

*"Materials-Cycle Optimisation in the  
Production of Major Finished Materials"*  
**CHAPTER 7: PHOSPHORUS, FLUORINE  
& GYPSUM**

by

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This chapter is part of a report made for the EC DGXII on a project entitled **"Materials-Cycle Optimisation in the Production of Major Finished Materials"**. This project aims at facilitating the identification of longer-term R&D needs for materials-cycle optimisation, especially by using wastes, co-products, or by-products from one process as inputs to other processes. Book publication is envisaged. Following is the list of chapters:

- Chapter 1: Summary and Overview (*Insead ref N°: 95/05/EPS*)
- Chapter 2: Alumina, Aluminium and Gallium (*Insead ref N°: 95/06/EPS*)
- Chapter 3: Copper, Cobalt, Silver & Arsenic (*Insead ref N°: 95/07/EPS*)
- Chapter 4: Chromium Sources, Uses and Losses (*Insead ref N°: 95/08/EPS*)
- Chapter 5: Zinc and Cadmium (*Insead ref N°: 95/09/EPS*)
- Chapter 6: Sulfur and Sulfuric Acid (*Insead ref N°: 95/10/EPS*)
- Chapter 7: Phosphorus, Fluorine and Gypsum (*Insead ref N°: 95/11/EPS*)
- Chapter 8: Nitrogen-based Chemicals (*Insead ref N°: 95/12/EPS*)
- Chapter 9: The Chlor-Alkali Sector (*Insead ref: N°: 95/13/EPS*)
- Chapter 10: Electronic Grade Silicon (EGS) for Semiconductors (*Insead ref N°: 95/14/EPS*)
- Chapter 11: Packaging Wastes (*Insead ref N°: 95/15/EPS*)
- Chapter 12: Scrap Tires (*Insead ref N°: 95/16/EPS*)
- Chapter 13: Coal Ash: Sources and Possible Uses (*Insead ref N° 95/17/EPS*)

All chapters are individually available as INSEAD Working Papers.

# CHAPTER 7. PHOSPHORUS, FLUORINE AND GYPSUM<sup>1</sup>

## 7.1. Summary

Phosphorus (like nitrogen and sulfur) is an essential element for all living systems. It is depleted from the soil by modern agriculture, because harvested crops are removed from the place where they are grown. For this reason, phosphorus must be replaced by synthetic fertilizer. There is, effectively, only one source of phosphorus for fertilizer, and that is from deposits of "phosphate rock" — one of several variants of the mineral apatite, consisting of calcium phosphate with traces of iron, silica and fluorine — located in several parts of the world.

Both phosphate rock and fluor spar are depletable resources. There is only a finite quantity that can be mined, and eventually it will run out. Phosphate rock is of biological origin, and phosphorus is recycled by geological processes, but only over millions of years. However, current consumption rates will exhaust the known reserves in two or three centuries, at most. But even on a shorter time scale, other problems arise. One is over-fertilization ("eutrophication") of rivers, lakes and estuarine zones, by the addition of phosphorus from runoff and sewage plants.

Another problem is that phosphate rock processing yields enormous quantities of wastes that are potentially recoverable, but which are virtually unrecovered at present. This results in unnecessary destruction of land, both for the disposal of phosphate process wastes and for the mining of other materials (gypsum and fluorites) that could easily be extracted from these wastes. A further problem of concern is that phosphates contain trace quantities of cadmium, a very toxic metal, that is not removed by the fertilizer manufacturing process and consequently ends up in agricultural soils where it can enter the human food chain. (See *Chapter 5, Zinc & Cadmium*).

Similarly, fluor spar mining and processing generate significant wastes that could be avoided if fluorine were recovered from phosphate wastes. Fluorine is an extremely reactive element, which makes it uniquely valuable as an intermediate for many chemical processes. Its very reactivity also makes its organic compounds (e.g. CFC's) extremely inert. Many of its inorganic compounds are toxic. It plays very little role in biological processes, except that it seems to have an affinity for phosphates, especially teeth.<sup>2</sup> The beneficial effects of small amounts of fluorides in drinking water as a tooth decay inhibitor are well-known, if not entirely understood. In any case it would be prudent to utilize available sources of by-product fluorine in preference to mining virgin sources.

Technologies for recovering both fluorine and gypsum-products from phosphate rock are known, but not widely employed. To some extent this might be changed by public investment directly in technology development. However, the most potent instrument for encouraging the needed development would be to increase the prices of virgin fluor spar and gypsum *vis a vis* the secondary product recovered from phosphate rock processing. A tax on phosphate rock waste disposal would probably be helpful in this regard, but a properly constituted resource-based tax (shifting taxation away from labor and more

towards raw materials) should accomplish this result.

**Goals of Public Policy:** Reduce emissions from phosphate mining and phosphoric acid production; maximize recovery of useful by-products (fluorine compounds, gypsum); reduce emissions of cadmium.

## 7.2. Sources and By-Products of Phosphates

**Table 7.1. Composition of phosphate rock from domestic producing field for use in superphosphate manufacture**

Constituent	In Florida land pebble <sup>(a)</sup>		In Tennessee rock <sup>(b)</sup>		In western rock <sup>(c)</sup>	
	66-68 BPL Percent	70-83 BPL Percent	66-68 BPL Percent	70-83 BPL Percent	60-68 BPL Percent	70-83 BPL Percent
P <sub>2</sub> O <sub>5</sub>	30.5—32.6(21)	32.8—36.5(40)	27.9—32.4(15)	32.8—37.5(25)	27.5—32.5(30)	33.0—37.9(34)
CaO	45.0—47.4(7)	46.1—50.2(18)	41.9—45.2(4)	45.3—50.8(13)	43.7—45.2(7)	44.2—52.2(8)
MgO	.1—0.5(6)	.8—1.0(5)	.1—0.3(3)	.0—0.2(5)	.0—1.2(7)	.0—0.5(2)
Al <sub>2</sub> O <sub>3</sub>	.7—1.1(6)	.8—1.8(18)	1.4—3.1(4)	1.2—2.7(13)	1.0—1.9(7)	.3—1.7(8)
Fe <sub>2</sub> O <sub>3</sub>	1.5—2.6(6)	.6—1.9(18)	1.8—3.4(4)	.9—3.4(13)	.8—2.7(7)	.3—1.3(8)
K <sub>2</sub> O	.1—0.5(6)	.1—0.3(5)	.4—0.6(3)	.2—0.4(5)	.2—0.6(7)	.1—0.3(2)
Na <sub>2</sub> O	.4—0.6(6)	.1—0.6(5)	.1—0.3(3)	.1—0.3(5)	.2—0.8(7)	0.4(2)
CO <sub>2</sub>	3.6—4.4(6)	1.5—3.3(18)	1.0—2.4(4)	1.1—3.7(4)	.8—4.1(7)	1.2(1)
SO <sub>3</sub>	1.1—1.3(6)	.2—0.9(5)	.0—1.2(3)	.4—0.8(5)	.1—1.4(7)	.3—1.8(2)
SiO <sub>2</sub>	7.3—9.8(6)	7.4—8.4(5)	8.6—16.8(3)	1.9—8.1(15)	5.6—17.3(7)	2.5—5.6(8)
F	3.3—3.9(21)	3.4—4.0(40)	2.9—3.7(15)	3.4—4.0(25)	<sup>(d)</sup> 2.9—3.8(30)	3.8—4.4(30)
Volatile matter <sup>(e)</sup>	4.8—7.0(6)	3.0—6.1(5)	2.8—4.0(3)	2.7—5.9(5)	2.2—8.4(7)	1.9—7.2(8)

<sup>(a)</sup> Data from "Superphosphate: Its History, Chemistry and Manufacture", USDA and RWA, 349 pp.(1964). Supt of Documents, U.S. Government. Printing Office, Washington, D.C. 20402. Figures are on moisture-free basis (105°C); The samples contained 0.2 to 1.3% moisture.

<sup>(b)</sup> Figures in parentheses show number of analyses included in the range.

<sup>(c)</sup> Total Fe

<sup>(d)</sup> One analysis showed 6.9%; the specimen contained considerable fluorite

<sup>(e)</sup> Water, organic carbon, carbonate carbon, and nitrogen

Source: Farm Chemical Handbook

Phosphate rock is the only significant source of phosphorus chemicals, including fertilizers.<sup>3</sup> The composition of phosphate rock varies only slightly from source to source, as indicated in Table 7.1, except for trace elements like cadmium. Note that fluorine is a relatively constant proportion of most samples, averaging 3-4% by mass. Phosphoric acid (P<sub>2</sub>O<sub>5</sub>) is the end product of phosphate rock processing (See Table 7.2.). The world's largest producer is the U.S. U.S. production of crude phosphate rock in 1988 (1992) was 162.3 MMT (154.9 MMT). This was beneficiated by washing and flotation to yield 45.4 MMT (47 MMT) of marketable rock. This material contained 13.833 MMT (14.1 MMT) phosphorus pentoxide (P<sub>2</sub>O<sub>5</sub>).<sup>4</sup>

Table 7.2. Phosphoric acid & processed phosphates (P<sub>2</sub>O<sub>5</sub> content)

Country	1988		1991		1992 Production				1992 Home Deliveries			1992 Exports			
	Prod	Cons	Prod	Cons	P <sub>2</sub> O <sub>5</sub>	DAP	MAP	TSP	DAP	MAP	TSP	P <sub>2</sub> O <sub>5</sub>	DAP	MAP	TSP
Austria	44	50	24	11	29.6			9.3			2.5	7.0			6.9
Belgium	320(a)	135(a)	320(a)	120(a)	355.0			20.0			19.7	235.3	34.0	38.5	12.9
Denmark	0	59	0	38											
Finland	209	185	157	121	189.0							92.3			
France	684	687	430	451	430.6							112.0	0.8	1.1	
Germany (W)	110	313	75	242								15.7	4.2	0.7	0.7
Germany (E)		1		0											
Greece	166	176	168	199	120.3			0.6			0.6				
Italy	214	405	101	201	48.6							1.2			
Netherlands	320	390	330	320	256.2	50.0	15.0		3.5	0.3		111.1	37.5	17.2	115.3
Portugal	24	28		6											
Spain	580	409	470	375	415.0	51.1	60.8	11.5	54.7	60.8	12.6	33.0			
Sweden	165	131	90	100											
UK	215	325	40	180	60.0							2.8	0.8	0.8	
Others	42(b)	42(b)													
<b>W. Europe</b>	<b>3093</b>	<b>3336</b>	<b>2205</b>	<b>2364</b>	<b>1904.3</b>	<b>101.1</b>	<b>75.8</b>	<b>41.4</b>	<b>58.2</b>	<b>61.1</b>	<b>35.4</b>	<b>610.4</b>	<b>77.6</b>	<b>58.3</b>	<b>135.8</b>
Bulgaria					43.8			31.8			13.0				19.0
Czechoslovakia					6.5							1.8	0.2		
Poland					306.1			60.3			12.5	4.7	40.8	2.5	48.4
Romania					267.0	60.6		20.1	25.6		16.8		34.8		3.5
<b>E. Europe</b>					<b>623.4</b>	<b>60.6</b>		<b>112.2</b>	<b>25.6</b>		<b>42.3</b>	<b>6.5</b>	<b>75.8</b>	<b>2.5</b>	<b>70.9</b>
Turkey	230	589	180	325											
US	10071	9262	10591	10151	11154.4	6164.7	1104.8	865.5	2231.3	625.6	363.5	478.8	3895.6	423.7	484.3
<b>World</b>	<b>28660</b>	<b>27724</b>	<b>26509</b>	<b>25930</b>	<b>24892.0</b>				<b>4856.7</b>	<b>2456.7</b>	<b>1760.9</b>	<b>3741.0</b>	<b>5743.0</b>	<b>1663.0</b>	<b>1627.0</b>

Source: Kemira, USBuMines

(a) Luxembourg included

(b) Cyprus

DAP = Diammonium phosphate

MAP = Mono-ammonium triphosphate

TSP = Triple superphosphate

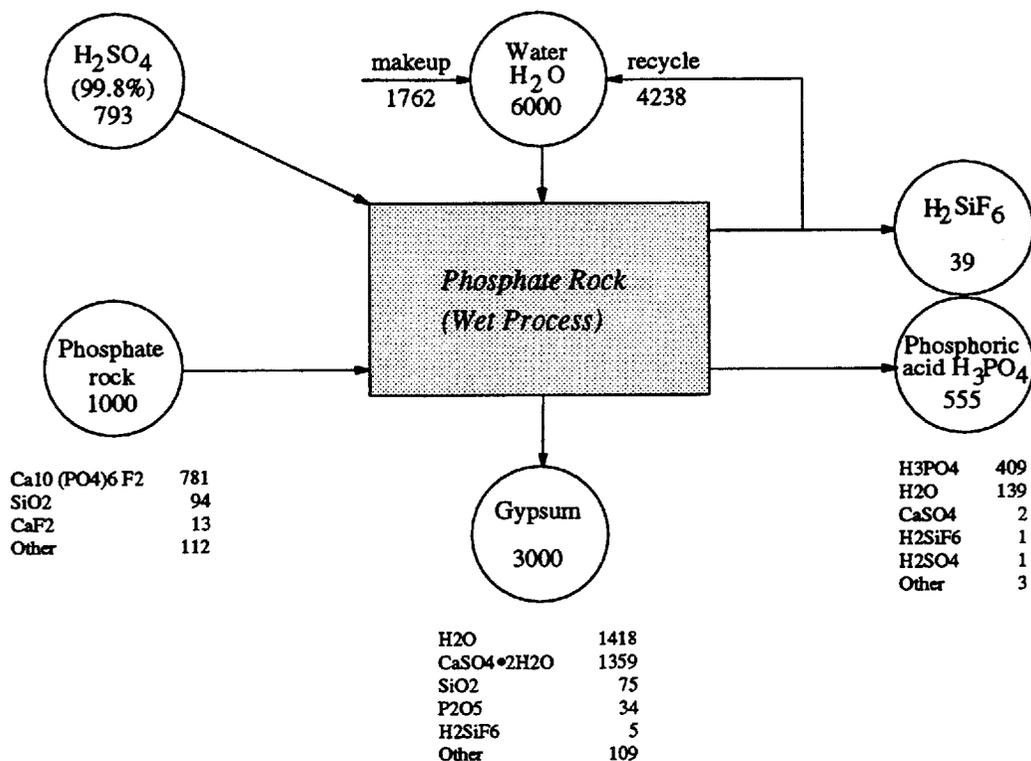


Figure 7.1. Materials balance for wet process treatment of phosphate rock concentrate

The phosphate rock was reduced by the so-called "wet process" — essentially digestion by sulfuric acid. The phosphate rock was reduced by the so-called "wet process" — essentially digestion by sulfuric acid. In 1988 (1992) 37.4 MMT (39.2 MMT) of phosphate rock were reduced to 30.6 MMT (33.8 MMT) fertilizer grade phosphoric acid with 10 MMT (11.2 MMT) phosphoric acid content. A schematic diagram of the "wet process" is shown in Figure 7.1. Phosphate rock processing in 1988 (1991) consumed about 25.5 MMT (25.4 MMT) of 100% sulfuric acid or 8.4 MMT of sulfur. This was more than 68% (67%) of total U.S. sulfur consumption in 1988 (1991) respectively (see Chapter 6 Sulfur). It is worth noting that approximately 1.8 kg of water is used in the process for each kg of phosphate rock processed. Of the 1.8 kg of water used, 1.4 kg is discharged. The remainder is water of hydration combined with calcium sulfate. The sulfur content of the sulfuric acid is disposed of as calcium sulfate ("phospho-gypsum") waste. According to Figure 7.1 about 3 kg of gypsum is produced per kg of phosphate rock, while 1.8 kg of process water used, of which 1.4 kg is discharged. The remainder is water of hydration combined with calcium sulfate. The sulfur content of the sulfuric acid is disposed of as calcium sulfate ("phospho-gypsum") waste. On this basis, phospho-gypsum production for 1988 (1992) would have been 75 MMT (72 MMT)

Actually, the US Bureau of Mines reports that phospho-gypsum generated by the wet process and disposed of on-site in the U.S. only amounts to 30 MMT per year [USBuMines 1991 "Phosphate Rock"]. This seems too low, and may be an underestimate. In addition, other mineral (mainly silica) wastes from phosphate rock processing in 1988 (1992) amounted to approximately 117 MMT (108 MMT), dry. Evidently this one process also accounts for virtually all of the waste from the entire fertilizer sector in the U.S. and most of the waste (in mass terms) from the whole U.S.<sup>5</sup>

The phospho-gypsum component of the waste is recoverable in principle and could be used for Portland cement and/or for building materials (e.g. plaster board). That is to say, the by-product phospho-gypsum could be used for exactly the same purposes as natural gypsum. It is not recovered for use in the U.S. due to the presence of contaminants. In fact, it is classified as a hazardous waste because of contamination by phosphoric acid and traces of radio-active elements. It is thus a major disposal problem for the phosphate fertilizer industry. In practice, natural gypsum is still mined on a large scale (see below).

At present, in the U.S. (also Morocco, Tunisia, Jordan and Israel) sulfuric acid is generally produced on-site at the phosphate rock processing facility. The waste heat from the exothermic sulfuric acid production process can then be utilized to generate electricity and concentrate the phosphoric acid product from 30% to higher strengths needed for producing ammonium phosphates (MAP, DAP) or merchant phosphoric acid (54%). However, in Europe, the practice has been to import beneficiated phosphate rock to a convenient continental site such as Hamburg, Rotterdam or Antwerp, where the sulfuric acid is also produced.

A significant by-product of phosphate rock processing in the U.S. in 1988 was 46,565 MT (0.047 MMT) of fluosilicic acid, with a fluorine content equivalent to 90,000 MT of fluorspar. This was largely (75%) used for municipal water fluoridation; the remainder was mostly consumed by the aluminum industry to produce aluminum fluoride, which is used in the Hall process. (See *Chapter 2, Aluminum*). A very small amount of fluosilicic acid is consumed in Europe, apparently from Swedish sources. However there is obviously no technical reason for failing to recover fluorine from Moroccan and other phosphates imported into Europe.

### 7.3. Uses of Phosphorus

Fertilizers (SIC 2873) accounted for 94% of all phosphorus used; of this 31% was consumed domestically and 63% was exported. Chemicals accounted for the other 6%, of which 5% was consumed domestically. Most of the phosphate rock that was processed domestically (94%) was converted into "wet process" phosphoric acid ( $H_3PO_4$ ). Elemental phosphorus production accounted for the remainder. Phosphorus production in the U.S. in 1991 was 0.25 MMT (0.615 MMT  $P_2O_5$  equivalent), of which 85% is reconverted to "furnace grade" phosphoric acid for chemical manufacturing. Some of this phosphoric acid goes back into fertilizer (to make triple superphosphate), but about 40% of it was used to manufacture sodium tripolyphosphate, or STPP ( $Na_5P_3O_{10}$ ), a detergent builder.

U.S. production of all sodium phosphates in 1991 was 0.4 MMT, with a phosphorus content of about 0.1 MMT. Detailed data for Europe are not available. Production of these chemicals has been declining since at least 1980. This appears to be due to the introduction of a competing type of detergent builder, namely zeolites together with polycarboxylic acid. These have virtually taken over the market in Germany, Italy, Switzerland and the Netherlands, due to concerns about the eutrophication of lakes, rivers and streams. Phosphate detergents have also lost some market share in the U.K. from 67% in 1991 to 54% in 1993. Declining use of phosphates also occurred in France, Belgium, Sweden and Denmark [ENDS Report 228, Jan. 1994].

Table 7.3. Composition of detergents

Components	Standard Detergents			Compact Detergents			
	With Phosphates (%)	Without Phosphates (%)	Difference	With Phosphates (%)	Compared to Standard Detergent	Without Phosphates (%)	Compared to Standard Detergent
Sodium Tripolyphosphate (TPP)	20-25	0	--	50	++	0	0
Zeolite	0	25	++	0	0	20 to 30	+
Polycarboxylates (PCA)	0	4	++	0	0	5	+
Organic Phosphonates	0 to 0.2	0.4	+	0	-	0.2	-
Sodium Silicate	6	4	-	5	-	4	0
Sodium Carbonate	5	15	++	4	-	15 to 20	++
Surface Active Agent	12	15	+	14	+	15	0
Sodium Perborate	14*	18	+	10**	*	13	*
Activator	0 to 2	2.5	++	3	++	5	++
Sodium Sulfate	21 to 24	9	--	4	--	5	-
Enzymes	0.3	0.5	+	0.8	++	0.8	+
"Antiredeposition" Agents	0.2	0.2	0	0.3	+	0.3	+
Perfume	0.2	0.2	0	0.2	0	0.2	0
Water	10	5	-	8	-	5	0
Total	100	100		100		100	

\* Tetrahydrate Perborate is used in standard detergents

\*\* Monohydrate Perborate is used in compact powders. Its power is much higher than Tetrahydrate Perborate

Source: Information Chimie n°341, Sept. 1992

However the so-called "compact detergents", introduced in 1988 may have actually reversed the trend. Whereas traditional detergents contained 20-25% STPP, the compact detergents increase this to 50% [Info Chimie 9-92]. See *Table 7.3*. The effect is that some consumers use less detergent, but with a higher phosphorus content. On the other hand, some European countries (e.g. Switzerland) do not permit phosphates to be used in detergents because of concerns about eutrophication of lakes.

Some phosphoric acid is used as a flavoring agent in the food and soft drink industry. A minor but growing use of phosphorus is in the manufacture of lubricating oil additives such as zinc dithiophosphate, which starts from phosphorus pentasulfide (made by direct reaction of phosphorus metal and elemental sulfur). This use accounted for 0.015 MMT of phosphorus metal in 1974; it is probably greater today.

The starting point for organic phosphate synthesis is phosphorus trichloride ( $\text{PCl}_3$ ). Production figures are not published, but on the basis of absorbing 1% of chlorine output (see chlorine below), we can conclude that about 0.03 MMT of phosphorus metal would have been required. The trichloride is later converted to phosphorus oxychloride ( $\text{POCl}_3$ ) by direct reaction with chlorine and phosphorus pentoxide  $\text{P}_2\text{O}_5$ . The oxychloride, in turn, is the basis of organic phosphate esters that now have many uses. The most important of them is the plasticizer tricresyl phosphate (TCPP). Phosphate esters are also used as flame retardants and fire resistant hydraulic fluids. Such phosphate esters totalled .043 MMT ( $\text{P}_2\text{O}_5$ ) in 1990 [USITC 1991]; detailed data for each chemical are not published, but the phosphorus content is rather small (8.5% in the case of TCPP). TCPP is also used as a gasoline additive.

All of the uses mentioned above are inherently dissipative. No more than 0.2 MMT of elemental phosphorus is embodied in chemicals used to manufacture other chemical products (mainly detergents). Uses of phosphorus are summarized in the pie-chart *Figure 7.2*. In most cases the dissipation does not occur within the chemical industry itself (SIC 28), however.

The only practical way to cut down on phosphate demand would be to discover ways of remobilizing biologically unavailable phosphates in the soil. This is a worthwhile object of agricultural research, but at present it appears to be rather a distant prospect at best. Thus, the most promising approach to minimizing environmental harm associated with the use of phosphates in industry is to focus on opportunities to utilize wastes and by-products from mining and production.

Fluoride emission factors for phosphate rock processing have been estimated by the U.S. Environmental Protection Agency (EPA) [Martin 1974]. Their relevance to other countries (e.g. Morocco) can be inferred from the fact that the same factors were adapted by the World Health Organization for its guidebook for "Rapid Assessment of Sources of Air, Water and Land Pollution" [WHO 1982]. The averages for "wet process" phosphoric acid plants with holding ponds for waste gypsum, with supernatant water recycling, are assumed to be 11.2 kg/tonne of anhydrous  $\text{P}_2\text{O}_5$ . For "wet process" plants with no ponds, dissolved fluoride emissions in waste water are assumed to be 22.2 kg/tonne.

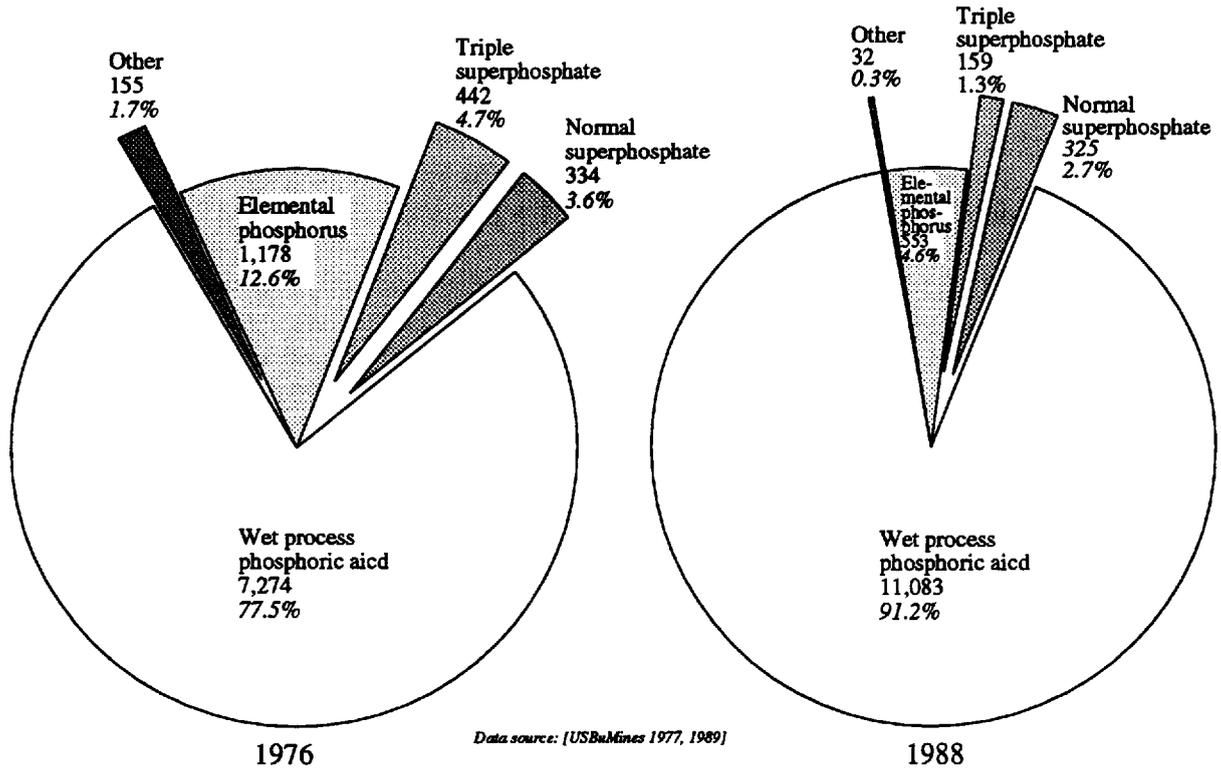


Figure 7.2. U.S. phosphorus production 1976 & 1988 (kMT). Data [USBuMines 1977, 89]

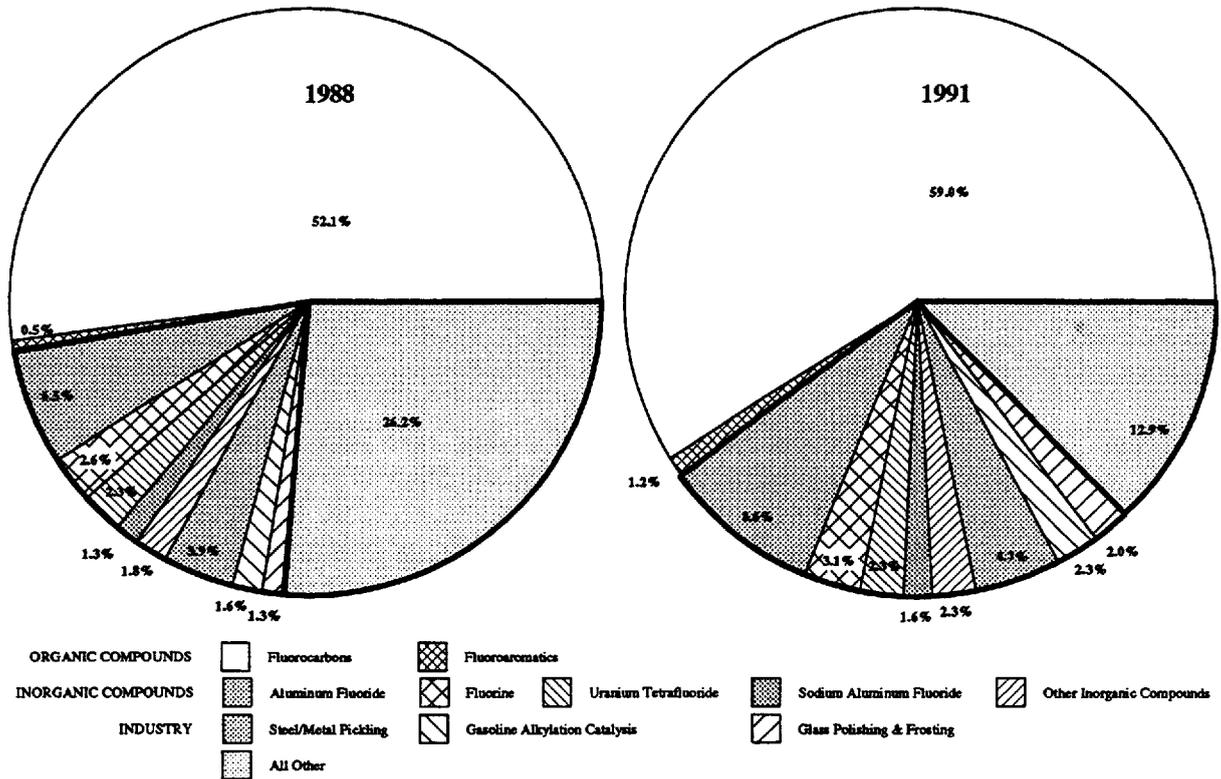


Figure 7.3. Western European consumption of hydrofluoric acid by end-use. Data source: ECOPLAN 1992

Based on western European production (1991) of 2.34 MMT of phosphoric acid, mostly from imported phosphate rock, it can be inferred that 52 KMT of dissolved fluorides were generated in Europe, of which about half may be stored in holding ponds and the rest was probably dumped into rivers. We do not know the fluorspar equivalent of this potential resource, but it seems possible that fluosilicic acid recovery could be considerably increased, replacing a significant fraction of imported fluorspar. See *Table 7.4.* on fluorspar mining and hydrofluoric acid production. Hydrofluoric acid uses in Europe are shown in *Figure 7.3.*

**Table 7.4. Hydrofluoric acid & fluorspar 1991 (kMT)**

<i>Country</i>	<i>HF Production</i>	<i>Acid Spar Production</i>	<i>1991 Consumption</i>
Austria			
Belgium	5.0		(a)
France	34.4	64	72.2
Germany (W)	72.9		153.1
Germany (E)			
Greece	8.8		18.5
Iceland			
Ireland			
Italy	54.4	16	114.2
Netherlands	7.2		15.1
Norway		16	
Spain	25.2	18	52.9
Sweden		(b)	
Switzerland			
United Kingdom	57.6		121
<b>W. Europe</b>	<b>265.5</b>	<b>124+(b)</b>	<b>547</b>

(a) from fluosilicic acid (b) +16 kMT fluosilicic acid

## 7.4. Sources and Uses of Fluorine

Fluorine is commercially extracted from a single mineral fluorspar, consisting of calcium fluoride, and various contaminants, notably silica. It is mined in a number of countries, especially China (by far the largest producer), Mongolia, Mexico, the former USSR and South Africa. Identified world resources of the mineral (as of 1991) were 365 MMT of contained fluorspar — of which 239 MMT were classified as "reserves" and the remainder currently subeconomic — as compared to 325 MMT in phosphate rock deposits. (Only 32 MMT of the latter are in domestic U.S. phosphates).

Most mined fluorspar must be beneficiated, usually by gravity separation or froth flotation. The beneficiation process generates significant wastes. There are three commercial grades, metallurgical grade (>60% "effective" CaF<sub>2</sub>), ceramic grade (85%-96% CaF<sub>2</sub>) and acid grade (> 97% CaF<sub>2</sub>). Metallurgical grade fluorspar is used as a flux in iron and steel-making, and in foundries. It reduces the melting point of slag, making it more liquid and also more reactive, thus making it more soluble for lime and other fluxes which can react with undesirable impurities (such as sulfur) in the metal. For this purpose silica is an undesirable contaminant, whence "effective" CaF<sub>2</sub> is calculated as actual CaF<sub>2</sub> minus 2.5 times actual silica content. Ceramic grade fluorspar is also used as a flux, mainly in the glass industry (it is also an "opacifier" for certain types of glass); small amounts are used in other industries.

Acid grade fluorspar is used to manufacture hydrofluoric acid (HF), from which most fluorine chemicals are derived. The process involves direct reaction with sulfuric acid, yielding calcium sulfate (gypsum) as a waste product. Approximately 3.6 tonnes of  $\text{CaSO}_4$  is generated per tonne of anhydrous HF product.

By far the largest use of HF is in the manufacture of chlorofluorocarbons (CFC's). The three major CFC's (CFC 11, CFC 12 and CFC 113) are in the process of being phased out, because of their ozone-depletion potential. Some of the possible substitutes are HFC's, which are more completely fluorinated molecules that contain no chlorine. Thus, the phaseout of CFC's does not necessarily imply a sharp reduction in demand for HF. In fact, the reverse is actually a (slight) possibility.

The technology for producing HF from impure fluosilicic acid ( $\text{H}_2\text{SiF}_6$ ) — the most likely fluorine-containing by-product of phosphate rock processing — is apparently not yet fully developed. One process that has been described in detail is a two-stage reaction. The first stage is to react the acid with ammonia, yielding ammonium fluoride and silica ( $\text{SiO}_2$ ), which precipitates out of solution. In the second stage ammonium fluoride reacts with calcium hydroxide (from lime and water), regenerating the ammonia and yielding solid  $\text{CaF}_2$ . The process is, of course, somewhat more complex than this simple description, due to the various filtration and drying stages that are needed in practice.

The virtue of the above scheme is that it produces the equivalent of commercial acid-grade fluorspar. Another process that has recently been developed by the Phosphate Engineering and Construction Co., of Lakeland Fla., is to react fluosilicic acid with phosphate rock itself. This yields marketable phosphoric acid and calcium silicon hexafluoride ( $\text{CaSiF}_6$ ). The latter is hydrolyzed to produce silica and calcium fluoride. These are separated by gravity (settling) and/or centrifuging. The latter is then converted to hydrofluoric acid (HF) in the usual way.

The virtue of the above schemes is that they produce the equivalent of commercial acid-grade fluorspar, which has a ready market. A short cut that avoids the production of solid  $\text{CaF}_2$  would, however, make sense. There are two possibilities. One is to develop fluorination processes that utilize ammonium fluoride as a starting point. This seems rather a distant prospect, at best. The other is to produce HF directly from ammonium fluoride. This could be done, in principle, by reacting it with sulfuric acid, yielding ammonium sulfate — a valuable fertilizer — and HF.

The aluminum industry has developed a process to make aluminum fluoride (for the Hall-Heroult electrolytic smelting process) directly from fluosilicic acid, by reacting it with aluminum hydroxide. We do not have any further details of this process, however.

Although *Figure 7.1*, describing phosphate processing in the U.S. indicates fluosilicic acid recovery, this is apparently not much practiced outside the U.S. Enhanced fluorine recovery would have two immediate and direct advantages. First, it would reduce both the need for mining and processing fluorspar, and the waste emissions from those processes. Second, recovery of fluosilicic acid (or silicon tetrafluoride) from phosphate rock processing would automatically reduce harmful fluorine emissions from phosphate rock processing facilities. We have no data on health problems arising from this activity in Europe. However anecdotal evidence suggests that the problem may be quite severe in some less developed countries.

A third possible benefit suggests itself: more sophisticated processing to increase recovery of fluorine from phosphate rock might also increase the technical and economic feasibility of removing the undesirable cadmium contamination from phosphate fertilizers used in Europe.

## 7.5. Gypsum Sources & Uses

As noted previously, about 100 MMT of the mineral gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) was mined globally in 1989. Production has been increasing at a steady pace. It is mined in over 80 countries. Reserves are large. Most production is consumed domestically, although the U.S. is also a large importer (from Canada and Mexico). Some countries have no known gypsum resources (e.g. Scandinavia). See *Table 7.5.* on gypsum mining.

The U.S. is the largest producer of natural gypsum (16 MMT). Other large producers include Canada, China and Iran. Production in Western Europe as a whole was 19.426 MMT while Eastern Europe accounted for another 4.5 MMT. In the U.S. about 8% of gypsum was used without calcination in agriculture (as a soil conditioner for alkaline soils). The remainder is calcined, by the low temperature process (159 degrees)



Of this, 13 % was used as a cement additive and the rest (79%) was used to make prefabricated wallboard products. Use as "plaster-of-Paris", for manual application, has largely disappeared.

Europe can be assumed to have a roughly similar use pattern, except that plaster for manual application continues to have a significant market, especially in housing renovation. Yet, it should be recalled that plaster-of-Paris once enjoyed a much wider range of uses. Before the discovery of Portland cement (c. 1815) it was used as mortar for stone buildings, as the basis for a form of concrete, and as a fireproofing agent.<sup>6</sup>

The French phosphate producer APC has a plant at Ottmarsheim, in Alsace on the Rhine River. At this plant the phospho-gypsum by-product is purified by double crystallization. The product is calcined and used to make plasterboard by PREGYPAN [Pichat 1982]. Since 1980, APC has developed a satisfactory single-crystallization purification process [ibid]. APC also has a phosphoric acid plant on the Seine River, near Rouen, in France. Wastes were towed by barge to the mouth of the Seine and dumped, causing pollution and distress to the local

**Table 7.5. Gypsum mining 1991 (kMT)**

Country	Gypsum Mines (MMT)
Austria	625
France	5569
Germany (W)	1850
Germany (E)	1850
Greece	500
Ireland	314
Italy	1250
Portugal	300
Spain	5500
Switzerland	218
UK	3990
<b>W. Europe</b>	<b>19426</b>
Bulgaria	400
Czechoslovakia	775
Hungary	115
Poland	1090
Romania	1595
Yugoslavia	550
<b>E. Europe</b>	<b>4515</b>
Turkey	250
USSR	4800
US	16000
<b>World</b>	<b>100000</b>

Source: [USBuMines 1991]

fishermen and tourists at Deauville. To avoid this necessity, APC developed a new product called "foamed" or "cellular" gypsum. It is very light (specific gravity 0.5), yet has good compression strength (10-15 bars) and good thermal insulation (0.12 watts per square meter per degree Celsius). It is also fire resistant, a good acoustic absorber, and an effective humidity regulator (since it takes up water from the air at high levels of external humidity, and releases it at low external humidity levels [ibid]). It can be poured into molds on a building site, or cast into blocks.<sup>7</sup> It hardens in 15 minutes. Houses have been built from this material in Douvrin and Rennes, France, and in Senegal [ibid].

Other uses of phospho-gypsum have been reported (e.g. at the International symposium on phospho-gypsum, Orlando Florida, Nov. 1980). Examples that do not require calcination include the following [Pichat 1982]:

- (1) Cement production. Gypsum regulates the setting of portland cement. About 5% of the mass of clinker typically consists of gypsum.
- (2) Phospho-gypsum (PG) can be mixed with slag or fly ash (see *Chapter 13 Coal Ash*) to make a quick-setting binder, as a partial substitute for lime. The combination 90% fly ash, 5% lime and 5% PG has been successfully used for roadbuilding in several locations.
- (3) Paper filler (e.g. as a substitute for kaolin). APC has a proprietary process.
- (4) Soil conditioner for tight clay soils. The  $\text{Ca}^{++}$  neutralizes the charges on the clay particles and encourages flocculation into a more granular form.
- (5) Reclamation of salt buildup in alkaline-clay soils. PG can displace the sodium ions that bind to clay particles, thus allowing them to be removed by percolation with ground water.
- (6) Drainage clearing. Pipes draining marshy lands can be clogged by ferric clay complexes. These can be flocculated by PG, reopening clogged drains.

To substitute wet phospho-gypsum for natural gypsum would primarily require dehydration. (The presence of trace quantities of uranium or thorium could be a problem in some locations). The major requirement, however, is heat. Much of the needed heat could be waste heat (or low grade fuels) from other processes, such as steel mills or petroleum refineries. The key to success is almost certainly to integrate the phosphate rock processing with other heat-generating activities.

Thus, it would make particular sense to integrate phosphate rock processing in Europe with petroleum or gas refining and/or non-ferrous metal refining. This would seem to be quite feasible, given that all of these processes tend to be located near major seaports or riverports. This would make it possible to convert the sulfur recovered from fuel processing directly to sulfuric acid at the same location where it will be used subsequently. Insofar as possible, view of the above uses for phospho-gypsum, it would make sense for a phosphate producer to locate near an agricultural area characterized by clay soils. Finally, it would also make sense

to co-locate with a building materials producer, a paper manufacturer, and possibly a fluorine chemicals user.

## References(7)

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## Endnotes(7)

1. We thank Philippe Pichat, of ADT, Paris, for providing us with important information with regard to current and possible uses of phospho-gypsum.  
  
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2. There seems to be evidence that some deposits of the mineral apatite were formed by metamorphic geological processes on accumulations of sharks teeth! This seems bizarre, but it might explain why apatite usually contains fluorine.
3. Some phosphorus is recoverable from high phosphate iron ores. These ores were not usable for steel-making until the so-called Thomas process was invented in the later 19th century.
4. Phosphorus pentoxide dissolved in water is phosphoric acid, the active ingredient in most phosphate fertilizers (e.g. "superphosphates"). It is not used, generally, in pure form.
5. It is important to emphasize this fact; to associate an undifferentiated "waste coefficient" with the "fertilizer sector" as a whole, in a country without a phosphate rock processing industry, would be grossly misleading. By the same token, it must be recognized that most countries (such as Morocco and Algeria) with significant phosphate rock processing sectors do not bother to control fluoride emissions, still less recover the fluorine for beneficial use. In most of the world this industry is extremely hazardous to workers and nearby residents.
6. Many 17th century buildings in Paris, especially the Marais district, were constructed — foundations included — from plaster-based concrete and mortar. These buildings have survived to the present day, with continuous occupancy and little or no need for renovation. In fact, these old buildings appear to be as durable, or more durable, than current construction.
7. The on-site pouring technology has been developed by the French construction firm, BOUYGES; the casting technique was developed by the construction firm GTM.