Recovery of Phosphors by Beneficiation Technology

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Abstract: Phosphorous is indispensable in the phosphoric acid industry, fertilizers, and elemental phosphorus production due to its high economic importance. The way to successfully upgrade phosphate ore was based on a full understanding of its mineralogy, mineral surface properties, mineral distribution and liberation. Most phosphate ores are not suitable for direct use in the acidulation process because they have relatively low P₂O₅ contents and generally contain many impurities. Thus, low-grade phosphate ores must be pretreated to reach a suitable phosphate concentrate by the following beneficiation techniques: flotation, attrition scrubbing and desliming, electrostatic separations, magnetic separation, gravity separation and calcination. Flotation was predominantly used for the beneficiation of phosphate ores, while calcination could be feasibly used when the fuel energy cost was low and the water source was limited. The chemical composition and texture of phosphate ores should be considered when applying attrition scrubbing and desliming, magnetic separation and gravity separation. Commonly, some of the above technologies should be combined to obtain excellent results.

Keywords: Phosphorous, Beneficiation, Flotation, Electrostatic separation, Gravity separation, Magnetic separation.

1. INTRODUCTION

Phosphorous is indispensable in the phosphoric acid industry, fertilizers, and elemental phosphorus production due to its high economic importance [1-4]. The only source for phosphorous was phosphate ores. Usually, there are five kinds of phosphate deposits: marine sedimentary (accounting for 80% of the world’s production), igneous, metamorphic, weathering sedimentary and biogenic deposits [5-8]. The phosphate deposits could increase to 30-35% P₂O₅ as the raw concentration ranged from 10%-30% [9-11]. Table S1 summarizes the leading phosphate reserves worldwide. China, Morocco, America and Russia have the most phosphate reserves, with values of 110 million t/a, 36 million t/a, 23 million t/a, and 14 million t/a, respectively [6, 12-14]. Following the expansion of these projects, phosphate mine production seemed to increase in other countries, such as Jordan, Morocco, Saudi Arabia and Senegal [5, 15-17].

Phosphate ores can also be divided into six kinds according to their major components: siliceous ores [18-20], clayey ores [21-23], calcareous ores of sedimentary origin [24-26], phosphate ores rich in organic matter [27-29], phosphate ores with multiple gangue minerals [14, 30], and igneous and metamorphic phosphate ores [5, 12, 16]. In other words, phosphate minerals can be grouped as primary or secondary minerals based on the phosphate cycle.

Mostly, the primary minerals were the original source of carbonate and alkaline igneous rocks [31-34]. The primary minerals transform into secondary minerals after treatment of the original sources. More than 200 kinds of phosphate minerals were found, and the apatite group was the most abundant, accounting for approximately 95%. Table S2 lists the abundant phosphate minerals and their occurrence [35-40].

2. PHOSPHORUS PROPERTIES

Mostly, phosphorous existed as phosphate ions (H₂PO₄⁻, H₂PO₄²⁻, HPO₄²⁻, and PO₄³⁻) in the aqueous solution. The real distribution of each species in the phosphorus (V)-water system was simulated by Minteq Visual software, and the results are shown in Figure 1. The fraction of each species changed with pH and concentration. The major species in the acidic and alkaline media were H₂PO₄⁻ and HPO₄²⁻. First, the concentration of the main component H₃PO₄ increased and then decreased as the pH increased. Then, H₃PO₄ was transformed to H₂PO₄⁻ as the pH increased and reached nearly 100% at pH 5. At the same time, HPO₄²⁻ was generated and increased to nearly 100% at pH 10 and then transformed to PO₄³⁻. In addition, the species were affected by the pH and concentration of phosphorous. When the concentration increased, the overall trend of each species hardly changed, while the percentage changed. The percentage of H₃PO₄ increased from nearly 20% to 42% at pH 2 as the concentration increased from 0.01 M to 0.09 M, and the same trend was observed for PO₄³⁻, while it had no effect on the formation of H₂PO₄⁻ or HPO₄²⁻.
3. BENEFICIATION

Usually, phosphate ore can be directly used to produce phosphate products such as phosphates and fertilizers through wet processes based on high-grade phosphate ores [23, 41-44]. With the growing demand for phosphate, high-grade phosphate ores have fallen short of demand; thus, some low-grade phosphate ores have attracted increasing amounts of attention. Most phosphate ores are not suitable for direct use in the acidulation process because they have a relatively low $\text{P}_2\text{O}_5$ content and generally contain many impurities [45-48]. Thus, low-grade phosphate ores must be pretreated to reach a suitable phosphate concentrate by beneficiation techniques. The advantages and limitations are summarized in Table S3 [6, 12, 17, 41, 49-51].

3.1. Flotation

Flotation technology has been widely used for the economic benefit of ores due to its exceedingly effective removal of impurities [23, 52-54]. Flotation reagents were selected according to the process design, whether apatite, calcite, dolomite, or quartz was collected [55]. During the direct flotation process, phosphate was selected as a floating mineral, and other gangue components were used for degradation and vice versa during the reverse flotation process. The collector properties significantly affected the process efficiency; therefore, the collector was selected after thorough investigation and literature review. Different simulation techniques could be used for efficient design using artificial intelligence. Various types of collectors, such as anionic, cationic [56], and amphoteric, have been thoroughly employed in beneficiation processes [57]. Commonly, anionic surfactants are used in direct flotation, and cationic surfactants are used in reverse flotation during the beneficiation of phosphates.

For the direct flotation process, the pH is an important parameter. $\text{Na}_2\text{CO}_3$ was mostly used to maintain a pH of 9.5 in the direct flotation process, and water was simultaneously applied to depress the float of silicate minerals. Finally, the pre-concentrated phosphate minerals were floated with the assistance of anionic surfactants [58-61].

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Figure 1: Distribution of phosphorus species in the phosphorus (V)-water system at 25°C at various pH values with concentrations ranging from 0.01-0.09 M.
Similarly, during the reverse flotation process, cationic surfactants assisted in floating silica while maintaining a weakly acidic environment, leaving the phosphates (dominant apatite) as underflow [62]. The flotation process and the type of surfactant used were selected according to the type and composition of the minerals. Mostly, the anionic reverse-flotation process was preferred for calcareous phosphates, whereas cationic reverse-flotation and anionic direct-flotation could be employed for the beneficiation of siliceous phosphates. Figure 2 shows a representative direct reverse two-step flotation process [41].

3.2. Attrition Scrubbing and Desliming

This technology is a physical process for cleaning clays adhered to the surface of phosphate ores [49, 60, 63]. It was mainly used for weathered ore or ore with more mud. At present, this technology is quite mature at home and abroad, especially for phosphate rock with a high weathering degree, and its separation effect is particularly obvious. The basic step of this technology was to wash the phosphate rock with water in the ore washing equipment, and after removing a large amount of slime from the ore, the qualified phosphorus concentrate could be obtained by screening and classifying processes. The scrubbing desliming process was simple and easy to perform, was purely a physical beneficiation method and did not cause environmental pollution because there was no chemical agent. In other areas with severe surface weathering, this technology was mostly used for pity ores, and good economic benefits could be obtained. A large number of industrial production practices have shown that the scrubbing desliming process has certain limitations in improving the concentrate grade, and a large number of tailings produced in the scrubbing process cannot be effectively utilized because of their fine particle size, resulting in the loss of phosphate rock resources in fine mud and the formation of resource waste. Currently, the combination of scrubbing and flotation technology is widely used for phosphate rock with a high weathering degree. After cleaning, predictable concentrated phosphate ores could be obtained. In some way, a high grade (above 32% P2O5) could be obtained after the gangue clays that are dominant in sesquioxide were removed. However, it should be noted that there was still a certain amount of phosphorus (up to 19%) remaining in the scrubbed tailings. If it is not treated effectively, it is a major environmental threat and waste of phosphate resources.

Attrition scrubbing of pebble phosphate samples (Dolomite rejection from central Florida pebble phosphate, top size of 1 mm and 2.97% MgO grade) was performed under different conditions of scrubbing time, pH, temperature and rpm. The results showed that the best scrubbing results were obtained for a scrubbing time of 20 min and an MgO content in the

![Diagram of Flotation Process](image)

**Figure 2:** Flotation process for the beneficiation of phosphate ore (Reprinted with permission from Sajid et al. (2022) Copyright (2022) Elsevier).
coarse product (concentrate) of approximately 1.72%, with a phosphate $P_2O_5$ recovery of 63.47% [63]. An Egyptian siliceous/calcareous sedimentary phosphorus with 21.80% $P_2O_5$, 10.93% acid insoluble and 16.61% loss on ignition was subjected to beneficiation by unsophisticated economic means. Through an integrated attrition scrubbing study, 52% of the phosphate was recovered, and 28.72% of the $P_2O_5$ was obtained [64]. The conventional desliming/flotation scheme used to process phosphate ores was tested and adapted to process one of the rejected streams of a niobium concentrator to produce a salable phosphate concentrate. The results showed that more than 32% $P_2O_5$ at a $P_2O_5$ recovery of 41% was obtained with desliming followed by reverse flotation of apatite and acid leaching [60].

3.3. Electrostatic Separation

Electrostatic beneficiation has been applied in the small-scale phosphorous industry since the 1940s and is also widely used in other small-scale mineral processing [65-68]. The recovery of phosphorous could be greater than 80% as the content of phosphorous ranged from 3% to 27% with fatty acids or fuel oils. For the whole process, the recovery efficiency was affected by the feed size, disk speed, splitter position, voltage, moisture content and electrode. To obtain excellent results, several enhancements, such as excellent recovery, significant upgradation, and efficient quartz removal along with dry operation, were investigated. This technology still fails to commercialize or be applied in large-scale production of phosphate owing to its high cost and low capacity.

3.4. Magnetic Separation

Magnetic separation has been successfully applied in the beneficiation of igneous apatite deposits because these minerals contain a high content of ferrous iron [69-72]. In Brazil, this technology has been used to successfully separate apatite from carbonate phosphate ores via consecutive low-intensity magnetic separation, desliming, flotation and high-intensity magnetic separation processes. It was concluded that this technology has great potential for the removal of magnetic gangues.

The benefits of high-phosphorus siderite ore include acid leaching dephosphorization, alkaline oxide-reinforced carbothermic reduction and magnetic separation. The results showed that phosphorous mainly existed as fluorapatite and could be removed effectively by sulfuric acid leaching. An iron concentrate with 70.83% Fe and 0.05% P could be obtained after the reducing reaction and magnetic separation process, and it could serve as a raw material for ironmaking [69]. Magnetic separation and flotation were combined to separate iron and phosphorus from a CaO–$SiO_2$–FeO–$P_2O_5$ slag. The results showed that with the addition of $B_2O_3$, the iron and phosphorus in the slag were enriched in the form of $Fe_3O_4$ and $Ca_{10}P_6O_{25}$ phases, respectively, under an Ar atmosphere. High grades of 92.84% $Fe_3O_4$ and 37.66% $P_2O_5$ slag were obtained, corresponding to recovery ratios of 85.8% for iron and 91.3% for phosphorus [73]. Phosphate ores (53–63 μm) from Rajasthan and Madhya Pradesh were subjected to two-stage high-gradient magnetic separation. The phosphorus and silica were coated by magnetite and remained in a nonmagnetic proportion after the first roasting stage, and the phosphorus was selectively coated again by the magnetite and consequently enriched in the final magnetic product in the presence of sodium oleate and sodium metasilicate. A final concentrate containing approximately 31.5% $P_2O_5$ and 8.8% $SiO_2$ was obtained under the optimized conditions, while the overall recovery of $P_2O_5$ was only 65.0% [74].

3.5. Gravity Separation

Gravity separation also belongs to the category of physical beneficiation, which mainly uses the density difference between different minerals to separate minerals with different densities in dense media, sinks more than heavy minerals, and floats more than light minerals [75-77]. A typical flowsheet of gravity separation for phosphate rocks is given in Figure 3 [12]. The density of different types of minerals generally varies, so the density of gravity separation in the sorting environment generally varies. Our country began to study and practice in the middle and late 20th centuries, and the results showed that the separation specific gravity was the key influencing factor of this beneficiation method and that the specific gravity should be controlled during the separation process. This technology has the characteristics of rapid separation and little environmental pollution. When treating phosphate ore with carbonate as the main gangue mineral, the weighting agent was magnetite, cinnamon iron or their mixture, so that the specific gravity of the prepared solution was between that of gangue minerals and that of phosphate minerals. During the separation process, minerals with a light specific gravity relative to the solution floated upward, whereas minerals with a heavy specific gravity sunk. By using the specific gravity difference caused by
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Journal of Composites and Biodegradable Polymers, 2024 Vol. 12

heavy liquid, the purpose of separating useful minerals from gangue could be achieved. For the current situation of phosphate rock resources, gravity separation could be performed before other separation operations as a preseparation operation, which could exclude most of the gangue in advance, and the concentrate could enter the next separation operation, thus improving the selected grade, reducing the operation pressure for the subsequent separation operation and improving the separation efficiency. The coarse phosphate minerals with a strip structure in the sedimentary phosphate rock were proven to be effectively removed by discarding the tailings through gravity separation. In this case, the energy consumption for grinding is drastically reduced. As an economical and environmentally friendly beneficiation technique, gravity separation has been increasingly popularized and applied by some phosphate mining enterprises in China. However, gravity separation technology has not been applied in large-scale industry due to its unsatisfactory $P_2O_5$ grade. Moreover, the high content of $P_2O_5$ in the tailings and low recovery were also limitations. To obtain qualified concentrates and to maximize mineral utilization simultaneously, it is necessary to combine these processes with flotation to form a joint beneficiation process.

3.6. Calcinations

Calcination is a chemical method that involves heating materials to a dissolved state in a roasting furnace, decomposing materials and removing volatile substances such as crystal water, carbon dioxide or sulfur trioxide. Calcination is mainly suitable for carbonate phosphorus removal. The basic principle behind this process is that phosphate rock is roasted at high temperature, and $CO_2$, $CaO$ and $MgO$ are decomposed by pyrolysis. Then, $CaO$ and $MgO$ are digested with water to form fine granular $Ca(OH)_2$ and $Mg(OH)_2$ attached to the ore surface, and the hydroxides of calcium and magnesium are removed by desliming and classification operations so that the phosphate rock is enriched. When collophanite contains a large amount of gangue minerals, such as $SiO_2$ and pyrite, and phosphate rock cannot be lifted by simple physical processes, calcination treatment is needed. The production of phosphates produced by calcination accounts for 10% of all phosphates produced worldwide. With this technology, calcareous minerals decompose during high-temperature roasting (approximately 950 °C), and then, phosphorous is recovered by extraction with $NH_4Cl$ or $NH_4NO_3$ solution [78-80]. However, because of its high energy cost, this technology is only suitable for some Mid-east countries, which have low energy costs and limited water sources. The energy cost was double or greater than that of the above physical beneficiation technologies.

4. CONCLUSION

A high-quality feedstock is essential for obtaining good quality products. Preferably, high-grade
phosphate minerals were used for the manufacturing of phosphate products. With the growing demand for phosphate, high-grade phosphate ores have fallen short of demand; thus, some low-grade phosphate minerals were replaced after beneficiation technology. Flotation was predominantly used for the beneficiation of phosphate ores, while calcination could be feasibly used when the fuel energy cost was low and the water source was limited. The chemical composition and texture of phosphate ores should be considered when applying attrition scrubbing and desliming, magnetic separation and gravity separation. Commonly, some of the above technologies should be combined to obtain excellent results.

FUNDING

There was no financial support for this work.

CONFLICTS OF INTEREST

All authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript.

AUTHORS’ CONTRIBUTIONS

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Jing Guo, and Bing Li. The first draft of the manuscript was written by Jing Guo and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Recovery of Phosphorus by Biotechnology


Received on 02-07-2024
Accepted on 05-08-2024
Published on 07-08-2024

DOI: https://doi.org/10.12974/2311-8717.2024.12.02

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