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## Comprehensive Recovery and Sustainable Development of Phosphate Resources

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### 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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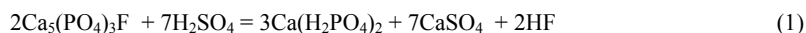
*Keywords:* Phosphate; Uranium extraction; Rare earths, Phosphogypsum; Sustainable development ; Comprehensive recovery

### 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):



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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 Anhydrate 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%  $\text{P}_2\text{O}_5$  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%  $\text{P}_2\text{O}_5$ . 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 BreyedHeurty [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

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