives).

8.2. The industrial base and technical know-how.

The well established world-scale phosphate industry in several ESCWA countries covers various stages of the technology starting from mining and ore-beneficiation to phosphoric acid and fertilizer production. Some of the countries of the region have had their phosphate industry for several decades while others started in the seventies and the eighties. Most of the countries have employed standard technologies such as Rhone-Poulenc, Prayon, Fison and Nissan. It is interesting to note in this respect that Tunisia has developed its own processing technology to suit its phosphate ore. In all cases mining and beneficiation procedures have to be adapted to fit the locality and quality of the phosphate deposits.

In some countries of the region, efforts were directed to develop the processing of some by-product of the phosphate industry and to find solutions for the environmental problems associated with phosphogypsum.

The emphasis on export whether of the beneficiated phosphate rock or for the phosphate products meant careful production control and the adherence to internationally acceptable specifications. This, of-course, demands deep understanding of the manufacturing process and the establishment of well-operated quality control procedures and laboratories.

In many countries research and development centers and activities exist to serve the phosphate industry. Such centers and activities are well established in Egypt, Iraq, Jordan, and Syria. Training programs form part of the activities of most of these centers. One such center with regional activities is the Moroccan center in Casablanca which has well staffed and equipped laboratories and pilot plant facilities to carry out wide-ranging R&D programs.

The well-established phosphate industry in the region, backed by highly qualified engineers, scientists, managers, economists and technicians with long-standing experience in the phosphate industry, can provide both the industrial base and the acquisition of know-how needed for the development of the industry. Table 8-3 gives the work force of the phosphate industry in the ESCWA region, both the present and the projected number and their division as professional and non-professional personnel. Of-course these

figures represent the present and projected need for the industry developing along the existing lines of manufacturing with possible additions of similar products. Nevertheless, they signify the availability of know-how and experience that can be build upon for any development in newer directions such as the down-stream industries.

8.3. The Regional market

The consumption of phosphatic fertilizers in the Arab region form less than 50% of production, and their use in kg per hector is among the lowest in the world. Both facts show that the Arab market is grossly underdeveloped and its agriculture is far from satisfying the need of the region. Beside, the need of the market for agrochemicals, such as pesticides, are almost completely dependent on imports. Hardly any local industry has been developed to meet the market needs for such products.

In addition to that, the wide range of industrial chemicals derived from phosphorus, which are needed by the local industry, are imported. Thus, inspite of the availability of the materials and the industrial base for the production of such industrially and economically important products, yet the phosphate industry has almost completely been developed for fertilizer production only. The items with large mark-up value that characterize most of the products of the down-stream phosphate industries have been completely overlooked.

The absence of detailed import figures makes it imperative to rely on subjective considerations in deciding the need for the various down-stream phosphate industry products that are of wide industrial applications and market interest.

The investment needs of the Arab phosphate industry to develop along its present lines of products, i.e., phosphoric acid and phosphate fertilizers, is expected to be more than doubled by the end of the nineties. With investments made available at such a rate, and expected to reach about 7 billion U.S. dollars by the year 2000, and considering that the export share of the volume of production is to rise from about 50% in 1990 to more than 64% for the same period, these are good indicators of the attractiveness of the phosphate industry for future investment. However, the general falling trend in the world prices for basic commodities, and the progressively rising prices of consumer products and other items of high mark-up value, make any call for investments to develop the manufacturing of such down-stream phosphate industry products highly appealing to the potential investors, especially so when considered with the relative advantages of the region mineral and energy industry and the great potential of developing a hitherto underdeveloped market.

8.4. The Future development.

Phosphorus science and technology present a vast field for future development in areas extending from genetic engineering and biotechnology, to composite materials and food industry. The progress of phosphorus-based industries over the second half of this century has assured scientists and industrialists of the great potentials that lie ahead in this field.

Areas of potential development and possible industrial applications and commercial significance cover such items as:

- Organic phosphorus polymers and copolymers,
- composite materials and asbestos-substitute phosphate fibers,
- new phosphorus-based catalysts,
- new pesticides, herbicides and fungicides,
- plant growth control agents,
- medical application of genetic engineering,
- biophosphates and metabolic control agents, etc.

It is of great importance, for countries with rich minerals resources to move up the ladder of industries based on these minerals and realize the fruits of the value-added products made from materials manufactured from these minerals.

The level of sophistication involved in the development of down-stream phosphate industry is not beyond the reach of a well established phosphate mining and fertilizer manufacturing industry, as that of the ESCWA region. The great potentials and the possibilities for future development, make the phosphate industry an ever-growing industry with no limits visible for the present or the foreseeable future.

One of the industry greatest future potential deserving special mention is the large number of minor constituents present in phosphate rock. As the extraction technology advances, then the need for some of these minor elements becomes such as to make their extraction economically feasible. The minor constituents of the phosphate ores for Iraq and Saudi Arabia, for which there are published figures though not as comprehensive as desired, are compared with those of global and regional interest in Table 8-4. Although the picture would be better understood if more comprehensive data are available and for other phosphorite deposits in the region, but in general they would not be expected to be different from those of other regions. Thus, any endeavour to develop these potential resources is a very interesting proposition.

Table 8-1
Phosphate Rock Export in the
ESCWA Region and in North Africa (1991)

unit 1000 tonnes

Country	Production capacity	production	% utilization	export	
				Qty	% of production
ESCWA region					
Egypt	1800	1367	76	764	56
Iraq	1700	1080	64	--	--
Jordan	8000	4850	61	4246	88
Syria	2500	1750	70	1600	91
subtotal	14000	9047	65	6610	73
North Africa					
Algeria	2000	1150	58	950	83
Morocco	25000	17814	71	9143	51
Tunisia	7000	6173	88	375	6
subtotal	34000	25139	74	10468	42
Total	48000	34186	71	17078	50

Source: Annual statistical Report, 1992, (ref.1).

Table 8-2
Phosphoric Acid Production Capacity Utilization
and Export in the ESCWA Region and in
North Africa (1991)

unit 1000 tonnes

Country	Production capacity	production	% utilization	export	
				Qty	% of production
ESCWA region					
Egypt	65	33	51	--	--
Iraq	416	139	33	--	--
Jordan	410	271	66	6.0	2
Lebanon	100	40	40	--	--
Syria	165	18	11	--	--
subtotal	1156	501	43	6.0	1
North Africa					
Algeria	115	57	50	--	--
Morocco	2772	2650	96	1337	50
Tunisia	1452	912	63	543	60
subtotal	4339	3619	83	1880	52
Total	5495	4120	75	1886	46

Source: Annual statistical Report, 1992, (ref.1).

Table S-3
The Work-Force of the Phosphate & Allied
Industries in the ESCWA Region
and in North Africa

unit 1000 tonnes

Country	1985	1990 ⁽¹⁾	2000 ⁽²⁾
ESCWA region			
Egypt	3800	4800	4850
Iraq	800	800	--
Jordan	500	630	1080
Lebanon	360	360	--
Saudi Arabia	120	200	--
Syria	1000	1500	1500
subtotal	6580	8290	
North Africa			
Algeria	500	1300	1300
Mauritania	--	250	250
Morocco	6800	8100	9250
Tunisia	3900	4447	4547
subtotal	1120	14097	
Total ⁽³⁾	1778	22387	

(1) estimated. (2) projected.

(3) Of these 25% directors and professional
65% technicians and skilled workers.

Sources: The Statistical Reference for Fertilizer Industry, 1987,
(ref.2).

Table 8-4
The Minor Constituents of Phosphorites

Elements	(PPM)				
	Iraq ⁽¹⁾	Saudi Arabia ⁽¹⁾ (range)	Israel ⁽²⁾	Crustal ⁽²⁾ Abundance	Average ⁽²⁾ Phosphorite
Ag	1.5		2	0.28	2
As		10-43	7	2.6	23
B				4.45	16
Ba			240	21	350
Be				2.8	2.6
Cd	71	4-33	25	0.2	18
Ce			6	60	104
Co			5	25	7
Cr	323	96-136	230	100	125
Cu		18-45	20	55	75
Ga				15	4
Hg ppb			0.05	80	55
La			35	30	147
Li			1	20	5
Mn			40	950	1230
Mo		9-12	40	1.5	9
Ni	43	23-40	90	75	53
Pb			5	13	50
Sc			1	22	11
Se				0.05	4.6
Sn				2	3
Sr	1804	760-960	2300	375	750
Ti	159		245	4400	640
U	58	37-75	110	1.8	120
V	109	69-179	155	135	100
Y	57	80-200	75	33	260
Yb	--	--	10	3	14
Zn	586	129-192	520	70	70

Sources : (1) Notholt, Sheldon & Davidson, (ref.15).
(2) Nathan, (ref.14).

Conclusions and Recommendations

The phosphate industry has been widely developed in the ESCWA region over the last two decades benefiting from a number of advantageous factors that could be summarized in the following points:

1. Surface or near surface deposits make for relatively easy and economic recovery of the phosphate ores.
2. Excessibility of the phosphate fields for most countries of the region.
3. Geographic location of the region on the western edge of Asia opens for the phosphate industry besides the European market, the enormous market potentials of Asia and Eastern Africa, areas of great need for phosphatic products.
4. Investment potentials for local capital in a rapidly and highly promising industry with widely open opportunity both for internal and intraregional trade as well as for export outside the region.

However, besides these positive points there are others on the negative side. Important among them are the following points:

1. The phosphate ores of the region are mostly of the relatively low grade which require beneficiation to produce phosphate rock quality.
2. The energy and material requirements for the phosphate industry are not cheaply available for some countries of the region. Also, industrial waste-disposal problems are not easily resolvable without some environmental effects to the region.
3. The complete reliance on the wet-process, phosphoric acid technology has confined the industry to the phosphatic fertilizers with very little activity in other products which are of high market value and hold great potential both for the region and for export.

This survey has demonstrated the technical feasibility of developing down-stream phosphate industries, and has shown quite clearly the importance and advisability of undertaking such actions as needed to realize the establishment of such industries in the region. The rationale behind this argument can easily be stated in terms of the importance of the phosphate industry of the ESCWA region to the world (as judged by its share of the world phosphate resources and of the phosphate trade), and also in terms of augmenting the value of the natural mineral resources and aiming at the more value-added phosphatic products. This should be viewed in terms of the great potentials for future developments not only in the possible utilization of hitherto unworked mineral deposits but

also in the promise of as yet underdeveloped regional market with great development expectations for a wide range of phosphatic products alongside the conventional phosphatic fertilizers.

With this aim in view and in the light of the facts and analyses presented in this study a number of recommendations could be made.

Recommendations

9-1. Modality for developing down-stream phosphate industries:

The proposed modality for developing down-stream phosphate industries in the region is based on flexible chemical manufacturing which requires close cooperation between the major phosphate producers and a number of small entrepreneurs.

The down-stream phosphate industries can be started as small-to-medium scale industries, even as pilot-plants that could be scaled-up as and when required. Such plants could produce a variety of products since the manufacturing technology is not very different for similar classes of compounds. The entrepreneurs could work on their own initiative, as well as in some cases especially at the beginning, the major producers may contract out to them on job-by-job basis to make such products as they require for their own marketing.

The primary role of the major producers besides giving the necessary financial supports, possibly through the provision of loans, is the supply of the basic materials needed by the down-stream manufacturers at preferential prices. Some of the basic materials, such as elemental phosphorus, purified phosphoric acid, phosphorus oxide, halides and sulphides, could be made within the major producer manufacturing complex either by the producer directly or through a subsidiary. These materials are to be produced on flexible basis by pilot-plants, and building up larger production capacities as demand grows. This is not unknown in the chemical industry, specially in the case where a potential market is being developed, as is the case here.

The proposed modality must be carefully studied by a team of specialists to present a policy paper that could form the basis for further action.

9-2. Regional cooperation:

The development of down-stream phosphate industries lends itself to many possible forms of regional cooperation. Besides the potentials of intraregional trade in phosphate-based products other than fertilizers, cooperation could be realized also at the manufacturing level. In this respect advantage may be taken of the availability of cheap energy in one country to be coupled with the availability of materials, such as potassium and chlorine,

in another.

Such regional cooperation could also be incorporated in the proposed modality. Whereby, a major producer in one country may undertake, directly or through a subsidiary, the production of some basic chemicals, such as elemental phosphorus or purified phosphoric acid, that can be made available to entrepreneurs supported by the major producer of another country. Also, marketing arrangements could form the channels of such cooperation. Furthermore, cooperation in R&D and in technology transfer could foster strong regional links in the future development of the phosphate industry.

9-3. Techno-economic studies:

To promote the establishment of down-stream phosphate industries careful techno-economic studies should be undertaken.

These pre-feasibility studies could help in decision making in the selection of those industries that may be considered valuable to the region. Examples of such industries are given here solely as illustrations.

1. Electric furnace production of elemental phosphorus:

This could be done by a small capacity plant attached to one of the phosphate complexes in a country with cheap electric power.

2. Purification of wet-process phosphoric acid:

The need for purified phosphoric acid has been amply demonstrated in spite of the limited quality that can be achieved through any of the purification processes, yet there are still interesting areas of applications for such acid. Pilot-plant scale purification unit whether by solvent extraction or precipitation seems to be a feasible proposition that deserves serious consideration in countries for which the availability of such acid could have an impact on some of its productive sector. One possible use is for stockfeed production.

3. Production of phosphorus compounds:

Compounds that are considered as the building block for phosphorus-based industry are phosphorus halides, oxide and sulphides. These can be made on a pilot-plant scale, and form a natural extension to the electric-furnace elemental phosphorus production unit. The availability of these basic materials is a must for the building of a viable down-stream industry for the production of such materials as organophosphate and organophosphorus compounds of varied application and uses, as for example in agrochemicals, pesticides, metal treatment, catalysts, corrosion inhibitors, etc.

4. Production of phosphate salts:

Phosphate salts other than those used as fertilizers, are of wide-ranging applications, e.g., in food industry, dentifrices, water treatment, cleaners and detergents, ceramics, etc. Some of these require for their production food-grade phosphoric acid which is obtained from electric-furnace elemental phosphorous. Others could be made using specially purified phosphoric acid from the wet process. Their varied applications and uses make it essential to plan carefully for the production of such salts that are considered of the widest possible need in the region.

9-4. Manufacturing manuals:

The availability of specialized how-to-do-it manufacturing manuals for selected number of products could help greatly in the promotion of building down-stream phosphate industries and would encourage the active participation of potential industrial entrepreneurs.

Examples of products to be covered are:

- specialized fertilizers including liquid fertilizers
- water-treatment agents
- boiler cleaners and corrosion inhibitors
- industrial cleaners and detergents
- electroless plating and metal plating with phosphate-based materials
- phosphates for ceramics, glass and cements.

9-5. Training programmes and workshops:

An active training programme in the technology, management and economy of the phosphate industry, especially orientated for the would be down-stream manufacturers, goes a long way in the promotion of such industries. Such programmes should be carefully developed and executed with the support and cooperation of the major phosphate producers and national R&D centers, both at the regional and country levels.

9-6. Reviews of future trends in the phosphorus industry:

Phosphorus chemistry and technology is a fast moving area of research and technical development. New products of great promise and new application of old products are daily occurrences. Therefore, the phosphate industry of the ESCWA countries with its great potentials and importance for the future development of the region must be kept actively aware of such development.

The proposed reviews may be undertaken by specialists from the region with the full support and cooperation of the major producers, future investors, national R&D centers and the universities. Such reviews may include areas of potential interest to the industry, e.g., organophosphorus polymers, phosphorous compounds and fibers in composite materials, genetic engineering and biotechnology involving phosphorus compounds and derivatives. The execution of such reviews by ad hoc groups formed from experts from the region could initiate greater cooperation in R&D and technology transfer that may eventually lead to closer regional links and the establishment of joined projects.

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