

Phosphorus and Phosphates

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INTRODUCTION

Phosphates, compounds of the element phosphorous, are produced from relatively abundant supplies of phosphate rock.

The major use of phosphate is to supply phosphorous, one of the three essential plant foods, nitrogen, phosphorus, and potassium. Phosphate rock extraction from its ore, and its subsequent conversion into fertilizer materials and industrial chemicals, is a relatively mature art. Single superphosphate, a mixture of monocalcium monohydrate and gypsum formed by the reaction of sulfuric acid with phosphate rock, has been used as a fertilizer since the mid-1800s. Phosphoric acid, derived by the treatment of phosphate rock with sulfuric acid so as to produce gypsum in a separable form, was manufactured in many locations by batch and countercurrent decantation methods in the 1920s.

Phosphoric acid produced by the later process is called the "wet process acid" to distinguish it from "furnace phosphoric acid,"

which is produced by hydrating the phosphorous pentoxide formed by burning elemental phosphorous in air. The "wet" processes utilized for the bulk of today's phosphoric acid and fertilizer production trace their origins to the early 1930s.¹

Higher-purity industrial and food-grade phosphates, until recently, were most often derived from furnace processes. New plants recover purified phosphoric acid suitable for food-grade uses from relatively impure wet process acid, using solvent extraction technology.

PHOSPHATE ROCK

Naturally occurring mineral products having sufficient phosphate content to be of commercial value are classified as phosphate rock. The grade or phosphate content of these products has been traditionally reported as percent $\text{Ca}_3(\text{PO}_4)_2$, which is referred to as bone phosphate of lime (BPL), tricalcium phosphate (TCP), or triphosphate of lime (TPL). Stoichiometric factors relating traditional rock analysis to other commonly used analytical

*Jacobs Engineering. D. W. Leyshon's contribution to the previous edition has been updated.

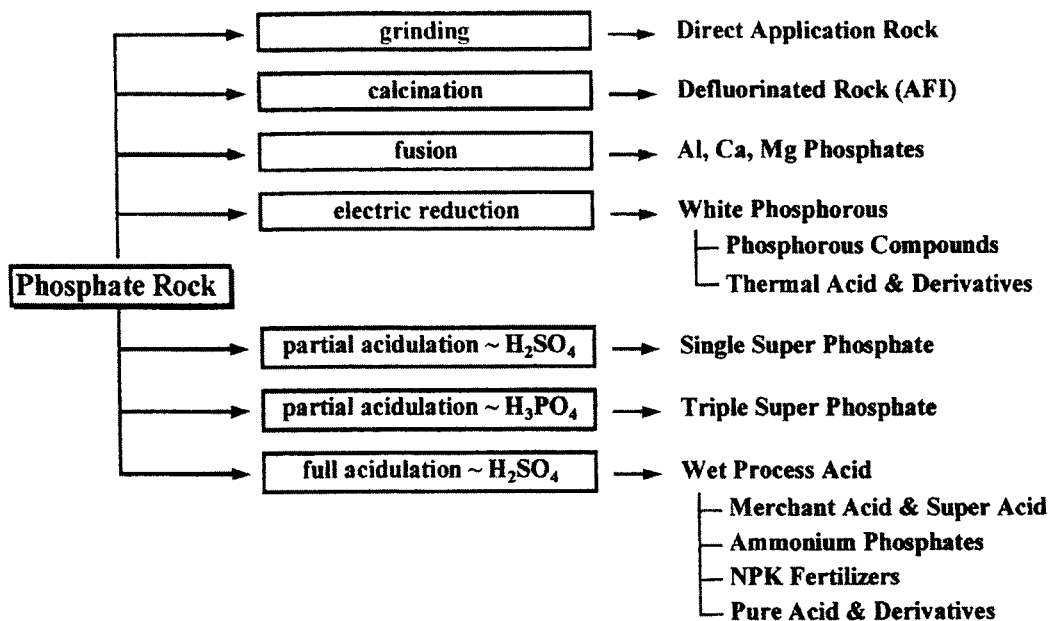


Fig. 23.1. Phosphate rock treatments and end products.

terms are 100.00 percent BPL = 45.77 percent P_2O_5 = 19.96 percent P.

International trade of phosphate rock is based on dry metric tons, whereas U.S. domestic sales are in short tons, on a dry or as is moisture basis. Specifications for purchased rock may address grade, particle size, moisture content, and chemical impurities such as CaO, MgO, SiO_2 , Al_2O_3 , Fe_2O_3 , F, Cl, Na_2O , and K_2O . The content of organic material and heavy metals is also of importance.

The treatments by which phosphate rock is commonly converted to fertilizers and chemicals are summarized in Fig. 23.1.

Minerals

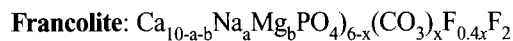
The most common and widely distributed phosphate minerals are the apatite group, with the general formula $Ca_{10}(PO_4)_6(X)_2$. The apatite is designated as fluorapatite, hydroxyapatite, or chlorapatite, when $X = F, OH,$ or Cl , respectively. The most abundant sedimentary apatite is carbonate fluorapatite (francolite). Relative to pure fluorapatite, francolite is characterized by the substitution of Na and Mg for Ca and of carbonate and fluoride for phosphate. An empirical formula for francolite

TABLE 23.1 Composition of the Fluorapatite–Francolite End Series

Constituent	Fluorapatite	Francolite
%CaO	55.60	55.40
% P_2O_5	42.20	34.00
% CO_2	—	6.30
%F	3.77	5.04
% Na_2O	—	1.40
%MgO	—	0.70

Source: McClellan.²

is given below and the chemical compositions of the end members of the fluorapatite–francolite series, as quantified by McClellan,² are given on Table 23.1.



Van Kauwenberg³ has described the mineralogy and alteration of phosphate ores in Florida. Mineralogical composition varies by particle size. Francolite and then quartz are the most abundant minerals for plus 20-mesh particles (pebble), while the reverse is true for particles in the 20–200-mesh fraction (flotation feed). In the minus 200-mesh size fraction (clay waste) quartz, francolite, wavellite, crandallite, goethite, dolomite, and a variety

of clay minerals such as smectite, kaolinite, illite, and palygorskite occur.

Resources and Ores

Naturally occurring phosphates exist, or originated, as accessory minerals in igneous rocks. Prolonged weathering gradually converts the water-insoluble apatite into dissolved compounds that accumulate in the world's oceans. Sedimentary marine deposits (phosphorites) are formed when phosphorous compounds are precipitated by chemical or biological reactions. Bernardi⁴ describes secondary enrichment as an important aspect in the formation of sedimentary deposits.

McKelvey⁵ reported that the earth's crust contains an average of 0.27 percent P_2O_5 , most of which occurs as apatite species. Sedimentary rocks, which predominate at the earth's surface, host the majority of commercial phosphate deposits discovered to date. Igneous rocks, which make up about 95 percent of the earth's crust, contain few phosphate deposits of commercial value. Guano deposits formed from the droppings of sea birds or bats are of minor importance, as are guano-related deposits. Northolt^{6,7} describes known phosphate deposits in the world, and estimates that identified phosphate resources in North America total more than 35 billion metric tons.

Resources are typically quantified as in situ tons of phosphatic material, without regard for economic criteria. However, it is preferable to quantify phosphate reserves as tons of phosphate rock recoverable according to specified economic, chemical, and regulatory criteria.⁸ The definition of phosphate reserves therefore requires an integrated program of geological exploration, laboratory testing, and classification using applicable criteria.

Significant commercial deposits of sedimentary phosphate ore occur in the United States, the Former Soviet Union, Morocco, China, Jordan, and Tunisia, and lesser deposits are mined in many other countries. Although phosphorite ores generally are classified as having siliceous or carbonate gangue minerals, soluble salts and organic material are also of concern. The phosphate content of the ores,

depending on conditions of deposition and secondary enrichment, ranges from 10 percent to more than 70 percent BPL. The recovery of by-products from phosphorite ores is uncommon; however, uranium has been extracted commercially from phosphoric acid.

The types of igneous rock in which commercial deposits of apatite have been found are nepheline-seyenite and carbonatites. The apatite deposits in Russia's Kola Peninsula are associated with nepheline-seyenite. Carbonatite deposits that are mined for their phosphate content include Siilinjärvi in Finland, Jacupiranga and Araxa in Brazil, Phalaborwa in South Africa, and Kapuskasing in Canada. By-product recovery from igneous phosphate ores is common. Nepheline ($NaAlSiO_4$) is recovered from the Russian ore, calcite from the Finnish ore, copper concentrate and baddelyite (ZrO_2) from the South African ore, and barite from Brazilian ore. A minor percentage of the world's phosphate rock production is recovered from guano-related phosphate deposits.

Mining

Phosphate ores are extracted from deep deposits by underground mining methods and from shallow deposits by surface mining methods. Underground mining tends to be more costly and therefore less common for phosphate deposits than surface mining. Because 1 ton of phosphate rock has only about 10 percent of the commercial value of 1 oz of gold, low-cost mining is imperative.

Sedimentary phosphate deposits are exploited by underground mining in China, Mexico, Morocco, and Tunisia. Generally, the flat laying ore is most economically extracted by room-and-pillar mining or long wall mining. Ore from deep sections of the igneous phosphate deposits in Russia's Kola Peninsula is mined by a block caving technique.

Many shallow deposits have unconsolidated ore covered by unconsolidated overburden. Large electric walking draglines are ideally suited for such deposits, as evidenced by their use at large capacity phosphate mines in the southeastern United States, Morocco, Jordan,



Fig. 23.2. Loading trucks with phosphate ore in Jordan.

Senegal, and Togo. Other deposits have overburden and ore that may be partially or fully consolidated. For these deposits, ripping or drilling and blasting are required to fragment the overburden and ore to the extent that they can be excavated. Power shovels, backhoes, and wheeled loaders are also commonly used for excavation. Figure 23.2 shows a hydraulic shovel loading phosphate ore into a haul truck in Jordan.

Bucketwheel excavators are used for overburden removal at phosphate mines in eastern North Carolina, Senegal, and Togo. One mine in central Florida has used cutter head dredges for both overburden removal and ore excavation.

The method of transporting ore from the mine to the beneficiation plant depends on ore characteristics, mining methods, and local infrastructure. Railroad transport has been practiced in Russia and Iraq. Haul trucks and belt conveyors are commonly used in China, Jordan, Mexico, Morocco, Russia, Syria, Tunisia, and the western United States. Slurry pipelines of 18–22 in. diameter, operating at less than 100 psig, are used exclusively in central Florida, north Florida, and eastern North Carolina. The pipelines may be extended up to 10 miles or more, by installing a series of centrifugal slurry pumps at 4000 ft intervals.

A typical Florida phosphate mining scheme, utilizing a dragline and slurry pipeline, is illustrated in Fig. 23.3. The dragline first exposes the phosphate ore (matrix) by stripping and casting the overburden into the adjacent mined area. The matrix is then dug by the dragline and placed in a slurry pit, where it is gunned with high-pressure water. Gunning the matrix, as shown in Fig. 23.4, transforms the unconsolidated ore into a slurry which is pumped to the beneficiation plant.

Beneficiation

Beneficiation, also known as mineral dressing or ore processing, may involve a variety of operations such as size reduction, size separation, mineral separation, dewatering, and thermal processing. Almost all phosphate ores require beneficiation to meet commercial specifications concerning particle size, moisture content, or chemical analyses.

The usual first beneficiation operation is size reduction, which may be achieved by crushing, grinding, or disaggregating by scrubbing and washing. Particle size reduction liberates mineral species so that they can be separated. Size separation usually follows size reduction. When gangue minerals are more indurated than the phosphate, it is often

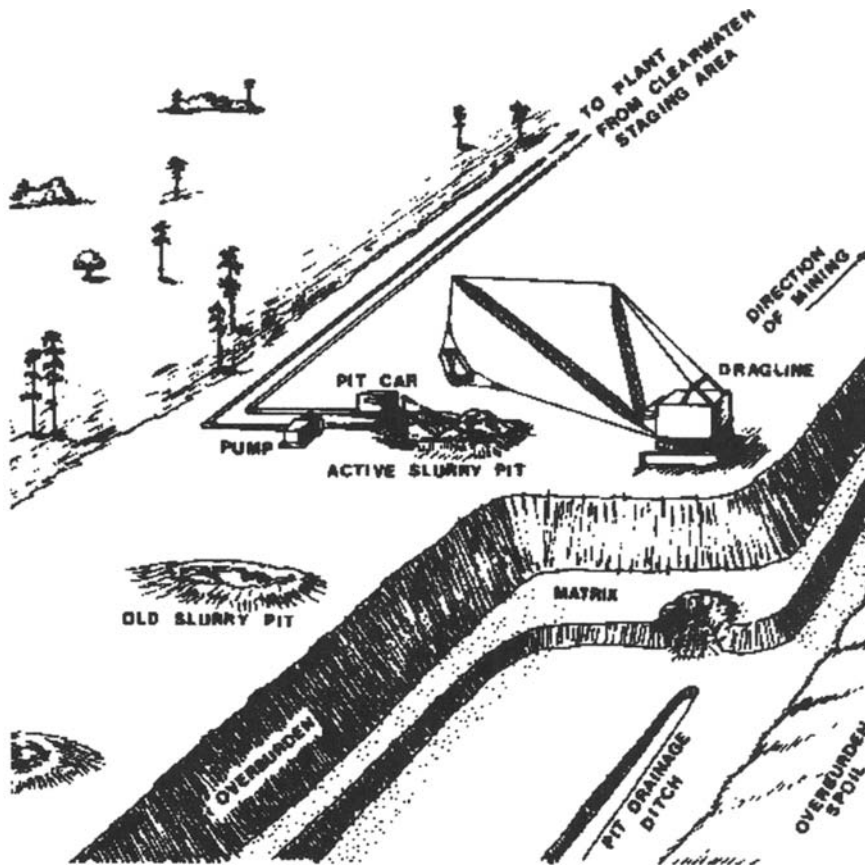


Fig. 23.3. Typical Florida phosphate mine.



Fig. 23.4. Gunning phosphate rock in a Florida mine.

practical to reject coarse waste material by wet or dry screening. Similarly, when gangue minerals are microcrystalline or softer than the phosphate, fine waste material may be rejected by wet or dry classification. Soluble chlorides, when present, must be removed from phosphate rock by washing with fresh water followed by dewatering.

Gangue minerals frequently have the same particle size as the phosphate mineral grains, and techniques such as heavy media separation, magnetic separation, or froth flotation are required. Heavy media separation is an appropriate process when liberation occurs at 16 mesh or coarser, and the phosphate mineral has a significantly higher density than the gangue (dolomite, calcite, quartz, shale). Low-intensity magnetic separation will remove highly magnetic minerals, such as magnetite,⁹ from phosphate. High-intensity magnetic separation will remove ankerite¹⁰ and other paramagnetic iron-bearing minerals¹¹ from

phosphate. Froth flotation is the most widely practiced operation for recovering phosphate rock from fines (-20 mesh). Variations of this process are used commercially to separate phosphate from barite, calcite, dolomite, feldspars, nepheline, phlogopite, and quartz. Flotation plants have been constructed and operated in Brazil, Canada, China, Finland, Jordan, Mexico, Russia, Senegal, South Africa and the United States. Dolomite flotation from phosphate is of increasing interest. In the United States, one commercial plant has a dolomite flotation circuit,¹² and other dolomite flotation processes have been demonstrated by pilot plant testing of Florida low-grade pebble.¹³

Electrostatic removal of quartz from apatite is technically feasible although it is impractical and costly.¹⁴

A generic scheme for mining and beneficiating central Florida phosphate ore is presented in Fig. 23.5 as a block flow diagram.

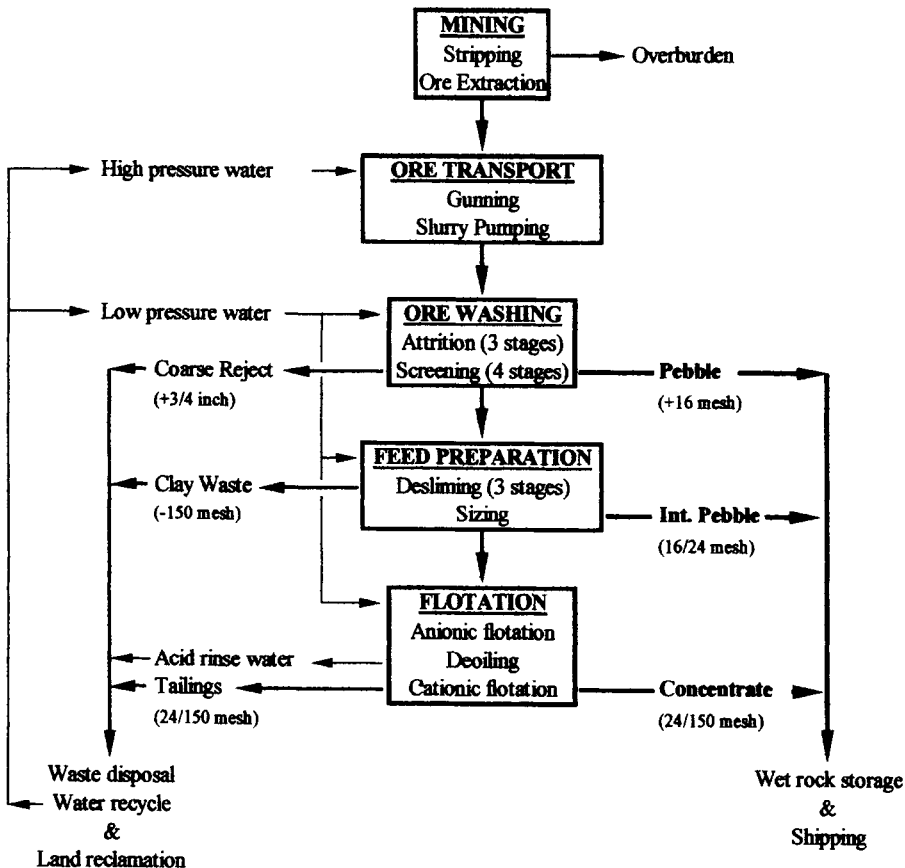


Fig. 23.5. Unconsolidated sedimentary ore beneficiation flow diagram.

Liberation of phosphate from the gangue occurs during ore transport and washing. First, a low-cost product, called pebble, is recovered by screening the ore at about 16 mesh. Secondly, a low-grade product (intermediate pebble) is recovered by sizing the flotation feed at about 24 mesh. Clays are removed from the flotation feed by three or more stages of desliming with hydrocyclones. Finally, a more expensive but higher grade concentrate is obtained by a two-stage flotation process. A rougher phosphate concentrate is recovered by direct flotation with anionic reagents. After deoiling with sulfuric acid and rinsing with water, the rougher concentrate is conditioned with cationic reagents and subjected to inverse flotation. The phosphate rock product, comprised of pebble, intermediate pebble, and flotation concentrate, dispatched to a chemical plant for conversion to phosphoric acid.

The initial beneficiation steps for consolidated phosphate ores generally differ from those of unconsolidated ores. Figure 23.6 depicts the flow diagram for the San Juan de la Costa phosphate mine in Mexico.

The high-grade ore, slightly more than 1 m in thickness, is extracted by room-and-pillar mining. Continuous miners rip ore from the mining face and load shuttle cars, which transfer the ore to feeder-breakers and a belt conveyor systems. Outside the mine, ore is loaded into haul trucks and transported to the beneficiation plant. Liberation of the phosphate is accomplished by crushing to 9 mm followed by grinding to 0.7 mm. Following grinding, the ore is deslimed, attrition scrubbed, and deslimed a second time to remove clays and carbonate minerals from the flotation feed. The feed is conditioned with anionic reagents and subjected to rougher and cleaner direct flotation using sea water. The concentrate is washed with fresh water to remove sea salt prior to use in the chemical plant.

Figure 23.7 presents a simplified mid-1980s flow diagram for the Siilinjärvi phosphate beneficiation plant in Finland. The low-grade igneous ore to this plant is carefully blended to avoid changes in plant feed characteristics. Liberation of phosphate is achieved by rod milling followed by closed

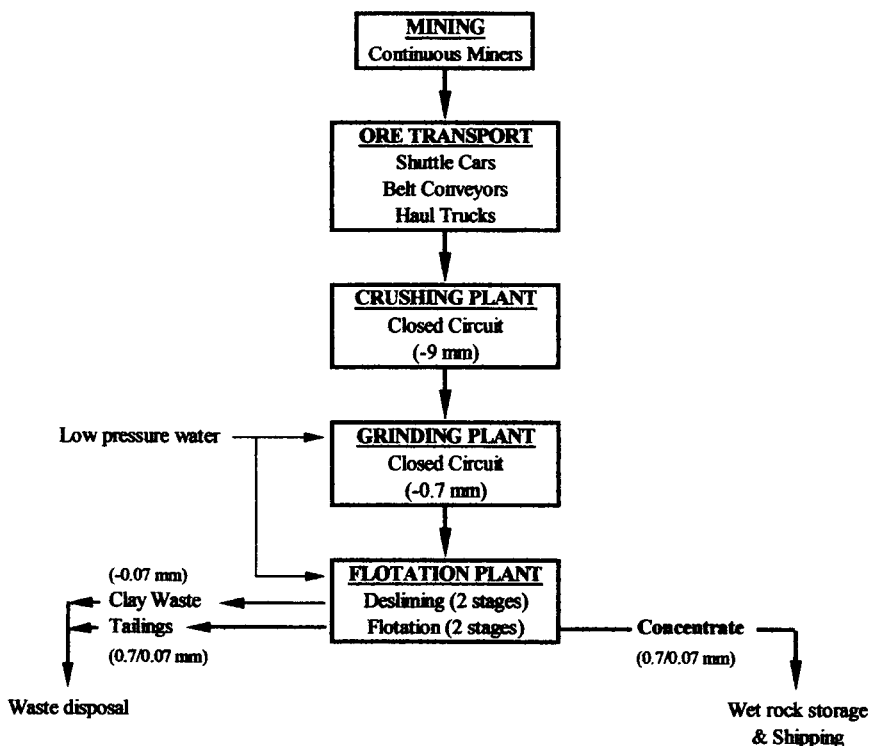


Fig. 23.6. Consolidated sedimentary ore beneficiation flow diagram.

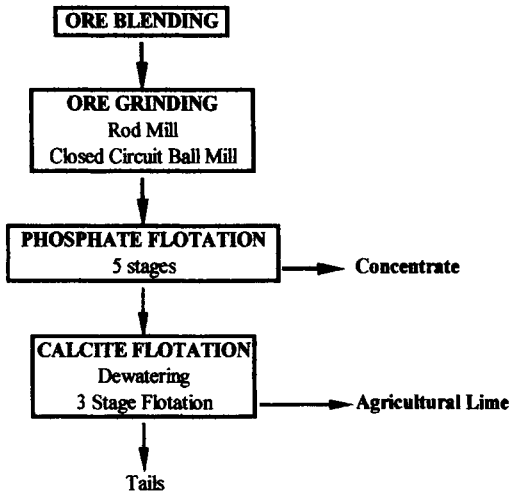


Fig. 23.7. Igneous ore beneficiation flow diagram.

circuit ball milling. The ground ore is conditioned without desliming, at pH 11, using an amphoteric flotation reagent. A phosphate concentrate is recovered by five stages of direct flotation. The tailings from phosphate flotation are dewatered, conditioned with anionic reagents, and subjected to three stages of direct flotation to recover calcite, which is used as agricultural lime.

Production and Value

The U.S. marketable production of phosphate rock over the last three decades is summarized in Table 23.2. Over the last two decades U.S. marketable production of phosphate rock has generally declined. If the post-1975 data were presented in constant dollars instead of current dollars, a more pronounced reduction in total value and a decline in unit value would be

TABLE 23.2 Phosphate Rock Value (United States Marketable Production)

Year	Total Value billion \$	Unit Value \$/metric ton
1975	1.107	25.00
1980	1.148	21.34
1985	1.236	24.31
1990	1.075	23.20
1995	0.947	21.75
2000	0.932	24.14
2004	1.003	27.12

Source: PHOSPHATE ROCK Annual Review, USBOM & USGS Mineral Industry Surveys.

evident. Because the unit value of phosphate rock has not kept up with inflation, it is increasingly difficult to justify the capital investment for new mines. Consequently, as U.S. phosphate mines have been depleted, their production capacities have not been replaced on a one-for-one basis. Nevertheless, as shown in Table 23.3, the United States remains the leading producer of phosphate rock.

The global demand for food stimulated increased fertilizer usage and consequently increased phosphate rock consumption through 1990. Over the last decade, rock production has been somewhat flat. Although production capacity has declined in the United States, new mine capacity has been added elsewhere. From Table 23.3 it is evident that significant increased phosphate rock production capability has been added in Morocco, China, Tunisia, Jordan, and the countries comprising Other.

Many countries use indigenous phosphate rock as a source of phosphorous for industrial

TABLE 23.3 World Production of Phosphate Rock (Million Metric Tons)

	1980	1990	2000	2001	2002	2003
United States	53.4	45.8	39.2	31.7	36.2	34.1
Morocco	18.8	21.2	21.6	21.8	23.0	23.3
China	10.7	17.3	19.4	21.0	23.0	24.5
USSR/Russia	24.7	36.9	11.1	10.5	10.6	11.1
Tunisia	4.6	6.6	8.3	8.1	7.6	7.9
Jordan	4.2	5.9	5.5	5.8	7.2	6.8
Other	22.2	22.8	26.6	26.5	28.2	29.0
Total world	138.6	156.5	131.6	125.4	135.8	136.6

Source: The International Fertilizer Industry Association (1990/2000).

TABLE 23.4 Major Exporters of Phosphate Rock (Million Metric Tons Exported)

	2000	2001	2002	2003
Morocco	10.5	10.9	11.1	11.0
USSR/Russia	4.5	3.4	3.3	3.3
China	3.4	4.9	3.1	3.6
Jordan	3.1	3.6	4.0	3.7
Syria	1.6	1.5	1.7	1.8
Togo	1.2	1.3	1.3	1.4
Tunisia	1.1	1.1	1.2	0.9
United States	0.2			

Source: International Fertilizer Industry Association.

chemicals and fertilizers. Few countries are self-sufficient and supplemental sources of phosphate rock are essential. The cost of imported phosphate rock is markedly influenced by freight, and therefore the low-cost producer is not necessarily the low-cost supplier.

The reduction in U.S. marketable production of phosphate rock has been accompanied by a reduction in exported phosphate rock. During the 1980s, U.S. phosphate rock exports declined from 14.3 to 7.8 million metric tons per year. As shown in Table 23.4, the decline in U.S. phosphate rock exports continued throughout the 1990s. Currently the United States is an importer of phosphate rock. Morocco has now replaced the United States as the major exporter of phosphate rock.

CHEMICAL PROCESSING OF PHOSPHATE ROCK

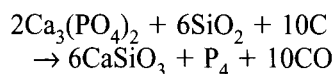
Phosphate rock is converted into usable chemicals by two methods. In the first, the rock is charged to an electric furnace with silica and coke to produce elemental phosphorus. The phosphorus then is converted into phosphoric acid and other compounds. In the second, the phosphate rock is reacted with sulfuric acid in a medium of phosphoric acid and calcium sulfate crystals to form dilute, impure phosphoric acid. The acid is separated and used to make fertilizers. This is known as the wet process method.¹⁵

The wet process is further divided into two subprocesses based on the type of calcium

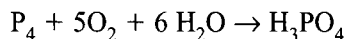
sulfate crystal produced. The dihydrate process wherein gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is produced has been the dominant process, but processes making hemihydrate ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) have become more important over the past decade.

Thermal Process for Phosphorus and Phosphoric Acid

The furnace or thermal process is shown in Fig. 23.8. The approximate reaction is:



The phosphorus leaves the furnace as a vapor and is condensed by direct contact with water. Phosphoric acid of high purity is made by burning phosphorus with air and hydrating the resulting P_2O_5 with water, according to the reaction:



If even less water is used for hydration, a product known as polyphosphoric acid results. Ordinary phosphoric acid is a solution of the monomer, H_3PO_4 , in water, and is called orthophosphoric acid. If a molecule of water is removed between two orthophosphate molecules, the dimer, pyrophosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$, is formed. Similarly, the trimer and higher polymers can be made. Superphosphoric acid is a mixture of orthophosphoric acid and polyphosphoric acid and is now made from wet process acid as described later in this chapter.

In 1990, there were about eight plants in operation, some with multiple furnaces, in the United States. By 2000–2001, only one plant remained. New emission standards, high capital and operating costs, and competitive lower-cost wet acid purification technology have spelled doom for most of the furnace plants. A more thorough discussion of electric furnace processing is to be found in the ninth edition of this *Handbook*.

Industrial Phosphates

Furnace phosphorus currently produced in the United States is consumed to make

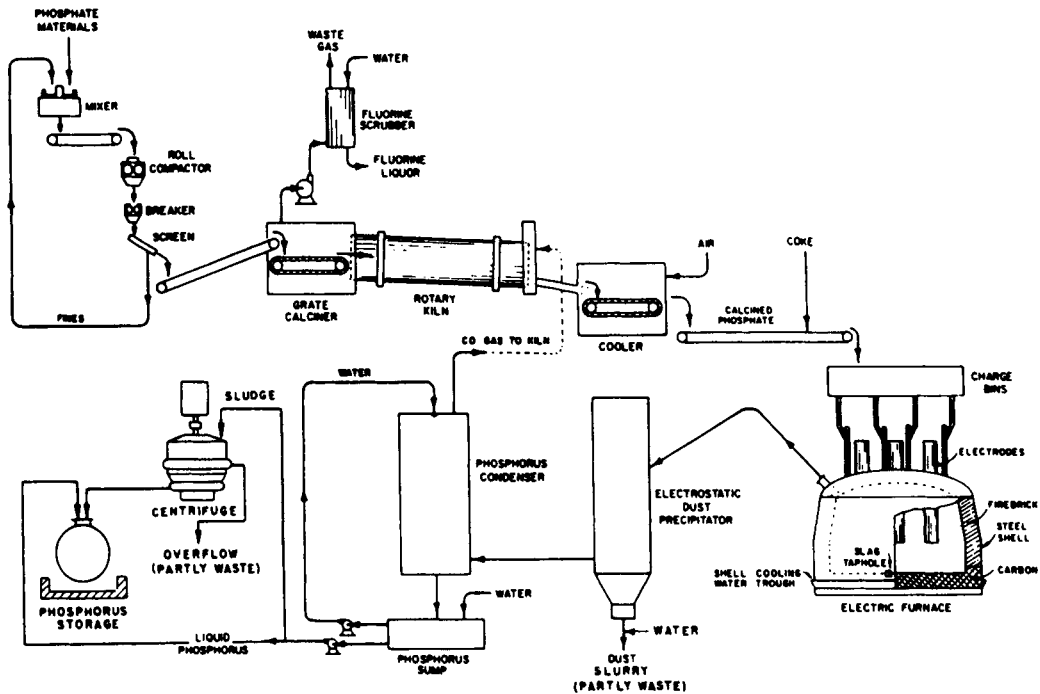


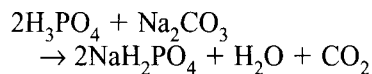
Fig. 23.8. Electric furnace process for production of elemental phosphorus.

compounds such as phosphorus pentoxide, phosphoric trichloride, and phosphorus pentasulfide, which find use in the preparation of drying agents, plasticizers, oil additives, fire retardants, and insecticides. These products are derived from phosphorus and, therefore, cannot be made from purified wet process acid so there is a continuing demand for a small amount of thermal product. However, for orthophosphoric acid use, the purified wet process acid is cheaper.¹⁶ This has now replaced furnace acid in soft drinks, candy, baked goods, and various other food products. It is also used for pickling metals.

The cheapest and most important salts of purified phosphoric acid are the sodium salts, made by reacting the acid with sodium carbonate or sodium hydroxide. Sodium phosphates may be classified in a general way as (1) orthophosphates, (2) crystalline condensed phosphates, and (3) glassy condensed phosphates.

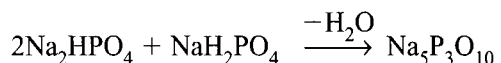
Three sodium orthophosphates can be prepared, depending on whether one, two, or three hydrogen atoms are replaced by sodium.

Monosodium phosphate is formed in the following reaction:



Sodium carbonate also is used to make disodium phosphate, Na_2HPO_4 , but sodium hydroxide must be used to replace the third hydrogen in trisodium phosphate, Na_3HPO_4 . The orthophosphates have a wide range of uses in industry.

Condensed phosphates are made by eliminating water from orthophosphates. The most important compound is sodium tripolyphosphate (STPP), made according to the following reaction:



The most important use of sodium tripolyphosphate is as a builder in detergents. However, legislative restrictions on the use of phosphorus compounds in household detergents have

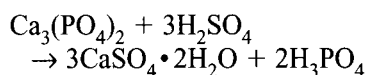
caused a Worldwide flattening of consumption.

Glassy condensed phosphates are represented by sodium hexametaphosphate, in which the O : P ratio is 3 : 1. There can be considerable variation in the Na₂O to P₂O₅ ratio.

The principal use of the condensed phosphates is to sequester metallic ions in water. They form water-soluble complexes with the metals and prevent metallic compounds from precipitating to cause discoloration, scale, and sludges.

Wet Process Phosphoric Acid

In the wet process, phosphate rock is reacted in a slurry of phosphoric acid and calcium sulfate crystals containing a controlled quantity of sulfuric acid. The simplified reactions for the dihydrate process is as follows:



Until 1969, virtually all wet process acid was made at maximum strengths of 26–32 percent P₂O₅, separating the calcium sulfate as gypsum containing two molecules of water. Since 1969, a substantial number of commercial hemihydrate process plants have been built in various modes. In the hemihydrate process, reaction conditions are higher in

temperature and phosphoric acid strength so that the stable solid phase is calcium sulfate with one-half molecule of water.

The hemihydrate process may be a single-stage process, known as HH, in which the hemihydrate solids are the waste product, or the process can have a second step in which the hemihydrate is recrystallized to gypsum, known as hemi-dihydrate (HDH). In the hemihydrate process, acid strengths of 38 percent P₂O₅ to about 42 percent P₂O₅ normally are produced although strengths up to 50 percent can be produced under somewhat more difficult circumstances requiring more filter area.

The neutralization reaction of the above equation is conducted in one or more strongly agitated reaction vessels, whether in a gypsum or in a hemihydrate mode. The system is highly exothermic and the slurry is maintained at 80–85°C for dihydrate processing, 95–100°C for hemihydrate, by evaporative or air cooling. During the reaction of phosphate rock with sulfuric acid, fluorine is evolved and must be scrubbed from the vent gas.

Table 23.5 lists the production of phosphoric acid in the recent past, and shows the substantial changes in location of P₂O₅ production over the last decade. The East and West Europe fertilizer industry was in a steep decline by 1999. North Africa and the Middle East are continuing to expand based on their

TABLE 23.5 Annual Production of Phosphoric Acid by Region

Region*	1999	2000	2001	2002	2003
<i>1000 mt P2O5</i>					
West Europe	1,623.1	1,275.1	1,244.0	1,157.4	1,117.3
Central Europe	556.7	544.4	487.9	545.2	546.6
Eastern Europe and Central Asia	2,295.9	2,424.6	2,197.2	2,507.0	2,546.6
North America	11,439.0	10,537.0	9,694.0	10,581.9	10,694.4
Latin America	1,679.3	1,683.2	1,551.8	1,358.1	1,460.2
Africa	5,432.9	5,258.4	5,600.2	5,922.9	5,952.1
West Asia	1,911.2	1,757.7	1,660.7	1,765.7	1,637.8
Asia	1,616.3	2,016.1	2,264.8	2,160.4	1,927.6
East Asia	1,500.0	2,200.0	2,805.0	3,492.0	4,632.0
Oceania	—	151.7	331.9	385.4	438.0
World total	28,054.4	27,848.2	27,837.6	29,875.9	30,952.7

*IFA regions as shown beginning in 2002 Processed Phosphates Statistics.

Source: Derived from IFA data, Processed Phosphates Statistics, 2001–2003.

huge reserves of high-grade phosphate. China, with substantial deposits, has now begun to develop these. The years 2000 and 2001 show a decline in overall P_2O_5 over the figures shown for 1997, illustrating the cyclic nature of the world wide phosphate business.

Dihydrate Process

The conventional dihydrate process, as operated over the last 70 years, was first demonstrated by the Dorr Company in the Cominco plant at Trail, British Columbia, in 1931.¹ The principles discovered at that time for making an acid strength of up to 32 percent P_2O_5 and a highly filterable gypsum crystal are still used today. The salient features of the process included maintaining H_2SO_4 content in the digestion acid of about 2.0–3.0 percent. Reaction slurry was recycled at a ratio of 10–15:1 relative to the volume of product slurry sent to the filter. The relatively higher recirculation of seed gypsum than had previously been practiced, together with control of the free sulfate, resulted in product acid well above the previous 22 percent P_2O_5 possible with batch and countercurrent decantation systems.

If the sulfate in the solution is allowed to exceed certain limits, depending on rock reactivity and particle size, the rock becomes coated with gypsum, and the reaction becomes uncontrollable. If the sulfate level is too low, the precipitated gypsum filters poorly and contains excessive quantities of crystallized (solid solution) P_2O_5 , leading to excessive P_2O_5 losses. Over the years, the process has evolved to employ increased slurry recirculation and different reactor configurations. In addition, several different filter designs are available.

The principal dihydrate processes in use as of 2000 are shown in Table 23.6. During the decade 1990–2000, many of the smaller plants and even some larger than 450 tons per day P_2O_5 plants have been shut down due to environmental or market conditions. This has resulted in more production in Morocco, Jordan, and India, and less in Europe. Most of the world's phosphoric acid is produced by the dihydrate method, but there is likely to be

TABLE 23.6 Phosphoric Acid Plants, Worldwide Dihydrate Process, 2000

<i>Process</i>	<i>Number of Lines 450 MTPD or Larger</i>
Prayon	20–25
Rhone Poulenc	10–15
Nissan H	7
Jacobs/Dorr–Oliver	7
Badger–Isothermal	7

increased production by the hemihydrate method because of advantages in some situations. The dihydrate processes listed have been modified over the years so that many slightly different configurations of the same process may exist.

The unique feature of each process is the reactor system configuration. The reactor or reactors normally provide from 2 to 6 hr detention for the gypsum slurry. This is about 0.8–2.5 m³ of reactor volume per ton of P_2O_5 per day, meaning relatively large vessels totaling 1500 m³ to over 2000 m³ in size for large plants. The individual reactor systems are described briefly below.

The objective of the reaction system is to produce a highly filterable gypsum crystal that washes well, and that also contains a minimum amount of insoluble P_2O_5 . The filterability of the gypsum slurry depends on the reactor configuration and on the rock source. Highly filterable gypsum slurries are produced from Florida, Togo, and Senegal phosphates. These rocks may provide more than double the P_2O_5 from a given filter when compared with gypsum produced from other sources. However, because phosphate rock is costly to transport, the use of local, less treatable phosphates can be quite economical. Table 23.7 lists the approximate filtration design rates for these groups of commercially available phosphate rock.

The advantages of the dihydrate process vs. the various, newer hemihydrate configurations are as follows.

1. The water balance permits the use of wet rock slurry feed. This eliminates the cost of drying the rock and the dust nuisance.

TABLE 23.7 Filtration Design Rates for Phosphoric Acid Produced from Various Rock Sources

<i>Rock Source</i>	<i>Tons P₂O₅ Produced per m² Active Area</i>
Togo	
Florida	7.5–9.0
Senegal	
Morocco Khouribga	
Western U.S.	4.5–7.0
Kola (USSR)	
North Carolina	
Morocco Safi	
Algeria	2.5–5.0
Tunisia	

This is the principal benefit that has deterred most Florida producers from using the hemi routes. Because gypsum has two moles of water of hydration vs. one half mole for hemihydrate, and because product acid strength is 26–28 percent P₂O₅ normally, the ground phosphate feed slurry can be as low as 65 percent solids for the dihydrate process. This still leaves enough makeup water for adequate washing of the gypsum. For hemihydrate processes the maximum moisture is generally considered to be about 15–18 percent in the feed rock. Such a low moisture would call for a dewatering step for ground Florida pebble rock. Producers in Florida have thus far chosen not to go this route because of the difficulty and expense of dewatering.

2. Dihydrate gypsum, in the case of most phosphates, filters at relatively higher P₂O₅ throughput rates than hemihydrate, comparing dihydrate filter performance at 28 percent P₂O₅ and hemihydrate at 42 percent P₂O₅.
3. Dihydrate plants are proven at huge outputs, in excess of 2000 metric tons per day P₂O₅, thus offering economies of scale.
4. A vast amount of operating data and experience exists on a wide variety of phosphate rocks for the dihydrate mode.
5. Capital costs for the dihydrate system can be less than for the two-stage hemi

processes even when evaporation and rock grinding are considered, because of the larger reaction vessels and two stages of filtration in the hemi process.

6. The yield across the filter for the dihydrate process, generally about 96 percent of the P₂O₅ fed, is about 3–4 percent above the single-stage hemi processes.
7. Dihydrate process maintenance costs are substantially less than those for hemi processes due to less severe process conditions. The on-stream factor is also higher for the average dihydrate facility.

Major Dihydrate Processes

Prayon Process. The Prayon process¹⁷ has evolved from the cascade system first used by the Dorr Company in the 1930s. Instead of round, steel vessels with rubber and brick lining, Prayon developed a multicompartmented reinforced concrete vessel, rectangular in shape, lined with a membrane and carbon brick in the early 1960s. The construction has proved to be exceedingly durable. A similar concrete construction is used by Jacobs and by Rhone Poulenc. A diagram of the Prayon Mark IV reactor configuration is shown in Fig. 23.9. The Prayon process uses vacuum cooling, a low-level vacuum chamber through which reaction slurry is circulated to maintain a reactor temperature of 80–85°C. There are numerous installations of large Prayon plants in the United States, although the center of process technology is Belgium.

Prayon also offers the Prayon–Central Glass process, a name derived from its Japanese origins. In this process, gypsum is crystallized in a dihydrate mode in the first stage. After separation of most of the P₂O₅ from the slurry by centrifugation or filtration, the gypsum is recrystallized to hemihydrate employing the sulfuric acid ultimately required in the first stage. The recrystallized hemi is quite low in P₂O₅ and impurities and suitable for by-product wallboard and plaster, and is readily washed in a second stage of filtration, followed by an agglomeration step that results in a semi-granular by-product. This process has allowed the Engis, Belgium, plant to continue

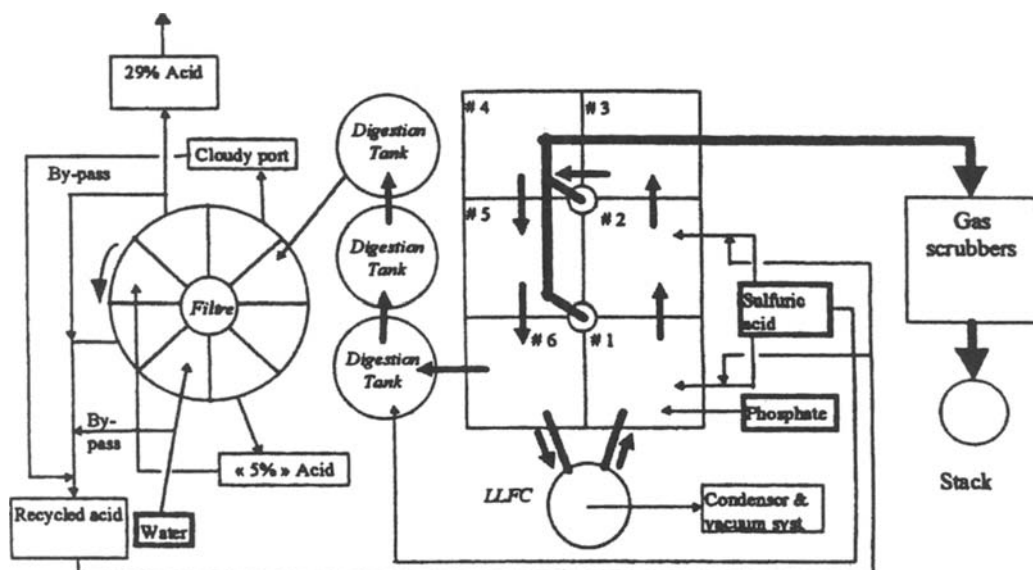


Fig. 23.9. Prayon Mark IV reaction and filtration system.

operation by converting all of its gypsum to a saleable product. The Prayon Mark III and Mark IV dihydrate processes are used in Florida and Louisiana in some eight lines operating between 1350 and 2000 tons per day P_2O_5 , and in one revamped plant in Jordan.

Speichim-Rhone Poulenc Process. Most of Rhone Poulenc's existing plants are of a single stirred vessel configuration. However, a two-vessel arrangement, the Diplo system,¹⁸ has been offered and retrofitted into several of the previous single reactor plants.

The original Rhone Poulenc Single Tank system is an exceedingly simple plant. It is air-cooled by passing a flow of air over slurry splashers, and does not have a filter feed tank, the slurry simply overflowing the reactor to a vertical pipe on top of the filter feed pump. The newer Diplo system is said to offer a better yield, higher P_2O_5 product acid strength, and a more filterable gypsum by providing a better concentration gradient for gypsum growth.

Rhone Poulenc installations are located in France, Belgium, Morocco, Senegal, Brazil, and China.

Nissan H Process. In this process, the rock attack is done under conditions favoring

the formation of an unstable hemihydrate. The slurry then is cooled and seeded to recrystallize to gypsum at high sulfate levels, producing a gypsum low in co-precipitated P_2O_5 . Yields in the 97–98 percent range are reported. The process, in operation since the 1960s, has been favored in many instances where the phosphogypsum can be used for wallboard or other building materials. Major installations are located in Japan and Morocco. A large plant at Pernis, Netherlands, has been closed and it appears that Nissan no longer offers phosphoric acid technology.

Jacobs Process. Jacobs Engineering acquired the Dorrco process technology in 1974 and has carried on the annular reactor design begun by Dorr in the early 1960s. The reactor configuration is a compromise between a multicompart system, as used in the earlier Dorr–Oliver cascade system and in the compartmented Prayon reactor, and the true single stirred vessel used by Rhone–Poulenc and Badger.

In the Jacobs system, the annulus of a large concrete tank is fitted with a series of agitators. There is baffling, but there are no walls between the agitators. High slurry



Fig. 23.10. Oswal phosphoric acid plant during construction—May 1999—in Paradeep, Orissa State, India.

recirculation rates are achieved by a combination of back-mixing and slurry pumping. Vacuum cooling normally is used. The Jacobs plants include a 1500 tons per day plant in Tampa, Florida, a 900 tons per day facility at Paradeep, India, and several smaller units. Figure 23.10 shows the Oswal Fertilizers and Chemicals construction site of the world's largest phosphoric acid plant^{19–21} 2650 metric tons per day P_2O_5 also at Paradeep, Orissa, in mid-1999. Figure 23.11 is a diagram of the reactor itself. Starting in the center foreground of the photo and moving clockwise, the large building, partially roofed, holds five 110 m two-belt filters, next is the wet grinding and screening structure. The concrete reactor tank, having 4350 m³ of slurry volume, is shown prior to the installation of the agitators. The three small cylindrical vessels are slurry vacuum coolers. Six evaporators with fluosilicic acid recovery are pictured next. The large tanks are for acid storage and clarification, and finally, on the far right, the cooling tower foundations. Slurry flow is clockwise around the annulus, into the center compartment, then to the long

narrow vacuum cooler feed compartment. The cooled slurry flows to the cooler seal compartment opposite the feed compartment. The bulk of the slurry recycles to the annular reactor with the net flow proceeding to the filter feed tank. In principal, the flow pattern is similar to the Prayon reactor system shown in Fig. 23.9. The ground phosphate rock is mixed with recycled cool slurry in the first position of the annulus followed by the addition of sulfuric acid diluted in a mixing tee with weak phosphoric acid from the filter.

Isothermal Process. The Badger-Raytheon reactor is a draft tube mixer within a vacuum vessel.²² All reactants are added to this vessel, which is under vacuum, and cooling and rock digestion are achieved simultaneously.

There are three lines in Florida, two in Mexico, and two in the Western United States. The system has low energy consumption, but lacks flexibility in that it works best with finely ground rock. It has also exhibited some difficulty in handling the high organic Mexican phosphate.

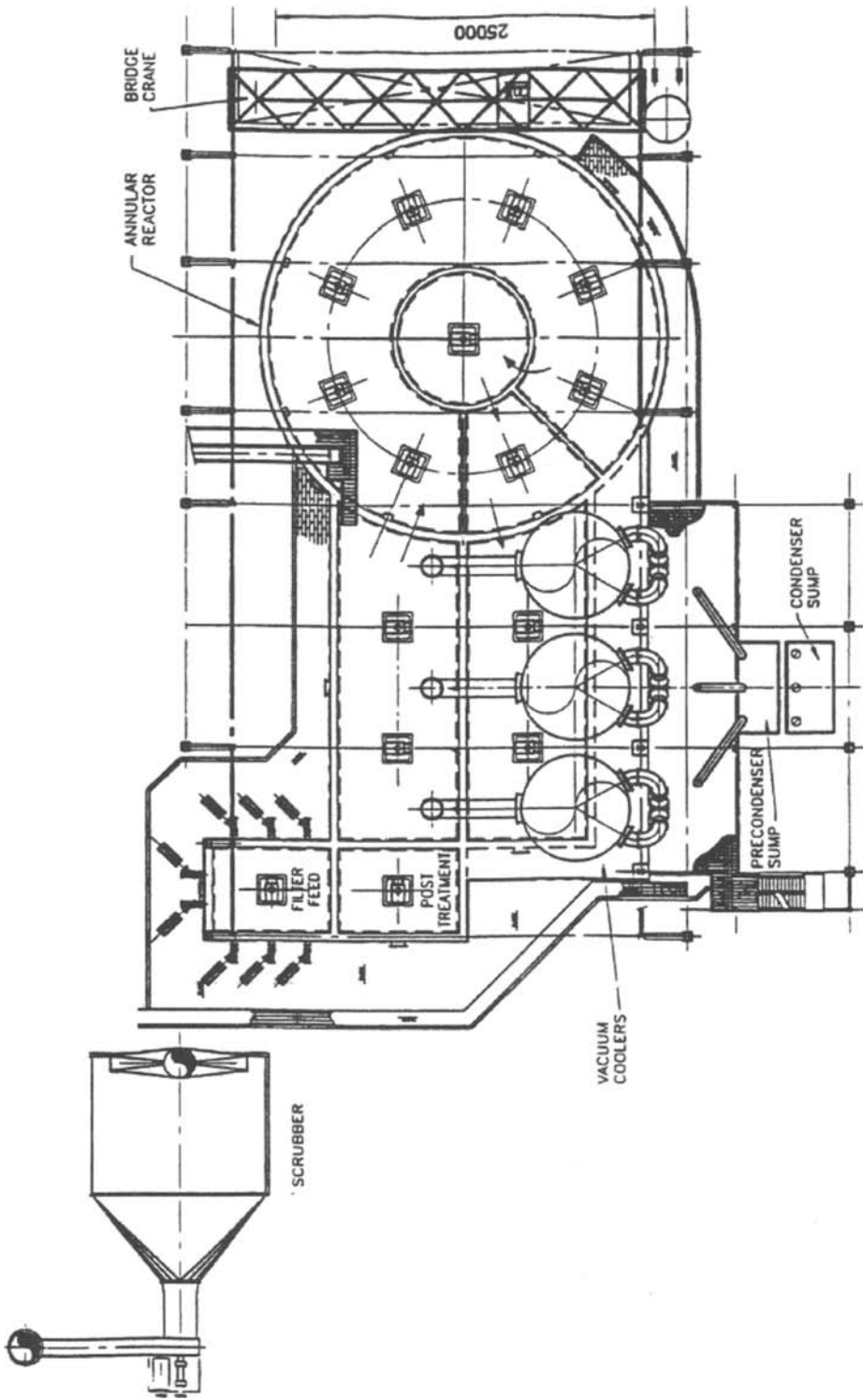


Fig. 23.11. Jacobson reaction system, 2500 tons per day P_2O_5 .

Hemihydrate Processes for Phosphoric Acid

Methods for making higher strength P_2O_5 acid have been known for a long time. The basic hemihydrate–dihydrate process shown in the Hydro Fertilizer flowsheet, Fig. 23.12, is similar to the initial process attempted in 1931 at the Cominco plant at Trail, BC. The hemihydrate–dihydrate process failed there, mostly because of inadequate filters, but the Dorr dihydrate process did emerge successfully.

The first large hemi plant of more modern times was the Kemira hemi-dihydrate two-stage plant at Siilinjärvi, Finland, which started operation in 1969, using the Dorr HYS process. After about four years of operation at 250 metric tons per day P_2O_5 , its rated design, the plant was expanded but operated in the dihydrate mode. In the hemihydrate

mode, filtration and recrystallization problems had plagued the plant, which operated on Kola rock.

Hemihydrate processes are available for new facilities and also for the retrofitting of existing dihydrate plants. Several conversions to higher-strength acid have been made, where the steam saved in evaporation can replace fuel. Plants that make super-phosphoric acid, or where sulfuric acid plant steam is not available, are likely targets for conversion.

The single-stage hemi process is similar to the front end of the hemi-dihydrate process (see Fig. 23.13). However, in this case, the hemi is sent to waste without deliberate recrystallization after washing. Yields for the single-stage process are generally below the yields of the dihydrate process, whereas yields for the two-stage hemi-dihydrate process are very high; see Table 23.8.

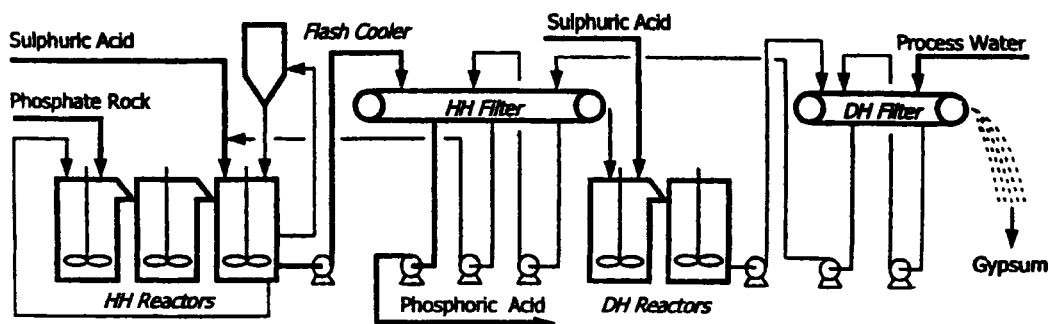


Fig. 23.12. Hydro fertilizer technology hemihydrate process.

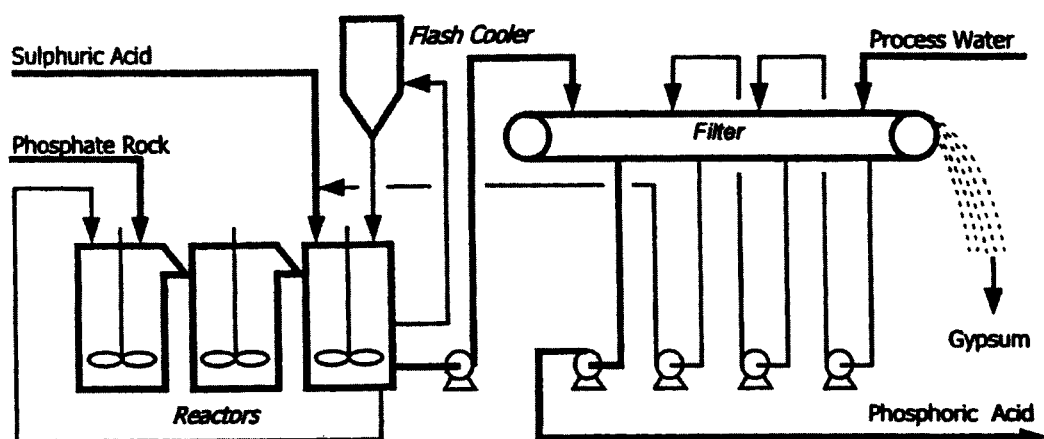


Fig. 23.13. Hydro fertilizer technology hemihydrate process.

TABLE 23.8 Range of P₂O₅ Yield through Filtration as % of P₂O₅ Fed*Phosphate Acid Process*

Hemi-dihydrate	98–99
Conventional dihydrate	95–97
Single-stage hemi	91–94

Table 23.9 lists the major hemihydrate plants operating in 2000. Many of the smaller facilities on the ninth edition list have been shut down. However, two major single-stage hemi plants have recently started operation. The Indo-Jordan facility has been particularly successful operating at full capacity from the initial startup, and up to 1000 tons per day P₂O₅ on two 80-m² Eimco belt filters.

The WMC plant^{23,24} extends proven hemi capacity to 1500 tons per day P₂O₅, but the plant has had to contend with a highly abrasive, low-grade rock, 23.5 percent P₂O₅ with over 35 percent SiO₂. In addition, the PCS (Occidental) single-stage hemi plant, in operation since the early 1980s, has been termed by some as one of the best phosphoric acid plants in the world. Also, the conversion at Arcadian has met the test of time.

The advantages of the hemihydrate processes compared with the conventional dihydrate processes are:

1. Energy savings due to higher product acid strength.

2. Higher P₂O₅ recovery and lower H₂SO₄ consumption for the two-stage process.
3. Lower capital cost for the single-stage process.
4. Hemi-hydrate recrystallized gypsum that is relatively pure, 0.2–0.4 percent total P₂O₅. This makes it more suitable for a cement additive or in wallboard.
5. Less rock grinding required.

Energy Savings in Phosphoric Acid. As has just been noted, the hemi processes provide energy savings due to the reduced steam consumption for evaporation. This steam, even though low-pressure, 2.0–3.0 kg/cm², has significant value for the co-generation of power. In some cases, the hemi process also saves rock-grinding power. On the other hand, dihydrate processes have the ability to use wet rock slurries and to absorb, in the process, more contaminated water resulting from rainfall collected off the waste gypsum stacks. The latter advantage may be important to maintaining a zero water balance and eliminating costly effluent treatment. The use of wet grinding and slurry feeding eliminates the fuel and electricity consumed in drying the rock.

Another energy-saving option is the use of hot water instead of steam for evaporation. This is an alternative, energy-wise, to the higher-strength hemi processes. Hot water normally is available from the heat of absorption of the sulfuric acid plant. Strengths of

TABLE 23.9 Major Hemihydrate Installations (2000)

Owner	Location	Year in Operation	Process	Product Acid Strength	Rock	Capacity P ₂ O ₅ (Million Tons per Day)
Chinhae	Korea	1990	N-H(C)(NDH)	45	FL	250
PCS (Arcadian)	U.S.	1980	N-H(C)(H)	40	Bou Cra	600
PCS (Occidental)	Florida	1980	Oxy(H)	38	FL	1400
Gresik	Indonesia	1984	Nissan C(HDH)	42	Jordan	550
Nam Hae	Korea	1988	Nissan C(C)(HDH)	42	FL/Jordan	1100
Yong Nam	Korea	1989	Nissan C(C)(HDH)	42	—	400
Copebras	Brazil	1987	Nissan C(C)(HDH)	—	Brazil	450
Coop Chem.	Japan	1987	Nissan C(HDH)	—	—	230
Yunnan	China	1992	N-H(HDH)	45	China	210
Inda-Jordan	Jordan	1998	N-H(H)	42	Jordan	750
WMC	Australia	2000	N-H(H)	42	Queensland	1500

N-H = Norsk Hydro; (C) = Conversion; (H) = Hemihydrate, single-stage; (HDH) = Hemihydrate-dihydrate.

40–42 percent P_2O_5 can readily be achieved. A few commercial installations exist in Europe. A more expensive alternative is offered in the HRS sulfuric acid process by Monsanto, which converts the absorption heat to low-pressure steam.

Unit Operations

In addition to the reaction step discussed above, there are a number of other unit operations used in producing wet process phosphoric acid.

Calcination. Phosphate rock normally is used as a dry rock or in slurry form. However, in some cases, particularly where the raw phosphate is high in carbonaceous matter or it is desirable to have a clean acid, the rock is calcined. Also, in a few cases, the phosphate rock is calcined, the product slaked, and free lime separated as a beneficiation step. Calcination is energy intensive and produces a less reactive rock and, in some cases, a less filterable gypsum. Therefore, the use of calcination is diminishing, and is being replaced by a wet oxidation step to produce green acid.¹⁶ In separating calcium carbonate, flotation, where it is successful, is favored over calcination because of its lower cost.

Rock Grinding. Until 1973, most phosphate was ground dry in roller or ball mills. In that year, Agrico, at South Pierce, Florida, converted one of its dry mills to wet slurry grinding and proved that the plant water balance could manage the rock at a 65–68 percent solids slurry. Since that time, most U.S. installations have converted to wet grinding.

Relatively fine phosphates, such as Kola, North Florida, Senegal, and Togo, can be processed unground as dry concentrates or as dewatered beneficiated product with 12–18 percent moisture. In the hemi processes, somewhat coarser feed, –20 mesh, may be tolerated. For dihydrate, it is desirable to feed from 1.5 percent +35 mesh (Tyler) to about 8 percent +35 mesh.

Filtration. The separation of phosphogypsum or hemihydrate from its mother liquor

has always been a difficult operation. The process has been subject to the formation of calcium sulfate, sodium fluosilicate, and other types of scale that clog the cloth and necessitate periodic filter washing. Filter cloth wear is severe, requiring cloth changes as often, in some cases, as two or three weeks apart.

Three types of filters have predominated over the past 20 years, the most widely used being the Bird–Prayon tilting pan filter shown in Fig. 23.14. The Ucego, a table filter with a peripheral side wall belt that leaves the filter to permit cake sluicing, has been popular worldwide since the late 1960s. In the late 1970s and the 1980s, belt filters became more readily accepted. The belt filter has been used on phosphoric acid since the 1940s and 1950s, but in the past it was plagued by mechanical problems and materials failures.

During the last decade, many successful belt filter installations have been made by Eimco, Filtres Philippe, Delkor, and Gaudfrin. Even in hemi service at Namhae, Indo-Jordan, and WMC, operating at 95°C or above, the belt filters appear to be successful. Because of their long narrow configuration, the belt filter is well suited as a supplemental filter and three have been installed in Florida for this purpose.

The filtration step is a countercurrent washing using two or three washes. Usually the final wash is a contaminated pond water or a cooling loop water, thus providing for, in most cases, a zero effluent plant.

Sizes of the Bird–Prayon and Ucego filter can be very large, over 200 m² of active surface area, allowing rates up to 1600–2000 metric tons per day P_2O_5 . Belt filters are, so far, 110 m² or less; however, they are relatively inexpensive because little alloy steel is used, and normally two belt filters would be less in first cost than one large tilting pan or table filter.

Evaporation. Phosphoric acid is used for downstream products mostly at 28 percent P_2O_5 , 40 percent P_2O_5 , and 54 percent P_2O_5 . Many plants also make clarified merchant grade acid (MGA), which, at 52–54 percent P_2O_5 , is a world traded product.

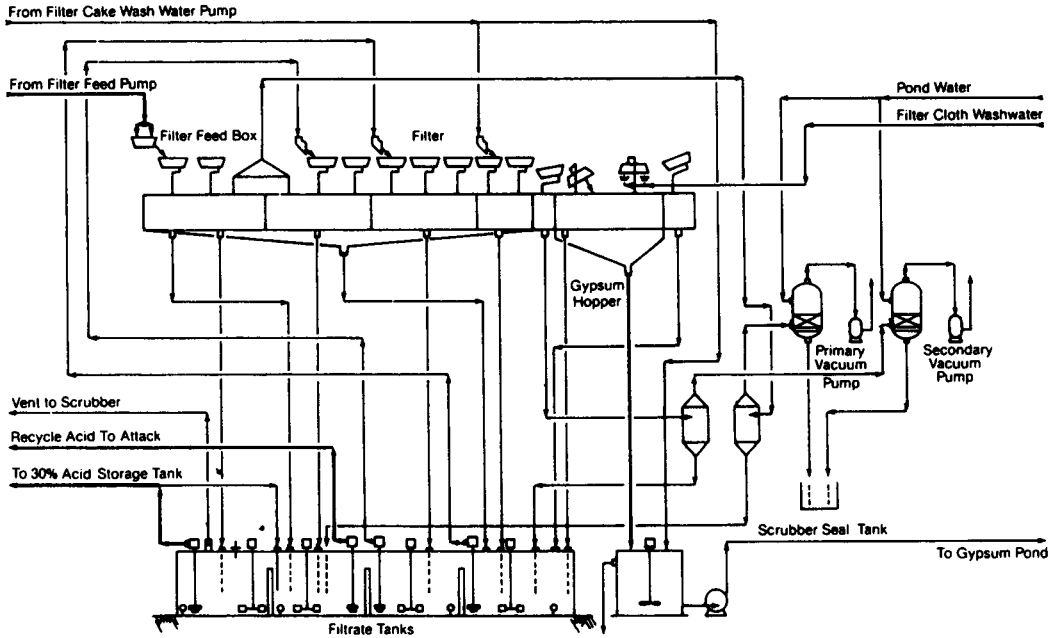


Fig. 23.14. Flow diagram of filtration section of a wet process phosphoric acid plant. (Prayon process, courtesy Davy McKee Corp.)

Evaporation normally is done under vacuum using forced circulation via an axial flow pump. Vacuum can be accomplished by steam ejectors, vacuum pumps, or with condenser water using an entraining condenser downleg. Heat exchangers normally have been shell and a tube, with graphite tubes in the United States. French practice has been to use carbon block exchangers, but these tend to scale more and are no longer in favor in many areas. Some newer shell and tube exchangers have been Sanicro 28 or Hastelloy G3 or G30. A flow sheet is shown in Fig. 23.15.

Typical analyses of wet process phosphoric acid made from North Carolina calcined concentrate are shown in Table 23.10.

Superphosphoric Acid

Solution fertilizers have become very popular in the United States. The principal source of P₂O₅ for these fertilizers is wet process Superphosphoric acid containing about 70 percent P₂O₅, where 35 percent or more of the P₂O₅ is present in the polyphosphoric form. When this acid is ammoniated and diluted, the iron, aluminum, and magnesium

TABLE 23.10 Typical Analyses, Wet Process Phosphoric Acid Made from North Carolina Calcined Concentrate

Component	Weight Percentage	
	Concentrated Acid	Superphosphoric Acid
P ₂ O ₅ , total	53.0	69.5 ^a
Solids	0.2	
Free water	22.0	
Fe ₂ O ₃	1.5	2.0
Al ₂ O ₃	0.7	1.0
F	0.6	0.3
MgO	1.1	1.3
SO ₄	2.7	3.7
CaO	0.1	0.2
Sp.g., at 75°F	1.68	2.0

^aAbout 36% of the total P₂O₅ is present as polyphosphates. (Courtesy Texasgulf, Inc.)

compounds naturally present remain in solution, sequestered by the polyphosphates. Clear solutions result, and there is no clogging of the sprays used for applying the fertilizer. When ordinary phosphoric acid is neutralized with ammonia, heavy sludges form, and the resulting solution is difficult to store and apply.

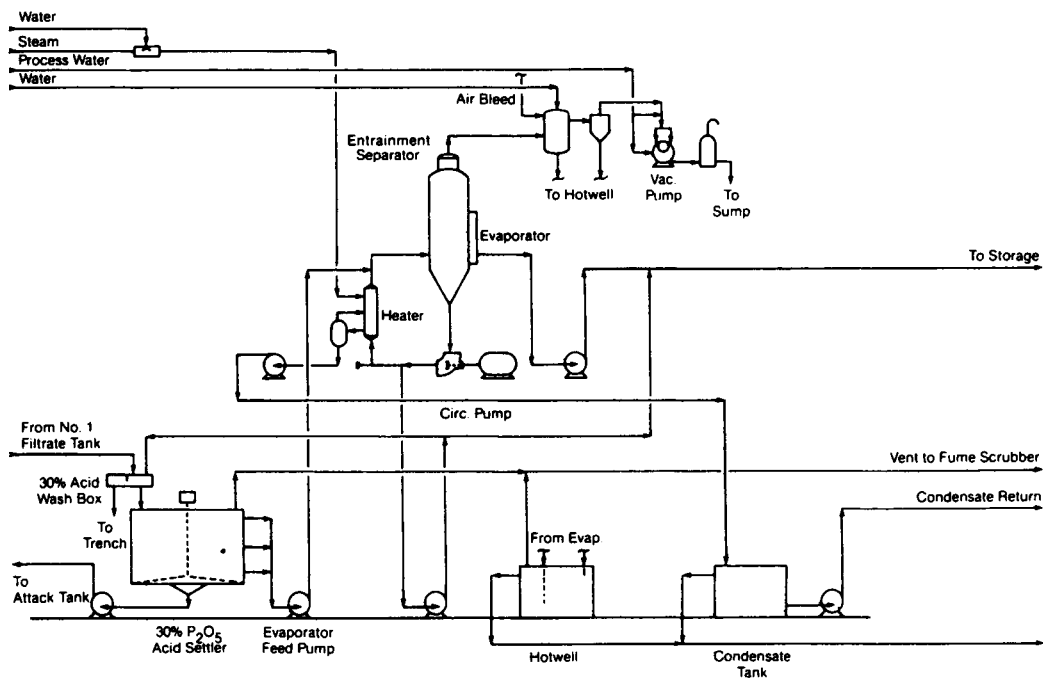


Fig. 23.15. Flow diagram of evaporation section of a wet process phosphoric acid plant. (Courtesy Davy McKee Corp.)

Superphosphoric acid is made by the additional concentration of clarified phosphoric acid in vacuum evaporators of the falling-film or forced-circulation type. High-pressure steam or Dowtherm vapor is used for heating. Corrosion is a problem, so the equipment is made from high alloy stainless steels. The acid is shipped in special insulated tank cars to the solution fertilizer plants, which are located close to the farm areas they serve. Organic matter contributes to sludge problems in making solution fertilizers; therefore, calcination of the phosphate rock used for making the acid is advantageous. Organics also may be removed by oxidation with nitric acid or ammonium nitrate,¹⁶ and several SPA producers have gone to such treatment to improve their product quality.

WET PROCESS ACID BY-PRODUCTS

Phosphogypsum

About 5 tons of gypsum on a dry basis are made for each ton of P_2O_5 produced in a wet process phosphoric acid plant. This material usually

is disposed of as a waste, by impounding it in old mine pits, stacking it in huge piles, or, in some cases, discharging it into very large rivers or river mouths. Phosphogypsum is sold to farmers in California for control of salt buildup in irrigated soils; a small quantity is sold to peanut farmers in the southeastern United States. However, there has been concern about the utilization of gypsum because of its low-level radioactivity in some instances. In addition, it contains fluosilicates and P_2O_5 so that utilization in building products, such as wallboard and blocks, has been limited to Europe and Japan, where natural gypsum is more costly than manufactured gypsum. In these cases, the phosphogypsum generally comes from a hemihydrate process producing a slightly purer form than natural gypsum.

Regeneration of SO_2 from gypsum has been done via the Krupp-OSW process, the most important facility formerly being the Fedmis plant in South Africa, which made about 300 tons per day H_2SO_4 and a similar amount of cement. Apparently, because of the high cost of cement and sulfur in this remote location, the plant was not economically viable and shut

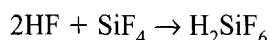
down in the late 1980s. Because of the present low cost of sulfur and its future abundance as a result of the removal of sulfur from sour natural gas and because of SO₂ removal processes in power generation, interest in sulfur recovery from phosphogypsum has waned.

The Florida Institute of Phosphate Research (FIPR) has studied phosphogypsum utilization at length, but the U.S. Environmental Protection Agency has prohibited its movement from its stacks (piles) because of its low level radiation. The FIPR hopes to show that its use in road building subsurfaces and as an additive to enhance digestion of municipal waste in landfills can be accomplished without harm to the public now or in the future.^{25,26}

Fluorine Recovery

Phosphate rock contains about 3.5 percent fluorine, some of which is recovered as a byproduct in manufacturing wet process phosphoric acid. During acidulation, the fluorine is released as hydrofluoric acid, HF, which reacts with the silica present as an impurity in the rock to form fluosilicic acid, H₂SiF₆. Some of the fluorine is lost with the gypsum as sodium or potassium fluosilicates, and some remains dissolved in the filter acid. When the acid is concentrated, much of the fluorine in the feed is boiled off, appearing as HF and silicon tetrafluoride, SiF₄, in the vapors.

Fluorine is recovered at the evaporator station by scrubbing the vapors leaving the flash chamber. The vapors pass through an entrainment separator to remove fine droplets of phosphoric acid and then into a spray tower where they are scrubbed with a weak solution of fluosilicic acid according to the reaction:



Part of the circulating solution is continuously withdrawn as a 20–25 percent aqueous solution of H₂SiF₆. The solution is shipped in rubber-lined tank cars and is used for fluoridation of drinking water, the preparation of fluosilicates, and production of AlF₃. These salts find use in ceramics, pesticides, wood preservatives, concrete hardeners, and aluminum production.

Uranium Recovery from Wet Process Phosphoric Acid

Uranium recovery was briefly described in the ninth edition. Since 1990, all uranium recovery contracts have expired in the United States and the recovery facilities moth-balled or scrapped. There is no indication the situation will change in the near future, because the reduced price of uranium no longer makes its recovery from phosphoric acid economical.

Animal Feed Supplements

Calcium phosphates for use in animal and poultry feeds are made from both furnace and wet process phosphoric acids. Dicalcium phosphate, CaHPO₄, containing 18.5 percent P, and mono calcium phosphate, Ca(H₂PO₄)₂•H₂O, containing 21.0 percent P, are made in large tonnages. Both grades are prepared by reacting phosphoric acid with pulverized limestone in a pug mixer. The limestone must be quite pure, and the phosphoric acid must have a low fluorine content, below 100 P to 1.0 F. If 54 percent P₂O₅ wet process phosphoric acid is used, it is defluorinated first by adding diatomaceous earth and then sparging the acid with steam. An alternate method is to use wet process superphosphoric acid, which has a low fluorine content. The superphosphoric acid is hydrolyzed by diluting it with water and heating. The pug mixer product is a fine granule, minus 12 mesh, which is dried and shipped in bulk to feed-mixing plants.

Purified Phosphoric Acid

Currently only one furnace acid plant remains in operation in the United States to supply elemental phosphorus and a few uses that cannot be satisfied by purified wet acid produced from wet process acid.

Wet process phosphoric acid made from calcined rock is preferred feed stock because it is devoid of the soluble organics and sludges present in acid made from sedimentary phosphates. However, calcination is expensive so that some plants are willing to go through laborious clarification to avoid it.

Clear acid is fed to a column or a battery of mixer-settlers and extracted with a solvent

such a butyl alcohol or tributyl phosphate. Generally, about three-fourths of the phosphoric acid transfers to the organic phase, leaving the impurities in the raffinate, which is sent to a fertilizer unit to recover its P_2O_5 . The yield of cleaned acid can be increased by adding another mineral acid such as sulfuric acid or hydrochloric acid to the extraction step.

After washing, the phosphoric acid is stripped from the solvent with water, and the solvent is returned to the extraction section. The phosphoric acid now is quite dilute and still contains small amounts of impurities.

The acid then is concentrated, and the impurities are removed by steam stripping and the addition of reagents and adsorbents followed by filtration. The exact details of the process vary, depending upon the process technology, which is proprietary, the impurities present in the feed acid, and the solvent used. Purified wet phosphoric acid is suitable for both industrial and food-grade use, although food-grade requires another level of purification over industrial or technical grade acid.

There are now several purified acid plants in the United States. Figure 23.16 is a photo of the PCS plant at Aurora, NC. That plant

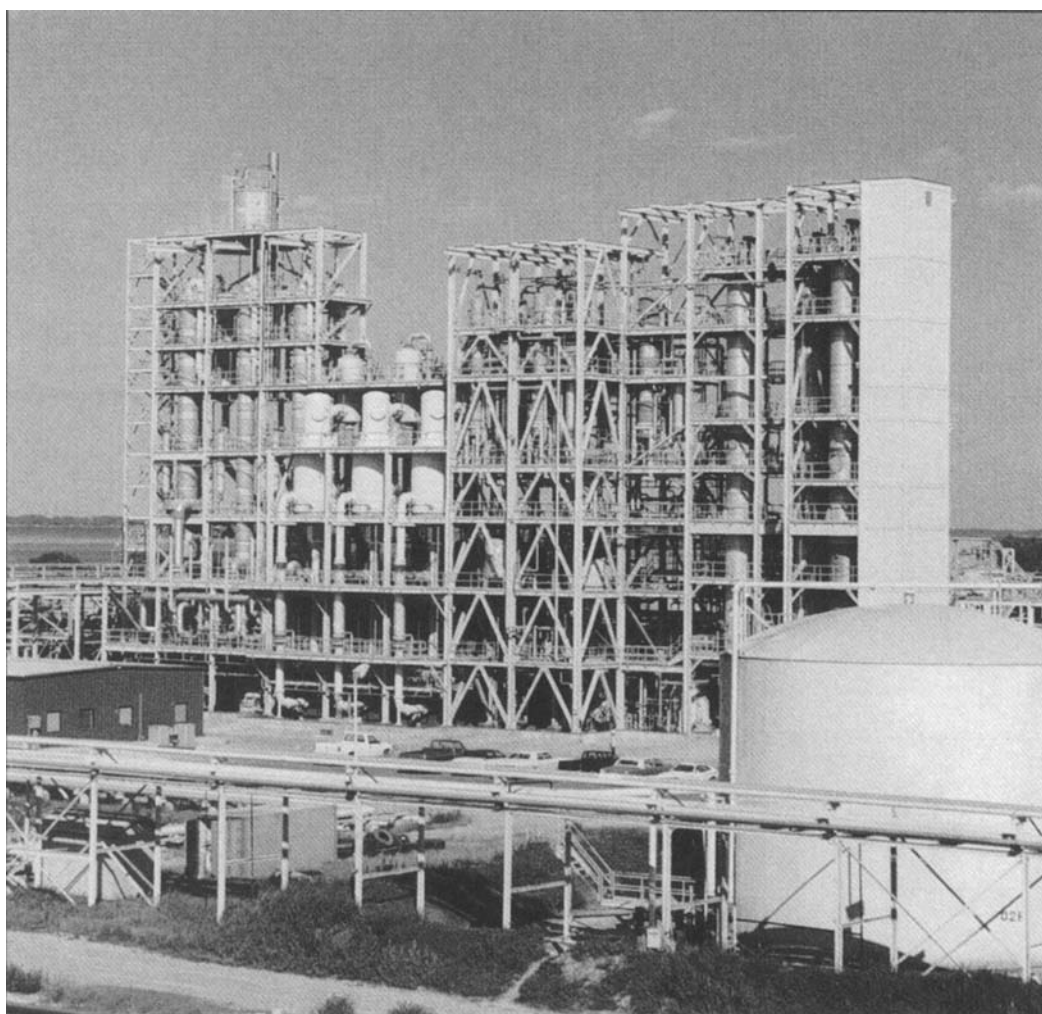


Fig. 23.16. Purified phosphoric acid plant for P.A. Partnership, Aurora, NC. (Courtesy P.A. Partnership and Jacobs Engineering.)

was expanded by adding a third train in 2001 and a fourth train in 2006. The Rhone-Poulenc purification plant at Geismar, LA continues in operation. There are also plants in Morocco, Belgium, Japan, and Israel.

Environmental Aspects

As implied earlier in this chapter, gypsum disposal is a problem that generally has defied an inexpensive solution. As a waste material, it is relatively benign, but P_2O_5 , sulfate, fluorine, low-level radioactivity, and other contaminants, including some heavy metals in small quantities, can leach from waste stacks into the nearby groundwater. In Florida, the underlying layers of limestone afford some protection, but

the EPA will require future stacks be lined with a membrane to prevent seepage. The “gypsum dilemma” has loomed as an increasing problem over the last decade.^{25–27}

Although dumping of waste gypsum slurries into the ocean still is practiced in some locations outside the United States, and harmful effects are generally difficult to quantify, there is continuing pressure from environmental groups to cease dumping into rivers and the seas.

Gaseous emission from phosphoric acid plants can be scrubbed with cool contaminated recycle cooling water to relatively low emission levels. However, to minimize cooling tower or cooling pond emission, fluorine recovery often is necessary on those streams that have a significant fluorine content.

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