

Review

Review of the Main Factors Affecting the Flotation of Phosphate Ores

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Abstract: The way to successfully upgrade a phosphate ore is based on the full understanding of its mineralogy, minerals surface properties, minerals distribution and liberation. The conception of a treatment process consists of choosing the proper operations with an adequate succession depending on the ore properties. Usually, froth flotation takes place in phosphate enrichment processes, since it is cheap, convenient, and well developed. Nevertheless, it is a complex technique as it depends on the mineral's superficial properties in aqueous solutions. Aspects such as wettability, surface charge, zeta potential, and the solubility of minerals play a basic role in defining the flotation conditions. These aspects range from the reagents type and dosage to the pH of the pulp. Other variables namely particles size, froth stability, and bubbles size play critical roles during the treatment, as well. The overall aim is to control the selectivity and recovery of the process. The following review is an attempt to add to previous works gathering phosphate froth flotation data. In that sense, the relevant parameters of phosphate ores flotation are discussed while focusing on apatite, calcite, dolomite, and quartz as main constituent minerals.

Keywords: sedimentary phosphate ore; igneous phosphate ore; mineral processing; froth flotation; surface charge; wettability; apatite; dolomite; calcite; quartz

1. Introduction

Phosphate ores are the only pronounced source of phosphorus. As a crucial component with high economic importance, phosphorus remains indispensable in the phosphoric acid industry, fertilizers, and elemental phosphorus production. The demand on phosphate has increased throughout the years. A total of 47 million tons P_2O_5 were consumed worldwide in 2019. This consumption is predicted to increase up to 50 million tons in 2023 [1]. As presented in Table 1, the worldwide leaders of phosphate mine production are China (110 million tons/y), Morocco (36 million tons), United States (23 million tons/y), and Russia (14 million tons/y). Countries such as Jordan, Saudi Arabia, Vietnam, Brazil, Egypt, Australia, and Senegal produce between 1 and 8 million tons/y. Phosphate mine production is expected to grow, especially in Jordan, Morocco, Saudi Arabia, and Senegal following projects expansions [1].

Conventionally, phosphate deposits are classified into five major categories: Marine sedimentary, igneous, metamorphic, weathering sedimentary, and biogenic [2]. Sedimentary deposits are predominant, providing 80% of the world's phosphate production. These deposit's grades range typically between 10% and 30% P_2O_5 and can be upgraded to (30–35%) P_2O_5 . Morocco, China,

Middle East, and United States host the biggest sedimentary deposits. Igneous deposits occur in Russia, Brazil, South Africa, Canada, and Finland with grades ranging between 4% and 15% P_2O_5 and can be upgraded to (35–40%) P_2O_5 [3,4]. Phosphate ores can also be classified based on their major gangue minerals as: (i) Siliceous ores if associated with silica, (ii) clayey ores if containing aluminum silicates, (iii) calcareous ores of sedimentary origin if containing carbonates as the major impurities, (iv) phosphate ores rich in organic matter, (v) phosphate ores with multiple gangue minerals, and finally, (vi) igneous and metamorphic phosphate ores if containing sulfides, magnetite, carbonates, nepheline, etc.

According to their genesis and based on the phosphate cycle, phosphate minerals can be grouped as primary or secondary minerals. The primary minerals represent the original and replenishing source of phosphorus. They occur in carbonatite and alkaline igneous rocks. Altered or disintegrated and decomposed by natural agents, the primary minerals are transformed into secondary phosphate minerals [5]. Hence, the igneous phosphate ores can hold a variety of phosphate minerals, which are seldom found in the sedimentary ores and vice-versa. Furthermore, there are more than 200 known phosphate minerals. The apatite group is the most abundant (95% of the phosphorus existing in the earth's crust). Examples of phosphate minerals are listed in Table 2. The impurities existing in sedimentary ores are likely to differ from the ones found in igneous deposits. Upgrading a phosphate ore of any type (e.g., sedimentary, igneous, etc.) consists of increasing its P_2O_5 content and eliminating the gangue minerals (it must contain over 30% P_2O_5 , with a CaO/ P_2O_5 ratio lower than 1.6%, SiO_2 content less than 3%, MgO content less than 1%, Fe_2O_3 content less than 7% [6,7]). The occurrence of impurities in the phosphate concentrate causes several complications and a frailty for phosphoric acid production, as presented in Table 3. Phosphate ore refinement is achieved by beneficiation processes, which depend on the characteristics of the treated ore (e.g., gangue minerals, particles size, hardness, etc.). Comminution and size separation, mineral separation, chemical and thermal techniques are the most common [2,8].

Froth flotation is a mineral separation technique used industrially since the late 19th century. Starting in 1940s, it has been included in phosphate ores enrichment processes. Froth flotation is based on the specific physicochemical properties of minerals surfaces, precisely the hydrophobicity and hydrophilicity of both valuable and unwanted gangue minerals. Hydrophobicity can be a natural characteristic, but for most minerals, including phosphate minerals, the intervention of specific reagents is required to control the flotation behavior and achieve satisfactory separation results [9]. Phosphate flotation was initially conducted using soap, then it evolved throughout the years with the development of reagents and the improvement of process parameters. Flotation is dynamic, it is based on the interaction of multiple scientific fundamentals such as surface and colloid chemistry, physics, crystallography, etc. [10]. The performance of a flotation system is vulnerable to a range of variables. These variables are gathered into three categories: (i) Operational, e.g., mineralogy/surface properties, feed rate, particle size, pulp density, temperature, etc. (ii) chemical, e.g., collectors, frothers, activators, depressants, pH regulators, and (iii) hydrodynamic, e.g., flotation cell design, agitation, air flow, etc. Phosphate flotation can be direct, reverse, or a succession of direct/reverse stages depending on circumstances. Direct flotation consists of floating the phosphate minerals by inducing hydrophobic surface properties. The opposite is the case during reverse flotation where gangue minerals are floated. Choosing the type of flotation depends on: (i) The phosphate mineral's initial grade, (ii) the economics of the reagents used, and (iii) the performance of the adopted flotation.

Froth flotation has been used to enrich sedimentary phosphate ores with siliceous impurities. It has replaced calcination in treating calcareous phosphate ores. It is also commonly used for processing igneous phosphate ores with usually less complications compared to sedimentary ores. Yet, igneous phosphate ores still present complications, as a single ore might hold numerous impurities and various types of phosphate minerals with different floatabilities [11]. Phosphate sedimentary ores usually contain apatite as the value mineral, carbonates, silica, and clays as impurities. The anionic-cationic flotation termed the "Crago technique" is the common method for upgrading siliceous

phosphate ores. This is used to upgrade Florida phosphate ores. In this process, francolite is floated using a fatty acid/fuel oil mixture. The rougher concentrate is scrubbed using acid to renovate the particles surfaces. The remaining silica is then floated using an amine reagent [12]. For calcareous ores, separation by flotation of carbonates (calcite and dolomite) and phosphates is challenging since the two mineral groups share similar surface chemical properties. There are also colloidal phosphate ores, sedimentary ores containing, in general, a very small grain sized apatite (cryptocrystal). The beneficiation of these ores is challenging. It requires fine grinding and the use of selective reagents since apatite is incorporated with gangue minerals, forming “collophanite”.

Table 1. Leading phosphate producers [13].

Top Phosphate Mine Producers	Deposit Types	Phosphate Minerals	Gangue Minerals	2019 Production (Million Tons)	Reserves (Million Tons)
China	Sedimentary (marine, weathered), Igneous (carbonatite/alkalic), Metamorphic, Guano	Collophane, fluorapatite, francolite, monazite	Dolomite, quartz, clay, calcite, goethite, chlorite, zircon	110	3200
Morocco	Marine sedimentary	Apatite	Quartz, dolomite, calcite, aluminum silicate minerals	36	50,000
United States	Sedimentary (marine, weathered), Igneous (carbonatite/alkalic), Metamorphic (metasedimentary), Guano	Francolite, monazite, wavellite, crandallite	Quartz, dolomite, calcite, magnetite, aluminum silicate minerals, goethite, ankerite	23	1000
Russia	Marine sedimentary, Igneous (carbonatite/alkalic)	Fluorapatite, hydroxylapatite, francolite, monazite	Magnetite, ilmenite, titanium magnetite, baddeleyite, forsterite, calcite, phlogopite, mica, titanium-augite, pyrite	14	600
Jordan	Marine sedimentary	N.A.	N.A.	8	1000
Saudi Arabia	Marine sedimentary	N.A.	N.A.	6.2	1400
Vietnam	Sedimentary (marine, weathered) Metamorphic (metasedimentary), Guano	Apatite	N.A.	5.5	30
Brazil	Igneous (carbonatite/alkalic), Guano	Fluorapatite, francolite, collophane, dahllite, monazite-(Ce), phoscorite, metavariscite, strengite, variscite	Calcite, magnetite, quartz, aluminum silicate minerals, pyrite, ankerite, fluorite, barite, quartz, carbonate	5.3	1700
Egypt	Marine sedimentary	Collophane, francolite, dahllite, wavellite, manganapatite	Pyrite, quartz, calcite, dolomite, goethite, chlorite, zircon, montmorillonite, gypsum, glauconite	5	1300
Peru	Marine sedimentary	Fluorapatite	Carbonates (calcite, dolomite), diatomite	3.7	210
Israel	Marine sedimentary	N.A.	N.A.	3.5	62
Tunisia	Marine sedimentary	N.A.	N.A.	3	100
Australia	Sedimentary (Marine, weathered), Metamorphic (metasedimentary), Igneous (carbonatite/alkalic), Guano	Fluorapatite, collophane, monazite, wavellite, dufrenite, millisite, churchite, xenotime, florencite, goyazite	Calcite, dolomite, quartz, hematite, goethite, quartz, Aluminum silicate minerals	2.7	1200
Syria	Sedimentary (marine, weathered)	N.A.	N.A.	2	1800
South Africa	Igneous (carbonatite/alkalic), Marine sedimentary	Fluorapatite, francolite, collophane, dahllite, monazite-(Ce), phoscorite, metavariscite, strengite, variscite	Calcite, magnetite, quartz, aluminum silicate minerals, pyrite, ankerite, fluorite, barite, quartz, carbonate, anatase, Au, Mn, aegirine, amphibole, pyroxene, arfvedsonite, vermiculite, serpentine, carbonatite minerals enriched in copper and iron	1.9	1400

N.A.: Not available.

Table 2. Abundant phosphate minerals and their occurrence.

Name	Types	Formula	Occurrence
Apatite	Chlorapatite	$\text{Ca}_5(\text{PO}_4)_3 \text{Cl}$	Ig, Mt.
	Hydroxylapatite	$\text{Ca}_5(\text{PO}_4)_3 \text{OH}$	Ig, Mt, Sd.
	Dahllite or Carbonate-hydroxylapatite	$\text{Ca}_5(\text{PO}_4, \text{CO}_3)_3 (\text{OH}, \text{O})$	Sd, Mt.
	Fluorapatite	$\text{Ca}_5(\text{PO}_4)_3 \text{F}$	Ig, Mt, Sd.
	Francolite or Carbonate-fluorapatite	$\text{Ca}_5(\text{PO}_4, \text{CO}_3)_3 (\text{F}, \text{O})$	Sd, Mt.
Monazite	Monazite-(Ce)	CePO_4	Ig, Mt, Sd. (Phosphate minerals containing REE).
Xenotime	Xenotime-(Y)	YPO_4	Ig, Mt. (Phosphate minerals containing REE).
Vivianite		$\text{Fe}_3(\text{PO}_4)_2 \cdot 8(\text{H}_2\text{O})$	Ig, Mt, Sd. Occurs in organically rich sedimentary deposits (clays and sandstones), hydrothermal replacement deposits, and in phosphate-rich granite pegmatites.
Variscite		$\text{AlPO}_4 \cdot 2(\text{H}_2\text{O})$	Sd, Mt. Occurs as a secondary mineral in hydrothermal replacement deposits and brecciated sandstones.
Wavellite		$\text{Al}_3(\text{PO}_4)_2(\text{OH}, \text{F})_3 \cdot 5(\text{H}_2\text{O})$	Sd, Mt. Occurs as a secondary mineral in the oxidized low-grade metamorphic rocks, epithermal veins, and in phosphate-rich sedimentary deposits.
Monetite		CaHPO_4	Ig, Sd. Occurs as coatings and cements in guano rocks and as coatings on phosphate minerals in granite pegmatite.
Whitlockite		$\text{Ca}_9\text{Mg}(\text{PO}_4)_6(\text{HPO}_4)$	Sd, Mt. Occurs in granite pegmatites; may be formed in caves from leached guano.
Brushite		$\text{Ca}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$	Sd. Occurs in cave guano deposits.
Struvite		$(\text{NH}_4)\text{Mg}(\text{PO}_4) \cdot 6\text{H}_2\text{O}$	Sd. Occurs in guano deposits; peat beds; organically rich sediments.
Variscite		$\text{Al}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$	Sd, Mt. Occurs in guano beds and metamorphosed sedimentary rocks.

Ig: Igneous rocks; Sd: Sedimentary rocks; Mt: Metamorphic rocks.

Table 3. Potential effects of phosphate impurities and their acceptable levels.

Impurity	Potential Sources	Acceptable Level	Desirable Properties	Undesirable Properties
Al_2O_3	Aluminum silicate minerals, wavellite, metavariscite, crandallite, variscite.	Up to 3% [7,14]	Low Al_2O_3 content improves the filtration rate by promoting the growth of gypsum crystals [15]. Reduces corrosion caused by fluoride ion [14].	High Al_2O_3 content impairs filtration, increases acid viscosity [14], decreases plant capacity, and P_2O_5 recovery [7].
Fe_2O_3	Goethite, magnetite, hematite, strengite.	Up to 2% [14]	Recoverable in case of excessive presence [14].	High Fe_2O_3 content causes excessive sludge formation, decreases the filtration rate, and influences the acid viscosity [14].
MgO	Dolomite, ankerite, phoscorite.	Less than 1% [7]	May have a nutrient value [14].	Increases the sulfuric acid consumption and impairs gypsum filtration [7].
Fluorine	Fluorite, fluorapatite, francolite.	Up to 4% [14]	Can be recovered as a by-product [14].	Causes corrosion, mud, slurry formation, and might impair gypsum filtration [15].
SiO_2	Quartz, Aluminum silicate minerals.	Around 2% [7]	Reactive silica forms with fluoride SiF_4 and fluosilicates rather than the harmful H_2SiF_6 [7,14].	High SiO_2 content causes wear and erosion of equipment and can impair the filtration of gypsum [7,15].
Chlorine	Chlorapatite.	Less than 0.03% (stainless steel equipment)	None.	Increases equipment erosion [7].
CaO	Calcite, dolomite, ankerite, fluorite, gypsum, crandallite, apatite.	$\text{CaO}:\text{P}_2\text{O}_5$ ratio less than 1.6 [7]	Improves the reactivity of the phosphate ore [15].	Increases the consumption of sulfuric acid and causes foam formation during the acid attack [15].

Table 3. Cont.

Impurity	Potential Sources	Acceptable Level	Desirable Properties	Undesirable Properties
Cadmium	Carbonate apatite (Cd substitutes Ca and/or is trapped in the structure during its formation by the sedimentation of phosphate rock) [16].	Up to 60 mg/kg P ₂ O ₅ (European union) [17]	None.	Does not pose notable problems in the production of phosphoric acid [7]. Toxic in specific end products (animal feed and fertilizers) [15].
Uranium	Following the sedimentation of the phosphate ore, U might substitute Ca in the apatite crystal and/or is adsorbed into it or forms uranium phosphate minerals such as phosphuranylite [18].	Typically, 4 Bq U per g P ₂ O ₅ .	Can be recovered as a by-product [14].	Hazardous to human health [7].

With the depletion of rich phosphate deposits of simple compositions and the abundance of complex poor phosphate reserves, research in phosphate froth flotation keeps evolving. At this stage, efforts are directed toward understanding what affects phosphate flotation and the different aspects that result in the success or the failure of a flotation operation. With these regards, the aim of this review is to focus on the factors affecting the flotation of sedimentary phosphate ores, as they provide 80% of the world's phosphate production.

2. Parameters Affecting Phosphate Flotation

2.1. Phosphate and Gangue Minerals' Surface Properties

Mineral surface properties are critical for flotation control as they represent the fundamental concepts behind the technological process. They allow to, both, predict and describe the physical and chemical superficial interactions of the mineral-reagent, mineral-medium, and mineral-mineral interactions.

2.1.1. Phosphate Minerals' Solubility and Surface Charge

The surface charge of phosphate minerals and their impurities (i.e., gangue minerals) is affected by many variables, e.g., pH and RPO values (reduction/oxidation potential). Respectively, the mechanisms governing the surface charge are complex rendering separation by froth flotation challenging in some cases. Minerals from the apatite group are the most abundant. It has been suggested that their active surface sites are formed by calcium hydroxyl ($\equiv\text{CaOH}$) and phosphorus hydroxyl ($\equiv\text{POH}$) groups [19]. It is considered that $\equiv\text{Ca-OH}^{2+}$ and $\equiv\text{P-O}^-$ are dominant surface groups [19]. The ions H^+ and OH^- are specifically adsorbed on the surface. Basically, depending on the pH, two different surface groups (both metal ions and ligands) can be adsorbed on the hydroxylated apatite surface. Hence, the adsorption of the flotation modifying agents on mineral surfaces is usually expressed in relation to pH being a critical parameter. The apatite's surface charge depends not only on pH but also on the concentration of various chemical species as well as on pretreatments. In this context, hydrogen, hydroxyl, calcium, fluoride, and phosphate are the apatite's potential determining ions [20]:

- H^+ and OH^- ions are critical as they control the solution pH and eventually the mineral's surface charge [19];
- Phosphate (PO_4^{3-}) decreases the mineral's surface charge under all pH conditions [20];
- Calcium makes the mineral more positively charged under all pH conditions [20];
- Fluoride is found to increase the surface charge in acidic medium and slightly decreases it in basic solutions following the possible formation of fluorite (CaF_2) and fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$), respectively [20].

The zeta potential expresses the electrical potential difference between the ion layer adsorbed onto the particle's surface and the bulk solution [21]. It enables prediction as to whether or not a reagent will bind to the particle's surface. The isoelectric point (IEP) is the pH value corresponding to a zero zeta potential. IEP values of hydroxyapatite, fluorapatite, francolite, and collophane in

different operating conditions are listed in Table 4. Parameters such as mineral purity, particles size, solid content, electrolyte, and measurement technique influence the IEP value.

2.1.2. Gangue Minerals' Solubility and Surface Charge

The most common impurities found in the sedimentary phosphate ores are carbonates (calcite and dolomite) and quartz.

- Calcite solubility and surface charge

Calcite solubility in aqueous medium leads to the release or deposition of Ca^{2+} and CO_3^{2-} on mineral surfaces depending on the solution pH. This latter and concentrations of Ca^{2+} , CO_3^{2-} , and HCO_3^- might fluctuate under the influence of dissolved atmospheric CO_2 . Moreover, the hydrated calcite surface can have both protonated anion sites ($>\text{CO}_3\text{H}$) and hydroxylated cation sites ($>\text{CaOH}$). Hence, in a froth flotation system, the solution pH controls the calcite surface charge. Nevertheless, it has been demonstrated experimentally that, when the calcium ions concentration was kept constant, the calcite surface charge was independent of pH [22]. The adsorption of Ca^{2+} and CO_3^{2-} onto the mineral surface (Figure 1) is represented through the following surface complexation Reactions (with or without the presence of CO_2) [22].

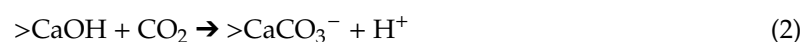
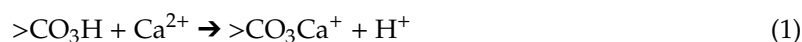


Table 4. The isoelectric point (IEP) values of phosphate minerals and their measurement operating conditions.

Mineral	Source	IEP	Purity	Wt%	Size (μm)	Electrolyte	pH Adjustment	Ref
Fluorapatite	Geological museum of Yunnan province, China.	3	>99%	0.1	<5	10^{-3} M NaCl	N.A.	[23]
	Africa.	4	High purity	0.02	<5	10^{-2} M KNO_3	HCl and NaOH	[24]
	Ontario, Canada.	5.5	39.18% P_2O_5	0.01	<43	10^{-3} M KNO_3	HCl and NaOH	[25]
	Ward's Natural Science Establishment, Canada.	3.9	37.8% P_2O_5	N.A.	<5	N.A.	0.1 M HCl and 0.1 M NaOH	[26]
	Madagascar in South Africa.	3.4	Pure	0.05	<38	N.A.	10% HCl and 10% NaOH	[27]
	Ward's Natural Science Establishment, Canada.	2.75	Mainly fluorapatite	0.01–0.1	<20	10^{-2} M KCl	HCl and NaOH	[28]
Carbonate-fluorapatite (Francolite)	Fort Dauphin, Tuléar province, Madagascar.	2–3	N.A.	0.01	<5	10^{-3} M KCl	NaOH and HCl	[29]
	Oulad Abdoun, Morocco.	4.8 ± 0.2	31.78% P_2O_5 prior to sieving	1	<50	0.5, 0.1, and 0.01 M KNO_3	HNO_3 and KOH	[30]
	Sinai Manganese Company Quseir (Red Sea, Egypt).	6.8	>99%	0.1	<45	10^{-2} M NaCl	N.A.	[31]
Hydroxyapatite	Ward's Natural Science Establishment, Canada.	4	High purity	2	≤ 20	10^{-3} M KCl	HCl and NaOH	[32]
	The Lisina deposit, Bosilegrad, Serbia.	<5	98.45%	0.1	<5	NaNO_3	HCl and NaOH	[33]
Collophane	Dayukou phosphate mine in Hubei Province, China.	6.5	92.05%	0.01	<2	10^{-3} M KCl	HCl and NaOH	[34]
	Shanxi Province, China.	6.4	High purity	0.005–0.01	<20	10^{-3} M KCl	HCl and NaOH	[35]
	Guizhou province, China.	2–3	94.51%	0.1	≤ 5	10^{-3} M KNO_3	HCl and NaOH	[36]
Apatite	Gregory, Bottley and Lloyd Ltd., United Kingdom.	3.9	Pure	0.05	≤ 5	10^{-2} M NaCl	HCl and NaOH	[37]
	Luiz Menezes Comércio e Exportacao de minerais (Brazil).	6.5	99%	2	<38	10^{-3} M KCl	HCl and NaOH	[38]
	Ward's Natural Science Establishment, Canada.	4.2	46.06% P_2O_5	0.01–0.1	<20	10^{-3} M KCl	HCl and NaOH	[39]

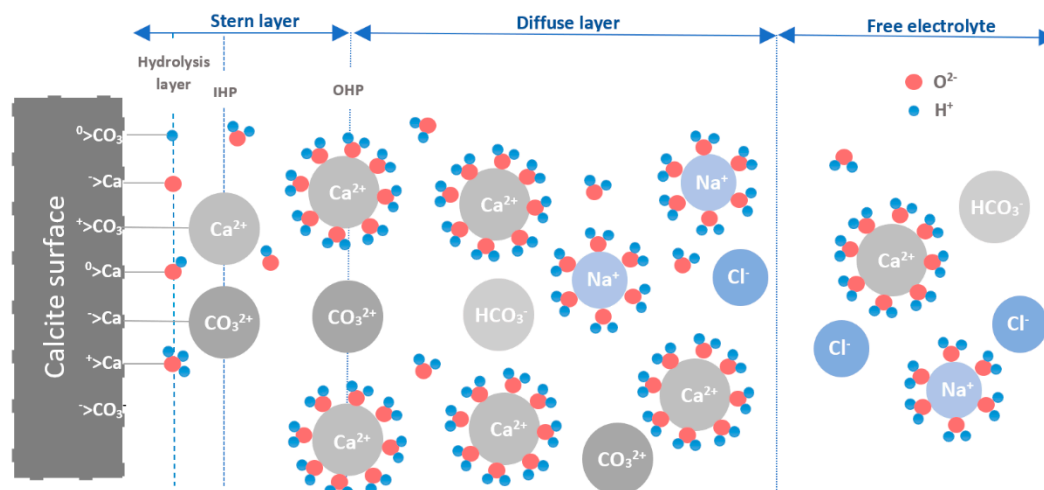


Figure 1. Illustration of the electrical double layer of calcite surface in water with NaCl as the electrolyte. IHP and OHP stand for the inner and outer Helmholtz planes, respectively [22].

To summarize, calcite surface determining ions (PDI) are the lattice ions Ca^{2+} and CO_3^{2-} . Mg^{2+} can also be considered as a PDI. The pH affects the zeta potential by moderating the equilibrium pCa for a given CO_2 partial pressure ($p\text{CO}_2$), therefore, it does not directly control the zeta potential [22]. Table 5 presents calcite IEP values and their measurement operating conditions.

Table 5. IEP calcite values and their measurement operating conditions.

Source	IEP	Purity	Wt (%)	Size (μm)	Electrolyte	pH Adjustment	Ref
Rongan mine in Guangxi province, China.	9.2	99.21% CaO	0.1	<5	10^{-3} M KCl	HCl and NaOH	[40]
Guangxi province and Hunan province, China.	9.5	98.91%	0.1	<2	10^{-2} M KNO_3	HCl and NaOH	[41]
Yunna province of China.	9.5	98%	0.01	<5	10^{-3} M KCl	HCl and NaOH	[42]
Shizhuyuan mine, Chenzhou, China.	10.3	>98%	0.05	<2	10^{-2} M KCl	HCl and NaOH	[43]

- Dolomite solubility and surface charge

The surface of dolomite resembles that of calcite. Dolomite is soluble in aqueous medium and the lattice ions Ca^{2+} , Mg^{2+} , and CO_3^{2-} are susceptible, depending on the solution pH, to either dissolve in the solution or precipitate on mineral surfaces. Moreover, the solution pH and concentrations of Ca^{2+} , Mg^{2+} , CO_3^{2-} , and HCO_3^- might fluctuate under the influence of dissolved atmospheric CO_2 . The species existing on the dolomite surface were investigated by some researchers. Figure 2 presents the calculated speciation at the dolomite–solution interface [44]. Based on these calculations, at a pH below 4, carbonate sites are protonated with predominantly $>\text{CO}_3\text{H}$ species. In higher pH conditions, $>\text{CO}_3^-$ dominates as deprotonation occurs. pH as well as the dissolved carbonate concentration influence the speciation at the dolomite metal sites. At a pH below 8, $>\text{MeOH}^{2+}$ species are dominant, however, once the pH exceeds 8 $>\text{MeCO}_3^-$ dominates. The study confirms the similarities between calcite and dolomite interfaces in aqueous solutions. It also indicates that the PDI for the dolomite surface are its lattice ions (as for calcite) being Ca^{2+} , Mg^{2+} , and CO_3^{2-} [44]. Table 6 presents IEP values of dolomite and their measurement conditions.

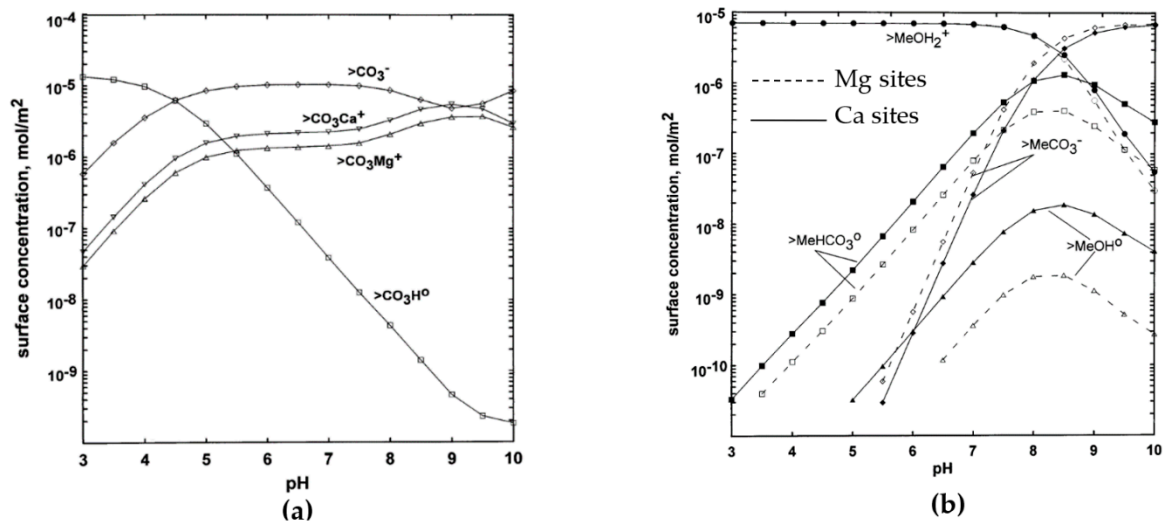


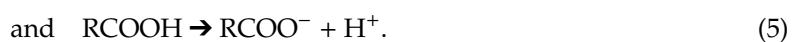
Figure 2. Calculated surface speciation of dolomite (0.01 mol/L NaCl, 10^{-3} M Ca^{2+} , and Mg^{2+} solution in equilibrium with $p\text{CO}_2 = 10^{-3.5}$ atm). (a) Carbonate sites, and (b) metal sites [44].

Table 6. IEP values of dolomite and their measurement conditions.

Source	IEP	Purity	Wt (%)	Size (μm)	Electrolyte	pH Adjustment	Ref
Wulonguan Mine in Hubei Province, China.	4.4	90.62%	0.01	<2	10^{-3} M KCl	HCl and NaOH	[34]
Sterling Hill Mine, New Jersey, USA.	4.8	relatively pure	0.01	D50 < 2.3	10^{-3} M NaCl	HCl and KOH	[45]
Ward’s Natural Science Establishment, Canada.	3.37	mainly dolomite	0.01–0.1	<20	10^{-2} M KCl	HCl and KOH	[28]
Ward’s Natural Science Establishment, Canada.	6.2	36.06% MgO, 60.27% CaO	0.01–0.1	<20	10^{-3} M KCl	HCl and NaOH	[39]
Selasvann, Norway.	7	20.62% MgO, 31.36% CaO	0.01	<43	10^{-3} M KNO_3	HCl and NaOH	[25]
Sinai Manganese Company Quseir, Red Sea, Egypt.	8.5	>99%	0.1	<45	10^{-2} M NaCl	N.A.	[31]

• Quartz solubility and surface charge

Quartz can be found as an impurity in most phosphate ores. Its superficial properties in aqueous solution resembles the properties of amorphous silica. Therefore, the two materials carry similar functional surface groups, and consequently, have the same reaction mechanism [46]. In the quartz-fatty acid flotation system, and in the absence of metal ions, the predicted Reactions are:



According to the reactions above, the adsorption of fatty acids on the quartz surface is nearly impossible. Though, in the presence of metal ions, quartz hydrophobicity can be achieved by surface reactions such as the ones presented below (Reaction 6, 7, and 8) [46]. Table 7 presents the IEP values of quartz and its measurement operating conditions.

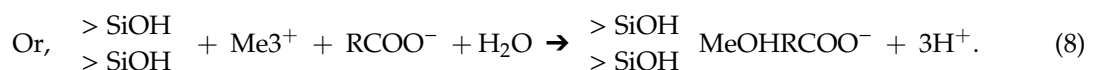
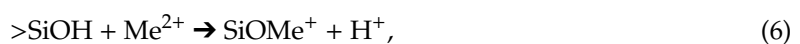


Table 7. IEP values of quartz and measurement conditions.

Source	IEP	Purity	Wt (%)	Size (μm)	Electrolyte	pH Adjustment	Ref
Ward's Natural Science Establishment, Canada.	Negative	96.02%	0.01–0.1	<20	10^{-3} M KCl	HCl and NaOH	[39]
SAC Co., South Korea.	2.1	99.2% SiO ₂	N.A.	<5	N.A.	0.1M HCl and 0.1M NaOH	[26]
Hubei province, China.	2	Relatively pure	0.05	<38	N.A.	10% HCl and 10% NaOH	[27]
Luanping county, Hebei province, China.	2	99%	0.05	<5	N.A.	HCl and NaOH	[47]

2.1.3. Wettability (Contact Angle)

Mineral wettability is critical to the establishment of an efficient froth flotation process. It conveys the mineral's floatability with or without the addition of collectors. The wettability is expressed by an empirical angle. It can be experimentally measured by various methods. For instance, a liquid drop is laid on a solid surface. The intersection of the liquid-solid and liquid-vapor interfaces forms the angle termed "contact angle". A hydrophobic surface retains a contact angle larger than 90° . A hydrophilic surface has a smaller contact angle [48]. The contact angle was first introduced by Tomas Young (1805) and can be calculated through its equation:

$$\gamma_{lv} \cos \theta_Y = \gamma_{sv} - \gamma_{sl}, \quad (9)$$

where γ_{lv} , γ_{sv} , and γ_{sl} represent the liquid-vapor, solid-vapor, and solid-liquid interfacial tensions, respectively, and θ_Y is the Young's contact angle.

However, the contact angles calculated through young's equation are usually different from the measured ones. The calculated θ_Y can be experimentally confirmed only in ideal conditions where the solid surface is physically and chemically homogenous, and the experiment is conducted under extremely controlled conditions. In reality, most measurements are done on heterogenous imperfect solid surfaces (especially for minerals). The advancing and the receding contact angles are other variations of θ . They are measured by expanding and contracting the liquid, respectively and the difference between these two is called the hysteresis (H), a very interesting and informative parameter:

$$H = \theta_a - \theta_r. \quad (10)$$

Table 8 presents phosphate minerals, calcite, dolomite, and quartz contact angles with water using different experimental methods. As already mentioned, the contact angle's precision depends on the sample preparation as its interface needs to be smooth and homogeneous and the measurement must be conducted in controlled conditions to avoid vibrations.

Table 8. Contact angle values of phosphate minerals, calcite, dolomite, quartz, and their measurement conditions.

Mineral	Source	The Contact Angle Type	Method	Contact Angle Value In °	Ref	
Fluorapatite	Ontario, Canada.	-	The captive bubble	36	[49]	
	Single crystal	Anemzy, Imilchil, High Atlas Mts, Morocco.	Static	The sessile drop	(001)	45.1
					(100)	58.9
					(101)	63.6
					(111)	72.8
	Yunnan and Hunan Province, China.	Static	The sessile drop	54.6	[51]	
Mineral powder	Gregory, Bottley and Lloyd, London.	-	Capillary penetration (Washburn method)	-425 + 150 μm -150 + 38 μm -38 μm	52.7 8.35 55.3	[52]
Carbonate fluorapatite	White pebbles	Central Florida, USA.	Advancing	The sessile drop	0	[53]
	Tan pebbles				10	
	Black pebbles				10	
Collophane	Mineral powder	Phosphate mine in Guizhou province, China.	-	Capillary penetration (Washburn method)	About 20°	[36]
Calcite	Calcite crystals (Iceland Spar)	Ward's Natural Science Establishment, USA.	Advancing	The sessile drop	21	[54]
	Single crystal	Yunnan and Hunan Province, China.	Static	The sessile drop	45.6	[51]
Dolomite	Selasvann, Norway.	-	The captive bubble technique	50.5	[49]	
	Haicheng of Liaoning Province, China.	-	-	11.67	[55]	
	Konya-Argit region, in Turkey.	-	The captive bubble technique	Between 5.68 and 7.68	[56]	
Quartz	Hand-picked	Xinjiang Keketuohai Rare Metal Mine, China.	Advancing	The sessile drop	Between 1.5 and 5	[57]
		Anqian iron mine, Liaoning Province, China.	Static	Sessile drop method	Between 22 and 25	[58]
	Mineral powder	Phosphate mine in Guizhou province, China.	-	Capillary penetration (Washburn method)	About 20°	[36]

2.2. Flotation Reagents

Flotation reagents, especially regulators (activators, depressants, and pH regulators) and collectors, impact the selective separation of phosphate minerals from impurities, which are usually carbonates (calcite and dolomite) and silicates (quartz). During the phosphate direct flotation process, gangue minerals are depressed and the phosphate mineral retaining a hydrophobic surface is floated. The opposite occurs during reverse flotation. Table 9 summarizes the reagents used in the phosphate reverse and direct flotation.

2.2.1. Gangue Minerals Reagents

- Calcite and Dolomite Reagents

Generally, anionic collectors are used for carbonates flotation. In the past decades and still in some cases today, anionic collectors' production depended on tall oil and oxidized petroleum as raw materials. However, these come with multiple downsides. Rather, vegetable oils such as rice bran, hydrogenated soybean, cottonseed, and jojoba oils represent a promising inexpensive source for fatty acids [59]. There are some cases when amphoteric collectors (e.g., aminopropionic acid [60,61], carboxyethyl imidazoline [62]) are used for floating carbonates. Moreover, nonionic collectors are generally used to improve the performance of ionic surfactants. They reduce the electrostatic repulsions between ionic head groups, generate hydrophobic chain interactions, and consequently, the adsorption of the ionic collector on mineral surfaces [29]. Table 10 presents the conditions and results where anionic and amphoteric collectors are used for the flotation of calcite and dolomite.

According to research conducted on different organic reagents used as dolomite depressants, carboxymethyl cellulose, citric acid, and naphthyl anthyl sulfonates are effective [63]. The β -naphthyl sulfonate formaldehyde condensate (NSFC) was used as a dolomite depressant during the anionic flotation of colophane at pH value of 9 [34]. NSFC was chemically adsorbed on the dolomite surface and barely adsorbed to colophane. However, NSFC's chemical toxicity is a severe limitation [34]. Additionally, *Bacillus subtilis* and *Mycobacterium phlei* have been tested as depressants of apatite and dolomite [64]. Results indicated the adsorption of both bacteria species on the minerals surfaces. They functioned as depressants for dolomite, as well as for apatite. Although these bacteria do not ensure apatite dolomite selectivity, a simulation of the flotation environment can provide a better choice of bacteria for this purpose.

- Quartz Reagents

Usually, the elimination of silicates minerals, such as quartz, is conducted using cationic collectors. Table 11 presents different reagents mentioned as silica collectors in the literature. Sodium silicate is reported as a performing quartz depressant. Silva et al. [65] investigated the mechanism of quartz depression using sodium silicate. They have found that at a pH value of 7, monomeric $\text{Si}(\text{OH})_4$ and polymeric species, resulting of sodium silicate hydrolysis, were adsorbed on the quartz surface. For a sample containing 97.2% SiO_2 , the quartz depression was observed at a dosage of 1000 g/t Na_2SiO_3 . Optimum floatability was obtained in the pH range from 5 to 8 using a dosage of 1500 g/t Na_2SiO_3 in the presence of 150 g/t amine. Under these conditions, quartz floatability was less than 10%. At a pH value of 11, floatability is high, suggesting that sodium silicate is not adsorbed onto the quartz surface. Moreover, starch exhibits a depressive effect on quartz flotation. Its flocculation property enables it to adsorb onto the quartz surface engendering its depression [66]. Nevertheless, starch is not an efficient depressant for quartz due to its low selectivity. It is still used in a number of concentrators as it is cheap in comparison to other effective reagents [67].

Table 9. Families of reagents used in phosphate flotation.

Selective Phosphate Flotation					
Apatite		Calcite and Dolomite		Quartz	
Collectors	Depressants	Collectors	Depressants	Collectors	Depressants
Anionic • Fatty acids, • Hydroxamates Amphoteric, Cationic.	• Fluosilicic acid, • Sulfuric acid, • Phosphoric acid and its derivatives, • Natural polysaccharides (Starch), • Synthetic polymers.	Anionic • Fatty acids, • Saponified vegetable oils, • Ester, Amphoteric, Nonionic.	• Natural polysaccharides (Starch, quebracho), • Synthetic polymers, • Inorganic soluble salts, • Citric acid, • Hydrofluoric acid.	Cationic • Amine collectors (Primary, Secondary, Tertiary amines), • Amine salts, • Quaternary ammonium salts. Amphoteric, Nonionic.	• Cationically modified polysaccharides, • Inorganic soluble salts (Sodium silicate), • Hydrofluoric acid.

Table 10. Collectors used for the selective flotation of carbonates (calcite and dolomite).

Type	Name	Supplier	Source	pH	Dosage	IRR (%)	P ₂ O ₅ Increase (%)	Recovery (%)	Ref
Anionic	V2711 Flotisor	Clariant	Gafsa-Metlaoui Basin; South of Tunisia.	5	0.2 kg/t	69.61 MgO	11.6	92.4 P ₂ O ₅	[68]
	Flotisor 7466		North Africa phosphate ore.	N.A.	0.6 kg/t	91.13 MgO	7.76	75.1 P ₂ O ₅	[69]
	Sulfoleic acid (SOA)	Zhuzhou Chemical Industry Research Institute	Pure calcite and fluorite minerals obtained from Xinyuan Mine, Chenzhou, Hunan, China.	9	6 mg/L	80.34 CaO	7.23	85.2 CaO	[70]
	Sodium dodecyl sulfate (SDS)	N.A.	Yichang, Hubei Province, China.	N.A.	0.4 kg/t	60.20 MgO	6.38	71.86	[71]
	saponified jojoba oil	Ferquima	The sedimentary phosphate deposit of Itataia, Brazil.	6.5	200 mg/L	N.A.	N.A.	N.A.	[72]
Amphoteric Collectors	dodecyl-N-carboxyethyl-N-hydroxyethyl-imidazoline	Lianyungang Chemicals Plant, Jiangsu Province, China.	Subbituminous coal obtained from Peabody Energy in the USA.	N.A.	0.4 kg/t	95.10	8.10	88	[31]
			Phosphate (francolite) from Quseir (RedSea, Egypt).	N.A.	0.4 kg/t	94.24 MgO	7.70	82 P ₂ O ₅	

IRR: Impurities-removal-ratio.

Table 11. Cationic collectors used for the selective flotation of silica (quartz).

Name	Supplier	Source	pH	Dosage (kg/t)	IRR (%)	P ₂ O ₅ Increase (%)	Recovery (%)	Ref
Alkyl amine salt (DAH)					66.01	5.50	85 P ₂ O ₅	
Ether-amine salt (GE-619)	N.A.	The Abyad area in Jordan.	5	1	48.31	4.75	80.11 P ₂ O ₅	[73]
Quaternary ammonium salt (CTAB)					15.54	2.67	95.45 P ₂ O ₅	
Flotigam EDA		Minas Gerais state, Brazil.	9	0.06	N.A.	N.A.	100 SiO ₂	[74]
Flotigan 2835-2L	Clariant, Switzerland.		9	0.06	N.A.	N.A.	87 SiO ₂	
Flotigam 7470		North Africa phosphate ore.	N.A.	0.42	37.14	7.76	75.1 P ₂ O ₅	[69]
Lilaflot D817M	AkzoNobel Surface Chemistry, USA.				71.32	N.A.	86.75 combustible	
Lilaflot 811		Peabody Energy in the USA.	Natural	3	65.32	N.A.	87.26 combustible	[70]
Dodecyl trimethyl ammonium bromide (DTAB)	Sigma-Aldrich, USA.				49.96	N.A.	90 combustible	

IRR: Impurities-removal-ratio.

2.2.2. Apatite Minerals Reagents

Apatite minerals are usually depressed in acidic medium. Studies showed that at a pH value below 4.5, apatite floatability is weak due to the dominance of Ca^{2+} , $\text{CaH}_2\text{PO}_4^+$, and H_2PO_4^- . The H_2PO_4^- species in the suspension occupies apatite's active sites and leads to a poor recovery. Therefore, inorganic acids are considered effective depressants with phosphoric acid being the most used as it does not cause any complication during the enrichment process. Phosphate salts can depress apatite, as well.

Always in acidic medium, using sulfate or oxalate salts is reported to further depress apatite. These reagents incite the precipitation of the dissolved Ca^{2+} , leading to apatite dissolution and a greater presence of phosphate ions in the suspension [75,76].

Additionally, a synthetic polymeric depressant "ACCO-PHOS 950" was developed by Cytec. The aim is to limit apatite loss during silicates flotation using amine collectors. The reagent proved to be effective when used on North Africa's high-grade phosphate ores [77]. Zhang and Snow (2014) [78] investigated sodium tripolyphosphate, fluosilicic acid, diphosphonic acid, starch and sodium silicate as apatite depressants candidates. The phosphate ore used contains 19.82% P_2O_5 and 40.28% Insol. Sodium tripolyphosphate gave promising results. Using it as apatite depressant yielded a final phosphate concentrate assaying approximately 31% P_2O_5 and up to 7% Insol with over 94% P_2O_5 recovery. During reverse flotation of silica from a fine-grained feed, starch effectively depressed the apatite.

2.3. Influence of Particle Size

Particle size is a main parameter in the flotation process. Particles of various sizes behave differently in the flotation system, directly affecting the recovery, selectivity, and overall performance. Usually, fine particles' flotation is less preferred compared to coarse mineral particles. Fine-grained minerals have a higher surface energy, leading to a nonselective reagent consumption, entrainment or entrapment of particles and an instability of bubble-particle aggregates. A study of the relationship between the phosphate particles size and flotation recovery was carried out by Gaudin et al. (1931). The results revealed that under similar operating conditions, particles of various sizes exhibit different flotation kinetics. The maximum phosphate minerals recovery was obtained when treating size fractions between 60 and 200 μm . Mineral liberation, which is related to the particle size, is also a parameter in the froth flotation of phosphate ores. Fine grinding is critical to attain greater liberation but will unfavorably affect the separation efficiency. Therefore, there is generally a compromise when choosing the particle size. A preforming flotation system requires an effective liberation of desired minerals without overgrinding the ore.

2.4. Influence of the Froth Stability

2.4.1. Froth Stability

The attachment of hydrophobic mineral particles to gas bubbles leads to the genesis of a concentrated mineral lather. The froth's stability is critical and is generally maintained using foaming agents (frothers). The froth must sustain the particle's weight, while resisting excessive coalescence and bursting. On the other hand, the proper functioning of the flotation process requires a manageable and easily suppressed froth for a practical recovery [79]. Froth stability is affected by the parameters such as gas flow rate, stirring rate, solid content, particle size, mineralogy, reagents type and dosage, and water's ionic strength. Farrokhpay et al. [80] noted that froth stability can be assessed through parameters such as froth half-life time, froth maximum height at equilibrium, dynamic froth stability factor, bubble growth across the froth phase, air recovery, and solid loading on bubbles on top of the froth surface, froth velocity, and froth rise velocity, etc.

Particle size and solid content: Liu et al. [79] investigated, in their recent study, the effect of particle size and solid content on fluorapatite, calcite, dolomite, and quartz froths stability. Using a setup

inspired from Lunkenheimer's report [81], they assessed the dynamic froth stability factor (Σ) for different particle sizes and solid contents. This factor is calculated using:

$$\Sigma = \frac{V_f}{Q} = \frac{S \times H_{max}}{Q} \quad (11)$$

V_f is the froth volume (cm^3), Q is the gas flowrate (cm^3/s), S is the cross-sectional area of the column (cm^2), and H_{max} is the maximum froth equilibrium height (cm).

Liu et al. [79] found that for fluorapatite, calcite, dolomite, and quartz the fine particles contribute to froth stability as a result of capillary mechanisms, whilst larger particles lead to froth rapture and instability. Additionally, they observed that increasing the solid content to a certain extent stabilizes the froth (Figure 3).

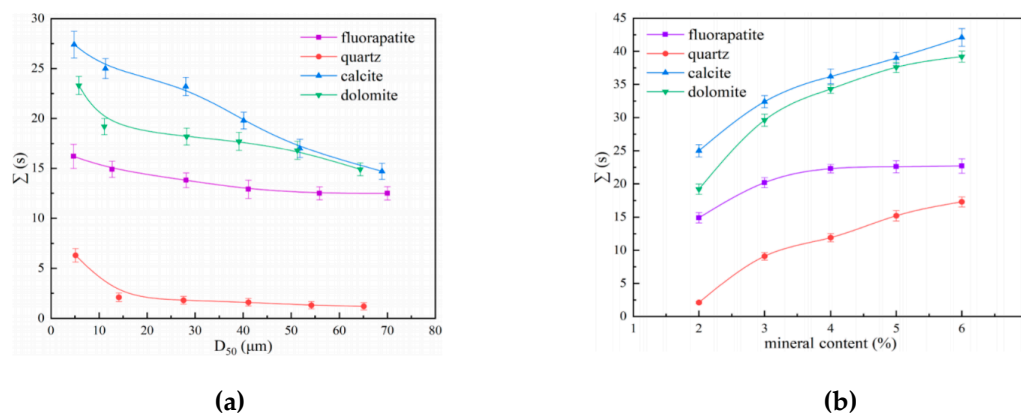


Figure 3. Effect of (a) particle size (b) solid content of fluorapatite, quartz, calcite, and dolomite on the dynamic froth stability factor [79].

Water's ionic strength/mineralogy: According to Liu et al.'s study [79], dolomite and especially the calcite froths stability were found to be superior than those of fluorapatite and quartz. It was demonstrated that Ca^{2+} and Mg^{2+} ions resulting from calcite and dolomite dissolution stabilize the froth. Moreover, the froth half-life time increased dramatically with the addition of Ca^{2+} ions up to $5 \cdot 10^{-4}$ mol/L Ca^{2+} but decreased rapidly thereafter.

Reagent type: The reverse flotation process widely used for upgrading siliceous phosphate ores are considered challenging, especially regarding froth stability. In most cases, cationic collectors are used to float the siliceous gangue. However, they produce an expanding overly stable froth that might entrain other minerals, causing lack of selectivity [59,79,82].

2.4.2. Bubble's Size

Hoang et al. [83] studied the effect of flotation time and froth height on the bubble's size. They found that the bubble's size increased with flotation time, contributing to the reagent's consumption and the decrease in the solid content leading to bubble coarsening. They also stated that the bubble's size increased with the froth height due to water film rupture resulting from low reagents concentration and hydrophobic particles existing in the water film.

3. Conclusions

Based on common scientific data, it can be deduced that the phosphate ores' enrichment was not as complicated as the enrichment of other minerals, namely, metal sulfides and oxides. The deposits already exploited have been high in P_2O_5 content, contained less impurities, and there were not as many strict quality regulations as there is today. With the depletion of these deposits, upgrading complex phosphate ores, while respecting rigorous criteria, is more and more challenging. Phosphate processing

regulations are not only about the concentrate's quality. They also cover environmental issues, such as CO₂ emission, polluting and toxic reagents, water and waste management.

- Huge carbon dioxide emissions are the main downside of thermal beneficiation techniques such as calcination. Hence, froth flotation was developed to replace it in many cases.
- Water recycling is already applied in most phosphate concentrator plants.
- Phosphate waste valorization is an interesting recent topic with numerous industrial opportunities. Hakkou et al. [84] mentioned multiple methods of phosphate wastes valorization. One way is the use of alkaline phosphate wastes (APW) to inhibit the acid mine drainage (AMD). Regarding its high calcite content, 15% APW was used to neutralize the acidity produced by pyrrhotite tailings' oxidation [85]. The APW were also assessed in the passive AMD water treatment [84]. Additionally, phosphate wastes with a size less than 1 mm, were tested in store-and-release (SR) covers to reclaim industrial mine sites [86].
- Flotation reagents can be environmentally harmful and highly toxic. For instance, different apatite depressants (organic and inorganic) are used in the reverse flotation of sedimentary phosphate ores. The most common ones are phosphoric and sulfuric acid and their derivatives. Using these inorganic depressants can entail, however, potential threats to the environment [87] (e.g., calcium phosphate scale formation and water eutrophication [88]). Organic depressants have been developed for apatite/carbonate separation, as well. Nevertheless, they are usually extremely toxic which limits their use [87].

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