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Comprehensive Recovery and Sustainable Development of Phosphate Resources

Patrick Zhang^{a*}

Florida Industrial and Phosphate Research Institute, 1855 West Main Street, Bartow, FL 33830, USA.

Abstract

It is well known that phosphate is a non-renewable 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 aware that there are many other valuable elements in phosphate ore, which 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 unconventional uranium resources, while rare earth elements in the world's annual production of phosphate rock (about 170 million tons) total nearly 100,000 tons. If these elements are not recovered during phosphate mineral processing and phosphoric acid manufacturing, they mostly end up in fertilizers and eventually being spread on farm lands, making it impossible to ever recover. Based on a review of selected research and development papers, the author provides his viewpoint of treating phosphate ore as an energy mineral, and suggests several approaches for recovering energy values from phosphate as well as for treatment and utilization of wastes associated with phosphate mining and processing.

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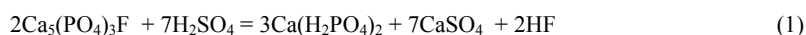
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1. Introduction

1.1. A Brief Introduction of Major Phosphate Fertilizers

Although calcined or lime-treated bones were applied to the fields to improve crop growth over 2000 years ago, and human wastes and animal manure were utilized for their phosphorus values by ancient farmers, the scientific understanding of the essential role of phosphorus in plants growth was first explained as late as 1799 by Erasmus Darwin [1]. Large scale phosphorus fertilizer production was made possible by the 1842 patented technology by John Bennet Lawes of Rothamsted for manufacturing superphosphate fertilizer [2]. The initial patent covers superphosphate fertilizer production by acidulating bones with sulfuric acid, which was expanded in 1848 to include sulfuric acid treatment of phosphate ore.

A simplified reaction for producing superphosphate is shown in equation (1):



* Corresponding author. Tel.: +1-863-534-7160; fax: +1-863-534-7165.

E-mail address: pzhang@admin.usf.edu

This process took off in the early 1850s in the U.S. and a number of other countries, initially using bones and later switching to mineral phosphate rock [3–4]. This fertilizer dominated the world's phosphate fertilizer market for more than 100 years.

Another variation of superphosphate fertilizer is the so called Single Superphosphate (SSP), which is still popular in some countries. The molecular formula of SSP is $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$. SSP is one of the most important fertilizers in Brazil. This P source is also produced in other countries in the world, especially in Australia, China, India and New Zealand. It accounts for 15% of the phosphate fertilizer use in India.

As the dominance of superphosphate diminished, di-ammonium phosphate (DAP) and mono-ammonium phosphate (MAP) fertilizers became more and more popular. The first step towards producing DAP and MAP is to make phosphoric acid from phosphate rock, which can be accomplished via either a thermal process or the “wet acid” process (usually referring to the manufacturing of phosphoric acid by reacting phosphate rock with sulfuric acid).

Although the first wet phosphoric acid plant was built in Germany as early as 1870 and in the U.S. in 1890, manufacturing of phosphoric acid during the early phosphate booming years was dominated by the thermal processes using either blast furnace or electric furnace, up till the middle of the last century.

However, since 1950, the wet acid process has quickly overtaken the thermal method as the primary technology for manufacturing phosphoric acid. As is shown in Table 1, today only about 5% of the world phosphate rock is consumed by the thermal process.

Table 1. World phosphate rock use distribution [5]

Use	Percent
Wet phosphoric acid manufacturing	71
Single super phosphate (SSP) production	13.5
Others, including animal feed, fused magnesium phosphate (FMP), triple super phosphate (TSP), mono-potassium phosphate (MKP), nitrogen-potassium-phosphorus (NPK), and nitrogen-phosphorus (NP)	10
Elemental phosphorus production	5
Direct application	0.5

The primary chemical reaction in the “wet acid” process may be expressed in the following equation using fluorapatite to represent phosphate rock and sulfuric acid as the reactant [6]:



Depending on the value of n , the process is defined as Dihydrate ($n=2$) process, Hemihydrate ($n=1/2$) process, or Anhydrite process. The term $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ in equation (2) is the so called phosphogypsum (PG).

When phosphate rock was first acidulated using sulfuric acid, it was done on batch scale producing an acid with only about 10% P_2O_5 and a dehydrate PG. The first continuous phosphoric acid manufacturing based on the dihydrate process was executed by Dorr [7–8]. Research work during 1932 resulted in the hemihydrate process capable of producing phosphoric acid with up to 50% P_2O_5 . However, this process did not receive enthusiastic endorsement at the time by the industry due to problems associated with the filtration process.

The majority of today's phosphoric acid plants is based on either the dihydrate or hemihydrate processes mainly developed or modernized by Dorr, Prayon, St. Gobain Rhone Progil, Fisons, Jacobs Engineering Group, Kellogg-Lopker, Nissan, Mitsubishi, and BreyerHeurty [9]. Another emerging process in recent years is the Hemi-Di process [10].

1.2. A Synopsis of Phosphate Mining and Beneficiation

Although some small operations do exist to recover and recycle phosphorus from various waste streams, phosphate rock is and will remain to be the only economical source of phosphorus for the production of phosphate fertilizers and phosphate chemicals. Phosphate mining expanded most dramatically from the 1970s–80s. For example, in the United States, it took about half a century (1902–1950) [11] for phosphate rock production to expand from an annual rate of 2 million to 10 million tons, while it only took 10 years (1964–1974) for the annual production to increase from 20 million to 40 million tons. Although the US production has declined in recent years to below 30 million tons per year, this decrease is more than made up with significant expansions of other major phosphate producing countries and new projects worldwide during the past decade. China, for example, more than doubled its phosphate rock production from 2000 to 2009; while Morocco expanded its phosphate mining by nearly 30% during the same period. Total world phosphate rock production surpassed 180 million

tons in 2010, and will probably keep increasing or at least maintain at that level for three main reasons: the ever growing population, the rapid living standard improvement in developing countries, and the demand for green energy crops.

Surface mining is the dominant method for extracting phosphate ores. Some countries, such as Morocco, China, Tunisia and Jordan, still enjoy the luxury of producing a significant amount of phosphate rock by simple washing and sizing, but this practice will end soon, because only about 2% of the world's phosphate deposits can be upgraded this way, as is shown in Figure 1. Indeed, all new phosphate mining projects involve deep beneficiation with flotation being the primary technology.

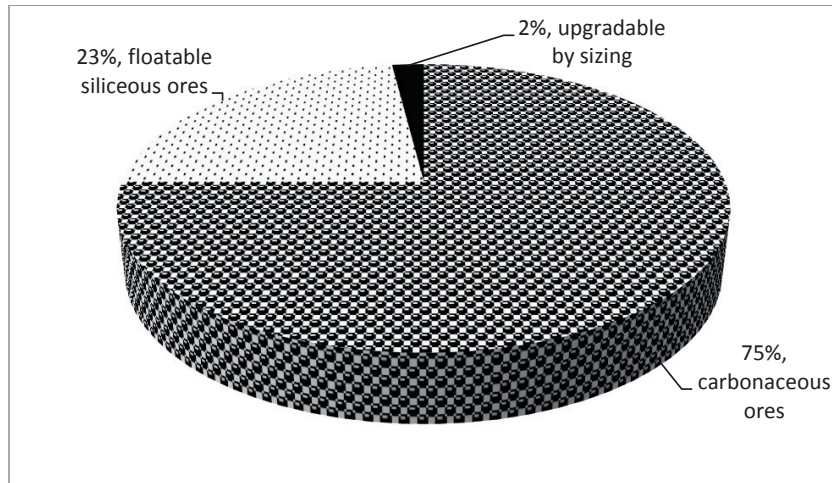


Figure 1. Types of phosphate ores based on beneficiation difficulty.

For the floatable siliceous ores, beneficiation methods include anionic flotation of phosphate and anionic flotation followed by cationic flotation to further reduce silica content. Calcination and heavy media separation practices for carbonaceous phosphate ores have been discontinued gradually, leaving fine grinding followed by flotation as the leading technology with the following three variations: 1) direct-reverse flotation in which bulk anionic flotation at high pH is followed by flotation of carbonates under slightly acidic conditions; 2) double reverse flotation involving flotation of carbonates under slightly acidic conditions followed by silica flotation at neutral pH; and 3) direct flotation of phosphate with carbonates/silica depressants. Iron containing minerals, such as magnetite and hematite, are often found in igneous phosphate deposits, and they are commonly removed by magnetic separation.

1.3. Various Valuable Elements in Phosphate

It is well known that phosphate is a non-renewable 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 aware that there are many other valuable elements in phosphate ore, which may play significant roles in the development of future energy, particularly clean 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 unconventional uranium resources [12], while rare earth elements in the world's annual production of phosphate rock (about 170 million tons) total nearly 100,000 tons.

Wherever there are rare earth-containing minerals, there is usually thorium. Thorium is detected in nearly all phosphate ores, though at low levels. Some scientists have long believed that thorium could provide the world with ultra-cheap and environmentally safe source of nuclear power. This approach is gaining momentum in recent years, particularly in India and China. The recently formed Weinberg Foundation in the United Kingdom also plans to push the promise of thorium nuclear energy into the mainstream political discussion of clean energy and climate change. According to Evans-Pritchard, "if China can crack thorium, it will have clean energy for 20,000 years" [13]. In his Sydney Morning Herald article titled "Safe nuclear power not a pipedream", Evans-Pritchard also talked in some details about China's thorium program with a start-up budget of \$350 million and a staff of 140 full-time scientists at the Shanghai Institute of Applied Physics, with a plan to increase the staff to 750 people by 2015.

Table 2 shows uranium and thorium contents in selected phosphate samples.

Table 2. Analysis of uranium and thorium in phosphate rock from different sources [14-15]

Sample	Number of samples	Median content of element, ppm	
		Uranium	Thorium
Florida, USA pebble, 1926-1935	11	208	14
Florida, USA pebble, 1946-1955	14	148	13
Florida, USA pebble, 1959-1964	12	127	17
Florida, USA Pebble, 1994	3	95	--
North Carolina, USA, 1957-1964	3	79	9
Utah, USA, 1936-1961	9	128	7
Idaho, USA	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

Rare earth elements (REE) have very specific critical uses in a multitude of markets. Many of these applications have no substitute materials and the move to green technologies has dramatically increased their demand. Table 3 summarizes various REE applications.

Table 3. Various uses of rare earth elements

Field	Uses
Green Energy	Rechargeable batteries; electric motors; fuel cells; solar cells; wind, hydro and tidal power turbines
Electronics	Computers; fiber optics; cell phones; digital cameras; DVD and CD players; lasers
Defense	Satellite communications; night vision gears; jamming devices; predator unmanned aircraft; tomahawk cruise missile; smart bombs; bunker Buster smart bomb; precision guided weapons; long range acoustic device and area denial systems
Magnetics	Computer hard drives; disk drive motors; headphones and speakers; microphones; refrigeration; electric motors, anti-lock brakes
Medical equipment	MRI machines; X-ray imaging; surgical lasers; surgical tools; computed tomography; electron beams
Glass & ceramics	Polishing powders; pigments and coating; tinted glasses; photo-optical glass; UV resistant glass
Chemical	Petroleum refining; catalytic converters; fuel additives; hydrogen storage; water filtration; air pollution controls; chemical processing
Lighting	LED lighting; color TV; flat screen displays; cell phone displays; fluorescent lighting

Rare earth elements have earned their reputation for being “rare” not because they are scarce in the Earth’s crust but because they “rarely” exist in mineral forms that can be mined and extracted. For example, the average concentration of the rare earth elements in the Earth’s crust (ranging from 150 to 220 ppm) is much higher than that of copper (55 ppm).

Although there are over 200 minerals known to contain appreciable amounts of rare earth elements, only three of them are economically significant. They include 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 REE. Xenotime is the primary mineral for heavy REE and yttrium.

Rare earth elements may also be extracted as a byproduct from the 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 the rare earths [16-18]. Table 4 shows lanthanide content in some phosphate rock [19-20].

Table 4. Lanthanide content in selected phosphate rock

Phosphate Rock Source	Ln ₂ O ₃ (%)
Kola, Russia	0.8-1.0
Florida, USA	0.06-0.29
Algeria	0.13-0.18
Morocco	0.14-0.16
Tunisia	0.14

Some phosphate ores or processing streams contain much higher REE concentrations than what are shown in Table 4. A Canadian phosphate deposit near Quebec, for example, contains about 1800 ppm (0.18%) of rare earth elements. Another

Canadian phosphate deposit in Ontario has an estimated content of 1.59% $\text{La}_2\text{O}_3 + \text{Ce}_2\text{O}_3$ [21]. In some recently discovered phosphate deposits in northern China [22], REE concentration (total R_2O_3) ranges from 1.5%~6.41%.

2. Treatment and utilization of wastes

2.1. Waste (Phosphatic) Clay (Slime)

Washing is the first step to upgrade phosphate minerals at a majority of the phosphate mines, particularly those in the US, Morocco, Jordan and Tunisia. This process generates huge volume of waste clay slurry, which is usually disposed of in large clay settling ponds. In Florida, for example, more than one ton of waste clay is generated for each ton of phosphate rock product, which translates to over 20 million tons (on dry basis) of waste clay per year. The waste clay is pumped into settling ponds as dilute slurry averaging 3% solids. Conventional impounding is still the dominant method for clay disposal.

The phosphatic clay slurry is perhaps the most difficult tailings to dewater. Three major factors are attributed to this problem, extremely fine particle size, high clay content, and the electrochemistry of the system. Table 5 indicates the fineness of the particles [23].

Table 5. Size distribution of some phosphatic clay samples

Sample	Weight (%) Distribution in Different Size (Micron) Fractions							
	+105	105x74	74x44	44x20	20x10	10x5	5x2	-2
Agrico-Saddle Creek	0	3	1	3	4	9	11	69
AMAX- Big Four	0	1	9	20	10	9	5	46
CF-Hardee	0	0	4	4	6	7	22	57
WR Grace-Four Corners	3	2	2	2	4	36	10	41
Mobil-Nichols	0	1	8	5	6	12	15	53
OXY-Suwannee River	3	3	1	1	1	6	11	74

Although impounding may be the most economical method of waste clay disposal, it has several 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 amounts are also lost through evaporation over the clay settling areas that can occupy up to 800 acres each.

Sustainable development calls for solutions to this big problem, which can be found with two approaches. The first approach is to develop technologies to reduce or eliminate settling ponds, and the other approach is to develop commercial uses. Significant progresses have been achieved on both fronts in recent years.

2.1.1. Disposal

Flocculation followed by deep cone thickening has found its applications for treating fine tailings worldwide. Recent lab studies and pilot testing has demonstrated its technical and economic feasibility for treating waste phosphatic clays in Florida [24-25].

The picture on the left in Figure 2 shows the thickened paste from the bottom of the thickener, and the picture on the right demonstrates the paste characteristics of the product using the slumping test method.



Figure 2. Sand/clay mix paste produced using deep cone thickener.

Long term consolidation measurements indicated that this sand/clay mix paste does not segregate due to the use of dual polymers.

2.1.2. Utilization

2.1.2.1. Use as Construction Materials

Several attempts were made to produce tiles using waste phosphatic clays with varying degrees of success [26-32]. The most comprehensive research on this topic was conducted by Alfred University [33]. An extensive series of experiments concerning ceramic tile body and glaze compositions and test evaluations were conducted on a number of ceramic tiles formulated with different phosphatic clay samples from the central Florida phosphate district, combined with fly ash, phosphogypsum or grog.

Conventional concrete suffers a number of deficiencies due to its lack of ductility and its susceptibility to long-term durability. One method of overcoming these drawbacks such as brittle failure mode and high permeability is to provide reinforcement of the concrete matrix at a smaller scale than the steel bars. The common approach to achieving this goal is the inclusion of a pozzolanic material, such as fly ash, silica fume, and blast furnace slag. The primary chemistry of these compounds is similar to that found in phosphatic clay. This has prompted researchers at University of Florida (UF) to propose an investigation of phosphatic clay as a concrete admixture [34]. The results indicated that phosphatic waste clay addition could improve the compressive strength of concrete significantly. Combining the waste clay with a suitable polymer has the ability to dramatically improve the ductility of concrete.

The aggregate market within the U.S. was 2.75 billion tons in 2001 and averaged 1.84 billion tons per year from 1971-2001. Therefore, a niche market of a few percent of the total aggregate market using phosphate clays could consume tens of millions of ton of the waste per year. This application may hold the most promising potential for phosphate clay utilization. Some encouraging results have been achieved. Small scale tests conducted by Vasan [35] indicated that it was feasible to produce a pelletized lightweight aggregate and ultimately a lightweight concrete from phosphate clays. It was estimated that up to 6-8 million tons of clay solids could be used annually. This research resulted in a four-step process for producing such aggregate: pumping clay slurry of 3-10% solids, drying of the slimes in a fluidized bed dryer, pelletizing the dried product, and kilning into a suitable lightweight aggregate. This application was also evaluated by several other organizations, with an IMC project being most detailed. The IMC technology involves drying the waste clay in fluidized bed, palletizing and kilning. Again, a consumption of 6-8 million tons/year solids was considered possible. Batch tests showed technical feasibility. The aggregates met ASTM specifications. In order to reduce drying costs, reduce the weight and improve strength of the aggregates made from waste phosphate clays, Dr. El-Shall [36] developed a flowsheet involving dewatering the waste clay by adding polymer and fibrous materials, further mechanical dewatering of the mixture to about 50% solids, extruding, and firing.

2.1.2.2. Alternative Fertilizers

A tremendous amount of phosphate is discarded with the waste clay, accounting for about 30% of the matrix phosphate in the case of Florida. Although it may be difficult to upgrade the phosphate to DAP feed grade, one should not give up hope of utilizing the phosphate value. For example, alternative fertilizers may be developed by agglomerating phosphate clay with bacterial materials to produce slow-release fertilizer, or agglomerating with sulfur to produce slow-release fertilizer.

2.2. Phosphogypsum

As is discussed above, depending on the value of n in the chemical reaction (2), the ‘wet’ phosphoric acid process is defined as Dihydrate (DH) ($n=2$) process, Hemihydrate (HH) ($n=1/2$) process, and Anhydrate process. The term $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ in the equation is simply referred to as Phosphogypsum (PG). The majority of the world’s phosphoric acid plants use the DH process, with a handful of HH plants and a few Hemidihydrate (HDH) installations. The HDH process is an innovative combination of the DH and HH processes. The tons of PG generated per ton of P_2O_5 produced are 4.9, 4.3 and 4.9 from the DH, HH and HDH processes, respectively.

Assuming that 70% of the world’s phosphate rock is consumed for making wet phosphoric acid, the annual PG production would amount to about 160-170 million tons!

Although the Florida style stacking with lining is getting adopted worldwide for PG disposal and may stay dominant in the phosphate industry for years to come, this practice is neither cost effective nor environmentally sound. As a matter of fact, it has the following major problems:

- Possible spills of acidic water from the top of PG stacks
- Potential groundwater contamination, particularly when sink holes occur

- Significant land occupation
- Likely odds of being located in highly sensitive, increasingly populated areas
- High costs of constructing, operating and closing.

Perhaps the only environmentally sound and sustainable way of dealing with the PG waste (or byproduct) is to find various uses. Both research work and commercial practices have demonstrated many beneficial uses for PG.

2.2.1. Utilization of PG in Agriculture

Agricultural use of PG has been studied extensively and practiced widely [37-42] because PG contains three of the essential elements for plants growth, calcium, sulfur and phosphorus. Numerous studies have demonstrated that use of PG enhances root growth thus helping plants absorb other nutrients, especially N [43]. Dissolution of PG in soil provides essential electrolytes to maintain hydraulic conductivities and increase infiltration rates thus preventing crusting and reducing erosion. The exchangeable Ca in PG can ameliorate subsoil acidity and Al^{3+} toxicity and reclaim sodic soils. PG is also known for its capability of improving soil structure by flocculating clays in soil.

The following examples speak volume for the potential of PG use in agriculture:

- Application of 500 lbs PG per acre tripled NCS31 peanut yield in Georgia, USA
- Use of PG more than doubled apple yield while increasing calcium content in Brazil
- Application of 176 lbs PG per acre nearly doubled crimson clover yield in Florida, USA
- Application of 4.5 ton PG per hectare on a sodic soil increased cotton yield by at least 40% in Kazakhstan.

2.2.2. Utilization of PG in Construction

Many uses have been found for phosphogypsum as construction materials. There are three major approaches for utilizing PG in cement. The first approach is direct use as PG based cement mortars. Hemihydrate PG was found to be more suitable than dehydrate PG for this purpose [44]. The second approach is high temperature treatment to convert dehydrate PG into hemihydrate, the treated PG is then used as cement retarder. Due to its energy consumption, this method has an economic disadvantage against natural gypsum. Another approach involves recovering sulfur from PG and using the clinker as the major component for making cement.

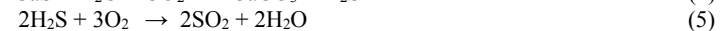
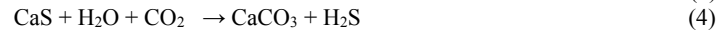
PG has been found to be suitable for making wall board or plaster, and building bricks and blocks [45]. Studies and testing of PG use as a road base materials have been well documented and publicized by the Aleffgroup and FIPR [46-49].

PG use as a road base material has a great economic advantage over conventional materials with a cost savings of up to 80% within economic transportation distance. The potential PG consumption for road building is huge. The US adds about 34,000 lane miles of new roads every year, while Florida adds 2,300 lane miles per year. Road base can consume over 4,000 tons of PG per lane mile, which translates to 140 million tons per year for US and 10 million tons for Florida alone.

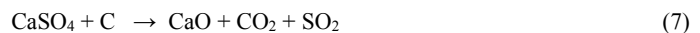
2.2.3. Utilization of PG as A Chemical Raw Material

PG is a viable raw material for recovery of sulfur and subsequent sulfuric acid manufacturing, as well as for production of ammonium sulfate. Both uses are currently viable economically in some parts of the world, and can be made feasible in many other places with some industry push and government supports.

Depending on market potential and prices for byproducts, sulfur recovery from PG could take two routes. Route 1 generates calcium carbonate as the major by-product through the following chemical reactions:



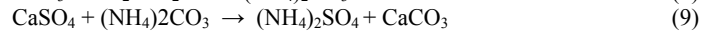
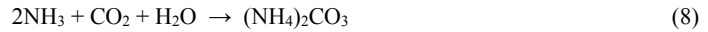
In the other process, lime (CaO) is generated as the major by-product by this reaction:



The most practical and economical approach, however, is the combination of sulfur recovery with cement production, similar to the OSW-KRUPP PROCESS or its modified versions [50]. In this process, dried PG, coke, sand and clay are mixed, ground and pelletized; the pellets are fed into a Krubb rotary kiln; the SO_2 from the kiln is treated and converted into

sulfuric acid; and the clinker from the kiln is mixed with gypsum to make cement. Several such plants are in operation currently in China.

The process for ammonium sulfate production can be expressed by the following two chemical reactions:



The Wengfu Group of China built a PG use plant with a capacity of 500,000 tons of ammonium sulfate per year. The plant started production in early 2011 and could consume 171,000 tons of PG annually [51]. A Brazilian company also expressed interest in building an ammonium sulfate plant using PG as raw material.

China recently adopted the 10-25 plan for PG use, drafted jointly by the Ministry of Land & Resources and the China Association of Chemical Mining. The plan calls for 30% use of PG produced by the year 2025. However, one province, Guizhou Province has already surpassed that national goal. The two largest phosphate producers in Guizhou province, Wengfu Group and Kailin Group, have reached 40% and 60% utilization of PG that they each produce, respectively. Their goal is to achieve zero PG accumulation by year 2025.

2.3. Wastes from Elemental Phosphorus Production

Although, only about 5% of the phosphate rock is consumed for elemental phosphorus production using the thermal process usually in electric furnace, a large amount of byproduct slag is generated in this process. All elemental phosphorus plants in the US are currently located in Idaho. Slags from these plants have been used extensively for construction purposes such as aggregate in concrete and asphalt, roadbed fill, backfill, and railroad ballast. However, these uses have been significantly reduced since the early 1990s, largely due to public perception of radiation. However, some plants consume all the slag produced. For example, the Kailin Group has no slag accumulation in their operation, with some used for mine cut reclamation and the rest utilized for making slag-PG bricks for construction purpose.

Another by-product of the electric furnace process is CO gas, which can be used for making methane by combining with the waste gas from an ammonia plant.

3. Comprehensive recovery of metal values from phosphate

3.1. Uranium from Phosphoric Acid

The historical ups and downs, major players and scale of operations for uranium recovery from phosphoric acid are clearly shown in Table 6.

Table 6. Uranium recovery from phosphoric acid facilities [52]

Acid Producer	Uranium Producer	Location	Capacity P2O5 (tons/year)	Capacity U3O8 (lbs/year)	Process	Operating Period
Farmland	Wyoming Minerals Corp.	Pierce, FL	450,000	400,000	WMC, DEPA-TOPO	1978 - 81
Freeport	Freeport Minerals Co.	Uncle Sam, LA	675,000	690,000	FMC, DEPA-TOPO	1978 - 99
Agrico	Freeport Minerals Co.	Donaldsonville, LA	360,000	420,000	FMC, DEPA-TOPO	1981 - 98
IMC	IMC	New Wales, FL	1,000,000	800,000	IMC, DEPA-TOPO	1980 - 92
CF Industries	IMC	Bartow, FL	720,000	600,000	IMC, DEPA-TOPO	1981 - 85
CF Industries	IMC	Plant City, FL	680,000	600,000	IMC, DEPA-TOPO	1980 - 92
W. R. Grace	Uranium Recovery Corp.	Bartow, FL	na	330,000	URC, OPAP	1976 - 80
Gardiner	Gardiner	East Tampa, FL	500,000	420,000	Gardiner, OPPA	1979 - 82
Western Fertilizer Corp.	Earth Sciences, Inc.	Calgary, Alberta, Canada	144,000	120,000	ESI, OPAP	1981 - 87
Chemie Rupel	Umipray	Purrs, Belgium	100,000	150,000	IMC – Prayon, DEPA-TOPO	1980 - 98

Although there is no uranium recovery plant in operation today, research and pilot testing efforts are intensive worldwide, which is particularly enhanced by the UxP (Uranium eXtraction from Phosphates and Phosphoric Acid) program lead by the

International Atomic Energy Agency (IAEA) and Aleffgroup [53-57]. The leading technology for uranium extraction from phosphoric acid is based on solvent extraction with DEPA/TOPO as the extraction reagent system [58-59]. DEPA stands for di(2-ethylhexyl) phosphoric acid while TOPO represents trioctyl phosphine oxide. A typical overall flowsheet for extracting uranium from phosphoric acid is shown in Figure 3 [60].

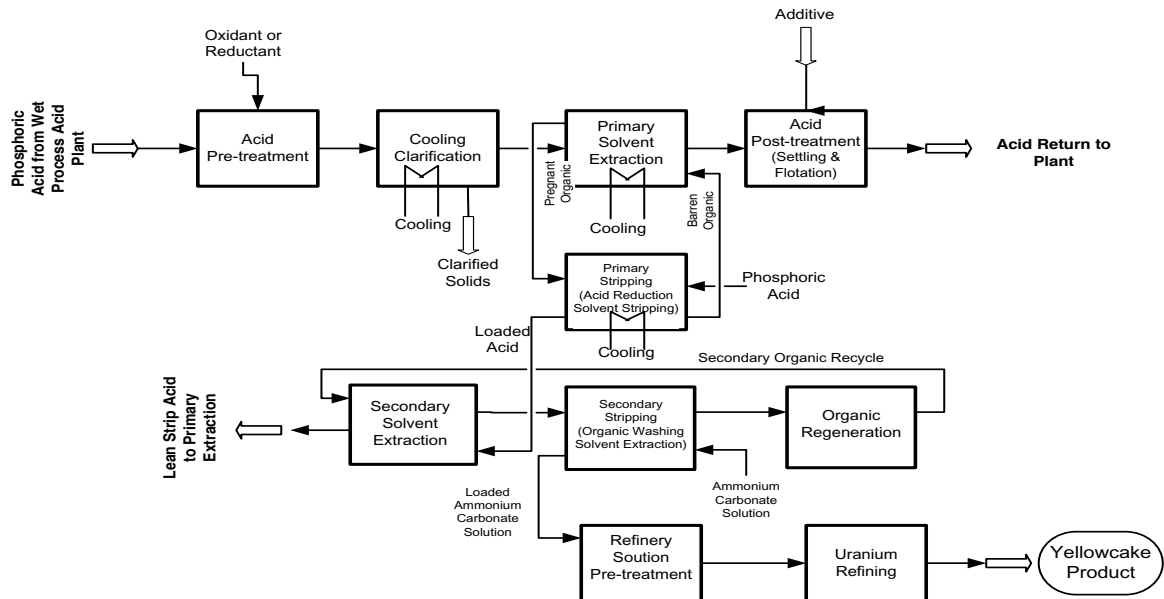


Figure 3. Overall process for uranium recovery from phosphoric acid.

Perhaps the most significant development in uranium extraction from phosphoric acid is the advancement of the ion exchange technology. Recently, UrTek successfully completed another round of pilot scale demonstration of U recovery from phosphoric acid based on the patented PhosEnergy (ion exchange) technology in two acid plants in the US [61]. Results of an engineering study based on this technology are expected to be available in mid-2013, but Uranium Equities estimates the cash operating cost of uranium production using the PhosEnergy Process to be \$20-25 per pound of U₃O₈, with a capital cost of \$100 per pound (U₃O₈). A Florida engineering firm has recently manufactured and shipped a few modular ion exchange plants to different clients. The ion exchange method does not have three of the vexing problems with the solvent extraction technology: emulsion, solvent loss, and crud formation.

3.2. Recovery of Rare Earth Elements from Phosphate and Phosphoric Acid

Until recently, research efforts had been sporadic to recover rare earth element from phosphate, and had not been put on the agenda of the research community, the industry or any governments. That lack of conviction was mainly attributed to the fact that in the wet phosphoric acid manufacturing process, only about 30% of the rare earth elements in the feed rock reported in the acid phase, with the rest ending up in the large volume of waste phosphogypsum. However, a good case can be made about the potential and viability of recovering rare earth from phosphate, not only from phosphoric acid, but also from other streams from the mining, beneficiation and acidulation streams. This case can be built using Florida as an example.

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 phosphogypsum waste.

Published analyses, decades old, of trace elements in Florida phosphate rock have shown that many of these vital rare earth elements 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 REE in Florida phosphate was conducted by Kremer and Chokshi [62] of Mobil Research & Development Corporation in 1989. The total REE 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 REE 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 REE versus 575 ppm in the flotation concentrate. The high REE concentration (336 ppm) in waste clay is another evidence of REE concentrating in fine phosphate particles.

Another set of data by the USGS [63] showed that Florida phosphate rock contained about 500 ppm REE, with 150 ppm lanthanum, 120 ppm cerium and 110 ppm yttrium. According to a report by the former USBM (May and Sweeney, 1983), Florida phosphogypsum contained 300 ppm REE, with 130-170 ppm gadolinium, 49 ppm cerium and 39 ppm lanthanum.

The Florida Industrial and Phosphate Research Institute (FIPR) recently completed a more detailed REE analysis in Florida phosphate. Under that project, two sets of samples were provided by companies A and B, each set consisting of eight (8) samples, including fine flotation feed, coarse flotation feed, flotation concentrate, pebble product, fatty acid flotation tails, amine flotation tails, waste clay (primary slime), and phosphogypsum.

Methods for the ICP-AES analysis of trace metals and rare earth elements in phosphate minerals were adapted from USGS [64]. Each material was sampled in duplicate and digested using 1:1 nitric acid at the same time on the same hotplate. These elements also seem to concentrate in the finer fraction of phosphate particles.

Total REE concentrations in various samples are listed in Tables 7.

Table 7. Total REE content in selected samples from two florida plants

Sample ID	Total REE, Plant A	Plant B
Flotation concentrate	608	901
Pebble	163	262
Amine flotation tails	153	335
Waste clay	122	346
Phosphogypsum	119	112

Mass balance analysis for plant A shows the following REE distributions: 61.9% in rock product, 19.6% in waste clay, and 18.2% in flotation tailings. For plant B the distributions are: 53.19% in rock product, 39.83% in waste clay, and 8.5% in flotation tailings. Based on these results, about 30,000 tons of REE are discarded with various phosphate mining and processing streams per year in Florida alone, which exceeds twice the current US demand for REE!

Results indicate that significant amounts of REE are present in both the waste clay and amine flotation tails. Since REE are mainly associated with phosphate minerals, they can be upgraded by concentrating phosphate in these streams. For example, REE in the waste clay could be upgraded by two folds by simply removing the fine clay minerals using hydrocyclone. Preliminary testing by Mosaic and FIPR showed that REE in the amine tails could be concentrated in several percent of the original mass using a gravity separation device.

The easiest and perhaps the most economical way of recovering the REE from phosphate is to extract them from the phosphoric acid. The key to success for this approach is to increase REE enrichment in the acid phase. Research work by the National Engineering Research Center for Rare Earth Materials of China [65] showed that REE leaching efficiency into the phosphoric acid phase could be increased to 75% by three methods: lowering leaching temperatures, reducing the solid/liquid ratio in the reactor, and adding surfactant to enhance gypsum crystal growth thus reducing REE adsorption. Of course, any change in operating parameters for REE recovery must be easy to implement, and have minimal impacts on phosphoric acid production.

Another ideal approach to recover REE from phosphate is to combine it with uranium recovery. In their 1976 US patent, Wamser and Bruen [66] disclosed a method for simultaneous recovery of fluorine, uranium and rare earth metal from phosphoric acid. Although the patent is based on phosphoric acid production by leaching phosphate minerals by hydrochloric acid, the approach may be applied to sulfuric acid leaching. As a matter of fact, some researchers have attempted to recover both uranium and rare earths from phosphoric acid made by sulfuric acid leaching [67-70].

3.3. Recovery of Thorium

Comprehensive recovery of the associated elements with rare earths minerals is being studied extensively. Major elements include Th, F, Nb, Sk and Sr. A majority of the world's thorium resource coexists with rare earths deposits. For example, in China, about 80% of the Th resource is found in two major rare earths formations. As the interest rises in using thorium in nuclear power plants, recovery of Th may become more important. One promising technology involves low temperature (230-300 °C) roasting followed by water leaching. Under these conditions, Th reports to the liquid phase, and is recovered by solvent extraction prior to REE extraction and separation.

4. Phosphate resources conservation

From the standpoint of sustainability, resource conservation is very important to any mining industry. This is even more critical to the phosphate industry, because phosphate is a non-renewable resource and essential to the survival of human being. At several points in the history, including the one during the past several years, concerns had been expressed about accelerated depletion of phosphate reserves thus causing food insecurity and starvation a few decades later. This concern was not based on scientific data, because we have about enough identified reserves for another 300-400 years [71]. However, this assurance does not change the fact that phosphate resource is finite and non-renewable.

4.1. Improving Phosphate Recovery in the Mining Process

The overall recovery of phosphate reserve in the mining process is within the low 80 percent range at its best worldwide. Some of this recovery loss is due to selective mining to bypass the difficult-to-process portions, but the majority is caused by the lack of instant information on the deposit as mining progresses.

The application of ore evaluation in the exposed mine face and in the dragline bucket can reduce phosphate loss significantly in the mining process. This has been brought close to reality by a continual research effort to develop laser based analytical tools for phosphate mining and beneficiation [72-73]. The FIPR Institute and an Israeli research team have long set the goal of developing a LIBS-based analyzer for remote analysis of ores and overburden before these materials are dug out or in transit to the beneficiation plant. The many years of research and development of the on-line LIBS analyzer have laid sound foundation for developing a remote LIBS, and the successful commercialization of the on-line LIBS ultimately boosted FIPR's resolution and confidence in funding research on remote LIBS.

Distant evaluation in the lab and field testing of a remote LIBS prototype demonstrated its feasibility for distant (from 5-25 m) real-time chemical analysis of phosphate minerals excavated by the drag line machine. Analytical data from the remote LIBS correlated well with laboratory analyses, giving a correlation coefficient of $R^2 = 0.915$ for P_2O_5 . It can provide the following useful information: differentiation between overburden, matrix and bed rock; analysis of the P_2O_5 content; and analysis of MgO content in matrix samples. This technology has great potential for improving both mining and beneficiation efficiency.

4.2. Recover of the Phosphate Values from Waste (Phosphatic) Clays (Slime)

A 1995 study of Florida waste clay shows the magnitude of phosphate loss in phosphatic clays, Table 8 [74].

Table 8. Major chemical compositions of phosphatic clays

Sample ID	P2O5 %	Insol %	Al2O3 %	CaO %	MgO %	Fe2O3 %
M010a	12.92	32.57	6.43	22.46	4.01	1.63
N010a	14.56	35.36	8.75	22.04	1.79	2.87
C010a	6.97	43.27	4.93	14.82	4.23	1.21
G010a	6.09	48.51	4.88	15.86	5.36	2.01

Several approaches were evaluated for recovering the phosphate values from waste clay, and the most promising method was found to be cycloning followed by flotation [75]. Batch sizing tests using a six-inch cyclone generated an underflow product of approximately plus 20 microns in size with 18% P_2O_5 , 0.5% MgO, and 3.3% Al_2O_3 . This cyclone also performed well under continuous operation, delivering a relatively sharp cut at 20 microns. A second stage cycloning further reduced the fines and unwanted components (Al, Mg, and Fe) from the primary underflow product. Selected cyclone underflow samples were further upgraded using three flotation techniques including direct amine flotation, fatty acid rougher-cleaner flotation and the standard Crago double float process. Table 9 summarizes some flotation results on a cyclone underflow sample analyzing 7.81% P_2O_5 , 72.88% Insol, 0.47% MgO, 1.15% Fe_2O_3 , and 2.47% Al_2O_3 .

Table 9. Flotation results using three flotation techniques

Item	Direct Amine	Rougher/Cleaner	Crago
%P ₂ O ₅	31.09	29.53	31.03
%Insol	7.84	10.10	7.35
%P ₂ O ₅ recovery	30.7	85.3	69.2
Reagent cost	5.00	3.41	4.57
\$/ton product			

Phosphate loss in waste clay is also significant at many phosphate mines worldwide and persistent efforts are being made to either reduce the loss in the first place or recover the lost values. In Brazil, phosphate recovered from the slime accounts for as high as 30% of the total rock production at some mines.

4.3. Improving P Recover from Carbonaceous Phosphates

As discussed in the Introduction, carbonaceous (MgO-containing) phosphate deposits account for roughly 75% of the world phosphate reserves. In the acidulation process for manufacturing phosphoric acid, MgO-containing minerals are fully dissolved and usually coexist in phosphoric acid by acid hydrolysis reaction to form Mg(H₂PO₄)₂. This is the main reason why magnesium causes various problems in the acid plant. Mg(H₂PO₄)₂ can greatly increase the viscosity of phosphoric acid, causing difficulty in ion diffusion and local concentration differences in the acidulation process, thus affecting the uniform growth of calcium sulfate crystals. High viscosity also reduces the filtration rate in separation of phosphoric acid from phosphogypsum.

Both the research community and industry have made great progresses in processing high-carbonates phosphate ores, particularly the dolomitic ores. The development and commercialization of the direct-reverse flotation process can be called a breakthrough. The basic flowsheet of the process is shown in Figure 4.

This process is becoming more and more popular in recent years [76-81]. Like the Crago “double float” process for siliceous phosphate, the direct-reverse flotation process for carbonaceous ores has the following distinct advantages: 1) it is suitable for flotation feed of varying grades; 2) it usually does not require depressants that may have environmental consequences; and 3) it is easy to operate.

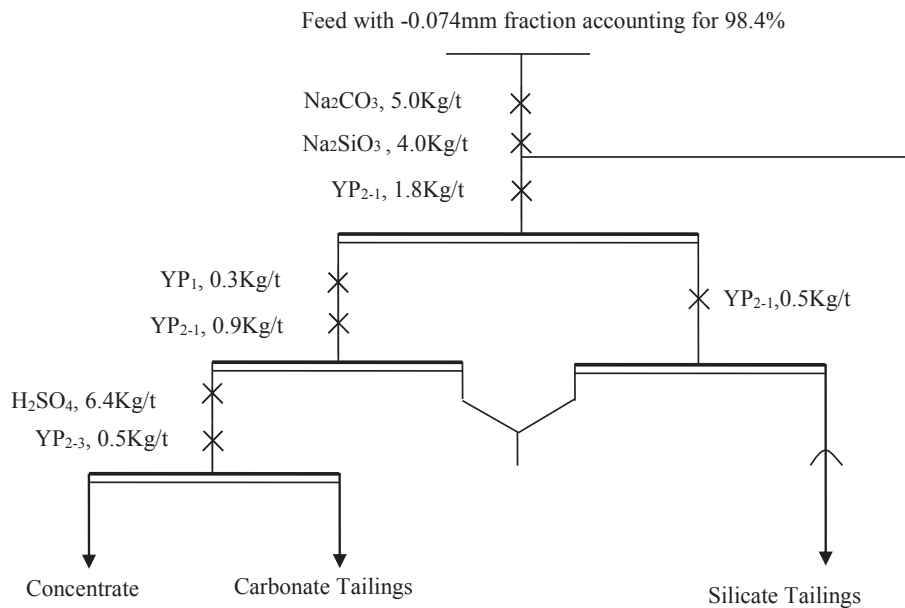


Figure 4. Direct-Reverse flotation flowsheet for dolomite removal [77].
YP₂₋₁ is the collector for direct flotation, and YP₂₋₃ is the collector for reverse flotation.

Currently, the major dolomite problem in Florida is with the pebble fraction. A 1989 FIPR study of the future phosphate resources in Florida showed that the ratio of concentrate to pebble would become higher and higher. Therefore, reducing MgO content in the concentrate by a small margin would allow blending of a large portion of the high-dolomite pebble. A rough estimate based on the study indicated that about 90% of the high-dolomite pebbles could be used, if the MgO content in the concentrate is reduced by 30%. The above rationale prompted FIPR to conduct a research project designed to develop techniques to reduce MgO content in the concentrate with minor modifications or no change to the current processing flowsheet. Successful methods developed under this project include adding a dolomite depressant in the rougher flotation step, dolomite flotation on the cleaner concentrate with grinding, and scrubbing the cleaner concentrate in quartz sand. These techniques could reduce MgO content in the final concentrate by over 20% [82].

5. Conclusions

Sustainability in phosphate mining and processing can be achieved by focusing on the following three areas:

- Increasing P_2O_5 recovery in the mining and beneficiation processes through providing instant analysis of mine face and developing more efficient technologies for processing carbonaceous ores.
- Utilizing wastes, particularly PG and waste clay. In the case of PG use, sulfur recovery combined with cement production, production of ammonium sulfate and construction materials present the best hope for large volume utilization. Waste clay has the potential to become a significant resource for phosphorus and rare earths, in addition to its uses as construction materials.
- Recovering metals values from phosphate, including uranium, rare earths, and possibly thorium.

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