

Review

Review on Beneficiation Techniques and Reagents Used for Phosphate Ores

Yaoyang Ruan, Dongsheng He and Ruan Chi *

Xingfa School of Mining Engineering, Wuhan Institute of Technology, Wuhan 430074, China; ruanyaoyang@163.com (Y.R.); csuhy@126.com (D.H.)

* Correspondence: rac@wit.edu.cn

Received: 30 January 2019; Accepted: 24 April 2019; Published: 25 April 2019



Abstract: Phosphate ore is an important raw material for manufacturing fertilizers and phosphorous chemical products. While most of the phosphate resources cannot be directly treated as feed stock due to the low grade of P_2O_5 and high content of impurities. In order to obtain a qualified phosphate concentrate, the beneficiation of the low-grade phosphate ore is, hence, of great necessity. Many beneficiation techniques can be employed to upgrade the P_2O_5 grade of phosphate ores based on their characteristics in chemical composition and texture. The flotation process is most widely applied to balance the P_2O_5 recovery ratio and cost. In this review, the dominant techniques for the beneficiation of phosphate ores are introduced. Moreover, the factors that affect the flotation of phosphate ore, including the properties of mineralogy, flotation reagents (depressants and collectors) and flotation medium, were systematically analyzed.

Keywords: phosphate ore; beneficiation; mineralogy; depressant; collector; interfering ions

1. Introduction

Phosphate ore is an essential raw material for manufacturing phosphoric industrial products, and it is irreplaceable. It has been widely utilizing in agriculture, chemical industry, food, pharmacy, etc. The world's phosphate reserves total up to 70 billion tons. Morocco has the biggest phosphate resources, a reserve of 50 billion tons, accounting for 71.43% of the total amount [1]. China, Morocco, the United States and Russia are the leading countries of phosphate production with a proportion of 79%. Other countries including Brazil, Jordan, Egypt and Saudi Arabia take up the rest of the production. There are four major types of phosphate resources according to the mineralization, viz., igneous deposits, metamorphic deposits, sedimentary deposits and biogenic deposits (guano accumulations). Approximately 75% of phosphate resources is attributed to sedimentary origin [2].

The high-grade phosphate ore will go through the wet process and pyrogenic process respectively to obtain the intermediate products of phosphoric acid and phosphorus, which can be used to produce various phosphate fertilizers and phosphates. The requirements for phosphate concentrate used in wet phosphoric process are (1) a P_2O_5 grade higher than 30%, (2) a CaO/P_2O_5 ratio less than 1.6, and (3) a MgO content less than 1% [3]. However, with an increasing population and a demand for phosphate, the high-grade phosphate ores with a low content of impurities are being depleted. Most of phosphate ores are not suitable for direct use in the acidulation process because they have a relatively low P_2O_5 content and generally contain a series of gangue minerals, mainly quartz, mica, feldspar, dolomite, calcite, clays and so on. Therefore, the industry of phosphate beneficiation is confronted with a great challenge, i.e., how to exploit these low-grade phosphate ores in economical and efficient way [4].

Since the low-grade phosphate ores must be pretreated to reach a qualified phosphate concentrate, the beneficiation techniques and reagents become extremely critical to achieve the selective separation of phosphate minerals. Based on the diverse compositions and texture of the run-of-mine, the

corresponding beneficiation processes and reagents are introduced. This paper comprehensively reviews the phosphate beneficiation techniques, reagents and the factors affecting phosphate flotation, aiming at providing a guideline for the development and utilization of phosphate ores in the future.

2. Beneficiation Techniques for Phosphate Ores

2.1. Flotation

Due to the high efficiency in the removal of silicate and carbonate gangue minerals, froth flotation is dominantly employed for the beneficiation of phosphate ore, especially for low-grade sedimentary phosphate rocks. Generally, direct flotation by anionic surfactants or reverse flotation by cationic surfactants are conducted to remove the silicate gangues from phosphate ores. During the direct flotation process, the pulp pH was adjusted to around 9.5 by adding soda ash, and a proper amount of water glass was required simultaneously to depress the float of silicate minerals. Then, the phosphate minerals turned out to be floated with the assistance of anionic surfactants. For the reverse flotation process, silica was floated using cationic surfactants in a weak acidic or neutral pH, and the phosphate minerals (dominantly apatite) were obtained from the underflow product. The superior adsorption of cationic surfactants on silica rather than apatite probably can be attributed to the more negatively charged surfaces of silica [5]. The conventional “Crago” double float process is used to remove silica twice from phosphate ore in Florida. Due to the higher fatty acid prices, lower feed grade and stricter environmental regulations, a new reverse “Crago” process comprised of amine–fatty acid flotation was developed [6], and its schematic flowsheet is given in Figure 1. For the removal of carbonate gangues, a high separation efficiency can be achieved using reverse anionic flotation at around pH 4.5 without the addition of a phosphate depressant [7].

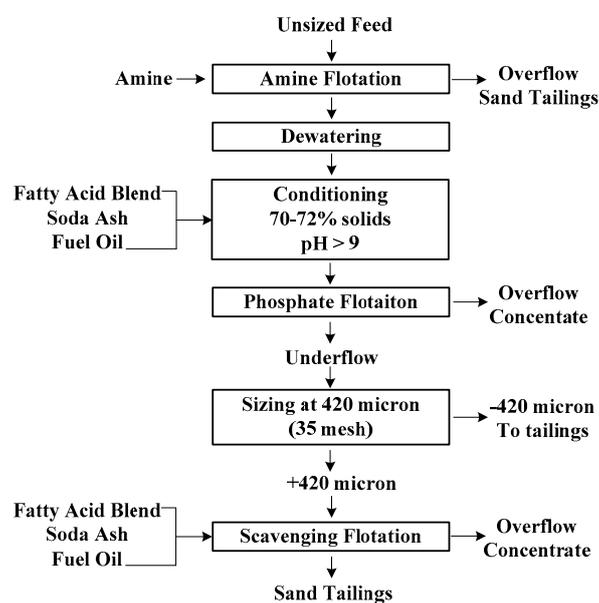


Figure 1. The reverse “Crago” double float process for beneficiation of Florida phosphate ore [6].

The phosphate ores mainly contain the siliceous phosphate rock, calcareous phosphate rock and calcareous-siliceous phosphate rock. Different types of phosphate ores should be subjected to specific flotation processes for upgrading according to the mineral composition characteristics. Both of the anionic direct flotation and cationic reverse flotation are applied for the beneficiation of siliceous phosphate rock, while the single anionic reverse flotation is preferred to beneficiate the calcareous phosphate rock. A two-step flotation process, named direct-reverse flotation (Figure 2) or double reverse flotation, is usually carried out to remove silica and carbonate gangue minerals stepwise from the calcareous-siliceous phosphate rocks [8].

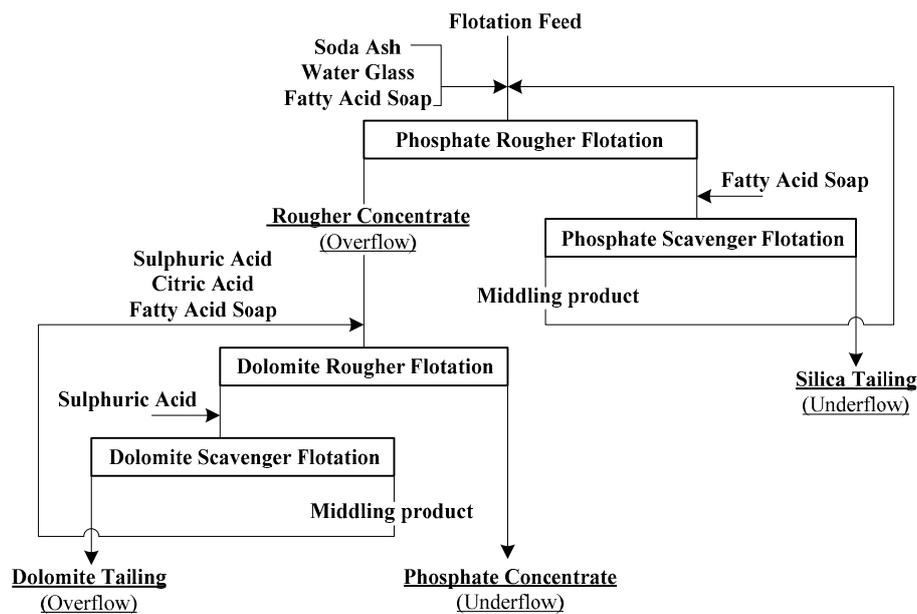


Figure 2. The direct-reverse flotation process for beneficiation of calcareous-siliceous phosphate ore [9].

However, it is found that the reagent consumption in direct flotation mid-low grade phosphate rocks is relatively higher and, thus, increases operating cost. At the same time, the recycled water is also difficult to reuse, and the high temperature is required sometimes, which results in the application of the direct process being highly restricted. Therefore, it is only suitable to beneficiate the low-grade phosphate ores. At present, the single reverse flotation is attracting concentrated focus and has been widely applied to beneficiate phosphate ores in China.

In some cases, an appropriate amount of silica in the phosphate concentrate is desired for the production of phosphoric acid by the wet process. As we know, the fluorine in phosphate ores will react with acid to generate HF and further corrode the surrounding facilities. However, this adverse effect can be greatly reduced, since the silica reserved in the flotation concentrate can react with HF to form SiF_4 and fluorosilicates [10]. The production practice has shown that it is economically feasible to obtain a qualified phosphate concentrate using single reverse flotation in case of the high-magnesium calcareous phosphate rock is mixed uniformly with a certain proportion of siliceous phosphate rock.

2.2. Attrition Scrubbing and Desliming

This technique is commonly used for the treatment of weathered phosphate ores that contains a relatively high content of clays. In this case, a coarse phosphate concentrate can be obtained after the elimination of fine-grained clays. This method has been successfully applied on the high-grade weathered phosphate ores in Dianchi area (Yunnan, China). As the weathered phosphate ores were crushed and sieved, the fraction of -25 mm was used to conduct the scrubbing and desliming; as a consequence, a high-quality concentrate with a grade of P_2O_5 above 32% was obtained after the gangue clays that dominant in sesquioxide ($\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$) were removed [11,12]. At the same time, this process has also been applied in the Crago flotation process for the preliminary enrichment of phosphorites ahead of the anionic-cationic flotation section [6,13].

However, it should be noted that there is still a certain amount of phosphorus remaining in the scrubbed tailings, and its grade is nearly up to 19%. If phosphorus slurry deposits into the tailings pond instead of being effectively recovered, it will cause a big waste of valuable resources and a nonnegligible environmental issue. He et al. confirmed that using a direct flotation can effectively recover the phosphorus from the scrubbed tailings in Yunnan and finally obtained a concentrate assaying 28.26% P_2O_5 with a recovery of 80.37% [12].

2.3. Electrostatic Separation

Electrostatic separation is always used to pre-concentrate grained phosphate minerals by discarding a certain proportion of silica. This approach can reduce the energy consumption of grinding and the cost of chemical reagents and water usage. Sobhy and Tao investigated the feasibility of using rotary triboelectrostatic separator in a dry beneficiation process of Florida phosphate ores [14]. Their results showed that a concentrate containing 30% P_2O_5 with a recovery of more than 85% was collected and that the acid insoluble rejection also reached almost 90%. The Saudi phosphate ores are always in grain size with 9–70 mm and can be upgraded by an electrostatic separator (COM Tertiary XRT B2400, GREANEX, Wilmington, DE, USA). In the laboratory experiment and industrial test, respectively, 60.2% and 44.65% of silica was demonstrated to be removed [15]. However, this method is usually restricted by the low capacity of the electrostatic separators and, thus, has not been applied for the large-scale production of phosphate concentrate.

2.4. Magnetic Separation

Magnetic separation is successfully applied for the beneficiation of igneous apatite deposits, which is abundant in ferrous minerals, such as magnetite or titanomagnetite. The beneficiation of apatite from the “Barreiro” complex carbonatite phosphate ore in Brazil can be realized by a consecutive low-intensity magnetic separation, desliming, flotation and high intensity magnetic separation process [16]. Meanwhile, it is confirmed that magnetic separation has a potential application on the treatment of coarse-grained sedimentary phosphate ore for the removal of magnetic gangues. Blazy and Jdid conducted a high-gradient magnetic separation (HGMS) on the Egyptian Abu Tartur high-grade phosphate ore in the size range of 38–210 mm. A concentrate assaying 31.2% P_2O_5 with a recovery of 70% was obtained through the removal of dolomite gangue minerals [17]. It was observed that the ferrous dolomite selectively entered into the magnetic product during the magnetic separation process, while the phosphate minerals remained in the nonmagnetic part. Another research also demonstrated that the removal of dolomite carbonates from a marine sedimentary phosphate ore (80–250 μm) can be achieved through magnetic the separation process [18].

The exploration of the magnetic separation process on the fine-grained rock phosphate ores was undertaken by Shaikh and Dixit [19], and the schematic flowsheet was given in Figure 3. Phosphate ores (53–63 μm) from Rajasthan and Madhya Pradesh were subjected to a two-stage high-gradient magnetic separation. In the first stage, the calcite/iron was coated by magnetite and effectively separated as the magnetic product under the effect of sodium oleate and dipotassium hydrogen phosphate. The phosphorite and silica remained in the nonmagnetic proportion. In the second stage, the phosphorite was selectively coated by the magnetite again and consequently enriched in the final magnetic product in the presence of sodium oleate and sodium metasilicate. A final concentrate containing about 31.5% P_2O_5 and 8.8% SiO_2 was obtained under the optimized condition while the overall recovery of P_2O_5 was only 65.0%. It can be seen from the above research that the phosphate recovery is low during the magnetic separation, and thus, this method is not efficient for the beneficiation of fine-grained phosphate ores.

2.5. Gravity Separation

Gravity separation is carried out according to the density difference between valuable minerals and gangue minerals. Because of the similar density of apatite and gangue minerals, it is usually difficult to recover phosphate minerals that are disseminated into fine grains. However, the coarse phosphate minerals with a strip structure in the sedimentary phosphate rock were proved to be effectively beneficiated by discarding tailings through gravity separation. In this case, the energy consumption for grinding is drastically reduced. The band-shaped phosphate rock in the Yichang (China) area contains an abundance of phosphate minerals which are mainly distributed ranging from

2 mm to 18 mm. It is feasible to adopt gravity separation to beneficiate this type of phosphate rock. The typical flowsheet of gravity separation for phosphate rocks is given in Figure 4.

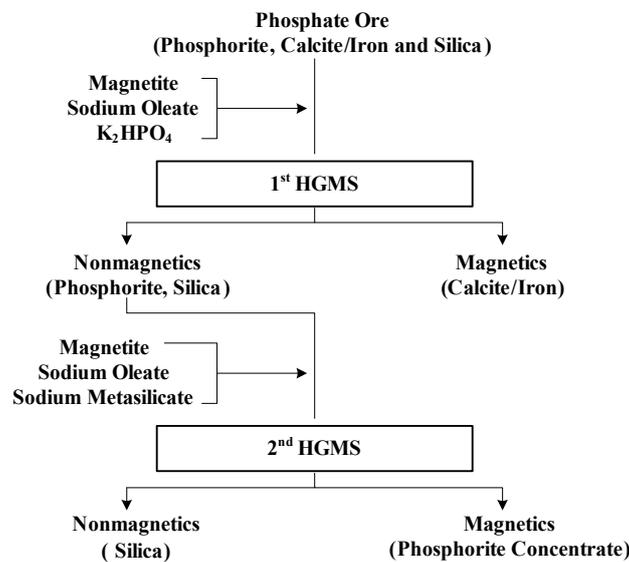


Figure 3. Schematic flowsheet of high gradient magnetic separation for Rajasthan and Madhya Pradesh rock phosphate [19].

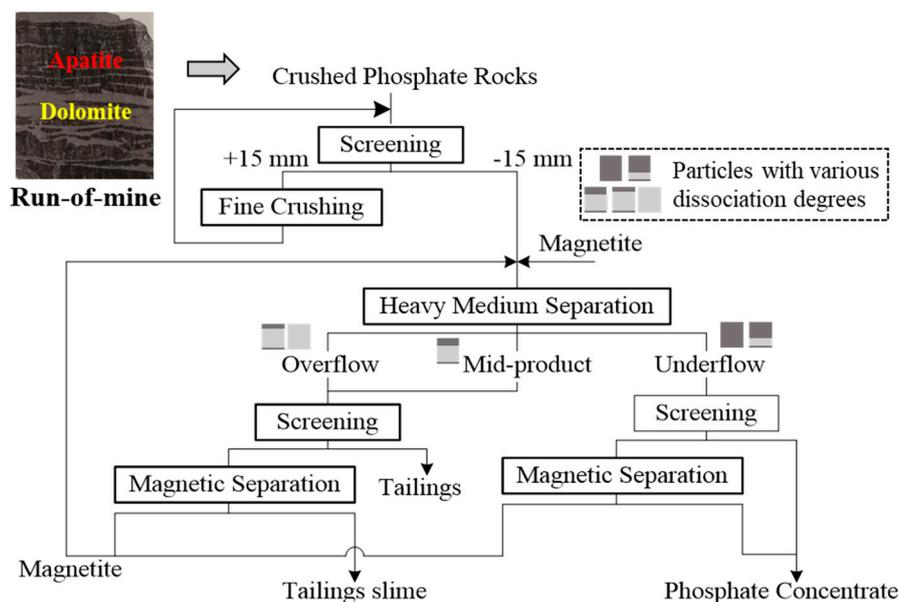


Figure 4. Schematic flowsheet of gravity separation for sedimentary phosphate rock characterized by a strip structure.

Through the addition of magnetite (nearly 92% passing 0.1 mm), the density of the pulp can be adjusted to 2.85–2.91 g/mL, which further facilitates the separation of the valuable and gangue minerals. After subjecting the pulp to gravity separation, the desired minerals are collected in the underflow through sedimentation while the gangue minerals report to the mid-product and overflow. This is often achieved by using a heavy medium cyclone. The mid-product and overflow product are usually merged in order to sieve out the coarse-sized tailings which can be used for mine backfilling. Magnetite contained in the underflow and overflow can be effectively recycled through a medium draining screen followed by magnetic separation. Afterwards, the nonmagnetic materials will be further subjected to concentration and filtration, and a fine-grained concentrate and tailing slime can be obtained. This

method has been successfully applied on the Yichang phosphate ore which contains 23.50% P_2O_5 . The content and recovery of P_2O_5 in the concentrate are up to 30.64% and 85.60% respectively. The annual capacity of the local plant has enlarged to 1.2 million tons since the year of 2008 in the Yichang area [20]. As an economical and environmentally friendly beneficiation technique, gravity separation is increasingly popularized and applied by some phosphate mining enterprises in China.

So far, the physical beneficiation processes such as scrubbing, gravity separation and electrostatic separation processes have not achieved large scale application because it is still difficult to obtain satisfactory phosphate concentrates. At the same time, the P_2O_5 content in the tailings is still high, which results in a low P_2O_5 recovery from these processes. In order 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 [21]. At present, the main combining processes which have been scaled up include the scrubbing-flotation process, the magnetic-flotation process and the gravity-flotation process.

2.6. Calcination

More than 10% of marketable phosphates are produced by calcination in the world [2]. During the calcination process, calcareous minerals are decomposed into calcium oxide and magnesium oxide at temperature about 950 °C, and carbon dioxide is released. Then, the calcined phosphate rocks are subjected to quenching by using NH_4Cl or NH_4NO_3 solution at a concentration of about 5%. Subsequently, the fine grained $Ca(OH)_2$ and $Mg(OH)_2$ are discarded as the slime phase after a classification by hydrocyclone, and the coarser high grade concentrate are successfully separated. For those phosphate ores containing organic matter, it is also an efficient technique for upgrading at a temperature of 650–750 °C [22].

However, it consumed large amounts of energy during the calcination, making this process only suitable for Mideast countries that have low energy cost and limited water sources. Compared to the total energy required for the physical beneficiation of phosphate ores, the consumption needed for calcination is doubled [2]. Furthermore, the solubility and reactivity of the calcined phosphate rocks may decrease during the manufacture of phosphoric acid by the wet process. Watti et al. [23] pointed out that the solubility of a calcined product sharply decreased with the increase of temperature because the dissolved P_2O_5 in a solution of citric acid varied from 9.32% to 3.55% when the treatment temperature increased from 25 °C to 1000 °C. It also has been revealed that the quenching process for the calcined ore was inefficient with the fine sizes and at low temperatures [24]. The above results showed that there are still some technical challenges remaining in the calcination of calcareous phosphate ore.

2.7. Acid Leaching

The calcareous phosphate ores can be also upgraded by acid leaching. In this process, the carbonate gangue minerals prefer to dissolve in the dilute acid solution, while the phosphate minerals remain in the leached residues. As a result, the separation of the phosphate minerals against carbonate gangue minerals is achieved. Using common mineral acids often results in the dissolution of P_2O_5 and causes the loss of P_2O_5 recovery while the leaching selectivity of the organic acids proves high. Therefore, the organic acids are preferred in the leaching process. The commonly used organic acids are lactic acid [25], formic acid [26] and succinic acid [27].

In order to obtain a satisfactory removal of the carbonate gangue minerals, it is necessary to optimize the leaching parameters such as the acid concentration, reaction time, particle size, solid to liquid ratio and reaction temperature [28]. Gharabaghi et al. [29] found that the leaching process for a low-grade calcareous phosphate rock should be optimized to obtain the qualified concentrate when using acetic acid. The best result was achieved by using 15 wt. % of acetic acid concentration at a liquid to solid ratio of 15:1, an optimum reaction time of 60 min and a leaching temperature at 40 °C. After leaching, the P_2O_5 content can be improved to 32.1% with the P_2O_5 recovery of 81%. Although the chemical leaching process of the calcareous phosphate rock is relatively simple and the qualified

concentrate can be obtained under the optimized leaching conditions, there are still some drawbacks, such as (1) the involved organic acids are costly, which greatly increases the production cost as well, and (2) the leaching process usually requires 30–60 min [30], which is much longer than other physical beneficiation methods. Abu-Eishah et al. [28] found that the demanded leaching time was more than 1.2 h to deal with the phosphate ores. The long leaching time greatly limits the capacity of plants and restricts the large-scale production of phosphates. As a result, the profit of plant has been reduced.

From the discussion above, beneficiation techniques and their applications for various phosphate ores are summarized in Table 1.

Table 1. Beneficiation techniques and their applications for various phosphate ores.

Beneficiation Techniques	Phosphate Rock Types	Applications
Flotation	Siliceous phosphate rock Calcareous phosphate rock Calcareous-siliceous phosphate rock	Widely applied in the beneficiation of various phosphate rocks on a large scale, especially for refractory sedimentary phosphate ore
Attrition scrubbing-desliming	Weathered phosphate ores	Used for discarding clay minerals and eliminating the detrimental effect of slimes on the subsequent flotation process
Gravity separation	Sedimentary phosphate rock characterized by a strip texture	Discarding gangues to achieve the preconcentration of phosphate minerals
Magnetic separation	Phosphate ores containing magnetic gangues	
Calcination	Calcareous phosphate rock	Acceptable for areas that have low cost energy and limited water resources
Electrostatic separation	Coarse grained siliceous phosphate rock	Mostly are experimental studies in laboratory scale
Acid leaching	Calcareous phosphate rock	

3. Factors Affecting the Flotation of Phosphate Ore

Satisfactory separation results can be easily obtained by a relatively simple flotation technique when beneficiating phosphate ore with a high degree of crystallinity. However, for the sedimentary phosphate ore characterized by fine grained dissemination and complex chemical composition, it is very difficult to obtain a high-grade phosphate concentrate with an acceptable recovery rate. In addition, as flotation is a gas-solid-liquid three-phase interface reaction process, there are many factors that can affect phosphate ore flotation, such as, mineralogical properties, flotation reagent properties and flotation medium properties.

3.1. Mineralogical Properties

3.1.1. Mineral Type

The influence of crystal chemistry properties on the floatability of apatites was systematically investigated by Rodrigues and Brandao [31], and the curves was illustrated in Figure 5. They stated that the floatability of different types of apatite decreased in the order of pegmatitic apatite (Durango, C. Grosso and Camisao), igneous apatite (Tapira and Catalao), metamorphic apatite (Monteiro), metasedimentary apatite (Itataia) and sedimentary apatite (Igarassu). The floatability of pegmatitic apatites is excellent with a value approaching 100% at a wide pH range. The maximum floatability was observed at neutral pH for the floatability of igneous and metamorphic apatites, and the floatability of metamorphic apatites decreased faster than that of igneous apatites under acid and alkaline conditions. Generally, the floatability of the metasedimentary apatite and sedimentary apatite is poor and the recovery is low in the whole variation range of pH value.

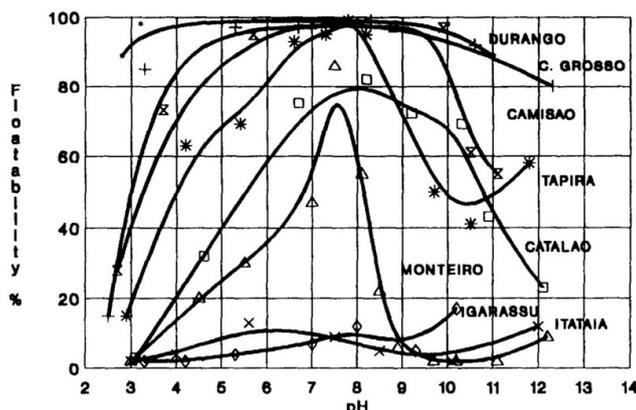


Figure 5. Microflotation curves of various apatite samples using 2.5×10^{-5} mol/L sodium oleate [31].

Through the determination of the unit cell parameters, it was found by Rodrigues and Brandao that the unit cell parameter of igneous, metamorphic and sedimentary-metamorphic apatite is higher than that of sedimentary apatite. The degree of crystallinity decreased in the rank regarding the geological origin: pneumatolitic-hydrothermal, pegmatitic, igneous, metasomatic, metasedimentary and sedimentary. It can be concluded that there is a positive correlation between the floatability and crystallization degree of apatite. They identified that apatites with a higher degree of crystallinity displayed much better floatability, while apatites with a lower crystallinity level needed a higher collector concentration to reach the same floatability corresponding to a highly crystalline one. The worse flotation performances of the apatites having lower crystallinity levels is believed to relate to their higher solubilities, and less stable mineral/water interfaces [31].

3.1.2. Mineral Granularity

It is known that the particle size distribution of the flotation feed has a significant effect on the separation efficiency. Generally, the processibility of coarse-grained minerals is better than that of the fine-grained ones. It is probably attributed to the high surface energy of the fine size, contributing to an increased dissolution from the surface of particles. Thus, the nonselective adsorption of the reagents and undesirable entrainment or entrapment of fine particles occurred [32]. Moreover, the commonly used collectors in phosphate plant, amine and fatty acids are sensitive to the minerals with a fine particle size. How to realize an efficient separation of fine particles is an urgent technical problem faced by the phosphate beneficiation plant. Recently, the effect of particle size on the flotation performance of phosphate ore has been reported.

The flotation selectivity of apatite from a phosphate ore as a function of particle size has been investigated by Santana et al. [32]. They found that the P_2O_5/Fe_2O_3 and P_2O_5/SiO_2 ratios of coarse fractions (+65, +100 and +150 mesh) were higher than the industrial requirements but that there were no satisfied selectivity observed when using finer fraction (−400 mesh). Another study reported by Santana showed that a phosphate concentrate with a high grade and satisfactory recovery were not feasible from both of the coarser (+65 and +100 mesh) and finer fractions (−400 mesh). The optimum particle size range for apatite flotation is from 37 μm to 105 μm [33]. Cationic flotation test conducted by Guo and Li showed that the P_2O_5 grade and recovery of 45–74 μm fraction are higher than those of −45 μm fraction about 2% and 5%, respectively [34].

Mineral liberation is closely related to the particle size in the flotation process of actual phosphate ores. However, there is a certain conflict between liberation and particle size for the beneficiation of fine-grained phosphate rocks because fine grinding is desired to achieve a higher liberation degree and the obtained fine particles will adversely affect the separation efficiency. On the contrary, the separation efficiency of coarse particle without adequate liberation is limited as well [35]. Therefore, the effective liberation of desired minerals as well as avoid overgrinding of ores is of great importance for the subsequent flotation process.

3.2. Properties of Flotation Reagents

A flotation reagent, especially depressants and collectors, has a great impact on the selective separation of phosphate minerals and gangues. During the flotation process, the surface of specific mineral becomes hydrophilic due to the hydrophilic film formed after the adsorption of depressant. Meanwhile, collector molecules are oriented on the surface of the floated mineral, causing the enhancement of hydrophobicity. For example, the addition of depressant for gangue mineral in the direct flotation of phosphate ore is often required. After the depression of gangues, the phosphate minerals can effectively react with collectors and become more gathered by attaching to the rising bubbles.

3.2.1. Depressants

(1) Depressants of Silicate Minerals

Sodium silicate is an effective depressant in the direct flotation of apatite from siliceous phosphate ore using fatty acids [36]. Compared to the infrared spectra of quartz in the absence and presence of sodium silicate at pH 7, the adsorption of dominant hydrolysis species $\text{Si}(\text{OH})_4$ was detected by Silva et al. [37]. The quartz depression mechanism was elucidated through the ligand exchange model, where pairs of electrons were shared by sites of the surface and species of silicate. Generally, the modulus and dosage of sodium silicate have a great impact on the depression of quartz occurred in flotation process [38].

The depression of quartz caused by adding NaHCO_3 in the pulp was also observed in both the cationic flotation using amine and the anionic flotation using sodium oleate and Ca^{2+} as activators. Sayilgan and Arol thought that the depression might result from the compression of the double layer or competitive adsorption of Na^+ and amine ions on the surface of quartz in the case of cationic flotation. For the anionic flotation, it was convincible that the activator calcium ions could react with the carbonate ions and precipitate, making the available concentration of $\text{Ca}(\text{OH})^+$ for quartz activation apparently reduced [39].

Starch exhibited a depression effect on the flotation of quartz. Pavlovic and Brandao identified that the adsorption of starch on the surface of quartz should be attributed to its flocculation property [40]. However, starch was not an efficient depressant for quartz due to the similar depression might have occurred in the flotation of apatite and dolomite. Considering the cost rather than the quality of the product, starch is still widely applied in the flotation of igneous phosphate ores in Brazilian concentrators [41].

(2) Depressants of Carbonate Minerals

In the phosphate beneficiation practice, carbonate gangues can be efficiently removed by a reverse flotation process with the addition of a phosphate depressant. However, for the upgrading of siliceous calcareous phosphate ore, two types of gangue minerals need to be removed by a double float process. In order to simplify the flotation process, attempts of the concurrent depression of silicate and carbonate gangues should be undertaken to achieve the phosphate enrichment at one stage. Therefore, it is of great importance to investigate the depressant for carbonate minerals. Zheng and Smith evaluated different organic chemical reagents which functioned as dolomite depressants in the flotation of single mineral and mixed apatite and dolomite, respectively. The results indicated that carboxymethyl cellulose, citric acid and naphthyl anthyl sulfonates were effective depressants for dolomite [42].

The selective separation of colophonane and dolomite using β -naphthyl sulfonate formaldehyde condensate (NSFC) as a depressant by anionic flotation at pH 9 was conducted by Yu et al. [43]. More significant changes were observed in the case of dolomite, and chemical adsorption occurred on the dolomite while a weak adsorption on colophonane through hydrogen bonds was identified. Although the high efficiency of dolomite depression can be achieved by NSFC, there is a critical obstacle for the large-scale application due to its chemical toxicity.

The depression effect caused by the adhesion of bacteria, namely *Bacillus subtilis* and *Mycobacterium phlei* on the anionic flotation of apatite and dolomite was elucidated by Zhang et al. [44]. It was found that these two bacteria adsorbed on the surface of dolomite and functioned as depressants for both of dolomite and apatite. It seems to be difficult for the separation of apatite from dolomite using these bacteria as depressant, but they can modulate the flotation environment and provide a new idea for the development of depressant for dolomite and apatite.

(3) Depressants of Phosphate Minerals

The depression of apatite can be achieved by adjusting the pH of pulp because the flotation behavior barely occurred at pH below 4.5 in an anionic flotation of apatite without the addition of any other phosphate depressant [5]. It is evident that the species of Ca^{2+} , $\text{CaH}_2\text{PO}_4^+$ and H_2PO_4^- are dominant at pH below 4.5 and that their concentration increases as the decrease of pH according to the solution equilibria of dissolved apatite. [45]. It can be deduced that the species of $\text{CaH}_2\text{PO}_4^+$ and H_2PO_4^- should be responsible for apatite depression. H_2PO_4^- prefers to bond with calcium ions exposed on the surface of apatite, resulting in the reduction of available active sites [44]. In that case, inorganic acids and various phosphate salts, such as potassium dihydrogen phosphate and sodium pyrophosphate, can be used as an efficient depressant for apatite [46,47].

In addition, it was reported that the addition of sulfate or oxalate salts can enhance the depression of apatite in acid media [48,49]. El-Mofty and El-Midany claimed that the dissolved Ca^{2+} can precipitate in the presence of oxalate or sulfate ions, causing more dissolution of apatite, and thus, more phosphate ions existed in aqueous solution [49]. Though sulfuric acid and its salts demonstrate a relatively strong depression on the phosphate minerals, it is easy to cause pipe fouling in production due to the formation of gypsum. Consequently, phosphoric acid is considered for application in the anionic reverse flotation for a beneficiation plant.

Aiming at enhancing the P_2O_5 recovery in cationic reverse flotation, various depressants including sodium tripolyphosphate, fluosilicic acid, diphosphonic acid and starch were evaluated by Zhang and Snow [50]. It was found that starch was an ideal phosphate depressant in the removal of fine (−35 mesh) silica from phosphate, while sodium tripolyphosphate may be the best one for the beneficiation of coarser (+35 mesh) feeds. The phosphate depression caused by a low molecular weight polyacrylamide containing both hydroxyl and carboxylic acid functional groups was also investigated by Nagaraj et al. [51]. The polymer demonstrated an excellent selectivity in the separation of apatite from siliceous gangue using reverse cationic flotation. Various depressants used in the flotation of phosphate ores are collected and presented in Table 2.

Table 2. Depressants used in the flotation of phosphate ores.

Mineral to Be Depressed	Name of Depressant	References
Silicate minerals	Sodium silicate	[36,52]
	Sodium and calcium lignin sulfonates	[53]
	Copolymers or terpolymers derived from acrylamide units and N-acrylamidoglycolic acid units	[54]
Carbonate minerals	Carboxymethyl cellulose, citric acid, naphthyl anthyl sulfonates	[42]
	β -naphthyl sulfonate formaldehyde condensate	[43]
Phosphate minerals	Potassium dihydrogen phosphate, sodium pyrophosphate	[46,47]
	Sodium tripolyphosphate, fluosilicic acid, diphosphonic acid, starch	[50]
	Cashew gum	[55]
	Sulfuric acid, phosphoric acid	[46,56]
	Alkyl phosphate acids, hydrofluoric acid	[57,58]
	Dipotassium hydrogen phosphate	[59]
	Cellulase enzyme	[60]
Iron/aluminum sulfate, tartaric acid	[61,62]	

3.2.2. Collectors

(1) Anionic Collectors

Long chain fatty acids are commonly used anionic collectors in phosphate flotation, especially for sodium oleate. With the aid of atomic force microscopy, the adsorption behavior of potassium oleate and the precipitation of Ca^{2+} ions on the surface of the apatite crystal were visualized. It is believed that the formation and precipitation of calcium dioleate occurred in the form of agglomerates on the apatite surface. The presence of agglomerates made the apatite surface rougher and heterogeneous, which contributing to the flotation behavior of apatite [63]. In the past decades, tall oil and oxidized petroleum were mainly used as the source of manufacturing anionic collectors for phosphate flotation. Due to the high temperature requirement, low flotation selectivity and relatively huge reagent consumption, alternative sources for fatty acids can be derived from the less expensive vegetable oil, such as rice bran oil, hydrogenated soybean oil, cottonseed oil and jojoba oil [9,41,64].

To further improve the solubility and selectivity of fatty acid soap at an ambient temperature, the modified fatty acids characterized by a multifunction group was designed and synthesized through chlorination, hydroxylation and etherification. The flotation results of a low-grade colophonite showed that the modified soybean oil had a better performance than a conventional fatty acid collector with a less dosage [65]. For those anionic surfactants with a low foamability, such as sodium dodecyl sulfonate and sulphosuccinate, they are mostly used as an auxiliary reagent to improve the flotation performance of reagent in practice [66].

(2) Cationic Collectors

In the practical flotation of phosphate ores, cationic collectors are dominantly used for the removal of silicate minerals. Guo and Li claimed that the alkyl amine salt (DAH) is a more effective collector for removing the silica from the fine siliceous calcareous phosphate ore as compared to the ether-amine salt or the quaternary ammonium salt (CTAB) [67]. The flotation behavior of pure quartz studied by Sahoo et al. indicated that cetyl pyridinium bromide and benzyl dimethyl tetradecyl ammonium chloride were more effective than the conventional cationic collector DDA and CTAB [68]. Flotigam EDA 3 ($\text{R-O-CH}_2\text{-CH}_2\text{-C-NH}_2$) and Flotigam 2835-2L ($\text{R-O-(CH}_2\text{)}_3\text{-NH-(CH}_2\text{)}_3\text{-NH}_2$), manufactured by Clariant, were selected as the collector for quartz flotation. It was observed that ether diamine was more effective in the flotation of medium and coarse quartz, while ether monoamine performed better in the case of fine fraction [69]. On the other hand, the above cationic collectors were used for the dephosphorization of an iron ore. Flotigam EDA at a dosage of 150 g/t led to a 0.201% phosphorus concentrate and mass recovery of 62.31%, while the use of Flotigam 2835-2L presented a phosphorous content of 0.31% and mass recovery of 90.24% [70].

The advantage of the cationic collector is that it can achieve the separation of valuable minerals from gangues at a low temperature with less consumption of the reagent. However, amine collectors are generally sensitive to the slimes contained in the run-of-mine ore. Additionally, attributed to the high foam viscosity, it is difficult to defoam during the flotation process when using an amine as the collector. Therefore, cationic collectors are suitable for the flotation of coarse-grained ores, but they show relatively poor performance in the separation of fine-grained materials.

(3) Amphoteric Collectors

This type of collector can be used for the removal of dolomite from phosphate ores. Their flotation selectivity is relatively high over a wide pH range and negligibly influenced by the dissolved species and temperature. It is reported that a phosphate concentrate assaying above 32% of P_2O_5 with a recovery around 90% can be obtained from a mixture of pure phosphate and dolomite minerals when using dodecyl-*N*-carboxyethyl-*N*-hydroxyethyl-imidazoline as the collector [71,72]. The separation of dolomite from Abu-Tartur phosphate ore using a similar amphoteric collector was conducted by Elmahdy et al. [73]. Under the determined optimal flotation parameters, a concentrate of 0.53% MgO and 31% P_2O_5 with a recovery of 90% was obtained. Measurements of the zeta potential and adsorption

in the absence and presence of amphoteric surfactant were performed to elucidate the mechanism. The results indicated that a much greater variation was observed on the calcite surface when compared to the case of apatite surface at an alkaline pH [74,75]. Therefore, the amphoteric surfactant can preferentially be adsorbed on the surface of calcite and can achieve the selective separation of calcite and apatite. However, most of the amphoteric collectors are limited to laboratory studies, and the real industrial application has been barely reported.

(4) Mixed Collectors

The mixture of various surfactants is the main research issue of the development of collector in the flotation of phosphate ore, especially for an ionic and nonionic surfactant mixture. Some mixed collectors used in phosphate flotation is presented in Table 3. It is well-known that mixed collectors are supposed to have a number of synergistic advantages over an individual surfactant. The presence of nonionic surfactants can enhance the adsorption of ionic surfactants on the surface of minerals due to the hydrophobic chain interactions and the reduction of electrostatic repulsion between ionic head groups [76,77]. The measurement of the contact angle of sodium oleate on the apatite surface in the absence and presence of the ethoxylated nonylphenol surfactant (NP-4) showed that the beneficial effect of the nonionic surfactant was achieved at low oleate concentrations (0.1–5 mg/L). It was further confirmed that the activity of ionic surfactants is enhanced with the addition of nonionic surfactant due to the synergistic effect in the formation of mixed micelles and the reduction of surface tension [78,79]. However, it should be noted that the excessive addition of the nonionic surfactant would cause an adverse effect on the flotation process. A decreased adsorption of reagent on apatite surface was found by Sis and Chander when using the mixture of sodium oleate and NP-4 at a weight ratio of 2:1 [80]. They thought that the adsorption decrease caused by nonionic surfactant could be attributed to the competition between the surfactants or the prevention of oleate ions from the precipitation as calcium oleate salt [80,81].

Mixing the anionic collector with nonionic surfactants is also desirable in improving the selectivity of the flotation process. It is reported that the alkyl-hydroxamic acid had a higher selectivity in phosphate flotation than the traditional fatty acid/fuel oil. When it was further used as a collector in the flotation of francolite together with alcohol, the francolite recovery was drastically enhanced [8]. Base on the high-speed video images which clearly exhibited the detachment of collector mixture drop from the quartz surface and then spread on apatite surface, the selective attachment of hydroxamic acid and alcohol collector mixtures in phosphate flotation was confirmed [82].

The effect of mixing anionic collectors with nonionic surfactants on the selective separation of Ca-bearing minerals, including calcite and francolite, has been investigated by Filippov et al. [76]. A synergetic behavior of mixed collectors of anionic surfactants such as alkyl hydroxamate (AERO 6493), di-2-(ethylhexyl) phosphoric acid (D2EHPA) and iso-tridecanol (PX4826) has been shown in the flotation data on francolite and calcite. It is noted that the difference in floatability of francolite and calcite was significantly enhanced at pH 8 when using a mixture of AERO 6493 and PX4826 without the presence of calcite depressant. Furthermore, synergistic effects of primary amine and PX4826 in terms of calcite and apatite recoveries by flotation at pH 8 were also observed [83]. The dephosphorization of magnetite ore by froth flotation showed that the anionic flotation response of apatite increased in the presence of nonionic ethoxylated nonylphenol with no effect on the magnetite flotation [84].

Table 3. Mixed collectors used in the flotation of phosphate ores.

Type of Mixed Collector	Primary Collector	Auxiliary Reagent	References
Anionic-anionic	Fatty acids	petroleum sulfonates and ethoxylated alcohol ether sulfates	[85]
	Fatty acids	alkyl aryl sulphonate and sulphated fatty acid	[86]
	Oleic acid	Sodium dodecyl benzene sulfonate and oxidized paraffin soap	[87]
Cationic-anionic	N-aminoethylpiperazine	Fatty acids	[88]
Cationic-nonionic	Primary amine (Cataflot)	Iso-tridecanol (PX4826)	[83]
Anionic-nonionic	Fatty acids	hydrocarbon oil such as kerosene or fuel oils	[89]
	Fatty acids	Esters of orthophthalic acid or maleic acid	[90]
	Fatty acids	Alkylphenol ethoxylates	[81,91]
	hydroxamate (AERO 6493), di-2-(ethylhexyl) phosphoric acid (D2EHPA)	Iso-tridecanol (PX4826)	[76]

3.3. Properties of Flotation Medium

The influence of flotation medium properties on beneficiation efficiency is significant as well, including pH, temperature and ions. For a determined flotation process, the pH and temperature of pulp are usually controlled in a certain range. However, interfering anions and cations are inevitably present, and their concentration varies based on the water quality and solubility of minerals, especially when recycled water is used. To figure out how various anions and cations affect the flotation performance of minerals, extensive efforts have been taken by many researchers. The effect of metal ions on the floatability of apatite was investigated by Ruan et al. [5], and the micro-flotation results were showed in Figure 6. It is seen that the appropriate amount of Ca^{2+} and Mg^{2+} can improve the floatability of apatite but had a negligible effect on the flotation performance of dolomite, whereas Al^{3+} , Fe^{3+} and excessive amounts of Ca^{2+} decreased the recovery of apatite in anionic flotation. The apparent decline of the apatite recovery caused by Al^{3+} and Fe^{3+} was attributed to the preferential precipitation of $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ on the apatite surface, and the hydrophilicity of apatite was enhanced [5].

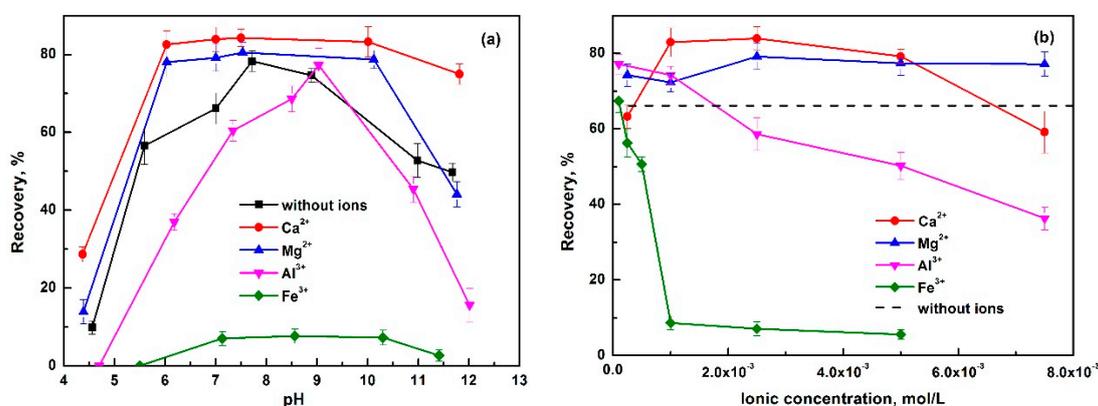


Figure 6. (a) Effect of pH on the floatability of apatite in the presence of metal ions at a concentration of 2.5×10^{-3} M; (b) Effect of ionic concentration on the floatability of apatite at neutral pH [5].

Teague and Lollback found that the recovery of P_2O_5 was inversely proportional to the hardness of the water used in grinding, conditioning and flotation, whilst the P_2O_5 grade of the concentrates

was observed to increase from 26.6% to 30.9% as the water hardness decreased [21]. The effects of Ca^{2+} , Mg^{2+} , PO_4^{3-} and SO_4^{2-} on the direct flotation of phosphate ore were investigated by Luo et al. [92]. An adverse influence of these ions on the flotation performance was ascertained, and the selectivity or beneficiation efficiency decreased as ion concentration increased. The authors explained that the Ca^{2+} and Mg^{2+} probably reacted with CO_3^{2-} to form insoluble salts and nonselectively precipitated on the surface of minerals, while PO_4^{3-} and SO_4^{2-} might have interacted with mineral surface through a chemical reaction or adsorption. Consequently, the magnitude of adsorption of the collector decreased, resulting in the efficiency reduction of beneficiation.

The effect of Ca^{2+} , Mg^{2+} , F^- and PO_4^{3-} on the flotation performance of apatite was evaluated by other researchers [16,93]. It was found that all the mentioned ions significantly contributed to the decline in apatite recovery. Santos et al. stated that Ca^{2+} and Mg^{2+} reacted with the apatite collector and caused the reduction of amount available for collection, while F^- reacted with the calcium present in fluorapatite and interfered the collector's function. Hence, it is necessary to minimize the ion concentrations in recycled water by pretreatment due to the detrimental effect on the flotation process caused by various anions and cations [94].

4. Summary

Flotation is dominantly used in the beneficiation of phosphate ores while calcination can be feasibly used in when the fuel energy cost is low and the water source is limited. The application of attrition scrubbing and desliming, magnetic separation and gravity separation should be referred to the characteristic of phosphate ores in chemical composition and texture. In that case, the pre-concentration of valuable minerals and cost reduction are achieved. For example, coarser phosphate concentrates are obtained when use attrition scrubbing, desliming and gravity separation to beneficiate weathered phosphate ores and banded structural sedimentary phosphate ores, respectively. Subsequently, the ultrafine components and overflow products are subjected to flotation for the further recovery of phosphate minerals.

The properties of mineralogy, flotation reagents and the medium have significant impacts on the flotation efficiency or selectivity of phosphate ore. Highly crystallized and coarse-grained phosphate ores have a good processibility. Hence, it is of great necessity to achieve a relatively high degree of mineral liberation and to avoid overgrinding concurrently. Depressants and collectors are the key reagents during the flotation process. Sodium silicate is mostly used to depress silica in a direct flotation. Organic chemical reagents including carboxymethyl cellulose and naphthyl anthyl sulfonates are effective depressants for dolomite. Inorganic acid and phosphoric salts demonstrate a depression effect on the floatability of phosphate minerals. Collectors used in phosphate flotation can be classified into anionic, cationic, amphoteric and mixed surfactants in terms of reagent type. Fatty acids are commonly used as anionic collectors, while cationic amines are used to remove silica in the flotation of phosphate ores. Mixed collectors like mixtures of ionic and nonionic surfactant exhibit more desirable performance than individual collector due to the beneficial effect caused by synergistic advantages. Additionally, the presence of Ca^{2+} , Mg^{2+} , Al^{3+} , Fe^{3+} , F^- , PO_4^{3-} and SO_4^{2-} showed a detrimental effect on the flotation performance of phosphate ores. Consequently, pretreatment should be taken to minimize the ion concentration if there is an excessive amount of interfering anions and cations.

Author Contributions: Writing—original draft preparation, Y.R.; writing—review and revise, D.H. and R.C.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. U.S. Geological Survey. *Mineral Commodity Summaries*; U.S. Geological Survey: Reston, VA, USA, 2018; pp. 122–123.

2. Abouzeid, A.-Z.M. Physical and thermal treatment of phosphate ores—An overview. *Int. J. Miner. Process.* **2008**, *85*, 59–84. [[CrossRef](#)]
3. Sis, H.; Chander, S. Reagents used in the flotation of phosphate ores: A critical review. *Miner. Eng.* **2003**, *16*, 577–585. [[CrossRef](#)]
4. Zafar, Z.I.; Anwar, M.M.; Pritchard, D.W. Innovations in beneficiation technology for low grade phosphate rocks. *Nutr. Cycl. Agroecosys.* **1996**, *46*, 135–151. [[CrossRef](#)]
5. Ruan, Y.; Zhang, Z.; Luo, H.; Xiao, C.; Zhou, F.; Chi, R. Effects of metal ions on the flotation of apatite, dolomite and quartz. *Minerals* **2018**, *8*, 141. [[CrossRef](#)]
6. Zhang, P.; Yu, Y.; Bogan, M. Challenging the “Crago” double float process II. Amine-fatty acid flotation of siliceous phosphates. *Miner. Eng.* **1997**, *10*, 983–994. [[CrossRef](#)]
7. Abouzeid, A.-Z.M.; Negm, A.T.; Elgillani, D.A. Upgrading of calcareous phosphate ores by flotation: Effect of ore characteristics. *Int. J. Miner. Process.* **2009**, *90*, 81–89. [[CrossRef](#)]
8. Miller, J.D.; Li, M.; Wang, X. Selective Flotation of Phosphate Minerals with Hydroxamate Collectors. U.S. Patent 6341697, 29 January 2002.
9. Ruan, Y.; Zhang, Z.; Luo, H.; Xiao, C.; Zhou, F.; Chi, R. Ambient temperature flotation of sedimentary phosphate ore using cottonseed oil as a collector. *Minerals* **2017**, *7*, 65. [[CrossRef](#)]
10. Al-Fariss, T.F.; Ozbelge, H.O.; Abdel Aleem, F.A.; Abdulrazik, S.M. Evaluation of Sandi phosphate rocks for wet process phosphoric acid production. *J. King Saud Univ. Eng. Sci.* **1992**, *4*, 33–44.
11. Li, H.M. Discussion of scrubbing and desliming of phosphate ore in Dianchi area. *Ind. Miner. Process.* **1986**, *6*, 52–53. (In Chinese)
12. He, H.; Yang, W.; Li, R.; Yu, L. Study on flotation of scrubbed tailings from phosphate ore. *Ind. Miner. Process.* **2015**, *11*, 4–10. (In Chinese)
13. Gallala, W.; Herchi, F.; BenAli, I.; Abbassi, L.; Gaied, M.E.; Montacer, M. Beneficiation of phosphate solid coarse waste from Redayef (Gafsa Mining Basin) by grinding and flotation techniques. *Procedia Eng.* **2016**, *138*, 85–94. [[CrossRef](#)]
14. Sobhy, A.; Tao, D. Innovative RTS technology for dry beneficiation of phosphate. *Procedia Eng.* **2014**, *83*, 111–121. [[CrossRef](#)]
15. Li, N.; Zhang, S.; Peng, H.; Fu, L.; Lu, Y. Application practice and evaluation of photoelectric separation in a phosphate mining industry. *Non Met. Mines* **2018**, *41*, 73–75. (In Chinese) [[CrossRef](#)]
16. Guimarães, R.C.; Peres, A.E.C. Interfering ions in the flotation of a phosphate ore in a batch column. *Miner. Eng.* **1999**, *12*, 757–768. [[CrossRef](#)]
17. Blazy, P.; Jdid, E.A. Removal of ferriferous dolomite by magnetic separation from the Egyptian Abu Tartur phosphate ore. *Int. J. Min. Process.* **1997**, *49*, 49–58. [[CrossRef](#)]
18. Bezzi, N.; Aifa, T.; Merabet, D.; Pivan, J.-Y. Magnetic properties of the Bled El Hadba phosphate-bearing formation (Djebel Onk, Algeria): Consequences on the enrichment of the phosphate ore deposit. *J. Afr. Earth Sci.* **2006**, *50*, 255–267. [[CrossRef](#)]
19. Shaikh, A.M.H.; Dixit, S.G. Beneficiation of phosphate ores using high gradient magnetic separation. *Int. J. Min. Process.* **1993**, *37*, 149–162. [[CrossRef](#)]
20. Wei, X.; Huang, Q.; Li, Y. Heavy-media separation industrial production practice of Yichang Huaguoshu Phosphorite. *J. Wuhan Inst. Tech.* **2011**, *33*, 48–52. (In Chinese)
21. Teague, A.J.; Lollback, M.C. The beneficiation of ultrafine phosphate. *Min. Eng.* **2012**, *27–28*, 52–59. [[CrossRef](#)]
22. Zafar, Z.I.; Anwar, M.M.; Pritchard, D.W. Optimization of thermal beneficiation of a low grade dolomitic phosphate rock. *Int. J. Miner. Process.* **1995**, *43*, 123–131. [[CrossRef](#)]
23. Watti, A.; Alnjar, M.; Hammal, A. Improving the specifications of Syrian raw phosphate by thermal treatment. *Arab. J. Chem.* **2016**, *9*, 637–642. [[CrossRef](#)]
24. Özer, A.K. The characteristics of phosphate rock for upgrading in a fluidized bed. *Adv. Powder Technol.* **2003**, *14*, 33–42. [[CrossRef](#)]
25. Zafar, Z.I.; Ashraf, M. Selective leaching kinetics of calcareous phosphate rock in lactic acid. *Chem. Eng. J.* **2007**, *131*, 41–48. [[CrossRef](#)]
26. Zafar, Z.I.; Anwar, M.M.; Pritchard, D.W. Selective leaching of calcareous phosphate rock in formic acid: Optimisation of operating conditions. *Min. Eng.* **2006**, *19*, 1459–1461. [[CrossRef](#)]

27. Ashraf, M.; Zafar, I.Z.; Ansari, T.M. Selective leaching kinetics and upgrading of lowgrade calcareous phosphate rock in succinic acid. *Hydrometallurgy* **2005**, *80*, 286–292. [[CrossRef](#)]
28. Abu-Eishah, S.I.; Muthaker, M.; Touqan, N. A new technique for the beneficiation of low grade carbonate-rich phosphate rocks by digestion with dilute acetic acid solutions: Pilot plant testing results. *Miner. Eng.* **1991**, *4*, 573–586. [[CrossRef](#)]
29. Gharabaghi, M.; Noaparast, M.; Irannajad, M. Selective leaching kinetics of low-grade calcareous phosphate ore in acetic acid. *Hydrometallurgy* **2009**, *95*, 341–345. [[CrossRef](#)]
30. Gharabaghi, M.; Irannajad, M.; Noaparast, M. A review of the beneficiation of calcareous phosphate ores using organic acid leaching. *Hydrometallurgy* **2010**, *103*, 96–107. [[CrossRef](#)]
31. Rodrigues, A.J.; Brandao, P.R.G. The influence of crystal chemistry properties on the floatability of apatites with sodium oleate. *Miner. Eng.* **1993**, *6*, 643–653. [[CrossRef](#)]
32. Santana, R.C.; Duarte, C.R.; Ataide, C.H.; Barrozo, M.A.S. Flotation selectivity of phosphate ore: Effect of particle size and reagent concentration. *Sep. Sci. Technol.* **2011**, *46*, 1511–1518. [[CrossRef](#)]
33. Santana, R.C.; Farnese, A.C.C.; Fortes, M.C.B.; Ataide, C.H.; Barrozo, M.A.S. Influence of particle size and reagent dosage on the performance of apatite flotation. *Sep. Sci. Technol.* **2008**, *64*, 8–15. [[CrossRef](#)]
34. Guo, F.; Li, J. Separation strategies for Jordanian phosphate rock with siliceous and calcareous gangues. *Int. J. Miner. Process.* **2010**, *97*, 74–78. [[CrossRef](#)]
35. Al-Wakeela, M.I.; Lin, C.L.; Miller, J.D. Significance of liberation characteristics in the fatty acid flotation of Florida phosphate rock. *Miner. Eng.* **2009**, *22*, 244–253. [[CrossRef](#)]
36. Qun, W.; Heiskanen, K. Batch flotation tests by fatty acid on a phosphate-iron oxide-silicate regolith ore sample from Sokli, Finland. *Miner. Eng.* **1990**, *3*, 473–481. [[CrossRef](#)]
37. Silva, J.P.P.; Baltar, C.A.M.; Gonzaga, R.S.G.; Peres, A.E.C.; Leite, J.Y.P. Identification of sodium silicate species used as flotation depressants. *Min. Met. Process.* **2012**, *29*, 207–210. [[CrossRef](#)]
38. Rao, D.S.; Vijayakumar, T.V.; Angadi, S.; Prabhakar, S.; Raju, G.B. Effects of modulus and dosage of sodium silicate on limestone flotation. *Maejo Int. J. Sci. Technol.* **2010**, *4*, 397–404.
39. Sayilgan, A.; Arol, A.I. Effect of carbonate alkalinity on flotation behavior of quartz. *Int. J. Miner. Process.* **2004**, *74*, 233–238. [[CrossRef](#)]
40. Pavlovic, S.; Brandao, P.R.G. Adsorption of starch, amylose, amylopectin and glucose monomer and their effect on the flotation of hematite and quartz. *Min. Eng.* **2003**, *16*, 1117–1122. [[CrossRef](#)]
41. Guimarães, R.C.; Araujo, A.C.; Peres, A.E.C. Reagents in igneous phosphate ores flotation. *Min. Eng.* **2005**, *18*, 199–204. [[CrossRef](#)]
42. Zheng, X.; Smith, R.W. Dolomite depressants in the flotation of apatite and colophonane from dolomite. *Min. Eng.* **1997**, *10*, 537–545. [[CrossRef](#)]
43. Yu, J.; Ge, Y.; Guo, X.; Guo, W. The depression effect and mechanism of NSFC on dolomite in the flotation of phosphate ore. *Sep. Purif. Technol.* **2016**, *161*, 88–95. [[CrossRef](#)]
44. Zheng, X.; Arps, P.J.; Smith, R.W. Adhesion of two bacteria onto dolomite and apatite: Their effect on dolomite depression in anionic flotation. *Int. J. Min. Process.* **2001**, *62*, 159–172. [[CrossRef](#)]
45. Somasundaran, P.; Wang, D.Z. *Solution Chemistry: Minerals and Reagents*, 1st ed.; Elsevier: Amsterdam, The Netherlands, 2006; pp. 58–60.
46. Elgillani, D.A.; Abouzeid, A.-Z.M. Flotation of carbonates from phosphate ores in acidic media. *Int. J. Min. Process.* **1993**, *38*, 235–256. [[CrossRef](#)]
47. Chen, Y.; Feng, Q.; Zhang, G.; Liu, D.; Liu, R. Effect of sodium pyrophosphate on the reverse flotation of dolomite from apatite. *Minerals* **2018**, *8*, 278. [[CrossRef](#)]
48. Al-Fariss, T.F.; Arafat, Y.; Abd El-Aleem, F.A.; El-Midany, A.A. Investigating sodium sulphate as a phosphate depressant in acidic media. *Sep. Purif. Technol.* **2014**, *124*, 163–169. [[CrossRef](#)]
49. El-Mofty, S.E.; El-Midany, A.A. Role of calcium ions and their interaction with depressants in phosphate flotation. *Chem. Pap.* **2018**, *72*, 2641–2646. [[CrossRef](#)]
50. Zhang, P.; Snow, R. Evaluation of phosphate depressants in the phosphate/silica system. *Miner. Metall. Process.* **2009**, *26*, 101–104. [[CrossRef](#)]
51. Nagaraj, D.R.; Rothenberg, A.S.; Lipp, D.W.; Panzer, H.P. Low molecular weight polyacrylamide-based polymers as modifiers in phosphate beneficiation. *Int. J. Min. Process.* **1987**, *20*, 291–308. [[CrossRef](#)]
52. Dho, H.; Iwasaki, I. Role of sodium silicate in phosphate flotation. *Min. Metallurgy Explor.* **1990**, *7*, 215.

53. Clifford, P.R.; Lloyd, G.M.; Zhang, J.P.; Richardson, S.G.; Birky, B.K.; Stewart, K.J. *An Investigation of Flotation Reagents*; Florida Institute of Phosphate Research: Bartow, FL, USA; p. 2008.
54. Nagaraj, D.R.; Rothenberg, A.S.; Lambert, A.S. Flotation Beneficiation Process for Non-Sulfide Minerals. U.S. Patent 4720339, 19 January 1988.
55. Ribeiro, R.C.C.; Correia, J.C.G.; Monte, M.B.M.; Seidl, P.R.; Mothe, C.G.; Lima, C.A. Cashew gum: A new depressor for limestone in the phosphate minerals flotation. *Miner. Eng.* **2003**, *16*, 873–875. [[CrossRef](#)]
56. Hanna, J.; Anazia, I. Fatty acid separation of siliceous carbonate phosphates. *Miner. Metall. Process.* **1990**, *10*, 84–90. [[CrossRef](#)]
57. Lehr, J.R.; Hsieh, S. Beneficiation of High Carbonate Phosphate Ores. U.S. Patent 4287053, 1 September 1981.
58. Hsieh, S.; Lehr, J.R. Method of Beneficiating High Carbonate Phosphate Ore. U.S. Patent 4486301, 4 December 1984.
59. Rao, D.V.; Narayanan, M.K.; Nayak, U.B.; Ananthapadmanabhan, K.; Somasundaran, P. Flotation of calcareous Mussoorie phosphate ore. *Int. J. Miner. Process.* **1985**, *14*, 57–66. [[CrossRef](#)]
60. Yehia, A.; Khalek, M.A.; Ammar, M. Cellulase as a new phosphate depressant in dolomite-phosphate flotation. *Physicochem. Probl. Miner. Process.* **2017**, *53*, 1092–1104.
61. Smani, S.M. Process for Enrichment by Flotation of Phosphate Ores with Gangues Containing Carbonates. U.S. Patent 4008151, 15 February 1977.
62. Mohammadkhani, M.; Noaparast, M.; Shafaei, S.Z.; Amini, A.; Amini, E.; Abdollahi, H. Double reverse flotation of a very low grade sedimentary phosphate rock, rich in carbonate and silicate. *Int. J. Miner. Process.* **2011**, *100*, 157–165. [[CrossRef](#)]
63. Paiva, P.R.P.; Monte, M.B.M.; Simao, R.A.; Gaspar, J.C. In situ AFM study of potassium oleate adsorption and calcium precipitate formation on an apatite surface. *Miner. Eng.* **2011**, *24*, 387–395. [[CrossRef](#)]
64. Santos, E.P.; Dutra, A.J.B.; Oliveira, J.F. The effect of jojoba oil on the surface properties of calcite and apatite aiming at their selective flotation. *Int. J. Miner. Process.* **2015**, *143*, 34–38. [[CrossRef](#)]
65. Huang, Q.; Huang, J.; Zhou, H.; Pan, Z.; Ping, X. Synthesis and application of a flotation collector for colophonite. In *Beneficiation of Phosphates: New Thought, New Technology, New Development*; Zhang, P., Miller, J., El-Shall, H., Eds.; SME: Denver, CO, USA, 2012; pp. 359–364.
66. Oliveira, M.S.; Santana, R.C.; Ataíde, C.H.; Barrozo, M.A.S. Recovery of apatite from flotation tailings. *Sep. Purif. Technol.* **2011**, *79*, 79–84. [[CrossRef](#)]
67. Guo, F.; Li, J. Selective separation of silica from a siliceous-calcareous phosphate rock. *Min. Sci. Technol. (China)* **2011**, *21*, 135–139.
68. Sahoo, H.; Rath, S.S.; Das, B.; Mishra, B.K. Flotation of quartz using ionic liquid collectors with different functional groups and varying chain lengths. *Miner. Eng.* **2016**, *95*, 107–112. [[CrossRef](#)]
69. Vieira, A.M.; Peres, A.E.C. The effect of amine type, pH, and size range in the flotation of quartz. *Min. Eng.* **2007**, *20*, 1008–1013. [[CrossRef](#)]
70. Nunes, A.P.L.; Pinto, C.L.L.; Valadao, G.E.S.; Viana, P.R.M. Floatability studies of wavellite and preliminary results on phosphorus removal from a Brazilian iron ore by froth flotation. *Miner. Eng.* **2012**, *39*, 206–212. [[CrossRef](#)]
71. Shao, X.; Jiang, C.L.; Parekh, B.K. Enhanced flotation separation of phosphate and dolomite using a new amphoteric collector. *Miner. Metall. Process.* **1998**, *15*, 11–14. [[CrossRef](#)]
72. Abdel-Khalek, M. Separation of dolomite from phosphate minerals by flotation with a new amphoteric surfactant as collector. *Trans. Inst. Min. Met. C* **2001**, *110*, 89–93.
73. Elmahdy, A.M.; El-Midany, A.A.; Abdel-Khalek, N.A. Application of amphoteric collector for dolomite separation by statistically designed experiments. *Trans. Inst. Min. Met. C* **2007**, *116*, 72–76. [[CrossRef](#)]
74. Hu, Y.; Wang, D. Flotation of apatite and calcite using α -amino aryl phosphoric acid as collector. *Nonferrous Met.* **1992**, *44*, 41–43. (In Chinese)
75. Hu, Y.; Xu, Z. Interactions of amphoteric amino phosphoric acids with calcium-containing minerals and selective flotation. *Int. J. Miner. Process.* **2003**, *72*, 87–94. [[CrossRef](#)]
76. Filippova, I.V.; Filippov, L.O.; Duverger, A.; Severov, V.V. Synergetic effect of a mixture of anionic and nonionic reagents: Ca mineral contrast separation by flotation at neutral pH. *Min. Eng.* **2014**, *66–68*, 135–144. [[CrossRef](#)]
77. Rao, K.H.; Forssberg, K.S.E. Mixed collector systems in flotation. *Int. J. Miner. Process.* **1997**, *51*, 67–79.

78. Javadian, S.; Gharibi, H.; Bromand, Z.; Sohrabi, B. Electrolyte effect on mixed micelle and interfacial properties of binary mixtures of cationic and nonionic surfactants. *J. Colloid Interface Sci.* **2008**, *318*, 449–456. [[CrossRef](#)]
79. Szymczyk, K.; Janczuk, B. The adsorption at solution-air interface and volumetric properties of mixtures of cationic and nonionic surfactants. *Colloids Surf. A Phys. Eng. Asp.* **2007**, *293*, 39–50. [[CrossRef](#)]
80. Sis, H.; Chander, S. Adsorption and contact angle of single and binary mixtures of surfactants on apatite. *Min. Eng.* **2003**, *16*, 839–848. [[CrossRef](#)]
81. Sis, H.; Chander, S. Improving froth characteristics and flotation recovery of phosphate ores with nonionic surfactants. *Miner. Eng.* **2003**, *16*, 587–595. [[CrossRef](#)]
82. Wang, X.; Nguyen, A.V.; Miller, J.D. Selective attachment and spreading of hydroxamic acid–alcohol collector mixtures in phosphate flotation. *Int. J. Miner. Process.* **2006**, *78*, 122–130. [[CrossRef](#)]
83. Filippov, L.O.; Duverger, A.; Filippova, I.V.; Kasaini, H.; Thiry, J. Selective flotation of silicates and Ca-bearing minerals: The role of non-ionic reagent on cationic flotation. *Min. Eng.* **2012**, *36–38*, 314–323. [[CrossRef](#)]
84. Rao, K.H.; Dwari, R.K.; Lu, S.; Vilinska, A.; Somasundaran, P. Mixed anionic/non-ionic collector in phosphate gangue flotation from magnetite fines. *Open Miner. Process. J.* **2011**, *4*, 14–24. [[CrossRef](#)]
85. Hughes, C.V. Enhanced Flotation Reagents for Beneficiation of Phosphate Ores. U.S. Patent 5962828, 5 October 1999.
86. Preller, G.S.; Schoeman, B.J.K. Flotation of Apatite. U.S. Patent 3405802, 15 October 1968.
87. Cao, Y.; Huang, G.; Yang, L.; Liu, S.; Deng, Q.; Gu, X. Process study on some low grade collophanite with high content of magnesium. *Non Met. Mines* **2016**, *39*, 63–66. (In Chinese)
88. Hefner, R.E., Jr. N-Aminoethylpiperazine Condensates for Beneficiation of Phosphate Ore. U.S. Patent 4301004, 17 November 1981.
89. Subrahmanyam, C. Method for Conditioning Phosphate Ores. U.S. Patent 4556545, 12 March 1985.
90. Dorrepaal, W.; Haak, G.M. Process for the Flotation of Ores. U.S. Patent 4200522, 29 April 1980.
91. Giesekke, E.W.; Harris, P.J. The role of polyoxyethylene alkyl ethers in apatite flotation at foskor, phalaborwa (South Africa). *Min. Eng.* **1994**, *7*, 1345–1361. [[CrossRef](#)]
92. Luo, H.; Liu, L.; Xie, B.; Ou, S. Effect of Ca^{2+} , Mg^{2+} , PO_4^{3-} and SO_4^{2-} on the flotation of phosphate. In *Beneficiation of Phosphates: New Thought, New Technology, New Development*; Zhang, P., Miller, J., El-Shall, H., Eds.; SME: Denver, CO, USA, 2012; pp. 33–38.
93. Santos, M.A.; Santana, R.C.; Capponi, F.; Ataíde, C.H.; Barrozo, M.A.S. Effect of ionic species on the performance of apatite flotation. *Sep. Purif. Technol.* **2010**, *76*, 15–20. [[CrossRef](#)]
94. Nanthakumar, B.; Grimm, D.; Pawlik, M. Anionic flotation of high-iron phosphate ores—Control of process water chemistry and depression of iron minerals by starch and guar gum. *Int. J. Miner. Process.* **2009**, *92*, 49–57. [[CrossRef](#)]

