CHAPTER 12.28

Phosphate Rock

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Phosphorus is essential to plant and animal life. It provides the material for skeletal bone structure in animals as well as the material for cell membranes in both plants and animals. The largest and least expensive source of phosphorus is obtained by mining and concentrating the phosphate rock from the numerous phosphate deposits around the world. The principal uses for phosphate rock are in the manufacture of fertilizer ingredients for food crop nutrition and the production of animal feed supplements to promote healthy and quick skeletal growth for meat-producing livestock.

Phosphorus is also one of the most abundant minerals in the human body, second only to calcium. This mineral is essential for the healthy formation of bones and teeth and is necessary for our bodies to process many of the foods that we eat. It is a part of the body's energy storage system and helps with maintaining healthy blood sugar levels. Phosphorus is also found in substantial amounts in the nervous system. The regular contractions of the heart are dependent on phosphorus, as are normal cell growth and repair.

EVOLUTION OF PHOSPHATE FERTILIZERS

The discovery of phosphorus, its role in agriculture, and the early development of phosphate fertilizers were well documented by Vincent Sauchelli (1942, 1951, 1965). Phosphorus was first discovered by a German metallurgist, who made it by heating urine into a solid state. Although as early as 2,000 years ago, Chinese farmers applied calcined or lime-treated bones to their fields to improve crop growth, and ancient farmers from many parts of the world used human wastes and animal manure as the primary source of phosphorus for crops, the essential role of phosphorus in plants' growth was first explained in a scientific manner by Erasmus Darwin in 1799 (Beaton 2010).

The first true phosphate fertilizers were made by acidulating bones with sulfuric acid. This process originated in Europe in the early 1800s. In 1842, John Bennet Lawes of the Rothamsted Experimental Station was granted a patent for the production of superphosphate from bones, and he began manufacturing and selling this fertilizer the same year. This patent was amended in 1848 to include sulfuric acid treatment of phosphate ore. The number of superphosphate plants in England reached 14 by 1853.

Large-scale phosphate fertilizer production was made possible by replacing bones with mined phosphate rock as the phosphate source. Small amounts of phosphate ores were mined in the mid-1840s in England, France, and Spain and in the 1860s in Norway and Germany. Phosphate rock mined in Ontario and Quebec, Canada, was shipped to England for processing between 1863 and 1895. In the United States, phosphate mining began in 1867 in South Carolina, followed by Florida in 1888, Idaho in 1906, Wyoming in 1907, and Montana in 1921.

To date, about 120 phosphate minerals have been identified, with apatite accounting for approximately 95%. Other commercial phosphate minerals include kribergite, guano, and vivianite. There are two primary routes for recovering the phosphate values from phosphate rock. In the thermal process, phosphate is reduced by carbon to elemental phosphorous gas and condensed in water. Today's predominant process is the "wet acid" process in which phosphate rock is acidulated with sulfuric acid.

Superphosphate

A simplified reaction for producing superphosphate is shown in the following equation:

$$2Ca_5(PO_4)_3F + 7H_2SO_4 = 3Ca(H_2PO_4)_2 + 7CaSO_4 + 2HF \qquad \textbf{(EQ 1)}$$

The first patent for this fertilizer was granted in 1842, and production started the same year in England. The product was readily soluble in water compared to the relatively insoluble bones or phosphate ores. This process took off in the early 1850s in the United States and several other countries, initially using bones and later switching to mineral phosphate rock. This fertilizer dominated the world's phosphate fertilizer market for more than 100 years.

Another variation of superphosphate fertilizer is the single superphosphate (SSP), which is still popular in some countries. The molecular formula of SSP is $Ca(H_2PO_4)_2 \cdot H_2O$. SSP is one of the most important fertilizers in Brazil. This

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phosphorous source is also produced in other regions, such as Australia, China, India, and New Zealand. It accounts for 15% of the phosphate fertilizer used in India.

Triple Superphosphate

Triple superphosphate (TSP) is made based on the following equation:

$$2Ca_5(PO_4)_3F + 12H_3PO_4 + 9H_2O = 9Ca(H_2PO_4)_2 \cdot H_2O + CaF_2 \qquad \textbf{(EQ 2)}$$

This high-analysis phosphate fertilizer was first manufactured in Germany in 1872. Limited triple production began in the United States in 1890, with large-scale production initiated in 1907. Currently, TSP accounts for a few percent of U.S. phosphate fertilizer production, though it accounts for a substantial percentage of worldwide use, representing more than 10% of the total phosphate fertilizer market.

Ammonium Phosphates

Ammonium phosphates are now the most popular phosphate fertilizers. Diammonium phosphate (DAP), $(NH_4)_2HPO_4$, is manufactured by reacting ammonia with phosphoric acid. The nitrogen to phosphate ratio in DAP makes it an excellent product for direct application or one that blends well with other fertilizer materials to produce a variety of NPK (nitrogen, phosphorus, and potassium) fertilizers. Monoammonium phosphate (MAP), $NH_4H_2PO_4$, is also a fertilizer manufactured from phosphoric acid and ammonia. "It is an ideal product for dry bulk blending with other fertilizer materials. MAP is a product-of-choice for manufacturing fluid blends or suspension fertilizers" (Griffith 2010).

Ammonium phosphates were first produced commercially in the United States in 1916. With the development of the dependable Tennessee Valley Authority process for producing granular DAP, DAP became the principal phosphate fertilizer in the United States by late 1960s. Today, DAP represents approximately 40% of phosphate use in the United States. On a worldwide scale, ammonium phosphates accounted for less than 5% of the world's production of phosphate in the early 1960s but have reached roughly 60% today.

Wet Acid Process and Phosphogypsum Production

The term *wet acid process* usually refers to the manufacturing of phosphoric acid by reacting phosphate rock with sulfuric acid. The first phosphoric acid plant was built in Germany in about 1870 and in the United States in 1890 (Beaton 2010). In the past decade, many new phosphoric acid plants have been constructed in major phosphate-producing countries such as Morocco, China, and the Middle East.

The primary chemical reaction in the wet acid process may be expressed in Equation 3 using fluorapatite to represent phosphate rock and sulfuric acid as the reactant (UNIDO and IFDC 1998):

$$Ca_{10}F_2(PO_4)_6 + 10H_2SO_4 + 10nH_2O \rightarrow 10CaSO_4 \cdot nH_2O + 6H_3PO_4 + 2HF \qquad \textbf{(EQ 3)}$$

Depending on the value of n, the process is defined as the dihydrate (n=2) process, hemihydrate (n=1/2) process, or anhydrate process. The term $CaSO_4 \cdot nH_2O$ in the equation is simply referred to as phosphogypsum (PG).

BRIEF HISTORY OF MAJOR PHOSPHATE MINING OPERATIONS

Phosphate rock is the only economical source of phosphorus for the production of phosphate fertilizers and phosphate chemicals. Most of the world's phosphate rock reserves are widely distributed marine phosphorite deposits. In 1847, phosphate rock was first mined in England and used for fertilizer. Between 1863 and 1895, phosphate rock was shipped from deposits in Ontario and Quebec, Canada, to England for processing.

In the United States, phosphate ore was first discovered in South Carolina in 1837, and mining there began in 1867. Extensive exploration of the vast phosphate rock deposits in Florida was carried out during the 1880s, and mining started in 1888. In the Western Phosphate Field covering the Rocky Mountain states, mining of phosphate began in 1906 in Idaho, in 1907 in Wyoming and Utah, and in 1921 in Montana. The North Carolina deposits were the latest to be exploited in the United States; mining started there in the mid-1960s.

Phosphate ore was discovered in Algeria and Tunisia in 1885, and mining initiated in 1889. The world's most abundant and rich phosphate reserve, the Moroccan deposits, was first identified in 1914 and mined in 1921. The major guano phosphate deposits were found in the Pacific Islands in the 1890s. Mining of the rich guano phosphate resource commenced in 1900 on Ocean Island, in 1906 on Nauru, and in 1908 on Makatea.

One of the largest igneous apatite deposits was discovered on the Kola Peninsula in Russia around 1930, and mining started shortly thereafter. Other major igneous deposits were found between 1960 and 1980 in Mexico; Brazil, Peru, and Colombia in South America; Israel, Turkey, Jordan, Iraq, and Saudi Arabia in the Middle East; Angola, South Africa, and Western Sahara in Africa; and in India and Australia. Many of these igneous deposits are being mined in Russia, Brazil, South Africa, Jordan, and Australia, accounting for nearly a quarter of the world's phosphate rock production.

By some estimates, China has the most abundant phosphate resource in the world. However, China was a late starter in phosphate mining, with its first mine initiated in the 1930s and made small progress up to the 1980s. During the past 15 years, China has transformed from the largest phosphate fertilizer importer into a net phosphate exporter. According to the International Fertilizer Association, China produced 51 Mt (million metric tons) of phosphate rock in 2005, against 38 Mt from the United States and 28 Mt from Morocco.

Currently, the leading phosphate-rock-producing countries are the United States, Morocco, China, Russia, Tunisia, Jordan, Brazil, and Saudi Arabia. Other producers of appreciable amounts include Algeria, South Africa, Togo, Israel, Nauru, Senegal, Peru, Australia, and Syria.

South Carolina, United States

Phosphate mining in America started in South Carolina. A phosphate mining company was formed in 1867, 30 years after phosphate was discovered in the state. After about 20 years of profitable mining, the state courts made it easy for anyone to obtain a mining permit. As a result, the profit margin dropped by more than 80%, and most companies shut down their mines there and moved to the new, more profitable source of phosphate in Florida.

Florida, United States

Although phosphate rock mining for fertilizer manufacturing started in England in 1847, the true "Phosphate Rush" originated in central Florida about 40 years later. It began with the river pebble of the Peace River, followed shortly thereafter by the discovery of the hard rock region near Dunnellon, and ultimately the land pebble districts. In 1892, there were 215 mining companies in Florida. By 1900, this number had dwindled to about 50 because of consolidation, and down to less than 10 by early 1990. Today, there are only two companies involved in phosphate mining in Florida. Mining of river pebble peaked in 1893 and ceased in 1908. Hard rock mining ceased in 1965 in the Ocala–Dunnellon region. Pebble mining quickly became the dominant form of mining, and this type of phosphate mining continues today in central and north Florida.

Tennessee, United States

When the "blue rock" was discovered in 1893, Tennessee was a formidable competitor with Florida in phosphate mining operations. But that competition was short lived because the easy-to-access, thick deposits ran out quickly and companies were forced to mine the rather thin seams of about 30 in. of thickness by underground mining. Mining of the brown phosphate rock started around 1896. By 1936, nearly all high-grade deposits in Tennessee were mined out, but phosphate mining continued well into the 1950s because the electric furnace method could process rock as low as 50 BPL (about 23% P_2O_5). *Bone phosphate of lime*, or *BPL*, is a term used by the phosphate industry to express phosphorous content in phosphate rock as percent of tricalcium phosphate, $Ca_3(PO_4)_2$. The most common term to express phosphorous content is *percent* P_2O_5, which can be derived by dividing BPL by 2.185.

Tennessee played a significant role in advancing phosphate mining and processing technologies. It pioneered the use of hydrocyclones for desliming, development of the flotation process, and optimization of the furnace acid technique.

Western United States

The Western Phosphate Field covers a large part of Idaho, a strip of Wyoming, a corner of Utah, and a tip of Montana. This Phosphoria Formation is a 350,000-km^2 area of the northern Rocky Mountains. Phosphate mining began in the early 1900s in southeast Idaho to supply fertilizer to the young agricultural industry. Most of the mines were underground and small. After World War II, technology changed and a growing demand fueled large-scale extraction of phosphate. At this time, open pit mining became the predominant phosphate mining method. Idaho production of phosphates currently constitutes more than 12% of national production. Today there are four open pit operations that produce more than 5 Mt of rock per year.

North Carolina, United States

The North Carolina deposits were the latest to be exploited; mining started in the mid-1960s. Currently, there is one phosphate mine in operation.

Morocco

Shortly after phosphate deposits were discovered in 1914, the Moroccan government established the Office Chérifien des Phosphates Group, commonly known as the OCP Group, and began mining in 1921. Owned solely by the government and managed in nearly the same way as a private company, the OCP Group has held a monopoly on mining, processing, and trading phosphate rock and phosphate fertilizers in Morocco for nearly a century. That monopoly recently showed some flexibility by allowing one private company to mine phosphate and by forming joint ventures with the European Union, India, and Pakistan. Until 1975, the OCP Group's primary business was mining and exporting phosphate rock, fully enjoying the luxury of having the most abundant high-grade ore that required only simple washing and sizing. That business model was revamped during the mid-1970s as accumulation of lower-grade rock made it economically advantageous to produce phosphoric acid or phosphate fertilizers locally. For example, Morocco exported zero phosphate fertilizer up to 1962 but put 75,400 t (metric tons) on the world market in 1976 and passed the one-million-ton mark by 2001. This trend is continuing. Today, Morocco produces well more than 15% of the world's total phosphoric acid. Many of its recent phosphate projects are entirely dedicated to deep processing. The OCP Group's Jorf Lasfar Complex, for example, turns out 2 Mt of P_2O_5 products per year, with 50% exported as phosphoric acid and 50% as fertilizers such as DAP, MAP, and NPK.

Russia

Russia started mining phosphate in the early 1930s and quickly became the world's second largest phosphate rock producer. It maintained that rank during the early 1980s. However, since the fall of the former Soviet Union, phosphate production quickly dropped to roughly 10 Mt a year, making Russia the world's fourth largest producer. Still, approximately one-third of Russia's phosphate rock production is exported.

The Khibiny Complex on the Kola Peninsula is the workhorse of recent phosphate mining in Russia, turning out more than 80% of its total production. This is an igneous deposit. Although the ore grade is not that impressive, the final concentrate analyzes up to 39% P_2O_5.

Russia also has a large sedimentary phosphate deposit in the Karatau Basin with a resource of about 8,000 Mt averaging 21% P_2O_5. In early mining, phosphate ore was crushed, ball milled, and screened to obtain a product of 23% P_2O_5 for elemental phosphorous manufacture. Other major sedimentary deposits are located along the southern margins of the Moscow Basin.

Tunisia

Tunisia is the second largest phosphate producer in Africa, turning out about 8 Mt per year of rock on average in recent years. Phosphate was first discovered in Tunisia in 1885 by an amateur French geologist. Subsequent extensive geological explorations revealed the existence of vast phosphate formations south and north of the so-called Kasserine Island. Like Morocco, the Tunisian government founded the Compagnie des phosphates et de chemins de fer de Gafsa in 1896 to establish a national phosphate industry in the country. The first phosphate was mined in Tunisia in the same year. Rock production reached an impressive level of 200,000 t in 1900.

After these early beginnings, the Compagnie des phosphates et de chemins de fer de Gafsa has gone through several transformations in its structure during the long course of its history before attaining its current status and becoming the Groupe Chimique Tunisien (GCT). GCT is now the world's fifth largest phosphate producer.

For many years, GCT has been gradually developing opencast mines to replace underground capacity to reduce costs. From 1978–1991, five opencast mines were opened. All Tunisian phosphate rock mines are now opencast. This move has resulted in significant savings in labor costs and increased productivity. Over the last decade, GCT has seen its merchant rock output rise from 6 Mt to more than 8 Mt per year.

Togo

Large-scale phosphate mining in Togo started in 1963 but has become the country's most important industry, with an annual production of more than 2 Mt. The phosphate deposit is a relatively thin layer ranging from 2 to 6 m, covered by a thick overburden of sand and clay up to 30 m. The phosphate rock grade, however, is one of the best in the world, analyzing about 36% with a minimal amount of Mg, Al, and Fe.

South Africa

South Africa is blessed with rich mineral resources. Its gold and diamond mining industries are formidable on a global scale. Many people do not realize, however, that the phosphate reserve base in South Africa ranks fourth in the world. The majority of South Africa's phosphate deposits are igneous in nature. The deposits are generally of low to medium grade with high Fe and Al contents.

The major Phalaborwa phosphate deposit was discovered in 1904. This phosphate resource was commercially mined in the early 1930s by South Africa Phosphates Ltd., which mined high-grade apatite pockets and sold them as a fertilizer product, but soon went bankrupt because of the less expensive Moroccan phosphate rock imports. The government later formed the Phosphate Development Corporation Ltd., which eventually became Foskor Ltd. New phosphate mining started in the early 1950s. Gradually, the fertilizer producers adapted their processes to the use of the igneous phosphate rock produced, and in 1976 a significant expansion enabled production of export-quality product. Today, approximately one-third of the phosphate rock is used domestically, one-third is exported as rock, and the remainder is acidulated for phosphoric acid and fertilizer ingredients for export.

China

In China, the Haizhou phosphate deposit (now the Jinping phosphate deposit) was found during the Tongzhi (1862–1874) period of the Qing dynasty. The Kunming phosphate deposit was discovered during a search for refractory clay for a smelting plant in 1931. The Jinping phosphate mine started operations in 1914 and was the first in China.

Before the founding of the People's Republic of China in 1949, the Chinese phosphate fertilizer industry was of little importance. Since then, Chinese geologists have conducted extensive geological reconnaissance, exploration, and evaluation of metamorphic phosphate deposits in the pre-Sinian system. As a result, huge amounts of phosphate deposits were identified in Yunnan, Guizhou, Sichuan, Hunan, and Hubei provinces, earning China the top spot in the world's phosphate reserves.

SSP was first developed in the 1950s, followed by furnace (or fused) calcium–magnesium phosphate (FCMP) fertilizer during the 1960s. High-concentrate phosphate and compound fertilizers such as DAP, MAP, TSP, and NP (nitrogen–phosphorous fertilizers) were developed quickly after the 1980s. During the past 10 years, the output of phosphate fertilizer in China increased in parallel with its gross domestic product (GDP) growth, with an average rate of 13.4% annually. The percentage of high-grade phosphate fertilizer also increased from 1% to more than 20% per year.

Until recently, SSP and FCMP were the primary phosphate fertilizers produced in China, because of the suitability of phosphate rock resources in China. The low-grade, silica- and calcium-containing, semi-self-melting phosphate rock is used for the production of FCMP in Hubei and Hunan. The waste rock of 20% P_2O_5 from the high-grade mines in Yunnan is also used for producing good-quality FCMP. SSP is another significant phosphate fertilizer in China for the benefits of S and Ca.

Although many of the new phosphate mining projects are coupled with producing high-grade fertilizers (DAP, MAP, and NPK), the production of SSP and FCMP will not see much decrease in China for three reasons:

1. These two varieties are relatively inexpensive.
2. Chinese farmers have gained tremendous experience in applying these materials.
3. These fertilizers also supply sulfur, calcium, and magnesium to soils.

Nauru

Phosphate (guano) deposits occupy about 90% of the island of Nauru. These deposits are of the highest grade, with the run-of-mine ore analyzing up to 40% P_2O_5. Nauru once possessed the highest GDP per capita in the world because of its rich phosphate deposits, but they have been nearly depleted.

Nauru was discovered in 1798 by a British sailor. Eleven years later, phosphate was discovered, and it turned out to be profitable for decades to come. In 1906, the Pacific Phosphate Company started mining phosphates with the support of the German government. After World War I, Nauru became a trust territory jointly administered by Australia, Britain, and New Zealand. The British Phosphate Commission was established to run the phosphate mining operations. After a brief pause during World War II, phosphate mining continued at an increasing rate. After the island achieved independence, the government-owned company Nauru Phosphate Corporation (NPC) was formed. NPC took over all phosphate operations in 1970. By the year 2000, the phosphate deposits were nearly depleted, leaving behind some small-scale operations.

Australia

Because of its membership in the Nauru Trust Territory and proximity to the best-quality phosphate rock from Nauru and Christmas Island, Australia had not given any priority to phosphate mining for a long time. Phosphate rock was first discovered in Australia in 1966. Exploration for rock phosphate was at that time encouraged because of the realization that the phosphate deposits at Christmas Island and Nauru were soon to run out. The Phosphate Hill rock phosphate deposit in northwest Queensland was first investigated extensively and targeted for the Queensland Phosphate Project. In 1975, BH South established a phosphate rock mine, a beneficiation plant, rail access, and port facilities. Because of production difficulties and various challenges, the operation was closed in 1978.

In 1980, Western Mining Corporation (WMC) acquired BH South's interests in Phosphate Hill and additional reserves. However, little activity took place during the 1980s and early 1990s. Recognizing that to achieve an acceptable return on investment the phosphate rock would have to be converted into either granulated TSP or ammonium phosphates, WMC decided to invest in a facility for the manufacture of ammonium phosphates. This proved to be a profitable proposition and placed Australia back on the map of the world's major phosphate producers by 2002.

Saudi Arabia

Saudi Arabia is a "sleeping giant" in terms of phosphate mining potential in the Middle East, with phosphate resources estimated up to 3,000 Mt averaging 18%–21% P_2O_5. The largest phosphate formation is the Sirhan-Turayf sedimentary deposit, which extends into Jordan, southern Iraq, and Syria. The best explored and largest deposit is at Al Jalamid, which has measured reserves of 213 Mt averaging 21% P_2O_5 and a stripping ratio of 2.3:1. Indicated resources amount to an additional 187 Mt, with 19.7% P_2O_5 and stripping ratios of 5:1 or less. The second most important deposit is in the Umm Wu'al north area with a total resource of 537 Mt averaging 19.35% P_2O_5 and a stripping ratio of less than 5:1. Saudi Arabia already has a large phosphate operation producing about 3 Mt of phosphate rock, and it is constructing another mining and chemical processing complex touted as the world largest integrated phosphate operation.

Brazil

Geological studies of Brazilian phosphate deposits were initiated as early as 1925, followed by extensive exploration from 1943–1969. However, many of the large phosphate complexes were established during the late 1970s. For example, Bunge's mine at the Araxá Complex began mining in 1977, whereas the largest phosphate mine, Fosfertil's Tapira mine, began production in 1978. Brazil is moving quickly toward self-sufficiency in phosphate fertilizers.

Jordan

Unlike some of its oil-rich neighbors, Jordan has phosphate deposits that are its primary natural resource and a major source of export income. Phosphate deposits cover nearly 60% of Jordan. At the current rate of about 8 Mt of phosphate rock, Jordan's proven reserve can sustain the industry for hundreds of years. Jordan Phosphate Mines Company (JPMC) was one of the earliest phosphate companies. Established in 1935 as a quasi-private company, JPMC has been the only player in phosphate mining and fertilizer production in Jordan. The company started mining in the 1930s from the Ruseifa mine. Mining at the El-Hassa mine was commenced during the 1960s. In the late 1970s, production started from the El-Abiad mine. The newest mine, the Eshidiya mine, was opened in 1988. Jordan is a world-leading phosphate rock exporter.

Canada

Even though phosphate rock from Ontario and Quebec was shipped to England for processing as early as 1863, there had been no major phosphate mining operation in Canada until 1999, when Agrium started its Kapuskasing phosphate operation in Ontario. Phosphate is mined from the Cargill deposit. This deposit was identified as a magnetic anomaly in 1954 and discovered to be a phosphate deposit in 1975. The Cargill deposit is an alkalic igneous complex. Some new deposits were discovered recently in Quebec, with significant amounts of rare earths or niobium. As a result, the Quebec government has recently approved a $750 million phosphate mine project (Topf 2015). The mine will produce phosphate rock product to be shipped from Sept-Îles, Quebec, to Norway, where Yara International will extract the phosphate to produce fertilizer.

Mongolia

Although there is currently no phosphate mining activity in Mongolia, its vast phosphate resources are worth mentioning. There are two phosphate reserve basins in Mongolia. The first area, the Khulosgul Basin, was discovered in the north of the country through geological exploration work from 1963 through 1986. The Zabkhan phosphate basin was discovered in the west of the country from 1987–1997. As a result of broad geological exploration work in Mongolia since 1963, more than 50 deposits have been discovered in the two basins, with an estimated total reserve base of approximately 5.7 billion t. Limited efforts have been made to utilize the phosphate rock by mechanical activation.

GEOLOGY, DEPOSITS, AND RESOURCES

Generally, phosphate minerals are found in igneous, metamorphic, and sedimentary deposits. In sedimentary marine ores, the phosphate is usually a carbonate fluorapatite. In igneous deposits, the phosphates have compositions close to that of fluorapatite. In some deposits, Ca-Fe-Al and Fe-Al phosphates are associated with apatite (McClellan and Germillion 1980). Currently, the apatites recovered from igneous and metamorphic rocks have commercial importance, but such apatites supply only a small fraction of the world market. On the other hand, sedimentary phosphates have been, and no doubt will continue to be, the major source of commercial raw material for the phosphate industry.

Sedimentary Phosphate Deposits

An enlightening description of the phosphate cycle is provided by Bateman (1952):

> The sedimentary cycle of phosphorus is puzzling and fascinating. Dissolved from the rocks, some of it enters the soil from which it is abstracted by plants; from there it passes to the bodies of animals and is returned via their excreta and bones to accumulate into deposits. Those in turn may undergo resolution and reach the sea, and there the phosphorus is accumulated or deposited by sea life, embodied into sediments and returned to the land on uplift, when a new cycle may start. Some of the phosphorus of the sea is absorbed by fish life, and the fish in turn are eaten by birds whose excreta have built up great phosphate deposits on islands of the Pacific.
>
> Commercial beds of phosphate are formed only under marine conditions in the form of phosphorite. The beds have been formed from early to recent geologic periods and extend with remarkable regularity over thousands of square miles. They are sparingly fossiliferous and are interlaminated with marine fossiliferous beds. These features together with their oolitic character indicate a marine origin.
>
> The great phosphate deposits of the world have been formed by the process of sedimentation. Those of Algeria, Tunisia and Morocco together yield the largest production in the world of the greatly desired

> mineral. The Moroccan deposits occur as horizontal beds along with limestone, marls and clays in which there are 3 to 4 beds up to 2.5 meters thick. The western United States deposits underlie parts of Utah, Wyoming, Idaho, and Montana and extend into Canada. The beds are in the Phosphoria formation of Permian age, and the chief bed is about 5 feet thick.... Other sedimentary phosphate deposits are found in Egypt and Russia. The large phosphate deposits of Florida, which supply most of the United States fertilizer and chemical consumption, are not strictly sedimentary beds but are pebble deposits derived from a sedimentary phosphate bed. The guano deposits of the Pacific islands also are not sedimentary.

These sedimentary apatites, because of their widely differing modes of chemical composition, display large variations in physical forms and types of associated gangue. Accordingly, these ores fall into one of the following three principal categories (Lehr and McClellan 1973).

Siliceous Ore

In this type, the major gangue mineral is quartz, chalcedony, or opaline forms of silica. In the United States, the Bone Valley deposit in central Florida, the upper unit of the Hawthorn Formation in north Florida, and the upper zone of the Hawthorn Formation in central Florida belong to this type. Phosphate ores in Australia and Senegal also fall under this category.

Carbonaceous Ore

This type of ore consists of phosphatic limestones or calcareous phosphates in which calcite, dolomite, or ankerite is mixed with the phosphate, or which occurs as intercalated seams. These include the lower zone of the Hawthorn Formation in central Florida; most of the phosphate deposits in Hubei and Guizhou provinces, China; the Karatau Formation in Russia; a majority of the Mongolian deposits; and some of the Moroccan phosphates.

Clayed Phosphate

Clayed phosphate ores are associated with gangue minerals containing mainly clays and hydrous iron and aluminum oxides. These gangue minerals are concentrated mostly in the silt and clay size ranges. Most of the phosphate ores in Morocco and Western Sahara, Tunisia, and Togo contain up to 40% clay, whereas the Florida phosphate matrix is composed of approximately one-third each of clay, phosphate, and sand.

Igneous Phosphate Deposits

Among the more economically important igneous apatite deposits being exploited commercially are the Khibina nepheline syenite massif near Kirovsk in the Kola Peninsula in Russia, the Jacupiranga Alkalic Complex in Brazil, and the Phalaborwa carbonatite in South Africa.

The most important deposit of igneous apatite mined today comes from the Kola Peninsula; the output is more than 9 Mt per year of concentrates with a P_2O_5 grade of 39% from an ore assaying 18% P_2O_5, 23.1% SiO_2, and 13.3% Al_2O_3 in a bonded phase of nephelinic syenites. Other important igneous phosphate ores are present at Phalaborwa in South Africa. The Igneous Complex is comprised of a suite of intrusive alkali rocks, which intruded granite gneiss, to form three coalescing and concentric lobes. The complex is about 7 km long and varies from 2 km to 4 km wide. The outermost zone consists of syenite with the intrusion being a feldspathic pyroxenite. The next zone consists of an apatite-bearing phlogopitic pyroxenite. Foskor operates an open pit for apatite extraction in a corner of this zone. The apatite varies from 0%–30% P_2O_5, averaging 7%, with the principal gangue minerals of diopside and phlogopite. The pyroxenite zone is followed by the foskorite zone, which consists of magnetite, serpentine, and apatite, assaying 6%–11% P_2O_5. Originally within the foskorite zone was a carbonatite core hill, which now has largely been excavated and is the large open pit of the Palabora Mining Company (PMC). In 1979 Foskor and PMC reached an agreement in which PMC would extend its open pit, with Foskor sharing the cost, and in return Foskor would receive certain types of ore mined by PMC. Foskor now produces phosphate rock from three sources: pyroxenite ore, foskorite ore, and PMC tailings (Schmidt 1999).

The Brazilian apatites also represent an important source of igneous phosphate ores. They are included in carbonatites (with simple carbonates as in Jacupiranga or as more complex ones with iron carbonates, phlogopite or vermiculite, titanium minerals, barytine, pyrochlore, etc.). The P_2O_5 contents are comparatively low, from 5% for Jacupiranga to 15% for Araxá.

World Reserves and Resources

How to classify mineral resources remains a topic of debate. This author believes in the simple way of defining phosphate deposits as reserves and resources, which also seems to be the dominant view in the United States. *Reserves* are the deposits that could be economically mined and processed to produce salable products under current economic conditions using available technologies. *Resources* are identified deposits that meet specified minimum physical and chemical criteria related to current mining and production practices, including those for grade, quality, thickness, and depth. Resources encompass reserves.

The International Fertilizer Development Center (IFDC) recently conducted a detailed study of world phosphate resources (Kauwenbergh 2010). Based on this study, the world has total phosphate reserves of 60 billion t, on the basis of 30% P_2O_5, and 290 billion t of resources. These numbers are close to U.S. Geological Survey (USGS) newly updated estimates of 67 billion t of reserves and 300 billion t of resources (Table 1). Table 2 lists reserves and resources of major phosphate-hosting countries based on the IFDC study.

UTILIZATION OF PHOSPHATE ROCK

World phosphate rock production reached nearly 200 million t by the year 2012 and has maintained at that level since. Table 3 shows phosphate rock production data for the major producing countries.

Figure 1 shows the distribution of various uses for phosphate rock in 2005. Wet-acid-based products account for about 71%, followed by SSP (14%), other non–wet-acid-based products (about 10%), elemental phosphorus (5%), and direct application.

The majority of phosphate rock requires deep beneficiation involving flotation prior to chemical processing. Figure 2 shows a simple classification of phosphate rock based on the degree of beneficiation difficulty. Figure 2 illustrates the importance of beneficiation/flotation in the processing of phosphate. All new mines being constructed or considered will include flotation, with the exception of the phosphate mine in Peru. More importantly, about three-quarters of the phosphate deposits are contaminated by carbonaceous minerals, which makes beneficiation more challenging.

Table 1 Updated world phosphate reserves and resources

Data Source	Reserves, billion t	Resources, billion t
International Fertilizer Development Center	60	290
U.S. Geological Survey	67	>300

Table 2 Major phosphate reserves and resources in the world

Country	Reserves, Mt	Resources, Mt
Australia	82	3,500
Brazil	400	2,800
Canada	5	130
China	3,700	16,800
Egypt	51	3,400
Israel	220	1,600
Jordan	900	1,800
Morocco	51,000	170,000
Russia	500	4,300
Senegal	50	250
South Africa	230	7,700
Syria	250	2,000
Togo	34	1000
Tunisia	85	1,200
United States	1,800	49,000
Other countries	600	22,000
World total	**60,000**	**290,000**

Source: USGS 2010–2016.

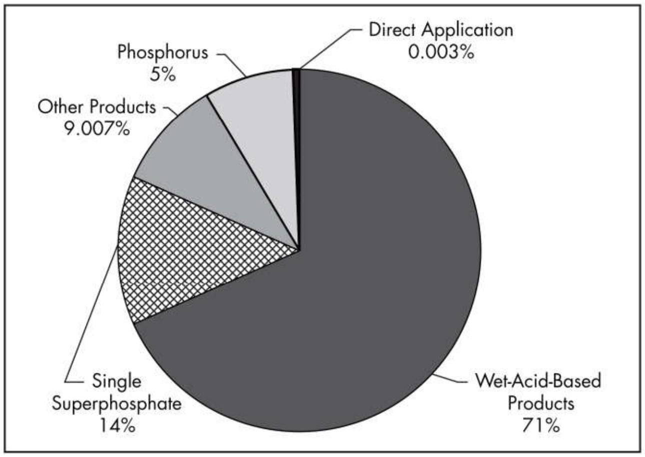


Figure 1 Distribution of various uses for phosphate rock

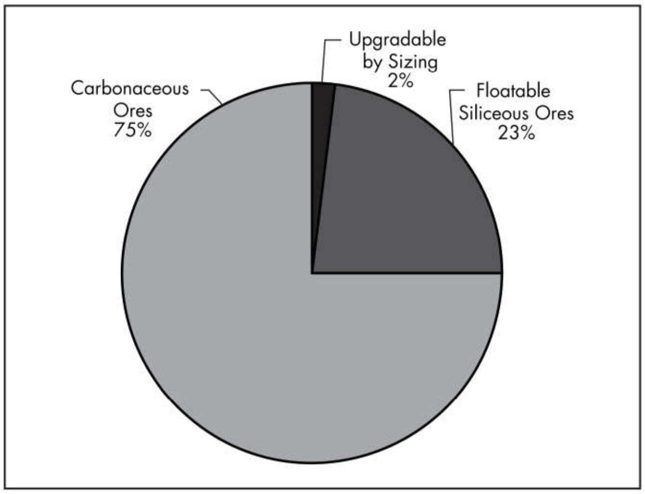


Figure 2 Classification of phosphate ores by beneficiation readiness

Table 3 Phosphate rock production, thousand tons

Country	2010	2011	2012	2013	2014	2015 (estimated)
Australia	2,095	2,519	2,000	1,919	2,600	2,600
Brazil	5,693	6,094	6,094	5,939	6,040	6,700
China	69,100	73,000	78,500	77,000	100,000	100,000
Egypt	3,435	4,746	5,738	5,315	5,500	5,500
India	2,000	1,910	1,154	1,211	1,110	1,100
Israel	3,078	3,118	2,871	3,437	3,360	3,300
Jordan	6,529	7,589	6,382	5,399	7,140	7,500
Morocco	25,655	27,821	26,844	25,489	30,000	30,000
Peru	791	2,544	3,209	3,547	3,800	4,000
Russia	10,844	10,304	10,282	10,743	11,000	12,500
Saudi Arabia	121	1,068	3,097	3,055	3,000	3,300
South Africa	2,499	2,468	2,065	1,925	2,160	2,200
Syria	3,765	3,542	1,780	898	1,230	750
Tunisia	8,132	2,510	2,607	3,284	3,780	4,000
United States	25,244	27,619	29,475	30,548	25,300	27,600
Others	15,629	14,104	14,578	13,584	11,980	11,950
Total	**182,111**	**190,957**	**196,676**	**193,293**	**218,000**	**223,000**

Source: USGS 2010–2016.

PHOSPHATE MINING AND BENEFICIATION TECHNOLOGY

During the late 19th century, phosphate mining operations in Florida involved wheelbarrows, picks, and shovels, followed by mule-drawn scrapers. Next came steam shovels and centrifugal pumps mounted on barges. Large-scale, more efficient mining was made possible only when draglines were introduced in the late 1920s.

The following numbers demonstrate how draglines increased mining efficiency. In the 1900s, it took 3–4 years to mine 15 acres with picks and shovels. Even a small dragline in the early days could mine about 5 acres a year. As draglines became larger, companies were able to mine 500–600 acres a year. Today, a dragline with an 80-yd bucket can mine up to 20 acres a month.

Phosphate ores usually require upgrading, that is, beneficiation, before they can be used for producing fertilizers (e.g., SSP, TSP, and FCMP) or products via the wet acid process. Early beneficiation methods included simple washing, screening, and crushing/grinding. A small amount of deposit could even be used directly.

In the 1920s and 1930s, separation advancements focused on improving washing and screening reduced the amount of phosphate rock discarded. The most dramatic change was the introduction of flotation technology in about 1927. Flotation of phosphate initially used oil as reagent and then changed to fatty acid flotation with oil as an extender. In Florida, the Crago "double float" process truly revolutionized phosphate beneficiation, in terms of both increasing P_2O_5 recovery and reducing silica content in the final concentrate. This process was adopted during the 1940s and is now the predominant beneficiation practice in Florida.

Study of the magnetic susceptibility of minerals dates to the late 1700s, and magnetic separation was used for nearly 200 years in upgrading iron ores. This separation technology finds its use in processing igneous phosphate ores in Brazil, Canada, and South Africa. Both high-intensity and low-intensity separators are used.

Limited gravity separation circuits are found in Florida beneficiation plants. Spiral separators are used to remove sand from the ultra-coarse (14 × 28 mesh) fraction. Heavy media separation was used to remove dolomite in the pebble fraction from the late 1980s to early 2000s, but these machines are no longer in use because of low separation efficiency and high operation costs.

The calcination process was employed in the western United States to remove carbonaceous materials from phosphate rock, and it is still used in Morocco to eliminate organic gangues.

Mining

Surface Mining with Dragline

Today, most phosphate rock is mined using large-scale surface methods. In the past, underground mining methods played a greater role, but their contribution to world production has declined. For example, in Idaho, phosphate mining has been transformed from 100% underground during the 1930s to nearly all surface mining today. Surface phosphate rock mining operations can vary greatly in size. Extraction may range from several thousand to more than 10 million tons of ore per year. In many cases, operations supply concentrate to a nearby fertilizer processing complex for the production of fertilizer products. The land area affected by the surface operations can vary widely, depending on the ore-body geometry and thickness. At similar extraction rates, mining of flat-lying thin ore bodies as found in Florida (United States) will affect a far wider area of land than the mining of thicker ore bodies as found in Brazil and Idaho. The depth of excavations may range from a few meters to more than 100 m. Currently, most phosphate rock production worldwide is extracted using opencast dragline or open pit shovel/excavator mining methods. This method is widely employed in parts of the United States, Morocco, and Russia. Underground mining methods are currently used in Tunisia, Morocco, Mexico, and India. Figure 3 shows a large dragline used for mining phosphate in Florida.

Figure 3 Surface mining of phosphate rock with dragline in Florida, United States

Surface Mining with Drilling and Blasting

In Khouribga, Morocco, the overburden in thickness of 16–17 m is drilled, blasted, and removed by dragline to the side of the mining area for subsequent reclamation. Small draglines, electric shovels, and bulldozers are used to recover the upper ore body. The intercalating limestone layer is blasted and removed to expose the Bed I phosphate, and then it is loaded onto trucks. The process is repeated to mine the Bed II phosphate deposit. At Vernal, Utah, mining begins with removal of topsoil and temporary storage for reclamation. Overburden is drilled and blasted with ANFO and shoved into mined-out areas. The ore is then drilled and blasted and loaded by shovel into trucks for transport to a feeder-breaker. The broken product at 25 cm is belt-conveyed to a 10,000-t live storage pile. Overburden in mined areas is contoured, covered with topsoil, and seeded.

Dredge Mining

Consideration of mining systems for the Santo Domingo, Mexico, project included bucketwheel excavators, draglines, scrapers, shovels, and dredges. A dredge-based system was favored primarily because the other systems could not operate effectively below sea level. Low operating and maintenance costs prompted the final selection of floating hydraulic cutter suction dredges with 27-in.-diameter suction heads. Two Ellicott dredges were used, each capable of pumping about 2,000 t/h of slurried solids to the floating primary beneficiation

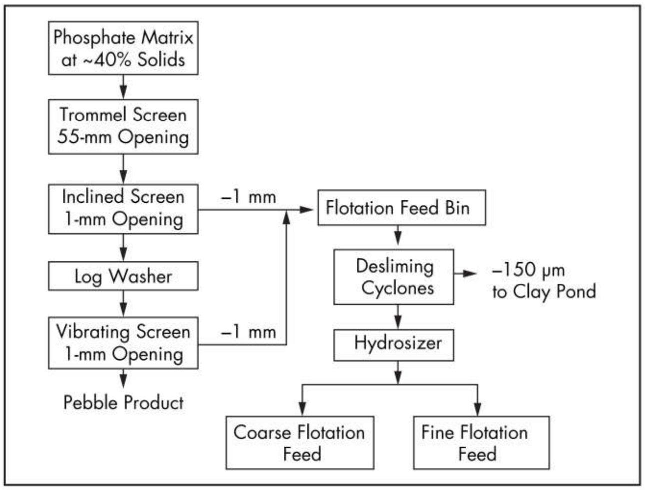


Figure 4 Simplified flow sheet of washing and sizing of Florida phosphate ores

plant. Dredge mining is also practiced at the Wingate Creek Mine in central Florida.

Materials Haulage

The three major methods of hauling materials in phosphate mining are pumping, trucking, and transporting using conveyer belts. In the United States, pumping is the predominant means of moving ore and tailings, with the longest pipeline running 87 mi. The J.R. Simplot Company transports phosphate rock slurry from its Smoky Canyon Mine in Wyoming to Pocatello, Idaho. OCP Group's recently constructed pipeline in Morocco is equally long.

PHOSPHATE MINERAL PROCESSING

According to the beneficiation difficulty, phosphate minerals may be classified into three categories: siliceous, carbonaceous, and magnetic. Typical siliceous phosphate ores are found in Florida, Morocco, and Jordan. Carbonaceous phosphate deposits are found all over the world (China, the western United States, the lower zone in central Florida, Saudi Arabia, and some parts of Morocco) and will constitute the source of most future phosphate rock production.

Beneficiation of Siliceous Phosphates

Washing and Sizing

Washing and sizing are commonly used on clayey ores as pretreatment steps prior to flotation. This operation is of paramount importance in Florida, because the phosphate ore as mined, known locally as the matrix, contains a high percentage of clay or clay-sized minerals. Figure 4 shows a simplified processing flow sheet. Details may vary significantly from mine to mine, particularly in sizing equipment and flotation feed size fractions.

The coarsest portion of the disaggregated matrix (+50 mm) is removed as waste by trommel screens because it usually represents lower phosphate grade and is likely to contain significant dolomite-cemented conglomerates. The portion of phosphate rock processed in the washer by disaggregation and simple screening is expected to diminish from the roughly 50% for the Bone Valley to about 20% as the mining moves to the south or west of the current Florida mining district. Because pebble production is relatively inexpensive, the reduction of this production has an unfavorable impact on costs. The disaggregation, which largely takes place in the pumps and transport lines, is completed by log washing at high percent solids to scrub residual clay from the mineral surface and is countercurrently washed away from the rock. Vibrating, plastic-coated screen decks permit the final removal of the pebble (1 × 55 mm).

For simplicity, Figure 4 does not show the split washing and sizing for the coarse (20 × 55 mm) and fine (1 × 20 mm) pebbles. The coarser washer pebbles are discarded when the dolomite content is too high, which is quite common when the draglines dig deeper.

The slurry containing flotation feed and clays, which represents the combination of pebble screen undersize, log washer overflow, and most other slurry streams created in the washer, is pumped through two stages of hydrocyclones with recycled water added to the first hydrocyclone underflow for dilution. This removes roughly 98% of the fine suspended clay particles from the flotation feed and creates a clay slurry waste containing 3% solids on average, which by themselves settle very slowly in clay ponds. Because roughly 30%–40% of the mined material weight is clay, these ponds represent a substantial capital investment in terms of both construction and reclamation when filled. These ponds also act as reservoirs for water recovery and recirculation. Most phosphate flotation plants separate the flotation feed (–1 mm to + 105 μm) into at least two size fractions with the split point at about 420 μm or 35 Tyler mesh.

In many other operations, washing and sizing produce the finished product. WMC in Australia uses water scrubbing to remove fine clays before shipping the low-grade rock (23.5% P_2O_5) to its chemical plant.

In Togo operations, the phosphate ore is first scrubbed with seawater and then wet screened at between 0.8 and 3 mm, depending on the quality of the ore. The clay is then removed using hydrocyclones. The high-ferrous product is further dried and upgraded using electromagnetic separation technology.

A large portion of the currently mined phosphate rock in Jordan only requires crushing and screening to become a salable product. In most operations, phosphate ore is first crushed and screened to reject the + 12.7 mm material. When the –12.7 mm fraction makes the grade of 66%–68% BPL, it is directly fed to rotary cascading dryers to produce a final product. The lower-grade ore requires beneficiation, which involves sizing and desliming at about 200 mesh using hydrocyclones.

Until recently, beneficiation of phosphate in Morocco has involved only crushing and sizing, except for the "brown" Youssoufia phosphate, which is calcined above 700°C to eliminate organic matter. At the Benguérir mine, located 70 km north of Marrakesh, the first treatment step is removing + 100 mm material, followed by crushing and wet screening at 10 mm, producing nearly 4 Mt per year of wet phosphate rock of –10 mm. Processing of phosphate ore at the Bou Craâ mine is almost as simple as it gets: ore is crushed and slurried with seawater, followed by sizing and desliming to remove unwanted materials. At the Khouribga mine, beneficiation is more complicated. High-grade ore is screened and stored, low-grade ore is treated using log washers and hydrocyclones, and lower-grade ore is calcined.

Crago "Double Float" Process

The Crago "double float" process shown in Figure 5 has been practiced in Florida for more than half a century. Modified versions or parts of the process are also practiced in other parts of the world. This process is particularly suitable for processing siliceous phosphates, where low-silica product is required. The flotation plant consists of several important processing steps:

1. Remove the flotation feed at a controlled rate from partially consolidated storage bins.
2. High solids condition the solids (65%–70%) with a pH modifier and anionic flotation reagent (namely, a vegetable-derived fatty acid) as a collector, a petroleum extender, and sometimes surfactants to impart desirable selectivity or frothing characteristics.
3. Dilute with clean, recirculated water to roughly 20% solids for the rougher flotation step of the bulk of the phosphate mineral from the sand.
4. Collect the froth concentrate and scrub the solids with sufficient sulfuric acid to free the fatty acid and fuel oil coating, and then rinse and dewater with clean, recycled water to provide a clean mineral surface for further separation.
5. Dilute with either fresh or very clean recycled water, adjust the pH to approximately neutral, and add a cationic flotation reagent (an amine, a light petroleum extender, and sometimes a surfactant) into a mixing tank or the feedbox of the flotation cells. (This cleaning flotation step is aimed at removing any fine sand inadvertently carried into the rougher concentrate by the relatively high reagent levels required to float the phosphate mineral.)
6. Partially dewater the cleaner cell underflow concentrate and hold it in bins until it is routed to the appropriate storage pile locations when chemical assays are available.
7. Combine the cell underflow tailing product from rougher flotation and the froth tailing product from cleaner flotation to create a combined tailing that is pumped to reclamation areas for land filling in the mine.

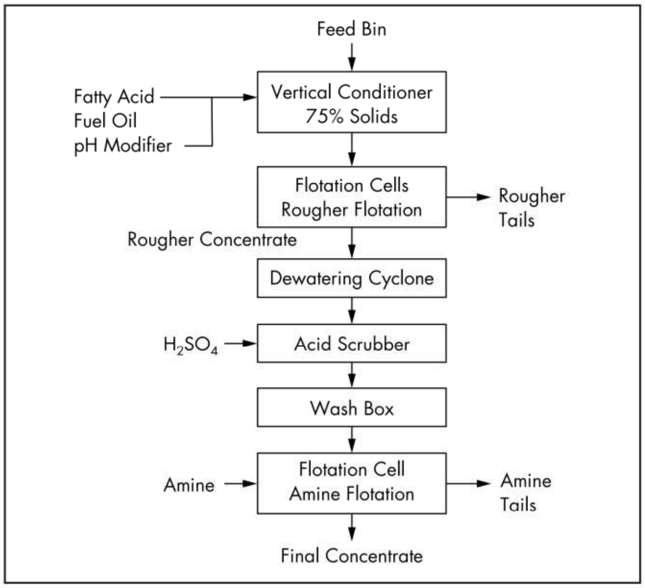
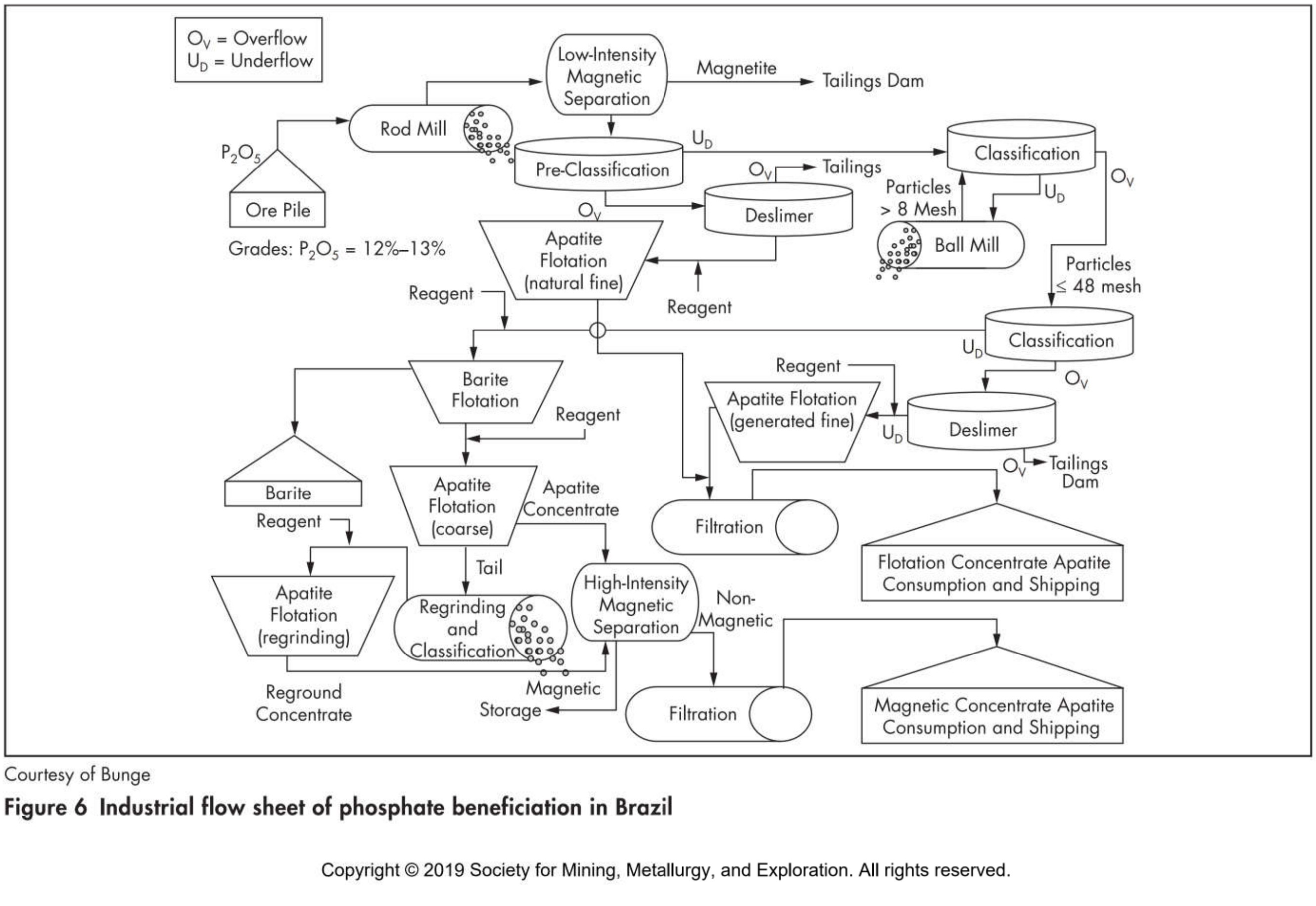


Figure 5 Simplified flow sheet of the "double float" process



Courtesy of Bunge

Figure 6 Industrial flow sheet of phosphate beneficiation in Brazil

Anionic Flotation Only

Outside Florida, direct flotation of phosphate using anionic collectors is the most prevalent practice. In Senegal phosphate operations, after desliming and sizing, the phosphate is upgraded using a tall oil fatty acid. The silica and the iron and aluminum oxides are depressed, and a high-grade concentrate analyzing up to 80% BPL is produced.

Foskor Ltd. of South Africa produces phosphate rock from three sources: pyroxenite ore, foskorite ore, and PMC tailings. The pyroxenite ore is crushed and milled to 15% + 425 µm and 20% –74 µm. The mill product is pumped to conditioners from which it flows to the flotation circuit, where apatite is floated using Wemco flotation cells. Flotation is done in a four-stage flotation circuit comprising rougher, scavenger, cleaner, and re-cleaner stages, with the recirculation of middlings. The pyroxenite process with only two reagents in the system is relatively simple and relatively trouble-free. A straight-chain petroleum sulfonate or sulfonic acid and a tall oil fatty acid are added to the pulp at the conditioners. From ore with a head grade of 7% P_2O_5, a concentrate with a P_2O_5 content of 39.6% is produced with a recovery of 70%. In the circuit for foskorite, flotation is also done in a four-stage flotation circuit comprising rougher, scavenger, cleaner, and re-cleaner stages, with recirculation of middlings, using Wemco flotation cells. Three reagents are used: sodium silicate ($Na_2O \cdot SiO_2$) as a dispersant, nonyl phenyl tetraglycol ether as a modifier and depressant, and a tall oil fatty acid as a collector. The average head grade of the foskorite is 7.5% P_2O_5, whereas the concentrate grade is 38.5% P_2O_5 with a recovery of 67%.

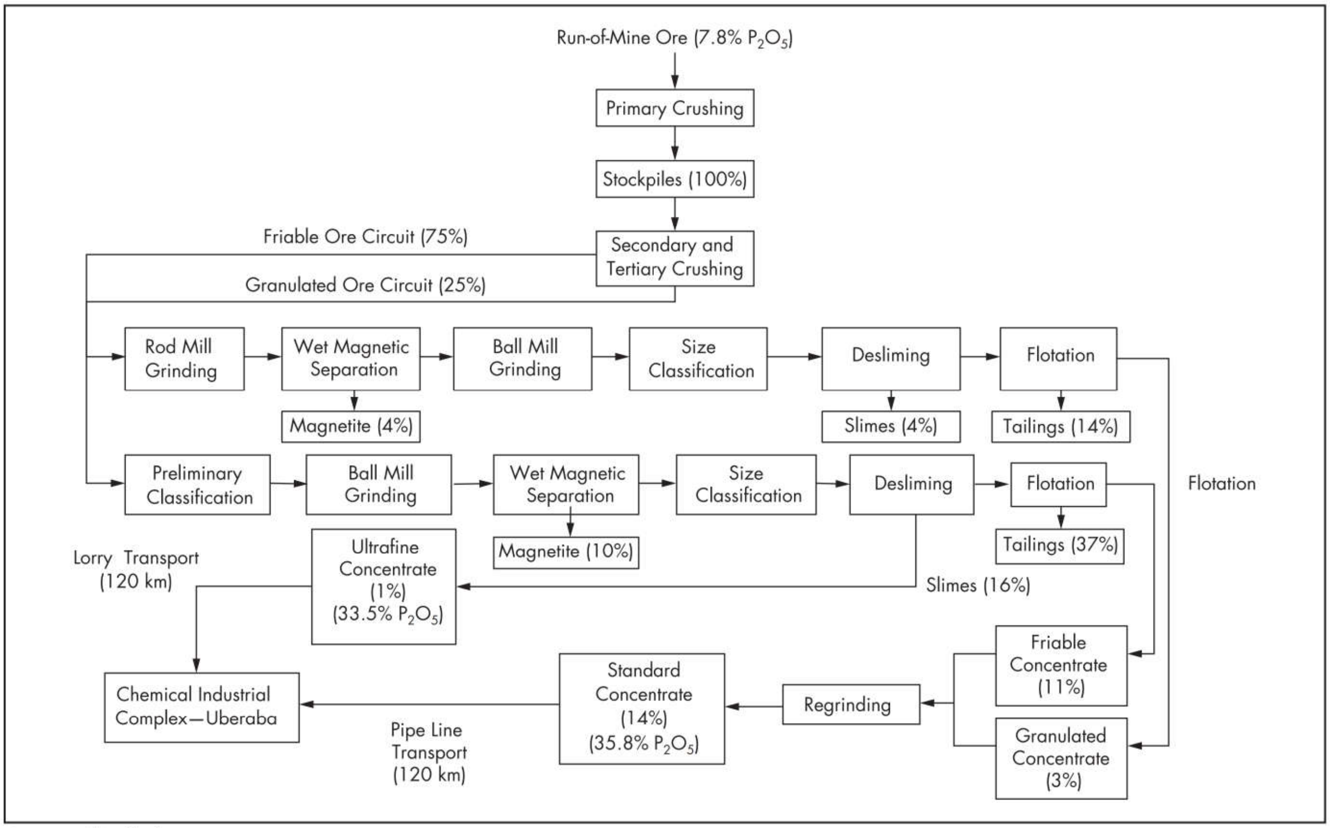
In Russia, a majority of the phosphate rock is turned out from the phosphate mines at the central Kola Peninsula. The mines are about half open pit and half underground. Phosphate ore is first crushed to –20 mm before being sent to the beneficiation plant. In the beneficiation plant, the feed is ground to approximately 55% passing 74 µm. Anionic rougher flotation is followed by several stages of cleaning and scavenging flotation.

Some low-grade phosphate ores in Jordan are treated by direct flotation using an aqueous blend of tall oil and diesel oil as phosphate collector, and sodium silicate as a dispersant for both clay and silica depressant for both fine and coarse fractions, with several rougher and cleaner stages.

Beneficiation of Igneous Phosphates with Iron

Brazilian igneous phosphate ores require numerous beneficiation steps using both magnetic separation and flotation. Flotation is typically carried out after a double desliming, generally with a roughing operation followed by one or two scavenging operations, with the froth being cleaned two or three times. The depression of carbonates and iron oxides is achieved at a pH of about 10 with causticized starch, and the flotation is carried out with fatty acids (tall oil). Concentrates of about 35% P_2O_5 with recovery ranging from 45% to 78% are obtained from different localities. The flow sheet shown in Figure 6 demonstrates the complexity of phosphate beneficiation operations in Brazil.

Another phosphate beneficiation flow sheet in Brazil is shown in Figure 7. The Brazilian phosphate industry makes extra efforts to recover phosphate from the "slime." Up to 35%



Courtesy of Fosfertil

Figure 7 Processing flow sheet of a Brazilian plant

of the product P_2O_5 is derived from the extremely fine fraction. Small hydrocyclones (2 in. diameter) are used to deslime, and fine flotation is carried out on the cyclone underflow.

At the newly opened Kapuskasing mine, the only phosphate mining operation in Canada, beneficiation is quite challenging, particularly at the beginning. Phosphate minerals are mainly fluorapatite with a small amount of crandallite. Gangue minerals are associated with iron, including iron sulfides, iron and titanium oxides, iron hydroxides, and iron and magnesium carbonates. Silica (mostly quartz) content ranges from 1% to 50%. After the strongly magnetic iron minerals are rejected using low-intensity magnetic separation (LIMS) and the weakly to moderately magnetic iron and titanium minerals are rejected using high-intensity magnetic separation (HIMS), the flotation feed goes through three stages of conditioning. Caustic starch is added into the first conditioner to both depress iron and adjust pH. In the second conditioner, a saponified tall oil is added as apatite collector. An optional third conditioner is used to further modify pH using NaOH. Flotation is conducted in mechanical cells. Flotation concentrate is dewatered with cyclones to 70% solids, followed by dewatering with belt filters to 85%–90% solids and drying with fluidized beds to 99.9% solids.

For Finnish igneous phosphates (which contain about 10% apatite, 22% calcite and dolomite, 65% phlogopite, and 3% amphibole and other silicates), the flotation process is carried out using substituted N sarcrosine (an amphoteric compound). Flotation is performed at a basic pH (8–11). The flow sheet adopted is grinding to 38.5% –74 µm, one roughing flotation stage, and five cleaning flotation stages. This flotation scheme is applied in the Siilinjarvi plant, achieving a concentrate of 33.7% P_2O_5 with a recovery of 85%.

Anionic rougher-cleaner flotation has been practiced in Mexico for many years. The flotation collector is a fatty acid emulsified with petroleum sulfonate and diesel oil.

Magnetic Separation

Magnetite, pyrite, hematite, and other iron-containing minerals are often associated with igneous phosphate ores. These minerals are usually removed using magnetic separation. Both high-intensity and low-intensity separation techniques are used. At the Phalaborwa Igneous Complex in South Africa, the pyroxenite zone is followed by the foskorite zone. This part of the ore body consists mainly of magnetite, serpentine, and apatite. The P_2O_5 content in this zone varies from 6%–11%. The magnetite must be removed using magnetic separation to upgrade the ore to commercial-grade rock. In the foskorite circuit, the crushed ore is conveyed to a 60-kt stockpile, reclaimed by three plough reclaimers, and conveyed to the milling plant. After copper flotation, Sala low-intensity magnets are employed to remove the magnetite after 750-mm and 100-mm Multotec cyclones remove the slimes. Magnetic separation is also conducted on the PMC tailings before phosphate flotation.

Magnetic separation as shown in Figures 6 and 7 is used in treating most Brazilian phosphate ores. The uniqueness of the Brazilian practice is that magnetic separation is used in both the front end and final stage of beneficiation.

At the Kapuskasing Phosphate Operations in Canada, magnetic separation is carried out on the final flotation product. The re-cleaner flotation concentrate is pumped to a reconditioned high-gradient magnetic separator (HGMS) purchased from the Iron Ore Company of Canada. The HGMS reduces the iron content from approximately 5% to less than 2%. HGMS product is pumped to a concentrate thickener.

At an Egyptian mine, phosphate ore is crushed and screened at 60 mm. The resultant oversize is discarded because of its high impurities. The –60 mm fraction is delivered to the beneficiation plant for further treatment. The first step of beneficiation is scrubbing and sizing to remove the +2 mm, a high-dolomite fraction. With further scrubbing, washing, sizing, and desliming, a 0.2 × 2 mm product is obtained. The –0.2 mm fraction is treated using a HIMS to obtain the fine concentrate. Magnetic separation is also practiced in Togo and Mexico.

Calcination

Calcining is used to treat phosphate rock to achieve one or more of the following objectives:

- Remove carbonaceous materials, dolomite, or calcite
- Remove organic matters
- Improve the reactivity of the rock
- Make low-grade, slow-release fertilizers

Calcination (at higher than 700°C) is widely used in Morocco to eliminate organic materials from the so-called brown or black phosphate rock.

During the last decade, calcination was studied and recommended to treat phosphate ores in Saudi Arabia, where the water supply is limited and energy is inexpensive. In the study, a Saudi phosphate ore containing 40%–50% carbonate and 16%–25% P_2O_5 was treated by calcination at 850°C for about an hour, followed by quenching with 5% ammonium nitrate (NH_4NO_3), 5% ammonium chloride (NH_4Cl), or water. Under the best test conditions, a concentrate containing 38% P_2O_5 was obtained.

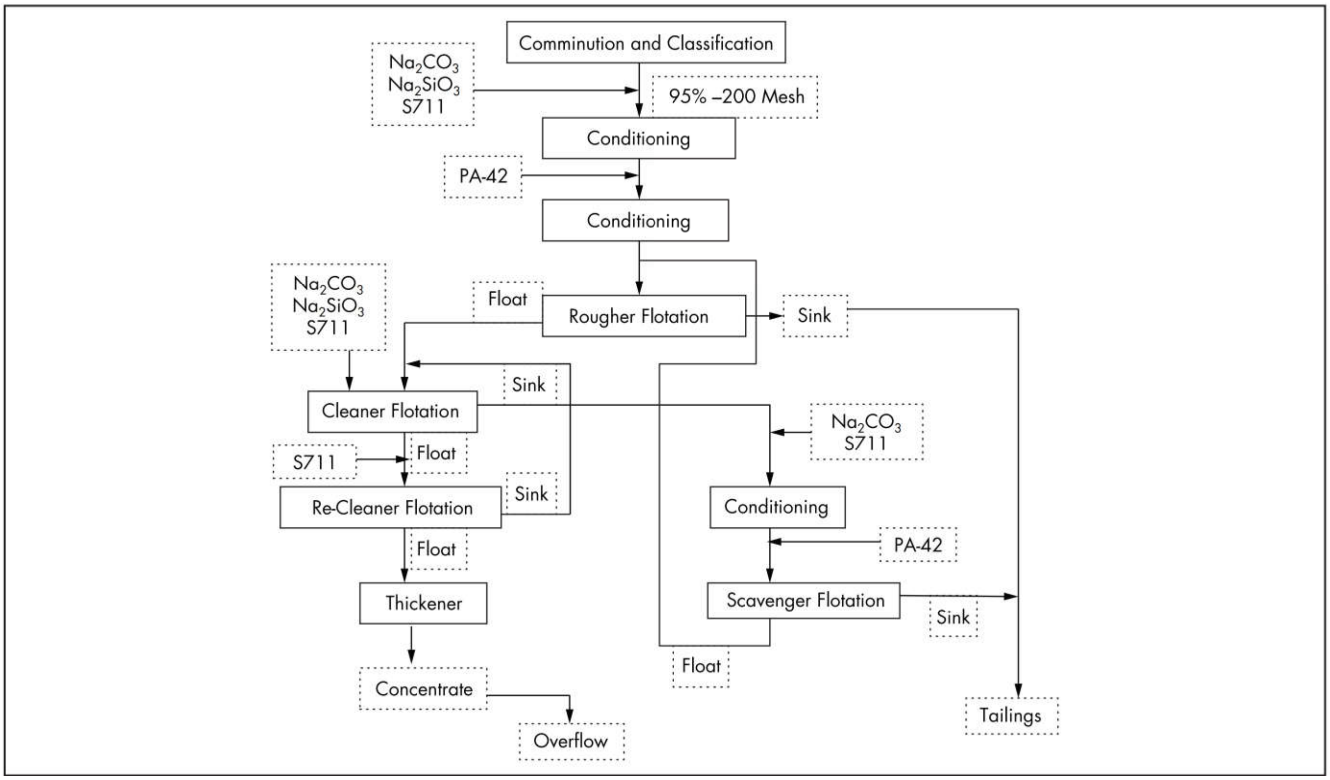
Two low-grade Indian carbonaceous ores were successfully upgraded using a continuous-flow calcination process. Phosphate recoveries ranged from 63% to 84.6%, with concentrate grades of 31.3%–38.5% P_2O_5. The roasting temperature was 900°C.

Although the process of making the popular FCMP in China is not defined as calcination, it is a thermal process. Some of the chemical reactions taking place in the FCMP process also occur in calcination kilns.

Beneficiation of Carbonaceous Phosphates

Sedimentary carbonaceous ore is, by far, the most widely present form of phosphate in the world and constitutes roughly two-thirds of present-day reserves. Some carbonaceous phosphates are beneficiated using a calcination process followed by elimination of CaO fines. Because of ever-increasing energy costs, more economical means are becoming increasingly attractive, including the froth flotation process. The difficulty, however, arises from the fact that the physicochemical properties of phosphatic minerals and carbonates are very similar. In the last three decades, numerous studies have been carried out to separate carbonaceous gangue from sedimentary phosphate ores. These processes include direct flotation of phosphate with depression of the carbonate gangue and reverse flotation of the carbonate gangue with depression of the phosphates.

China is quite successful in processing sedimentary carbonaceous phosphates using flotation technology, perhaps because most of its phosphate deposits (about 80%) belong to this category. The Chinese phosphate resources have three distinct characteristics: old geological age, a high content of



Source: Gao and Gu 1999

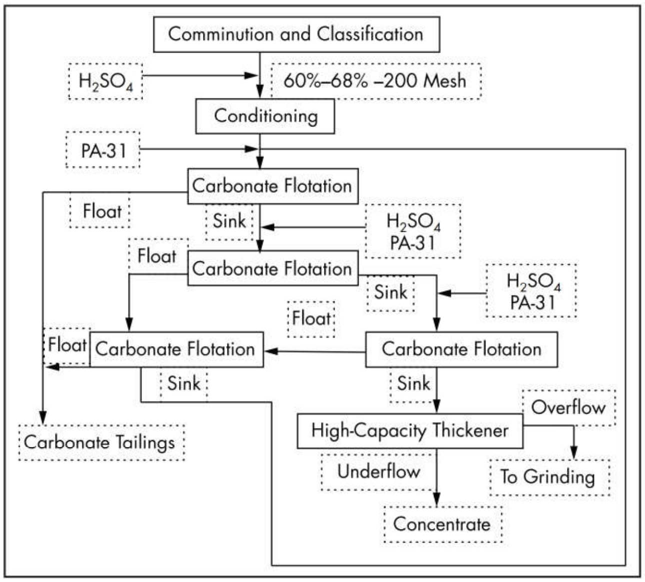
Figure 8 Processing flow sheet for Dayukou carbonaceous phosphate ore

dolomite and other impurities, and fine dissemination. Before beneficiation, fine grinding is usually required to liberate impurity minerals from phosphate.

Figure 8 shows the processing steps at the Dayukou phosphate mine in Hubei Province, China. The phosphate ore contains 17%–18% P_2O_5 and 4%–5% MgO. Phosphate, dolomite, and silicate in the ore were intergrown as extremely fine particles. To achieve the desired degree of liberation of phosphate from gangue minerals, the ore must be ground finely to 90% passing 200 mesh. For such fine particle sizes, it was once considered almost impossible to separate dolomite from phosphate by the flotation method. This beneficiation plant was put into operation in 1996. The success of the "direct flotation" process was attributed to the S series depressants developed by China Lianyungang Design and Research Institute (CLDRI). These depressants are effective for both carbonates and silicates. The S series depressants were derived from a by-product of the petroleum industry. The phosphate collector PA-42 is derived from waste material from vegetable oil processing. The flotation section of the process is in a closed circuit. The underflow of first cleaning flotation is subject to a scavenging operation, which is a key step for effective rejection of MgO impurity.

Figure 9 shows a "reverse flotation" process for processing carbonaceous phosphates in China. The Wengfu phosphate project in Guizhou Province, China, is currently the largest integrated phosphate fertilizer complex in China, producing 2.5 million t/yr of rock, 800,000 t/yr of TSP, 800,000 t/yr of sulfuric acid, and 300,000 t/yr of P_2O_5 as phosphoric acid. The run-of-mine ore containing about 30% P_2O_5 and 4%–4.5% MgO is crushed and then ground to about 60% passing 200 mesh for mineral liberation. The feed slurry of 40% solids is conditioned with H_2SO_4 as a pH modifier and PA-31 as dolomite collector, and is then subject to carbonate flotation to remove dolomite as a froth product. The rougher sink is cleaned and refloated to further reject dolomite. The concentrate analyzes 36% P_2O_5 and 0.95% MgO at the overall P_2O_5 recovery of 95%.

The Vernal, Utah, phosphate operation recently reached a capacity of 1.4 million t/yr. Although the ore body (4.5–6 m in thickness) is overlaid by 29 m of overburden, and beneficiation involves fine grinding and complex flotation steps, Vernal boasts the lowest cost phosphate production facility in North America. Primary grinding using the semiautogenous grinding mill brings the ore down to 35 mesh. The + 35 mesh fraction is sent to the secondary grinding circuit with ball mill. The –35 mesh (–420 µm) material from the secondary grinding is the flotation feed. The flotation feed is deslimed using hydrocyclones to remove the 400 mesh (37 µm) primary slime. The cyclone underflow is sized at 200 mesh using hydrosizers, generating a primary flotation feed (35 × 200 mesh) and a secondary slime (200 × 400 mesh). The flotation includes many steps. In the primary step, rougher flotation feed is conditioned in a three-stage tank system at a natural pH ranging from 7.5 to 7.9. This product is cleaned in a single four-cell flotation bank identical to those used in the rougher circuit. Final concentrate grade averages 30.8% P_2O_5 with an MgO content of 0.8%. Two-thirds of the phosphate production comes from the primary circuit. Primary rougher and cleaner tails are combined as the scavenger flotation feed for recovering the P_2O_5 loss in the primary tails. This feed is also conditioned at a natural pH ranging from 7.5 to 7.9 and



Source: Gao and Gu 1999

Figure 9 "Reverse flotation" process at Wengfu, China

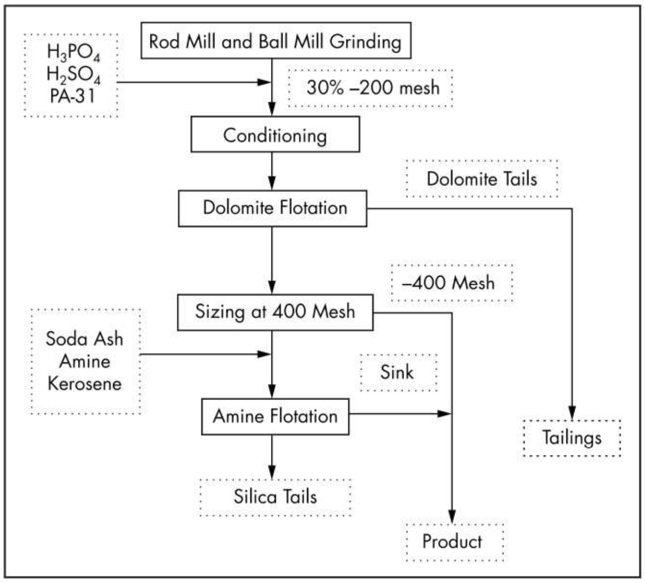


Figure 10 CLDRI fine flotation process for Florida dolomitic phosphate pebbles

70% solids with a fatty acid collector, a petroleum sulfonate, a diesel fuel, and a frother. The scavenger cleaner concentrate averaging 26.8% P_2O_5 and 2.2% MgO is acid-scrubbed prior to dolomite flotation using a dolomite collector. A frother is required to stabilize the carbonate flotation circuit.

CLDRI Process for Florida Dolomitic Pebbles

Under Florida Industrial and Phosphate Research (FIPR) Institute funding, IMC Phosphates conducted two major projects to develop an economically feasible process for high-dolomite phosphate pebbles in Florida. The CLDRI worked with IMC as the primary subcontractor for laboratory development and pilot-scale evaluation of flotation processes for dolomitic pebbles. As a result, the CLDRI process was developed. Figure 10 shows a typical flow sheet of the CLDRI process, which involves grinding, dolomite flotation, sizing, and silica flotation. Unlike most previous processes, the CLDRI process does not require the desliming step after grinding, thus reducing phosphate loss. Pilot-plant testing on two Florida samples achieved encouraging results similar to or better than those obtained in laboratory tests. An economic analysis was conducted based on the pilot testing results for a 272-t/h (300-stph) battery limit plant. The estimated variable (production rate dependent) costs (including raw materials, electric power, reagents, consumables, severance tax, dam building, services, and contract maintenance) add up to \$13.80/t (\$12.52/st) of concentrate. Fixed costs (including labor, overhead, depreciation, supplies, taxes, and insurance) total an estimated \$3.42/t (\$3.10/st) of concentrate. Total operating costs, which are the sum of variable and fixed costs, are estimated at \$17.22/t (\$15.62/st) of concentrate. These numbers suggest that the CLDRI process is economically feasible under the current conditions. The battery limit plant includes silica flotation, which reduces the concentrate acid insolubles from 19%–6%.

In the CLDRI fine flotation process, the H_3PO_4-H_2SO_4 mixture serves dual purposes as a pH modifier and a phosphate depressant. Dolomite flotation is conducted at pH about 5. The dolomite collector PA-31 is a saponified fatty acid containing a plasticizer to improve dispersion of the collector.

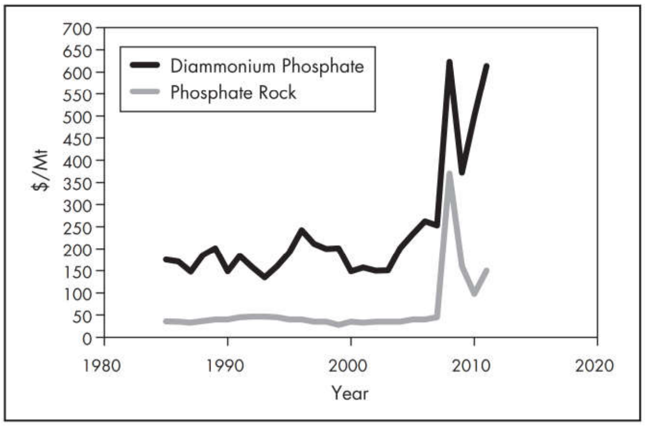


Figure 11 Historic phosphate prices

PHOSPHATE MARKET

Phosphate is mainly traded as finished products such as fertilizers (DAP, MAP, SSP, etc.), phosphoric acid, animal feeds, and industrial chemicals. However, Morocco, Jordan, Tunisia, and Peru export large amounts of phosphate rock. Like the price for other mineral commodities, the price for phosphate rock varies cyclically, as demonstrated in Figure 11.

CURRENT PROBLEMS AND FUTURE DEVELOPMENTS

World production of phosphate rock is exceeding 200 million t/yr. Regardless of the source of the ore, the quality of the rock concentrates produced is a major criterion for its subsequent use and/or processing operations. For instance, in acidulation processes for production of phosphoric acid, a set of physical and chemical quality factors is highly important and must be met before using the produced phosphate rock. The contents of iron, aluminum and magnesium oxides, silica, and chlorine, for example, should not exceed certain limits (Lehr and McClellan 1973). From the chemical point of view, the iron and aluminum content (expressed as R_2O_3) is the principal cause of sludge and postprecipitation in phosphoric acid production (Lehr and McClellan 1973). The ratio R_2O_3/P_2O_5 should be less than 0.095 if solid fertilizer products meeting specifications are to be produced (Lawver et al. 1978). Magnesium is the most undesirable impurity in phosphate ore. It precipitates fluorine as colloidal particles that blind the gypsum filters. It also raises the viscosity of superphosphoric acid (Lehr and McClellan 1973). Consequently, magnesium should be removed from phosphate rock feed to phosphoric acid production plants. The MgO content in acid plant feed should not be higher than 1.0% (McClellan and Germillion 1980). Chlorine is also a particularly harmful impurity in phosphate ores because of its corrosive action on plant equipment. Generally, chlorine contents higher than 0.1%–0.2% cannot be tolerated in acid-grade concentrates except in SSP manufacture where a higher level of chlorine may be used (Everhart 1971).

It is also important to maintain the correct balance of Si to F during the production of phosphoric acid to ensure that the fluorine is removed as silicon tetrafluoride, which is less corrosive than hydrogen fluoride (Frazier and Lee 1972). Also, the weight ratio of CaO/P_2O_5 should not exceed 1.6 to avoid high sulfuric acid consumption during the acidulation (Frazier and Lee 1972).

On the other hand, the minor elements such as Cu, Mn, and Zn contribute to postprecipitation of insoluble phosphate. Other elements, such as Cd, Pb, Cr, As, Hg, Se, and V, are either toxic or harmful in agricultural products

In its recently updated strategic plan for 2012–2015, the FIPR Institute assigned high priority to research on two of the major waste products from phosphate mining and processing, phosphatic clay and PG. Phosphatic clays are a major problem. They occupy large land areas, which are difficult to reclaim for either economic or environmental purposes. They also waste phosphate and clay minerals. PG is also wasted resource. Pond water associated with PG stacks poses a significant environmental hazard.

Because of limited space, this chapter focuses only on the metallurgical problems as related to beneficiation and chemical processing of Florida phosphates. These may be summarized as follows:

- Developing methods for reducing or eliminating clay settling ponds
- Recovering phosphate from phosphatic clays
- Developing technologies for solving the dolomite problem
- Reducing the magnitude of the process water problem
- Reducing the accumulation of phosphogypsum in the stacks
- Developing an alternative to the Crago process
- Extracting all useful elements from phosphate

Developing Methods for Reducing or Eliminating Clay Settling Ponds

The Florida phosphate matrix (ore) is composed of roughly one-third each of phosphate, clay, and sand. The clay must be removed before upgrading phosphate using flotation. Therefore, approximately 1 st ton of clay waste (phosphatic clay) is generated for each ton of phosphate rock product. This translates to nearly 100,000 stpd of waste clay produced in Florida. Under current practice, phosphate clay slurry with an average solids content of about 3% is pumped through pipelines to clay storage ponds where the clay slowly settles.

Although impounding is the most economical method of waste clay disposal, it has several major disadvantages. Clay settling ponds occupy about 40% of mined lands and generally have limited use after reclamation, causing adverse economic impacts. The waste clay not only ties up a large amount of water but a significant amount of water is also lost through evaporation over the clay settling areas that can occupy up to 800 acres each. The impacts of clay settling ponds on the hydrological systems must be better defined. Wetlands created on clay ponds are not accepted by the Florida Department of Environmental Protection as suitable for replacing wetlands destroyed during mining.

A near-term approach to achieve this goal is to develop rapid dewatering methods for instantaneous reclamation of mine cuts. The long-term solution is to develop alternative minerals processing technologies that would not create waste clay in the first place. For example, direct leaching of the phosphate ore (matrix) would not produce waste clay. This may be accomplished by continuous-circuit, vat, heap, or in situ leaching. The former U.S. Bureau of Mines (USBM) conducted a pilot-scale evaluation of continuous-circuit leaching of phosphate matrix in a five-tank reactor (White at al. 1978). The results from that study may be summarized as follows:

1. Phosphate recovery from the matrix ranged from 80% to 90%.
2. Sulfuric acid consumption based on P_2O_5 content was 10% higher than in commercial plants processing concentrates.
3. Total impurity (Al and Fe) content in product phosphoric acid was 60% higher than in commercial filter acid.

Another problem with this approach is the total operating cost, which was not analyzed but should be much higher than processing concentrate. Today, the industry spends about \$20 on beneficiation and \$70 on chemical processing per ton of phosphate rock in the near term.

Biohydrometallurgy may also offer some solutions. It has been demonstrated that phosphate rock can be leached by bacterial solutions to produce either phosphoric acid or elemental phosphorus. The practical and economic feasibility of bioprocessing for phosphate remain to be determined, but preliminary studies indicate they are not likely to be feasible or practical.

Whether traditional leaching or bioleaching was used, the resultant phosphoric acid would be contaminated by Fe, Al, and Mg. Acid purification steps would be necessary if the acid were used to make high-grade DAP. Hydrometallurgical approaches to purify the acid, such as solvent extraction and ion exchange techniques, would be needed.

Recovering Phosphate from Phosphatic Clays

Phosphate mining in central Florida generates approximately 1 st of phosphatic waste clays for each ton of phosphate rock produced. Based on this ratio, approximately 1.5 billion st of phosphatic clays have been generated by the Florida phosphate industry over the years. In many cases, phosphate content in the phosphatic clays is higher than in the matrix. About one-third of the phosphate mined has ended up in the clays.

Table 4 Concentration of P_2O_5 in phosphatic clays

Year	Author/Organization	% P_2O_5 in Clays
1954	Tyler and Waggaman, National Academy of Science	20.0
1966	Stanczyk and Feld, U.S. Bureau of Mines	12.5
1969	Davenport and Watkins, Tennessee Valley Authority	17.7
1982	Ardaman and Associates	4.6–17.9
1987	Davis et al., U.S. Bureau of Mines	6–15.9
2001	Zhang et al., Florida Industrial and Phosphate Research Institute	9.0

Many investigators have verified this enormous loss of phosphate (Table 4.)

Phosphatic clays are extremely fine, with more than 50% a few micrometers in size. Therefore, traditional beneficiation techniques, such as flotation and gravity separation, are not suitable for upgrading the phosphate component. Again, leaching or other hydrometallurgical processes may be needed for recovering the phosphate values from the clays.

Developing Technologies for Solving the Dolomite Problem

Among the deleterious materials (Fe_2O_3, Al_2O_3, CaO, MgO, F) in phosphate rock feed for phosphoric acid production, MgO is the most common and the one that causes the most problems. Generally, the phosphate rock acidulation process requires a feed of less than 1% MgO. This feed requirement has not been achieved in Florida at a commercial scale by removing magnesium from rock containing more than 2% MgO. Phosphate rock that does not meet the requirement consumes too much sulfuric acid per ton of P_2O_5 produced in the wet phosphoric acid process. In addition, MgO in the wet acid reduces the filtering capacity and ties up an equivalent amount of P_2O_5 when acidulated. MgO also causes problems in the production of DAP, which has a strict requirement for the minor element ratio, of which Mg is a constituent.

With the depletion of the higher-grade, easy-to-process Bone Valley deposits, the central Florida phosphate industry has moved into the lower-grade, more contaminated ore bodies from the southern extension of the Hawthorn Formation. Phosphate deposits in the southern extension may be divided into two zones: upper and lower. Rock in the upper zone can be processed readily using the current technology; however, the lower zone is highly contaminated by the magnesium-containing dolomite. Geological and mineralogical statistics show that nearly 50% of the phosphate resource would be wasted if the high-dolomite deposits were bypassed in mining.

Reducing the Magnitude of the Process Water Problem

Process water is essential to the operation of phosphoric acid plants. It is used as makeup water for phosphoric acid manufacture, to convey the PG to the stack, to remove the heat generated during phosphoric acid manufacture, and to scrub all the exhaust gases within the chemical complex to prevent the discharge of undesirable gases to the atmosphere. In the course of serving all these functions, the process water becomes acidic and reaches equilibrium for all the materials found in both the phosphate rock and the sulfuric acid. While the plants are designed to operate with a negative water balance, periods of excessive rainfall may make it necessary to treat and discharge surplus water. Treatment before discharge involves a two-stage neutralization with lime to remove fluoride and phosphate, followed by aeration to remove ammonia, and then the addition of sulfuric acid to reduce the pH to 6–7. Even after treatment, the conductivity of the treated water is higher than allowed and fresh water must be added before process water can be discharged to the surface waters of the state. Ammonia concentrations are also too high. Finding or developing a technology that would significantly remove or reduce any or all of the soluble salts, or raise the pH of the process water economically, would be desirable.

Double liming is also expensive, at about $20 per 1,000 gallons of process water. Reverse osmosis (RO) is now being used to obtain higher quality for discharge water. However, the major contaminants in the process water, particularly ammonia and phosphate, reduce RO efficiency significantly. Selective precipitation, ion exchange, and solvent extraction could play a role in treating the process water.

Reducing the Accumulation of Phosphogypsum in the Stacks

PG has the potential to become a major asset to the state of Florida. PG is a by-product of phosphoric acid manufacture. For every ton of phosphoric acid produced, approximately 5 tons of PG are produced. If acceptable uses can be found for PG, it may have the benefit of improving the environment, economy, and welfare of the citizens of the state. Research has demonstrated that using PG in both road building and agriculture offers substantial economic benefits without creating excessive risks. Other uses that are environmentally and/or economically desirable are also possible. The major barrier to using PG is concern about the low level of radiation associated with it. Since it is highly unlikely that methods can be developed that would use all PG production, it is desirable to find methods that will reduce its rate of production.

Some efforts have been made in reducing PG production by manipulating the chemistry, such as the MonoCal and DiCal processes. However, dramatic PG reduction requires entirely different hydrometallurgical processes.

Developing an Alternative to the Crago Process

The Florida phosphate reserves that can be economically processed with current technology may last for only about 20–30 years at the present mining rate. While development of a viable dolomite separation process is critical to extending the life of Florida's phosphate reserve, improvement in P_2O_5 recovery from the currently mined siliceous phosphates is equally important. Phosphate recoveries from the flotation feeds in most plants in Florida do not exceed 85%, with <80% being more common. Assuming that Florida's total production of flotation concentrate is about 20 Mt/yr at 32% P_2O_5 from feeds averaging 7% P_2O_5, an improvement of 1.8% P_2O_5 recovery translates to an additional 1 Mt of phosphate rock.

In the Crago process, sized flotation feed is dewatered and conditioned at about 70% or higher solids with fatty acid/fuel oil at pH ~9 for 3 minutes. The phosphate is then floated to produce a rougher concentrate and a sand tailing. A significant amount (30%–40%) of silica is also floated in this step. The rougher concentrate goes through a dewatering cyclone, an acid scrubber, and a wash box to remove the reagents from the phosphate surfaces. After rinsing, the de-oiled rougher concentrate is transported into flotation cells where amine is added. The silica is finally floated at neutral pH.

In this conventional process, about 30%–40% by weight of the sands in the feed are floated twice, first by fatty acid and then by amine. The Crago process is, therefore, inefficient in terms of collector utilization. One of the major drawbacks of this process is the de-oiling process. De-oiling consumes a significant amount of sulfuric acid, which calls for special safety cautions and equipment maintenance. Insufficient de-oiling, which is a frequent phenomenon, often causes loss of phosphate and poor concentrate grade. De-oiling also causes loss of fine phosphate particles, amounting to more than 1% phosphate recovery in most operations. Another problem with the Crago process relates to the amine flotation step. Not only are amines more expensive than fatty acids, but they are also very sensitive to water quality, particularly the clay content in water.

Direct flotation using anionic reagents was practiced on high-grade phosphate flotation feeds in some U.S. plants and is still being used in a Mexican plant. Research efforts have also been directed at developing an anionic flotation process for phosphate, but the interest has faded because of the stringent requirement for Insol (at 4%–5%) content in beneficiated phosphate rock product in the past. However, that requirement has recently been relaxed, with chemical plants now accepting concentrate analyzing as high as 10% Insol, which an anionic rougher-cleaner process could achieve without sacrificing much flotation recovery.

Another driving force for an anionic flotation process is its environmental friendliness. The environmental benefits of such a process are evident: eliminating the use of sulfuric acid and amines for phosphate beneficiation, reducing water and energy usage, and curtailing the total discharge of chemicals to the environment. An anionic flotation process also offers improved phosphate recovery. With companies having difficulty getting permits for new mines or for expansion of existing mines, there is a growing interest in extracting as much phosphate as possible from each acre mined.

Extracting All Useful Elements from Phosphate

It is well known that phosphate is a nonrenewable resource essential for plant growth and crop production, and it is therefore vital to feeding the fast-growing population of the world. But it is not widely known that there are many other valuable elements in phosphate ore that may play significant roles in the development of future energy, particularly green energy, high-tech equipment, and advancement of various key technologies. These elements include rare earths, uranium, and thorium. Uranium in phosphate accounts for more than 80% of the world's unconventional uranium resources, whereas rare earth elements (REEs) in the world's annual production of phosphate rock (about 200 Mt) total about 100,000 t, assuming an average REE concentration of 500 ppm. If uranium is not recovered during phosphate mineral processing and phosphoric acid manufacturing, it mostly ends up in fertilizers and eventually is spread on farm lands, making it impossible to ever recover it. Except for the two "waves" of uranium recovery from phosphoric acid when the uranium price was high, millions of tons of these critical elements have been discarded with fertilizers and other processing streams.

Uranium content in the world's phosphate rock products ranges from 50 to 200 ppm, averaging about 100 ppm, as shown in Table 5 (Menzel 1968; El-Shall and Bogan 1994). Worldwide, unrecovered uranium from phosphate totals about 20 million kg (based on 200 Mt rock production) per year. Using the same average uranium concentration of 100 ppm, total uranium in the world's 290 billion t of phosphate resources amounts to 29 billion kg. Florida phosphate ranks on the top in terms of uranium content, which is why in the past, most uranium extraction plants from phosphoric acid were built in Florida. The next-generation uranium extraction plants may also start in Florida.

A majority (about 65%) of the uranium in sedimentary phosphate exists in the tetravalent state in isomorphous substitution with calcium ion, because the ionic radius of U^{4+} is 0.97Å, very close to that of Ca^{2+}, which is 0.99Å. Uranium in hexavalent (+ 6) state is held by chemisorption on the phosphate surface as $UO_2 \cdot HPO_4$. Some uranium in phosphate, particularly that in in igneous phosphate, is associated with REEs and thorium.

Rare Earth Elements in Phosphate

Although there are more than 200 minerals known to contain appreciable amounts of REEs, only three of them are economically significant: bastnaesite, monazite, and xenotime, with bastnaesite and monazite accounting for about 95% of the current sources for light rare earths. Some rare-earth-bearing clays are also significant sources for REEs. Xenotime is the primary mineral for heavy REE and yttrium.

REEs may also be extracted as a by-product from processing of minerals, such as copper, gold, uranium, and phosphate ores, with phosphate having a great potential. Certain phosphate deposits, specifically the fluorapatite ores, contain significant amounts of REEs (Jorjani et al. 2008; Becker 1983; Preston at al. 1996). Table 6 shows the lanthanide content in some phosphate rock (Altschuler et al. 1967; Bliskoyskii et al. 1969).

Some phosphate ores or processing streams contain much greater amounts of REEs than shown in Table 6. A Canadian phosphate deposit near Quebec, for example, contains about 1,800 ppm of REEs. In recently discovered phosphate deposits in northern China (Xia 2011), REE concentration (total R_2O_3) ranges from 1.5% to ~6.41%.

Table 5 Analysis of uranium and thorium in phosphate rock from different sources

Sample	Number of Samples	Median Content of Element, ppm	
		Uranium	Thorium
Florida, United States, pebble, 1926–1935	11	208	14
Florida, United States, pebble, 1946–1955	14	148	13
Florida, United States, pebble, 1959–1964	12	127	17
Florida, United States, pebble, 1994	3	95	—
North Carolina, United States, 1957–1964	3	79	9
Utah, United States, 1936–1961	9	128	7
Idaho, United States	5	151	8
Peru, washed rock, 1961–1964	7	106	8
Morocco, 1937–1943	5	141	8
Tunisia, 1927–1955	6	48	23
Jordan, 1956–1963	6	48	0
Egypt, 1936–1937	6	122	6
Senegal	6	107	17

Source: Menzel 1968; El-Shall and Bogan 1994

Table 6 Lanthanide content in selected phosphate rock

Phosphate Rock Source	% Ln_2O_3
Kola, Russia	0.8–1.0
Florida, United States	0.06–0.29
Algeria	0.13–0.18
Morocco	0.14–0.16
Tunisia	0.14

Table 7 Total REE content in two sets of Florida samples

	Total Rare Earth Elements	
Sample Identification	Plant A	Plant B
Final concentrate	608	901
Pebble product	163	262
Flotation feed	160	209
Cleaner tails	153	335
Rougher tails	40	20
Waste clay	102	346
Phosphogypsum	118	112

Fate of Uranium in the Acidulation Process

In phosphoric acid manufacturing using the dihydrate process, about 90% of the uranium in the phosphate rock feed reports to phosphoric acid and 10% ends up in PG, versus 80% and 20%, respectively, using the hemihydrate process. Therefore, the dihydrate process favors uranium recovery. Past uranium recovery plants all used phosphoric acid produced from dihydrate-based acid plants.

Rare Earth Elements in Florida Phosphate

The Florida phosphate ore (matrix) is mined in open pits using large draglines. Phosphate matrix is first transported to the beneficiation plant and, after several washing and separation steps, is turned onto four streams: pebble product, flotation concentrate product, sand tailings, and waste clay. In the chemical processing plant, the combined pebble/concentrate rock product is reacted with sulfuric acid producing a relatively concentrated phosphoric acid and PG by-product.

Decades-old published analyses of trace elements in Florida phosphate rock showed that many of the vital REEs are present. Though only present in trace amounts, because of the tonnage of phosphate produced, these elements are still significant in aggregate mass and have not been recovered.

A comprehensive investigation of REEs in Florida phosphate was conducted by Kremer and Chokshi (1989) of the Mobil Research and Development Corporation. The total REEs in Florida phosphate matrix analyzed 282 ppm (88 ppm neodymium, 68 ppm cerium, 57 ppm yttrium, and 49 ppm lanthanum, accounting for 90%). Distributions of REEs in the mining and chemical processing streams were also determined, showing 40% in waste clay, 37.5% in PG, 12.5% in phosphoric acid, and 10% in sand tailings. Data further indicated that REEs were concentrated in fine phosphate particles, as the pebble product analyzed 284 ppm REEs versus 575 ppm in the flotation concentrate. The high REE concentration (336 ppm) in waste clay is evidence of REEs concentrating in fine phosphate particles.

Another set of data by the USGS (Altschuler et al. 1967) showed that Florida phosphate rock contained about 500 ppm REEs, with 150 ppm lanthanum, 120 ppm cerium, and 110 ppm yttrium. According to a report by the former USBM (May and Sweeney 1983), Florida PG contained 300 ppm REEs, with 130–170 ppm gadolinium, 49 ppm cerium, and 39 ppm lanthanum.

The most recent characterization of REEs in Florida phosphate was conducted by the FIPR Institute (Zhang 2012). In this study, two sets of samples were collected from two operating mines, with each set consisting of eight samples, including fine flotation feed, coarse flotation feed, flotation concentrate, pebble product, fatty acid flotation tails, amine flotation tails, waste clay (primary slime), and PG. Total REE concentrations in various samples are listed in Table 7. REE mass balance was calculated based on chemical analysis and plant mass flow rates. For Plant A, the mass balance analysis shows the following REE distributions: 61.9% in rock product, 19.6% in waste clay, and 18.2% in flotation tailings. These distributions add up to 99.7%. For the Plant B samples, mass balance analysis shows the following REE distributions: 53.19% in rock product, 39.83% in waste clay, and 8.5% in flotation tailings. These distributions add up to 101.25%.

Other Elements of Interest

Recovery of iodine, fluorine, and magnesium have been commercialized. Some recently discovered phosphate deposits in Canada contain economically recoverable niobium.

REFERENCES

Altschuler, Z.S., Berman, S., and Cuttitta, F. 1967. Rare earths in elements—Geochemistry and potential recovery. In *Intermountain Association of Petroleum Geologists Annual Conference Guidebook No. 15*. Salt Lake City: Intermountain Association of Petroleum Geologists. pp. 125–135.

Ardaman and Associates. 1982. *Evaluation of Phosphatic Clay Disposal and Reclamation Methods. Volume 1: Index Properties of Phosphatic Clays*. FIPR Publication 02-002-003. Bartow, FL: Florida Industrial and Phosphate Research Institute. p. 68.

Bateman, A. 1952. The formation of mineral deposits. *Science* 115(2990):442–443.

Beaton, J. 2010. History of fertilizer. In *Efficient Fertilizer Manual*. Mosaic. www.back-to-basics.net/efu/pdfs/HistoryofFertilizers.pdf. Accessed May 2012.

Becker, P. 1983. *Phosphates and Phosphoric Acid: Raw Materials, Technology, and Economics of the Wet Process*. New York: Marcel Dekker.

Bliskoyskii, V.Z., Mineev, D.A., and Kholodov, V.N. 1969. Composition of lanthanides in phosphorites. *Chem. Abstr.* 72:34390-d.

Davenport, J.E., and Watkins, S.C. 1969. Beneficiation of Florida pebble phosphate slime. Size distribution of constituent minerals. *Ind. Eng. Chem. Process Des. Dev.* 8(4):533–539.

Davis, B.E., Davis, E.G., and Llewellyn, T.O. 1987. *Recovery of Phosphate from Florida Phosphate Slimes*. Report of Investigation 9110. Washington, DC: U.S. Bureau of Mines.

El-Shall, H., and Bogan, M. 1994. *Characterization of Future Florida Phosphate Resources, Final Report*. FIPR Publication No. 02-082-105. Bartow, FL: Florida Industrial and Phosphate Research Institute.

Everhart, D.L. 1971. Evaluation of phosphate rock deposits. Presented at the Society of Economic Geologists Meeting, New York, March 1971.

Frazier, A.W., and Lee, R. G. 1972. Stabilization of polyphosphate fertilizer solutions. *Fert. Solut.* 16(4):32–43.

Gao, Z., and Gu, Z. 1999. Plant practices of phosphate. In *Beneficiation of Phosphates: Advances in Research and Practice*. Edited by P. Zhang, H. El-Shall, and R. Wiegel. Littleton, CO: SME. pp. 289–301.

Griffith, B. 2010. Phosphorus. In *Efficient Fertilizer Use Manual*. Plymouth, MN: Mosaic.

Jorjani, E., Bagherieh, A.H., Mesroghli, S., and Chehreh Chelgani, S. 2008. Prediction of yttrium, lanthanum, cerium, and neodymium leaching recovery from apatite concentrate using artificial neural networks. *J. Univ. Sci. Technol. Beijing* 15(4):367–374.

Kauwenbergh, S.J. 2010. *World Phosphate Rock Reserves and Resources*. Muscle Shoals, AL: International Fertilizer Development Center.

Kremer, R.A., and Chokshi, J.C. 1989. *Fate of Rare Earth Elements in Mining/Beneficiation of Florida Phosphate Rock and Conversion to DAP Fertilizer*. Research report. Nichols, FL: Mobil Mining and Minerals.

Lawver, J.E., McClintock, W.O., and Snow, R.E. 1978. Beneficiation of phosphate rock: A state of the art review. *Miner. Sci. Eng.* 10(4):278–294.

Lehr, J.R., and McClellan, G.H. 1973. Phosphate rocks: Important factors in their economic and technical evaluation. Presented at the CENTO Symposium on Mining and Beneficiation of Fertilizer Materials, Istanbul, Turkey, November.

May, A., and Sweeney, J.W. 1983. *Evaluation of Radium and Toxic Element Leaching Characteristics of Florida Phosphogypsum Stockpiles.* Report of Investigation No. 8776. Washington, DC: U.S. Bureau of Mines.

McClellan, G.H., and Germillion, L.R. 1980. The role of phosphorous in agriculture. *Proceedings of Symposium at the National Fertilizer Development Center, Tennessee Valley Authority*, Muscle Shoals, AL, June 1–3, 1976.

Menzel, R. 1968. Uranium, radium, and thorium content in phosphate rocks and their possible radiation hazard. *J. Agric. Food Chem.* 16(2):231–234.

Preston, J.S., Cole, P.M., Craig W.M., and Feather, A.M. 1996. The recovery of rare earth oxides from a phosphoric acid by-product. Part 1: Leaching of rare earth values and recovery of a mixed rare earth oxide by solvent extraction. *Hydrometallurgy* 41:1–19.

Sauchelli, V. 1942. *Manual on Phosphates in Agriculture*. Baltimore: Davison Chemical.

Sauchelli, V. 1951. *Manual on Phosphates in Agriculture*. Baltimore: Davison Chemical.

Sauchelli, V. 1965. *Phosphates in Agriculture*. New York: Reinhold Publishing.

Schmidt, C. 1999. Foskor phosphate beneficiation. In *Beneficiation of Phosphates: Advances in Research and Practice*. Edited by P. Zhang, H. El-Shall, and R. Wiegel. Littleton, CO: SME. pp. 325–334.

Stanczyk, M.H., and Feld, I.L. 1966. *Chemical Processing of Florida Phosphate Rock Slime.* Report of Investigation 6844. Washington, DC: U.S. Bureau of Mines.

Topf, A. 2015. Quebec okays $750M phosphate mine. *Mining.com*. March 19. www.mining.com/quebec-okays-750m-phosphate-mine/. Accessed November 2015.

Tyler, P.M., and Waggaman, W.H. 1954. Phosphatic slime—A potential mineral asset. *Ind. Eng. Chem.* 46:1049–1956.

UNIDO and IFDC (United Nations Industrial Development Organization and International Fertilizer Development Center), eds. 1998. *Fertilizer Manual*. Dordrecht, The Netherlands: Kluwer Academic Publishers.

USGS (U.S. Geological Survey). 2010–2016. Phosphate rock. In *Mineral Commodity Summaries [various years].* Reston, VA: USGS.

White, J.C., Goff, T.N., and Good, P.C. 1978. *Continuous-Circuit Preparation of Phosphoric Acid from Florida Phosphate Matrix.* Report of Investigation 8326. Washington, DC: U.S. Bureau of Mines.

Xia, X.H. 2011. The distribution characteristics and potential of endogenetic phosphate rock in north China. Presented at the Beneficiation of Phosphates VI Conference, Kunming, China, March 6–11.

Zhang, P. 2012. Recovery of critical elements from Florida phosphate: Phase I. Characterization of rare earths. Presented at the ECI International Conference: Rare Earth Minerals/Metals—Sustainable Technologies for the Future, San Diego, CA, August 12–17.

Zhang, P., Snow, R., Yu, Y., and Bogan, M. 2001. *Recovery of Phosphate from Florida Phosphatic Clay.* FIPR Publication 02-096-179. Bartow, FL: Florida Industrial and Phosphate Research Institute. p. 67.