8

Phosphates

The element phosphorus, a nonmetal, is relatively rare in nature. In fact, phosphorus is less than one tenth of one percent of the mass of the earth's crust. Common mineral forms of phosphorus include apatite, wavellite, vivianite, and phosphorite. The most important sources of phosphorus are phosphorite or phosphate rock. Phosphate rock consists of the mineral apatite, an impure tricalcium phosphate, mixed with clay and other elements.

Forms of Phosphorus

Elemental phosphorus is made commercially in several different forms called allotropes. These occur within three major categories: white or yellow phosphorus; red phosphorus; and black or violet phosphorus. Other phosphorus compounds are used by industry in the production of steel, china, and baking powder.

The white form of phosphorus is a soft, waxy solid that is made from phosphate rock. White phosphorus combines readily with other elements and ignites in air. Because it is unsafe to handle out of water, it is stored and shipped underwater. White phosphorus is poisonous and can cause serious burns. It is used to manufacture phosphoric acid and other phosphate compounds. The white form glows in the dark when it is exposed to air (phosphorescent). The name phosphorous comes from a Greek word meaning "light bearer."

Red phosphorous is a brownish-red powder prepared by heating white phosphorus to a high temperature ($250^{o}C$). Red phosphorus does not burn as readily as the white form and is neither poisonous nor phosphorescent. However, red phosphorus should be handled carefully at certain temperatures and conditions, because it can change to white phosphorus. The red form of

phosphorus is used to manufacture wooden and paper safety matches, pesticides, smoke bombs, and fireworks.

Black (violet) phosphorus resembles the mineral graphite. It is prepared by heating white phosphorus under high pressure.

Phosphoric acid (H_3PO_4) is a basic chemical used in drugs, animal feed, and fertilizers. According to the U.S. Bureau of Mines, nearly 93 percent of the phosphate rock sold or used in the U.S. in 1991 was for the manufacture of wet-process phosphoric acid, single superphosphate, and triple superphosphate; the balance (approximately 7 percent) was used to produce elemental phosphorous.[1]

Sources of Phosphate Rock

Although phosphate minerals are common throughout the world, occurrences that can be profitably beneficiated to a marketable product occurs in South America and the Pacific Islands as well as Africa, China, the Middle East, the United States and Russia. China, Jordan, Morocco, the United States, and Russia are the principle world producers of marketable phosphate rock.

In 2000, nine companies operated seventeen phosphate rock mines in the U.S. Florida is the main source of phosphate rock in the U.S. It supplies 25 percent of the world and 75 percent of the U.S. demand for phosphate.[2] Other large producing states are North Carolina, Utah, and Idaho. Eastern companies from Florida and North Carolina produce approximately 84 percent of the marketable phosphate rock mined in the United States and process most of the refined mineral in fertilizer upgrading facilities. The balance is principally used to manufacture elemental phosphorus.

8.1 Process Overview

There are two products from phosphate rock - elemental phosphorus and phosphoric acid. The following describes the general mining and processing steps for both then followed by specific steps for each.

8.1.1 Phosphate Rock Mining

The primary method of mining and exploration of phosphate rock is surface mining. Surface mining consists of clearing the site of brush, initial removal of topsoil and overburden, ore removal, and reclamation.

Eastern phosphate comes from surface mining and is sometimes extracted through a mechanized open cast mining technique using electric walking draglines with various bucket capacities. The overburden, which consists of sand, limestone and other materials, is stripped away by the draglines. Overburden and topsoil are placed in temporary piles for subsequent use in reclamation and/or dam construction. In the West, ripping and drilling usually loosen the

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[1] U.S. Bureau of Mines, *Minerals Yearbook Volume 1. Metals and Minerals*, Phosphate Rock, 1992
[2] Florida Institute of Phosphate Research, 1997-1999 Report, *Mining and Beneficiation*

uncovered phosphate. It is then loaded into dump trucks for hauling to the crushing and screening plant, which is usually located at the mine site.

To keep mining practices from permanently destroying wildlife habitat, all states including Florida, where most phosphate rock is mined, require the reclamation of mining areas. The two stages of reclamation are contouring and revegetation. Contouring is the stage in which the mined land is reshaped to resemble pre-mining topography and drainage. The mine areas are contoured using the removed overburden, topsoil and mill tailings. Revegetation provides for the replacement of native habitat. This may require reforestation. The entire cycle, from pre-mining activities through reclamation, varies by mine and typically requires approximately two years.

A western phosphate rock opencast mine is comprised of clays, marls, limestones, and cherts with phosphate-rich beds. The mineable beds range from one to three meters in thickness and have an average grade of 22-28 percent phosphorus pentoxide (P_2O_5). Six benches of overburden and phosphate are drilled with rotary blasthole drills and blasted. The exposed phosphate is loaded by an electric shovel or wheeled loader into trucks for haulage to the primary crushing station. In the east, draglines are used to remove waste and ore or matrix, which is a combination of sand, clay, and phosphate rock, and slurry the matrix to be piped to a washer plant for initial sizing.

8.1.2 Phosphate Ore Beneficiation

Phosphorus-based materials are used mostly in fertilizers, detergents, foods and beverages and metal treatment coating. Elemental phosphorus is used as a process input to produce a wide array of phosphorus chemicals. Most phosphorus is converted to a derivative including phosphorus sulfides and halides, phosphorus pentoxide, and phosphoric acid. An electric furnace for the production of phosphorus consists of a sequence of four operations:

- Preparing the furnace burden
- Charging and operating the furnace
- Collecting the liquid products
- Collecting the gaseous products

Beneficiation Plant

The primary activities that occur in an eastern beneficiation plant include:

> **Testing -** The washer plant yields a pebble phosphate product and fine flotation feed. The pebble product is tested to determine the concentration of magnesium oxide (MgO). If the MgO concentration is less than one percent, it is considered a product and no further beneficiation is required. If the MgO concentration exceeds one percent, the ore is directed to a patented heavy media separation plant for MgO removal.

> **Flotation** - The flotation feed is sent to the flotation plant, where the ore is passed through hydraulic sizing over screens and separated into three sizes. Different flotation

methods are used for each size of material. The flotation products are then combined with the pebble product, and shipped off-site to phosphoric acid plants and to other customers.

Washing - The washer plant generates oversized debris and undersized clays, which are considered wastes and managed on-site. The flotation plant generates tailings, which are stored in on-site tailing piles before being used as backfill for reclamation and in clay pond construction.

Preparation of Raw Materials

Storage and preparation of raw materials consists of stockpiling, screening and crushing, briquetting, calcining, and proportioning of the shale ore, coke, and silica. Shale ore arrives at the plant by truck. The ore is conveyed to the stacker for distribution on one of two storage piles. Ore is then collected from the piles by a reclaimer that deposits it on a conveyer belt. The conveyor belt carries the ore to crushing and screening. Ore is screened to remove oversized material. It is then crushed to a uniform size and sent to the briquetting process. Fugitive dust from screening and crushing is collected by baghouses.

The briquetting process presses the crushed material into briquettes similar to the size and shape of charcoal briquettes. The briquettes are then routed to the calciners where they are heated to burn organic material, remove water, and harden. The calcined briquettes, called nodules, are cooled and either stockpiled for later use or fed directly to proportioning. Calciners are fueled by carbon monoxide, which is generated by electric arc furnaces used for electrothermal processing. Air emissions from the calciners go to one of two sets of scrubbers for removal of particulates and radionuclides. The primary scrubbers remove particulates and the secondary scrubber removes polonium 210, a radionuclide.

The nodules are routed from the calciners to the proportioning building where they are mixed with silica and coke, creating a mixture called burden. The burden is sent to feed bins on each furnace. Fugitive dust from transfer points at the calciners and the proportioning building is collected by baghouses.

Electrothermal Beneficiation and White Phosphorus Production

Once the raw materials are prepared, the burden is fed to furnaces through feed chutes located on top of the furnaces. The chutes distribute burden uniformly about the electrodes. Silica is used as a flux agent to bind with the calcium present in the phosphate ore and form slag. Coke then reacts with the phosphate ore to form carbon monoxide and ferrophosphorus. The furnace offgas, which contains elemental phosphorus, carbon monoxide and particulates, passes through an electrostatic precipitator (ESP) for particulate removal. Gas passes through a primary condenser where the phosphorus is cooled by water sprays and condensed to a liquid. Each furnace is equipped with a precipitator and primary condenser. The majority of the phosphorus is condensed in the primary condenser. The gas stream leaving the primary condenser is combined with the gas streams from the other primary condensers at the carbon monoxide header. The combined gas stream, which is primarily carbon monoxide, flows to a second condenser for additional phosphorus removal. A carbon monoxide stream from the secondary condenser is

used as fuel for the calciners. Excess carbon monoxide goes to the roof flare and to the flare pit. Elemental phosphorus is gravity fed from the condenser to sumps in the furnace building. Phosphorus in the sumps is kept under water to prevent contact with air. Phosphorus is transferred from the sumps to one of seven storage tanks at the phosphorus loading dock. Phosphorous is transferred by pumping water into the top of the sumps to displace the phosphorus and force it out the bottom of the sump and into the bottom of the storage tanks. The phosphorus displaces water from the top of the storage tank and the water flows back to the sumps to form a closed-loop system. Phosphorus is pumped from the storage tanks into railcars for off-site shipment. The phosphorus dock also processes sludge generated at the furnace building sumps, storage tanks, and in the returning railcars. The sludge is dried in a centrifuge and stored before being pumped back to the furnaces for phosphorus recovery.

The furnace burden must be porous enough to allow gases to escape from the reaction zone near the bottom of the furnace. Several agglomeration methods must be employed to prepare phosphate rock fines for the electric furnace. The fines must be sintered and then crushed to size and screened. The ore is screened to remove oversized material. Another agglomeration method is nodulizing. In this process, phosphate fines are heated in a rotary kiln to incipient fusion. The tumbling in the kiln causes the material to cohere and form spheroidal agglomerates. A final method of agglomeration is formation of pellets by tumbling. The pellets can then be calcined in a rotary kiln.

The agglomerated phosphate rock is charged to an electric arc furnace with coke as a reductant and silica as a flux. The reduction generates a calcium silicate slag and ferrophosphorus, which are trapped and carbon monoxide off-gases that contain volatilized phosphorus. Dusts are removed from the off-gases using dry separation techniques such as electrostatic precipitation. Phosphorus is removed by condensation in the presence of recirculation water above the melting point of phosphorus. The carbon monoxide gases are subsequently burned and phosphorus is then decanted from the water and stored for sale. The recirculating water is neutralized and a purge of mud and soluble impurities is removed and disposed.

8.1.3 Elemental Phosphorous

Red Phosphorus Production

Although red phosphorus is usually manufactured by a batch process, continuous methods are now being used. In the batch process, white phosphorus is converted to red phosphorus in a steel or cast-iron vessel. The liquid phosphorus, which is protected by a layer of water, passes into the vessel, which is then closed. The vessel is heated gradually so that unconverted liquid phosphorus does not boil violently and erupt. A reflux condenser is used to retain the phosphorus. The mass remains fluid until almost half of the phosphorus has turned into red phosphorus. As the process continues, the mass thickens and solidifies. The mass is cooled and red phosphorus is removed. The material is then wet-ground and boiled with sodium carbonate solution to remove any traces of white phosphorus, which is flammable in air. The red phosphorus is sieved, washed on a rotary filter, vacuum dried, and stabilized by one of two methods. In the first method, red phosphorus is suspended in a sodium aluminate solution and then aerated. In the second method, magnesium oxide is precipitated onto the red phosphorus.

8.1.4 Phosphoric Acid

About 95 percent of the commercial grade wet-process phosphoric acid is used to produce fertilizers and animal feed. A small portion of the phosphate acid is used as a feedstock in chemical processing operations. Typically, the fertilizer and feed plants are co-located with the phosphoric acid facilities. There are two processes for producing phosphoric acid: (1) the wet process, and (2) the furnace process. Wet-process acid, produced directly from phosphoric ores, is characterized by relatively high production volume, low cost, and low purity. It is used primarily in fertilizers. Furnace or thermal acid, manufactured from elemental phosphorus, is more expensive and considerably purer than wet-process acid. It also is produced in much smaller quantities, almost exclusively for applications requiring high purity, such as that used to produce carbonated beverages and pharmaceuticals. In the United States, there are 16 facilities that use the wet process and four facilities that use the furnace process. The furnace process is not discussed in this report because it is beyond the first sellable product.

Wet Process Phosphoric Acid - The wet process methods include digestion, filtration and concentration. Phosphate rock is dissolved in sulfuric acid. The slurry from this operation is sent to filters where solids are collected, washed, and sent to phosphogypsum stacks. The acid is concentrated by evaporation.

The wet process for phosphoric acid production consists of three operations: digestion, filtration, and concentration. Beneficiated phosphate rock is dissolved in sulfuric acid to chemically digest the calcium phosphate. The product of this operation is a slurry that consists of the phosphoric acid solution and a suspended solid, calcium sulfate, commonly known as phosphogypsum. The slurry is routed to a filtration operation where the suspended phosphogypsum is separated from the acid solution. The acid isolated during filtration is concentrated through evaporation to produce "merchant grade" (54 percent) phosphoric acid. The phosphogypsum is re-slurried in recycled process wastewater and sent to disposal in phosphogypsum stacks.

Only five percent of raw product acid is purified. Purification of wet-process acid is accomplished by two primary methods: (1) solvent extraction and (2) chemical precipitation. In the production of sodium phosphates, almost all wet-process acid impurities may be induced to precipitate as the acid is neutralized with sodium carbonate or sodium hydroxide. The main exception, sulfate, may be precipitated as calcium or barium sulfate. Most fluorine and silica can be removed with the sulfate filter cake as sodium fluorosilicate by the addition of sodium ion and control of the Si/F ratio in the process.

In the double-neutralization process for wet process acid purification, sodium fluorosilicate is precipitated and removed by filtration at a pH of 3 to 4. Upon raising the pH to between 7 and 9, insoluble phosphates of iron, aluminum, calcium and magnesium form and separate. Iron can be precipitated as hydrous ferric oxide, reducing the phosphate loss in the second filter cake. Both the fluorosilicate and metal phosphate filter residues tend to be voluminous cakes that shrink when dewatered. The recovery of soluble phosphates trapped within the cakes is difficult.

The double-neutralization process is used in the production of high volume detergent-builder phosphates since the phosphate precursor solutions occur at pH 7 to 9. The more acidic salts, however, require an additional filtration to eliminate discoloration caused by remaining traces of ferric oxide that precipitate at higher pH.

The increasing cost differential between the sulfur used in the manufacture of wet-process acid and the electricity needed for thermal acid has encouraged the development of new processes for purifying wet-process acid. These new processes are mostly based on solvent extraction using organic solvents with low viscibility in water. Crude wet-process acid is typically concentrated and clarified prior to extraction to remove sludge-forming components and improve partition coefficients. Chemical precipitation of sulfate, silicate, and fluoride may also be used as a prepurification step preceding solvent extraction.

Organic-phase extraction of H_3PO_4 is accomplished in a series of countercurrent mixer-settlers with extraction generally limited to 50 to 75 percent of the feed acid P_2O_5 content. Higher extraction results in sludge precipitation in the settlers and in the depleted raffinate stream. Raffinate is stripped of residual solvent and used in fertilizer production.

The acid is washed from the organic stream by water or aqueous alkali in another series of countercurrent mixer-settlers, stripped of residual solvent, and concentrated to the desired P_2O_5 level. The solvent is recycled to the extraction section. Many variations of this basic scheme have been developed to improve extraction of phosphate, but also to reject impurities in the raffinate stream. Numerous patents have been granted on solvent extraction processes.

Of all the impurities in phosphate rock, magnesium (Mg) can be one of the most troublesome. In the manufacture of phosphoric acid, high magnesium content increases sulfuric acid consumption and results in lower production rates and yields. High magnesium content in phosphate ore will mean that some ore will not be mined and just left in the ground and some of the ore that is mined will have to be discarded. While a number of techniques for magnesium removal have been proposed, no satisfactory solution to the problem has been adopted.

8.2 Summary of Inputs/Outputs

The following lists the inputs and outputs for phosphate mining and processing. Figure 8-1 illustrates the phosphate mining process with its major inputs and outputs.
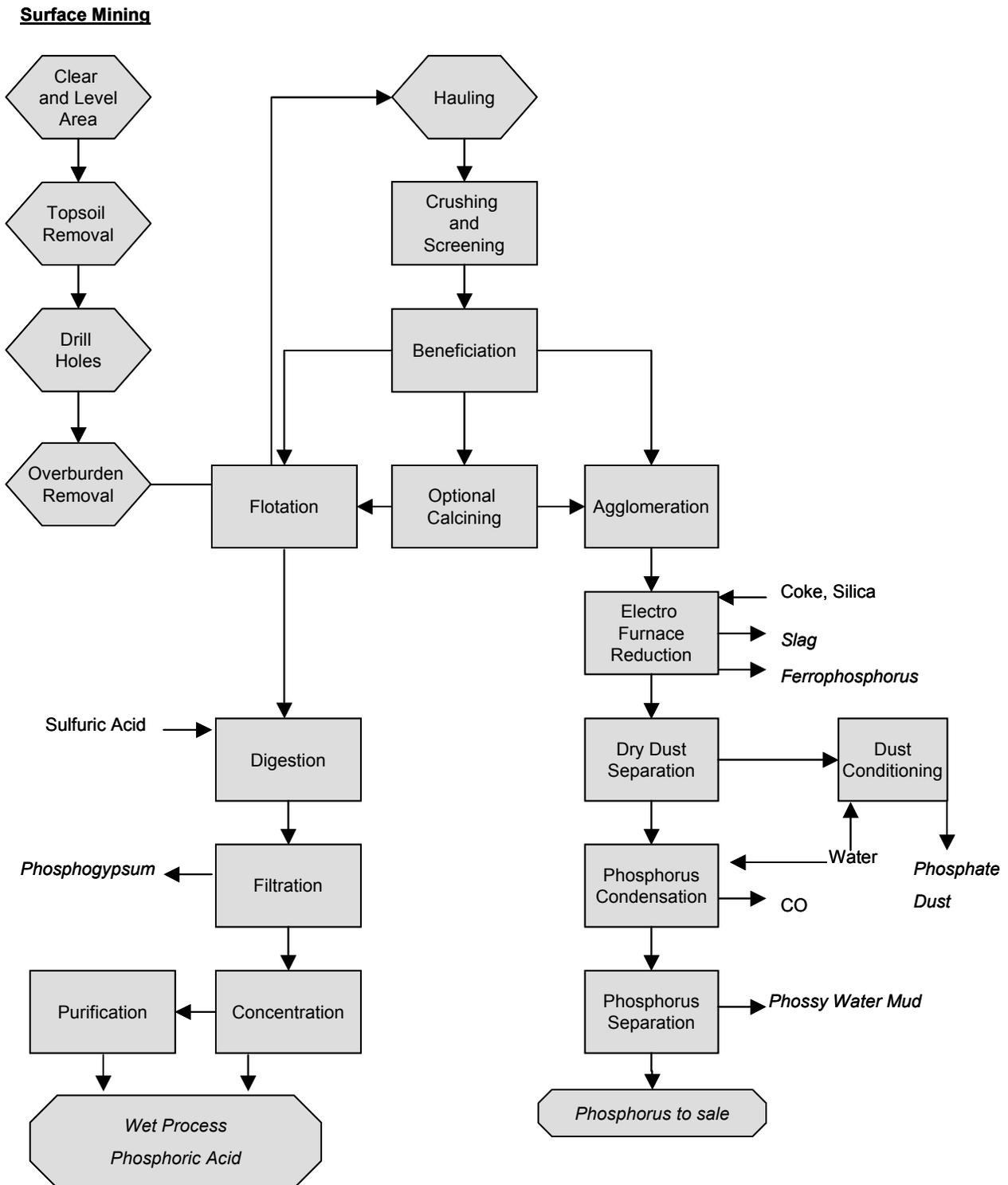
Inputs	**Outputs**
Electricity	Slag
Fuel Oil	Ferrophosphorus
Coke	Dust
Silica	Carbon Monoxide
Water	Phossy Water Mud
Sulfuric Acid	Phosphogypsum
Soda Ash	Phosphoric Acid

Figure 8-1. Phosphate Rock Mining Flow Diagram
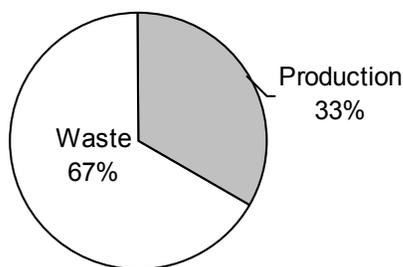
Surface Mining

8.3 Energy Requirements

8.3.1 Materials Handled

Materials handled referst to the amount ore and waste material that must be handled in mining. Figure 8-2 shows the amount of phosphate rock mined in relation to the amount of waste materials mined. When looking at energy requirements in mining and processing the tonnage of materials which must be handled drives energy consumption in mining operations. For example, in 2000 the amount of phosphate rock crude ore produced was 154 million tons. The materials handled is typically one-third phosphate, one third sand, and one third clay. This brings the total material handled in 2000 to 308 million tons.

Figure 8-2. Materials Handled for Phosphate Rock Mining

Source: U.S. Department of the Interior, U.S. Geological Survey, *Minerals Year Book*, Mining and Quarrying Trends, 1994,1995,1996, 1997, 1998

8.3.2 Energy Requirements

The energy requirements for preparing phosphate rock vary significantly from mine to mine due to the type of mining and type of phosphate being mined. A major energy source for phosphate mining is purchased electric energy. In 1997, phosphate mining consumed 15.2 trillion Btu.[3] Table 8-1 shows the type and quantity of fuels consumed during phosphate rock preparation. Electrical energy is used to power draglines, shovels, pumps, and other miscellaneous beneficiation equipment. Fuel oil is consumed by bulldozers, portable mining equipment, and dryers. Dryers are usually gas-fired, but use oil as a standby fuel. Power consumption is a function of material handling requirements and therefore depends on the deposit's stripping ratio, the ore's concentration ratio, distance from mine to beneficiation plant, and water contents prior to drying. In Florida, the estimated energy required per ton of ore was 9 kilowatt-hours for mining, 11 kilowatt-hours for benefication, and 3 kilowatt-hours for waste disposal per ton of ore. In fuel oil this equates to 0.017 gallons for mining, 0.003 gallons for benefication, and 0.01 gallons for waste disposal, per ton of ore.[4]

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[3] U.S. Department of Commerce, Bureau of Census, Census of Mineral Industries, Subject Series, *Fuels and Electricity Consumed*, 1992
[4] U.S. Department of Interior, Bureau of Mines, *Mineral Facts and Problems*, p. 197-221, 1985

Table 8-1. Phosphate Rock Production and Energy Consumed by Type [a]				
	Units	**1987**	**1992**	**1997**
Marketable Phosphate Rock Production	Million tons	45.1	51.8	50.6
Energy Consumption				
Coal	Thousand tons	Withheld	Withheld	Withheld
Fuel oil [b]	Thousand bbl.	343.8	Withheld	323.7
Gas	Billion Cubic Feet	3.8	2.1	0.7
Gasoline	Million Gallons	Withheld	2.8	1.4
Electricity Purchased	Million kWh	2,600	2,900	2,900
Electricity generated less sold	Million kWh	0	0	Withheld

[a] Phosphate Rock is SIC Code 1475 (1997 NAICS Code 212392)
[b] Summation of distillate and residual fuel oil
Sources: U.S. Department of Commerce, Economics and Statistics Administration, Bureau of the Census, Census of Mineral Industries, *Industry Series*, Phosphate Rock.
US Department of the Interior, US Geological Survey, *Minerals Year Book*, Statistical Summary, 1997 & 1994

Due to a lack of current information on the energy requirements of mining and processing, the *SHERPA Mine Cost Estimating Model* along with the *Mine and Mill Equipment Cost, An Estimators Guide* from Western Mine Engineering, Inc. was used to estimate the equipment-level energy requirements of mining and processing phosphate.

Table 8-2 shows the estimated energy requirements for a surface phosphate mine in the U.S. This phosphate mine operates over a 25-year lifetime with a 137.5 million-ton output at the end of its life. The mine runs 365 days per year with three shifts per day of 8.00 hours, which gives it a daily production rate of 21,153.85 tons. The daily waste production is 12,443.41 tons.
The results from the SHERPA mine model and cost guide show that the draglines are the most energy intensive piece of equipment used and consume the most energy in the surface mining of phosphate. The draglines operate on electric energy and account for 79 percent of the total energy used per ton in phosphate surface mining.

Table 8-3 shows the energy requirements to process phosphate. Processing of phosphate is not as energy intensive as other minerals. Flotation is the most energy intensive process and consumes the most energy. Flotation alone accounts for 65 percent of the total energy required per ton to process phosphate. The total energy required to both mine and process phosphate was 70,670 Btu per ton. Mining requires 98 percent of the total energy needed, while beneficiation uses the remaining two percent.

Table 8-2. Estimated Energy Requirements for a 15,068 ton/day Surface Phosphate Mine					
Equipment (Number of Units)	Daily hours/ unit	Energy Consumption			
		Single Unit (Btu/ton)	All Units (Btu/hour)	All Units (Btu/day)	All Units (Btu/ton)
Draglines [a] (2)	24.00	27,500	34,500,000	829,000,000	55,000
Hydraulic Monitors [a] (2)	24.00	5,280	6,630,000	159,000,000	10,600
Pumps [a] (28)	24.00	140	2,460,000	59,000,000	3,910
Pit Cars [a] (1)	24.00	140	87,800	2,110,000	140
Total			43,700,000	1,050,000,000	69,600

a   Calculated at $0.049 per kWH: average for Rocky Mountain Region, 1999
Note: Mine operates over a 25-year lifetime with a 137.5 million-ton output at the end of its life. Mine runs 365 days per year with 3 shifts per day of 8.00 hours. Operates at a daily production rate of 21,153.85 tons per day. The daily waste production is 15,068 tons per day.
Sources: BCS, Incorporated estimates (September 2002) using the Western Mining Engineering, Inc. *SHERPA Mine Cost Software* and *Mine and Mill Cost, An Estimators Guide*
Conversations with Industry Contacts

Table 8-3. Estimated Energy Requirements for Beneficiation of Phosphate					
Equipment (number of Units)	Daily hours/ unit	Energy Consumption			
		Single Unit (Btu/ton)	All Units (Btu/hour)	All Units (Btu/day)	All Units (Btu/ton)
Flotation [a] (5)	24.00	140	439,000	10,500,000	700
Screens [a] (4)	24.00	70	176,000	4,210,000	280
Trommel [a] (1)	24.00	87	55,300	1,300,000	87
Total			669,000	16,000,000	1,070

a   Calculated at $0.049 per kWH: average for Rocky Mountain Region, 1999
Sources: BCS, Incorporated estimates (September 2002) using the Western Mining Engineering, Inc. *SHERPA Mine Cost Software* and *Mine and Mill Cost, An Estimators Guide*

8.4 Emissions

Elemental Phosphorus

Although there are no significant emissions from phosphate rock beneficiation plants, emissions in the form of fine rock dust may be expected from drying and grinding operations. Phosphate rock grinders can be considered a source of particulates or fugitive dust. Because of the extremely fine particle size, baghouse collectors are normally used to reduce these emissions.

Air emissions from the calciners go to one of two sets of scrubbers for removal of particulates and radionuclides. The primary scrubbers remove particulates and the scrubber removes polonium 210, a radionuclide. Fugitive dust from transfer points at the calciners and the proportioning building is collected by baghouses. Air emissions from furnace operations result from normal furnace operation, furnace venting, and slag tapping. The electrothermal process generates carbon monoxide, which is used as fuel at the calciners or vented to the flare pit. Furnace venting occurs during furnace maintenance/repair or process upsets. During maintenance/repair, the furnace is vented to the roof flare. Emissions to the flare bypass the carbon monoxide header. These emissions consist primarily of phosphorus pentoxide. Emissions from process upsets, such as furnace over-pressurization, are vented to a pressure relief valve. These emissions are also primarily phosphorus pentoxide. Emissions from slag tapping are vented to the atmosphere through a Medusa scrubber followed by an Anderson scrubber. Furnace off-gas may contain elemental phosphorus, carbon monoxide, and particulates. Electrostatic precipitators (ESP) are used to remove the particulates. Dust slurry from the four ESPs is discharged to ponds that are dredged. Furnace offgas is not considered to be hazardous.

8.5 Effluents

Elemental Phosphorus

Mining activities can alter the topography and vegetative land cover, affecting the volume and rate of surface water run-off. The run-off increases the variability in stream flows and can dramatically effect aquatic life.

Effluents produced in the mining and beneficiation of phosphate rock are contained in the water suspensions leaving the washer plant. These suspensions are the phosphatic clays and sand tailings. The major effluent is that of the phosphatic clays, which contain a suspension of clays and very fine solids. These phosphatic clays are impounded in slime ponds to allow settling and clarification to occur. Clear water is returned from the ponds to the beneficiation plant. These are not generated when producing elemental phosphorus.

When phosphate rock is calcined, fluoride is produced. The fluoride produced is scrubbed with water or dilute hydrofluoric acid. Quantities of phosphate rock effluents are shown in Table 8-4. The phosphate rock effluents generated during extraction and processing include:

Table 8-4. Effluents From Phosphate Beneficiation	
Effluent	**Quantity (metric tons/year)**
Precipitator Slurry	160,000
Phossy Water	670,000
Furnace Scrubber Blowdown	410,000
Furnace Building Washdown	700,000
WWTP Liquid	1,520,000

Source: U.S. Environmental Protection Agency, Office of Solid Waste, *Identification and Description of Mineral Processing Sectors and Waste Streams*, Phosphate ore, April 1998.

- *Precipitator slurry* - Although not all processing plants may generate this waste, some plants do. In these cases, the elemental phosphorus product exits the furnaces as a gas, along with the carbon monoxide produced in the furnace reaction during the processing stage. The furnace off-gas also includes solids and solids that have volatilized

in the furnace and condenses as the off-gas cools. Electrostatic precipitators are used to remove these furnace off-gas solids prior to the water spray condensers that remove the elemental phosphorus as a liquid. These solids can be collected in a vessel at the bottom of the precipitator, known as the slurry pot, where water is added with a mixer to form what is termed precipitor slurry. The slurry pot acts as a gas seal on the precipitators to prevent in-leakage of air. Some elemental phosphorus condenses in the slurry pot and the solids contain low volatile metals such as cadmium and zinc in elevated levels. In the past, precipitator slurry has been sent to ponds where the solids settle out and the water is recycled. A facility can produce 43 million gallons of precipitator slurry each year. This waste sometimes exhibits cadmium toxicity.

- *NOSAP slurry* - As part of waste minimization efforts, some companies have modified electrostatic precipitators and the slurry pots. Lime slurry is added to the slurry pot to control the pH of the slurry to a set point of pH 12. The lime reacts with the phosphorus to form phosphites and phosphine gas, thus reducing the concentration of phosphorus to below 1000 ppm. The lime also prevents the metals from becoming leachable.[5]

- *Phossy water* - Phossy water may be reactive. It is possible that phossy water could exhibit toxicity for cadmium. As a result of its contact with phosphorus, phossy water contains suspended phosphorus and other dissolved solids. Due to the presence of elemental phosphorus, the solids in phossy water may spontaneously oxidize and ignite if dewatered. A company can generate as much as 89 million gallons of phossy water per year. Solids in phossy water settle out and may be considered a hazardous waste.[6]

- *Furnace scrubber blowdown* – A company can generate this waste at the rate of 43.4 million gallons per year. Management for this waste may include treating in a tank and sending the sludge to disposal impoundments. This waste may exhibit the characteristics of toxicity for cadmium and corrosivity prior to treatment.[7]

- *Furnace building washdown* - This waste is generated from numerous sources in the furnace building. Water is used in the following: condensing elemental phosphorus from the furnace off-gas stream; water seals on pressure relief devices and overfill protection systems; electrical transformer and furnace cooling; furnace tapping fume scrubber systems; conveying and storage operations to keep phosphorus under water cover; slurrying and transporting electrostatic precipitator solids; cleaning (rinsing) of process equipment to ensure maximum performance; and other miscellaneous uses such as pump packings and steam condensate. These streams are collected in a tank and referred to as furnace building washdown. This stream is generated continuously during process operations. The furnace building washdown occasionally exhibits toxicity for cadmium

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[5] U.S. Environmental Protection Agency, Office of Solid Waste, *Identification and Description of Mineral Processing Sectors and Waste Streams*, p. 281-303, April 1998
[6] Ibid.
[7] Ibid.

and contains elemental phosphorus. A company can generate approximately 79 million gallons of this waste each year.[8]

- *Sludge* – Sludge is generated in the sumps and consists of a phosphorus water emulsion and particulates not removed by the ESPs. Generally, sludge is distilled in iron retorts of steam heated vessels to recover phosphorus. Recovered phosphorus is added to the product and phosphorus free residues from the retorts are landfilled. The sludge is sometimes processed with sludge generated from furnace building sumps, storage tanks and returning railcars. The sludge is dried in a centrifuge and stored before being pumped back to the furnace for phosphorus recovery. This waste is not considered hazardous.

- *Waste filter media* – This waste is generated by scrubbers. The waste filter media is washed to reduce radionuclide levels before off-site disposal. Filter media wash water is discharged to the wastewater treatment tank and then to the calciner ponds. This material is not considered a hazardous waste.

- *Cooling water* - Cooling water is generated from cooling of furnace domes by direct water spray. This material is not considered a hazardous waste.

- *Surface impoundment waste liquids* - This waste is not expected to be hazardous.

- Non-contact cooling water – This is generated by the cooling of the grates that transport briquettes. The noncontact cooling water is discharged via a permitted outfall. This waste is a non-uniquely associated waste.

- *Process wastewater* – This waste is considered a special waste by RCRA.

- *Waste water treatment plant (WWTP)* –The generation rate for this waste stream is 1,520,000 metric tons per year.[9]

Phosphoric Acid -Wet Process

Process waste waters and phosphogypsum are the primary waste streams from the wet process. These wastes have been classified as RCRA special wastes, and are exempt from Subtitle C regulation. Generally, across the industry more than 90 percent of the water used is recycled. Because production and cooling are primary uses, water is generally recycled through cooling ponds. The constant reuse and recycling of water results in buildup of acidity to the point that the recalculated water has significant acid values that make it valuable for reuse.[10]

Phosphogypsum is created when sulfuric acid is reacted with phosphate rock to make the phosphoric acid used in fertilizer. In Florida alone, more than 900 million tons of

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[8] U.S. Environmental Protection Agency, Office of Solid Waste, *Identification and Description of Mineral Processing Sectors and Waste Streams*, p. 281-303, April 1998
[9] Ibid.
[10] U.S. Environmental Protection Agency, Office of Solid Waste, *Identification and Description of Mineral Processing Sectors and Waste Streams*, April 1998

phosphogypsum are currently stock-piled in Florida in stacks. A phosphogypsum stack can be as high as 200 feet and cover as many as 400 acres of land. Currently there are 20 of these stacks in Florida. Thirty million new tons of phosphogypsum are produce yearly.[11]

Waste scale is also generated at rate of 41,700 to 208,300 metric tons per year and is generally sent to a cooling bond.[12]

Phosphoric Acid Furnace Process

Approximately 0.28 kg per kkg of product of arsenic sulfide is formed during product purification.[13]

8.6 By-products and Solid Waste

Elemental Phosphorous

The quantity of phosphate rock solid waste generated is shown in Table 8-5. The phosphate rock solid wastes generated during extraction and processing include:

- *Anderson Filter Media (AFM)* - AFM is a felt-like material that is used in the Anderson scrubbers to filter fine particulate. Anderson Cleanable Media High Efficiency Air Filter scrubbers are used in series with the Medusa Scrubbers to further clean fumes from furnace tapping and phosphorus dock loading operations. AFM is used in these scrubbers to filter fine particulates. The AFM is generated at a rate of 420 cubic yards per year. The material can contain cadmium, arsenic, chromium, lead, and selenium and is considered a hazardous waste.

Table 8-5. By-products from Phosphate Ore	
By-product	**Quantity (metric tons/year)**
Anderson Filter Media	460
Slag	2,867
Dust	4,400
Furnace Offgas Solids	24,000
Wet process Waste Streams	~125,000

Source*:* U.S. Environmental Protection Agency, Office of Solid Waste, Identification and Description of Mineral Processing Sectors and Waste Streams, lead and zinc, April 1998.

- *Surface impoundment waste solids* – These are generated, but this waste does not exhibit characteristics of a hazardous waste.

- *Slag* - Slag contains trace amounts of radioactive materials in a stable, calcium silicate matrix. For every pound of white phosphorus produced, four pounds of slag are produced. In 1991, 2,867 metric tons per year were generated. Slag is tapped into the slag pit that is located next to the furnace building.

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[11] Florida Institute of Phosphate Research, 1997-1999 Report, *Chemical Processing*

[12] U.S. Environmental Protection Agency, Office of Solid Waste, *Identification and Description of Mineral Processing Sectors and Waste Streams*, April 1998

[13] U.S. Environmental Protection Agency, Office of Solid Waste, *Identification and Description of Mineral Processing Sectors and Waste Streams*, April 1998

- *Dust* - Phosphatic dusts may be slightly enriched in radioactivity as well as volatilized-reduced heavy metals. Phosphatic dusts are normally sold for blending with fertilizer materials and are classified as byproducts. Management includes storage in a wastepile and offsite landfill disposal. Dust is generated at a rate of 4,400 metric tons per year.

- *Furnace off-gas solids* - These solids may be toxic for cadmium. In addition, the waste may also contain cyanide. The generation rate for furnace offgas solids is 24,000 metric tons per year. Air emissions from the calciners are sent to scrubbers for removal of particulates and radionuclides. This waste may is recycled and is classified as sludge.[14]

- *Spent furnace brick* - This material is not considered a hazardous waste.

- *Waste ferrophosphorus* – This material is tapped from the furnaces. It is tapped into chill molds inside the furnace building and allowed to cool. After cooling, the ferrophosphorus is crushed and screened. This material is not considered a hazardous waste.

- *Wet process waste streams* - During the production of phosphoric acid, process wastewater and phosphogypsum are the primary waste streams from the wet processing. In addition, waste scale from the wet process is generated at a rate of 41,700 to 208,300 metric tons per year and is generally sent to a cooling pond. This waste is not expected to be hazardous. This does not apply in the production of elemental phosphorus.

- *WWTP Sludge/Solids* - This material is not considered a hazardous waste and does not apply in the production of elemental phosphorus.

8.7 Hazardous Waste

Elemental Phosphorus

Wastes generated from the extraction, beneficiation and processing of phosphate from phosphate-bearing ore considered hazardous and/or toxic by RCRA are as follows:

- Anderson filter media
- Precipitator slurry
- NOSAP slurry
- Phossy water
- Furnace scrubber blowdown
- Furnace building washdown

Ancillary hazardous wastes may be generated at on-site laboratories and may include used chemicals and liquid samples. Other hazardous wastes may include spent solvents (e.g., petroleum naptha), acidic tank cleaning wastes, and polychlorinated biphenyls from electrical transformers and capacitors.

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[14] U.S. Environmental Protection Agency, Office of Solid Waste, *Identification and Description of Mineral Processing Sectors and Waste Streams*, p. 281-303, April 1998