Effects of Metal Ions on the Flotation of Apatite, Dolomite and Quartz

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Abstract: The effects of Ca^{2+}, Mg^{2+}, Al^{3+}, and Fe^{3+} on the flotation behaviors of apatite, dolomite and quartz were investigated through a micro-flotation test, and the influence of calcium ions on the flotation of these minerals was further elucidated by solution chemistry study, zeta potential measurement, and X-ray photoelectron spectroscopy (XPS) analyses. The results indicate that an 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 and dolomite. The studied metal cations can activate quartz at a particular pH. It can be inferred from solution chemistry and zeta potential measurement that the influence of metal ions on the flotation of different minerals should be attributed to the adsorption of various hydrolysis species on the mineral surfaces. XPS analyses reveal that calcium ions can enhance the adsorption of anionic collector on apatite and quartz surfaces, and there are no apparent changes to be observed on the surface of dolomite in the absence and presence of calcium ions at a concentration of 2.5×10^{-3} M, which was in good agreement with the micro-flotation results.

Keywords: metal ions; flotation; apatite; dolomite; quartz

1. Introduction

Flotation has been widely used for the separation and purification of finely disseminated minerals, and its separation efficiency strongly depends on the selectivity during the flotation process. On the other hand, due to the water quality, dissolution of minerals and consumption of grinding medium, a certain amount of metal ions, such as Ca^{2+}, Mg^{2+}, Al^{3+} and Fe^{3+}, are inevitably present in the pulp of the actual flotation system [1,2]. Extensive research [2–9] has proven that the floatability of various minerals can be adversely affected by metal ions in the pulp.

Currently, more than 60% of the world's marketable phosphate is upgraded by the flotation process [10]. Fatty acids are commonly used as anionic collectors in phosphate flotation but their use is sensitive to the metal ions [5,11]. Santos et al. [12] reported that calcium and magnesium ions contributed significantly to the decline of apatite recovery and P_2O_5 grade. They identified that the metal ions can react with fatty acid, resulting in reagent consumption. Al-Thyabat and Al-Zoubi [13] pointed out that the presence of Ca^{2+} and Mg^{2+} in water was detrimental to phosphate flotation. It was explained that the collector would react with free divalent metal ions in the pulp to form metal carboxylate complexes or precipitates on both quartz and phosphate instead of selectively reacting to the calcium sites on the surface of phosphate particles. Elgillani and Abuozeid [14] claimed that the dissolved Ca^{2+} in the system should be responsible for the reduction of apatite depression by its effect on the stabilization of apatite, causing the removal of carbonates from phosphate minerals to be less

efficient. Sis and Chander [11] observed the detrimental effect of Ca^{2+} on the hydrophobicity of apatite by contact angle measurement, as the contact angle decreased with the increase of Ca^{2+} concentration.

However, the majority of previous research was focused on the treatment of actual phosphate ore in the presence of divalent calcium and magnesium ions, and the mechanism of the detrimental effects of metal ions, including Al^{3+} and Fe^{3+}, still remains to be determined. Moreover, it is well-known that apatite is the main valuable mineral in actual phosphate ore while the major carbonate and silicate gangue minerals are dolomite and quartz, respectively [15]. Therefore, to further understand the effects and mechanism of metal ions on the flotation of the phosphate ore, it was necessary to first explore the effects of metal ions on the flotation behaviors of apatite, dolomite, and quartz, separately.

The effects of Ca^{2+}, Mg^{2+}, Al^{3+}, and Fe^{3+} on the flotation of apatite, dolomite, and quartz were systemically investigated by micro-flotation tests. Based on the solution equilibrium constants, the distribution diagrams for the hydrolysis species of polyvalent metal ions at the initial concentration of 2.5×10^{-3} M were obtained, in order to interpret the different flotation behaviors of various minerals caused by metal ions in aqueous solution. Furthermore, the adsorption mechanisms of hydrolysis species of Ca^{2+} on apatite, dolomite, and quartz were evaluated by zeta potential measurement and X-ray photoelectron spectroscopy (XPS).

2. Materials and Methods

2.1. Pure Minerals

The crystal apatite was sorted from Madagascar in South Africa while the pure quartz and dolomite samples were taken from Hubei province in China. The mineral purities were examined by X-ray diffraction (XRD) analysis and the results (seen in Figure 1) indicated that the phosphate mineral occurred in the form of fluorapatite and that there were no other minerals detected other than the three pure minerals. Prior to the batch flotation experiments, the samples were successively subjected to hammer crushing and grinding with an agate mortar. The samples were sieved to obtain the fractions of -0.074 mm and -0.038 mm, which were used for micro-flotation tests and zeta potential measurements, respectively.
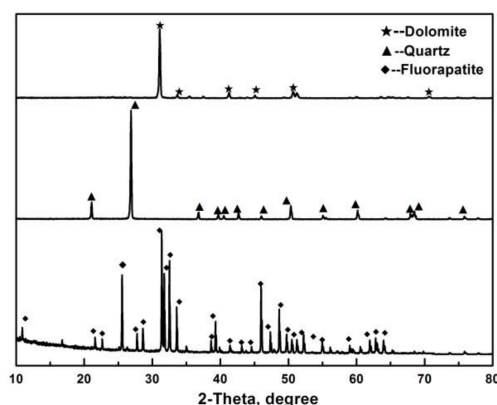

Figure 1. The XRD patterns of apatite, dolomite, and quartz.

2.2. Reagents

Cottonseed oil bought from the local market was chosen as an anionic collector for the flotation experiment after being saponified by sodium hydroxide [16]. Analytical grade calcium chloride, aluminium chloride, magnesium chloride hexahydrate, and ferric chloride hexahydrate were purchased from Sinopharm Chemical Reagent Co., Ltd., Ningbo, China. These chemical compounds were used to generate various metal ions in aqueous solution with the objective of investigating their effects on the flotation of apatite, dolomite, and quartz. Hydrochloric acid and sodium hydroxide

solution, at a concentration of 10%, were used for pH adjustment, and distilled water was used throughout the experiments.

2.3. Micro-Flotation Test

The flotation test was conducted in a laboratory flotation machine with a 50 mL cell and the concentration of cottonseed oil soap was fixed at 60 mg/L (2.14×10^{-4} M). Precisely 2.00 g of pure mineral was conditioned for 5 min in the cell with 50 mL aqueous solution at a determined pH and metal ion concentration. The pulp was aerated with a flowrate of 0.1 L/min, and the sample was floated for 5 min with impeller speed of 2000 rpm. Subsequently, the froth product was filtered, dried, and weighed to calculate the recovery.

2.4. Zeta Potential Measurement

The electrophoretic measurements were performed by a zeta potential analyzer (Zetasizer Nano-ZS90, Malvern, UK). Fifty milligrams of the -0.038 mm fraction sample was suspended in 100 mL solution at the determined pH and calcium ion concentration (2.5×10^{-4} M and 2.5×10^{-3} M). The mineral particles were dispersed for 10 min by ultrasonic agitation at room temperature. The final pH of the solution was measured and recorded. Subsequently, the suspension was centrifuged and the supernatant was taken for zeta potential measurements. Each measurement was repeated three times to provide an average value.

2.5. X-ray Photoelectron Spectroscopy (XPS) Analyses

Samples and the float products with 60 mg/L cottonseed oil soap in the absence and presence of 2.5×10^{-3} M Ca^{2+} were collected and dried at ambient temperature. The XPS analyses were carried out with a Thermo Scientific (Waltham, MA, USA) ESCALAB 250Xi spectrometer using a monochromatic Al Kα source ($h\nu$ = 1486.8 eV). The pressure of the analyzer chamber was less than 2×10^{-9} Torr. High-resolution spectra were obtained with a pass energy of 30 eV. The binding energy of C1s at 284.8 eV was used to calibrate the spectrometer. Spectra were analyzed using XPS Peak software (version 4.1, Hongkong, China), and the lines were fitted with a Gaussian–Lorentzian product function after Shirley background subtraction. The Gaussian–Lorentzian mix ratio was taken as 20% for all lines.

3. Results and Discussion

3.1. Flotation Behavior of Pure Minerals in the Presence of Metal Ions

The effect of pH and ionic concentration on the floatability of apatite in the presence of different metal ions is shown in Figure 2. It can be seen from Figure 2a that apatite recovery in the absence of metal ions dramatically increased with increasing pH values (4.5–8.0), and then decreased as the pH continuously increased. The maximum recovery of 78.27% was achieved at pH around 8.0 Ca^{2+}, and Mg^{2+} exhibited a beneficial effect on the floatability of apatite as the recovery in the presence of Ca^{2+} and Mg^{2+} was higher than that without metal ions. Al^{3+} and Fe^{3+} were proved unfavorable to the flotation of apatite, especially for Fe^{3+} since the apatite recovery was less than 10% over the entire pH range.

Figure 2b further demonstrates the effect of the concentration of various metal ions on the flotation performance of apatite at neutral pH. It was clear that a proper concentration of Ca^{2+} in solution can promote the recovery, which was in accordance with the findings of Horta et al. [17]. Another similar result was reported by Tohry and Dehghani when they investigated the influence of Ca^{2+} on the reduction of apatite content for the beneficiation of a siliceous-phosphorus iron ore [18]. The beneficial effect caused by Mg^{2+} was observed for the entire concentration range, as the curve of Mg^{2+} was above the baseline (i.e., no metal ions). Increasing the Al^{3+} concentration resulted in a steady decline in apatite recovery. The presence of Fe^{3+} sharply reduced the floatability of apatite above concentrations of 10^{-5} M to 10^{-4} M and little recovery was observed when the concentration was more than 5×10^{-3} M.
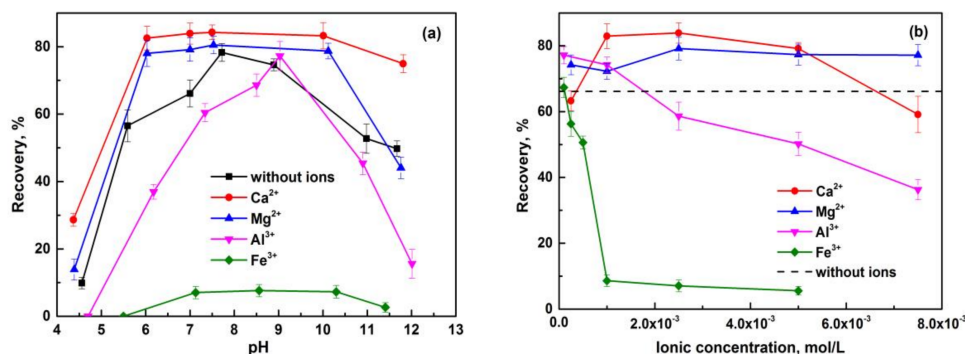
Figure 2. (**a**) Effect of pH on the floatability of apatite in the presence of metal ions at a concentration of 2.5×10^{-3} M; (**b**) Effect of ionic concentration on the floatability of apatite at neutral pH.

The flotation results of dolomite in the presence of metal ions are plotted in Figure 3. It was found that the floatability of dolomite was excellent in distilled water, as the recovery rate was around 80% over the entire range of pH (5.9–11.3). Ca^{2+} and Mg^{2+} had a marginal effect on the flotation performance of dolomite until the pH of the solution changed from 10 to 11, which agrees with the results reported by Zhang et al. [19]. The floatability of dolomite was affected by Al^{3+} and Fe^{3+}, especially in the pH range 6.0–7.0. It is evident that Al^{3+} and Fe^{3+} have a depression effect on the flotation of dolomite, but the depression reduced as the pH increased.

The results given in Figure 3b clearly depict the depression effect of metal ions on dolomite flotation as a function of concentration at neutral pH. Ca^{2+} and Mg^{2+} had a negligible effect on dolomite flotation when the concentration was no more than 2.5×10^{-3} M, but exhibited a detrimental effect when the concentration exceeded 5×10^{-3} M. Al^{3+} and Fe^{3+} would strongly depress the flotation of dolomite even at a low concentration. The depression effect caused by these metal ions could be attributed to reaction of cations with fatty acid into precipitation, decreasing the concentration of the collector available for adsorption onto the dolomite surfaces [20].
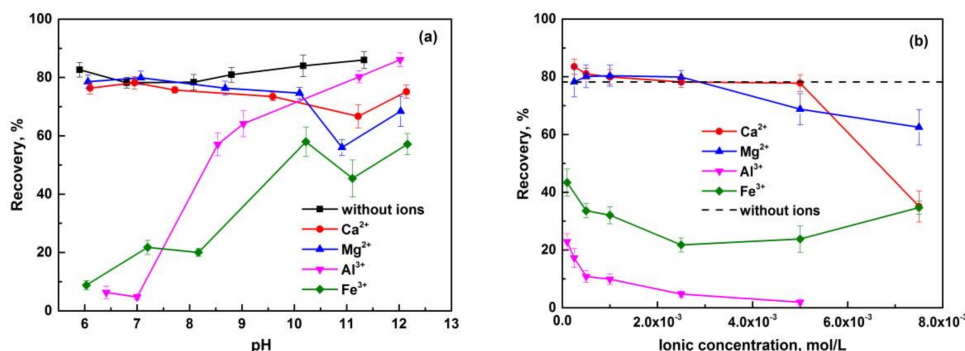

Figure 3. (**a**) Effect of pH on the floatability of dolomite in the presence of metal ions at a concentration of 2.5×10^{-3} M; (**b**) Effect of ionic concentration on the floatability of dolomite at neutral pH.

Pure quartz cannot be floated without being activated using anionic collectors, such as fatty acids. Figure 4 presents the flotation results of quartz after activation by various metal ions. For Mg^{2+}, Al^{3+} and Fe^{3+} as activators, the recovery of quartz increased to maximum at pH 9–10 then decreased with increasing pH. Quartz started to float at pH of 9.0 and a sharp improvement of recovery was observed from 9.5 to 11.5 in the presence of Ca^{2+}, which was in agreement with the adsorption of calcium species on quartz surfaces reported by Ananthapadmanabhan and Somasundaran [21]. Moreover, it is evident from Figure 4a that the activation abilities caused by metal ions can be determined in the order of $Ca^{2+} \geq Mg^{2+} > Fe^{3+} > Al^{3+}$.

The concentration of various metal ions significantly affected the flotation behavior of quartz as well. Figure 4b shows that quartz recovery increased as the ion concentration increased, and then decreased with the further increase of concentration. Therefore, it can be concluded that the favorable condition was Ca^{2+} and Fe^{3+} at a concentration of 2.5×10^{-3} M, whereas the concentration was 10^{-3} M for Mg^{2+} and Al^{3+} under the desired pH for activation.
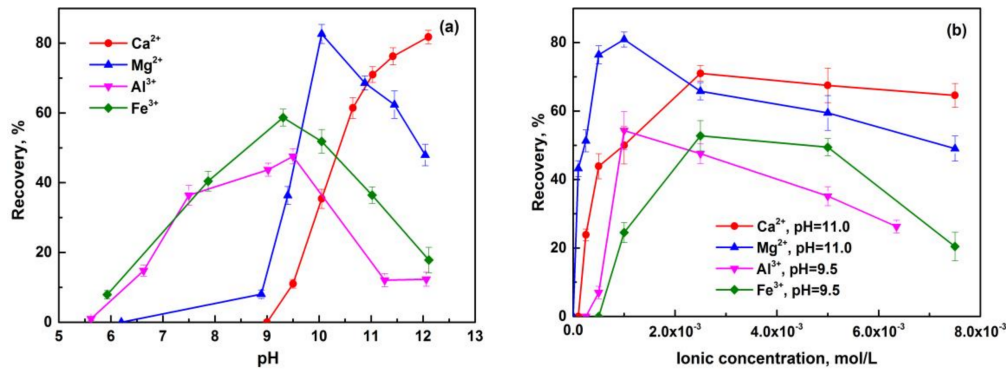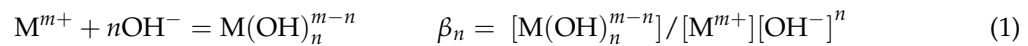

Figure 4. (**a**) Effect of pH on the floatability of quartz in the presence of metal ions at a concentration of 2.5×10^{-3} M; (**b**) Effect of ionic concentration on the floatability of quartz at the desired pH.

On the basis of the results and discussion above, metal ions affected the floatability of apatite and dolomite similarly, suggesting that their flotation selectivity would be poor at moderate metal ion concentration in neutral and alkaline conditions. Meanwhile, unintentional activation of quartz by metal ions would result in phosphate grade reduction. Thus, it is necessary to reduce the pulp metal ion concentration when beneficiating the phosphate ore by flotation.

3.2. Hydrolysis Equilibria of Metal Ions

The flotation behavior of apatite, dolomite, and quartz varies with the change of pH in the absence and presence of metal ions, thus the hydrolysis species are thought to be responsible for the different flotation behaviors. To interpret the influence of polyvalent metal ions on the flotation behavior of apatite, dolomite, and quartz, the concentration of each hydrolysis component was calculated based on the solution equilibria of the cations. Distribution diagrams for 2.5×10^{-3} M Ca^{2+}, Mg^{2+}, Al^{3+}, and Fe^{3+} as a function of pH were obtained to evaluate the interactions between the mineral surface and hydrolysis species.

In homogeneous systems, the hydrolysis of polyvalent metal ions is shown below [22].

$$M^{m+} + nOH^- = M(OH)_n^{m-n} \qquad \beta_n = [M(OH)_n^{m-n}]/[M^{m+}][OH^-]^n \tag{1}$$

Thus,

$$[M] = [M^{m+}] + [MOH^{m-1}] + [M(OH)_2^{m-2}] + \cdots + [M(OH)_n^{m-n}] = \\ [M^{m+}](1 + \beta_1[OH^-] + \beta_2[OH^-]^2 + \cdots + \beta_n[OH^-]^n) \tag{2}$$

where $\beta_1, \beta_2, \ldots, \beta_n$, are cumulative stability constants, [M] represents the initial concentration of metal ions in solution.

The concentration of free metal ions is given by

$$\log[M^{m+}] = \log[M] - \log(1 + \beta_1[OH^-] + \beta_2[OH^-]^2 + \cdots + \beta_n[OH^-]^n) \tag{3}$$

When metal ions start to precipitate in solutions, the concentration of free metal ions can be calculated by:

$$\mathrm{M(OH)}_m = \mathrm{M}^{m+} + m\mathrm{OH}^- \qquad K_{sp} = [\mathrm{M}^{m+}][\mathrm{OH}^-]^m \tag{4}$$

$$\log[\mathrm{M}^{m+}] = \log K_{sp} - m\log[\mathrm{OH}^-] \tag{5}$$

The concentration of other species can be obtained by Equation (1),

$$\log\left[\mathrm{M(OH)}_n^{m-n}\right] = \log\beta_n + \log[\mathrm{M}^{m+}] + n\log[\mathrm{OH}^-] \tag{6}$$

With reference to Equations (3), (5) and (6), and the relevant stability constants shown in Table 1, the concentration of hydrolysis species of Ca^{2+}, Mg^{2+}, Al^{3+}, and Fe^{3+} was calculated and the species distribution diagrams of various metal ions as a function of pH at the ionic strength of 2.5×10^{-3} M can be plotted (Figure 5).

Table 1. The stability constants of the metallic ionic hydroxyl complex.

Metal Ions	Stability Constants				pK_{sp}, $\mathrm{M(OH)}_m$
	$\log\beta_1$	$\log\beta_2$	$\log\beta_3$	$\log\beta_4$	
Ca^{2+}	1.40	2.77	/	/	5.22
Mg^{2+}	2.58	1.00	/	/	11.15
Al^{3+}	9.01	18.70	27.00	33.00	33.50
Fe^{3+}	11.81	22.30	32.05	34.30	38.80

As shown in Figure 5, it can be seen that Mg^{2+} and Fe^{3+} begin to precipitate when the pH is up to 9.8 and 2.1, respectively. $Al(OH)_3$ precipitation is the dominant species in the pH range 3.8–11.8, whereas $Ca(OH)_2$ precipitation does not exist in an aqueous solution over the entire pH range. Therefore, Al^{3+} and Fe^{3+} were in the form of insoluble metal hydroxide throughout the pH range of micro-flotation tests. $Al(OH)_3$ and $Fe(OH)_3$ could preferentially precipitate on the mineral surface [23], and the hydrophilicity of apatite and dolomite was enhanced, resulting in the reduction of the adhesion of surfactant molecules on the mineral surface. That is why the floatability of apatite and dolomite decreased in the presence of Al^{3+} and Fe^{3+}, as shown in Figures 2 and 3.
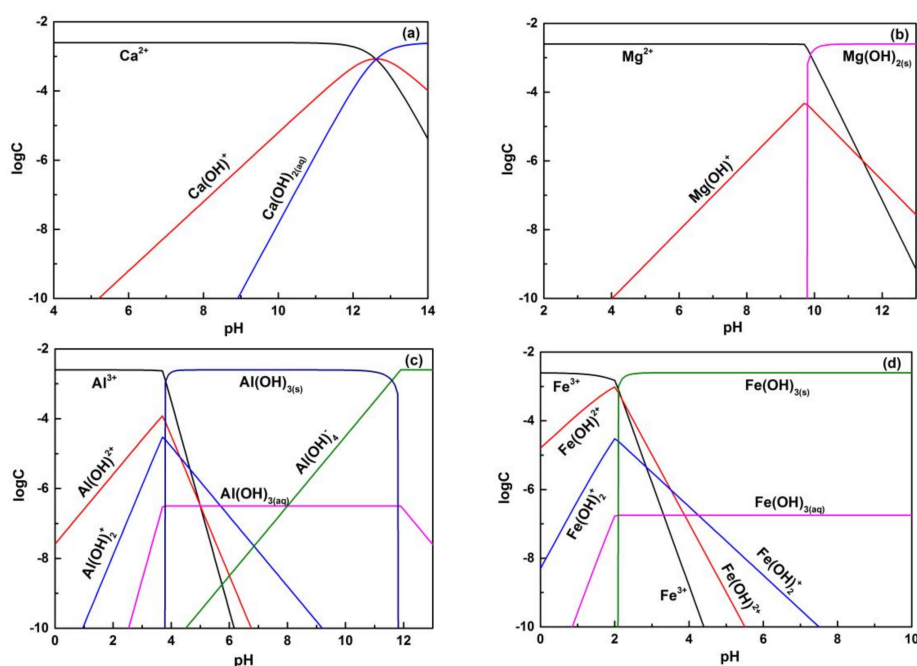

Figure 5. The logC–pH diagram for hydrolysis species of (**a**) Ca^{2+}; (**b**) Mg^{2+}; (**c**) Al^{3+}; (**d**) Fe^{3+} with the initial ionic concentration of 2.5×10^{-3} M.

As the dominant species around the neutral pH, divalent calcium, and magnesium ions were specifically adsorbed on the mineral surface in apatite and dolomite flotation. It can be speculated that the adsorption of Ca^{2+} or Mg^{2+} on the apatite surface can increase the active sites which react with the carboxylate ion of fatty acid soap, contributing to the improvement of apatite floatability. The high recovery of dolomite was mainly attributed to the relatively high concentration of cations in the surface lattice [24], thus a low concentration of Ca^{2+} and Mg^{2+} exhibited a negligible influence on the flotation performance of dolomite. However, in the case of high concentration, the extra divalent metal ions in the bulk would react with fatty acid soap, reducing the amount available for dolomite collection [12].

The activation of quartz by metal ions was attributed to the chemisorption of hydroxides on the mineral surface. Han et al. [25] investigated the activation of quartz as a function of pH in the presence of 10^{-4} M metal ions and sulfonate collector, and the first hydroxy species were found to be responsible for the increase of quartz recovery under a particular pH. As shown in Figure 4a, the maximum quartz recovery was obtained at a pH of about 12.2 in the presence of Ca^{2+} and 10.0 for Mg^{2+}. The species distribution diagrams of Ca^{2+} and Mg^{2+} indicate that $Ca(OH)^+$ and $Mg(OH)^+$ increase to the maximum at pH of 12.4 and 9.8, respectively. Furthermore, it can be seen that the maximum recovery of quartz coincided with the conditions for the maximum concentration of the first hydroxy species of calcium and magnesium. Meanwhile, the logC–pH diagram showed that it was the precipitate of $Al(OH)_3$ and $Fe(OH)_3$, instead of free metal ions, that was the major species in the pH range 4.0–10.0 and is likely the reason why the activation of Al^{3+} and Fe^{3+} on quartz was lower than that of Ca^{2+} and Mg^{2+}.

3.3. Zeta Potentials of Pure Minerals in the Presence of Calcium Ions

As the precipitations of $Mg(OH)_2$, $Al(OH)_3$, and $Fe(OH)_3$ were generated in solution under certain pH conditions, the accuracy of potential measurements of pure minerals would be affected by the coating of these metal hydroxides on the mineral surface. Hence, the effect of calcium ions on the zeta potential of minerals was studied. Previous studies were focused separately on the zeta potential measurements of apatite [26,27], dolomite [24,28], and quartz [29] in the presence of calcium ions. In fact, the zeta potentials varied due to different ionic strength, experimental apparatus, sample preparation process, etc. The effects of calcium ions on the zeta potentials of apatite, dolomite, and quartz as a function of pH were of great necessity to investigate simultaneously in this study. The results are shown in Figures 6–8.

It can be seen from Figure 6 that the isoelectric point (IEP) of apatite was about 3.4 in distilled water, which was almost in agreement with the value of pH = 3 obtained by Hu and Xu [30]. The IEP values shift to 4.3 and 9.6 in the presence of calcium ions at concentrations of 2.5×10^{-4} M and 2.5×10^{-3} M, respectively. Amankonah and Somasundaran [26] identified that the shifts could be attributed to surface reaction and/or bulk precipitation. Besides, the apatite surface was more positively charged with the increase of calcium ion concentration, and a relatively great variation of zeta potential was observed at pH 4–10 while small changes were shown above pH 11 in the presence of Ca^{2+}. This indicates that calcium ions were mainly and specifically adsorbed on the apatite surface in the form of divalent cations at a particular pH range (pH < 10).
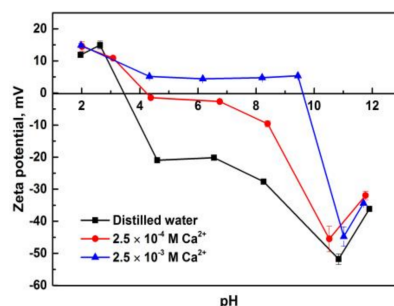

Figure 6. Zeta potential of apatite as a function of pH in the absence and presence of calcium ions.

Due to the dissolution of dolomite in acid conditions, the measurement was conducted with a pH above 9, and the results are plotted in Figure 7. Though the IEP of dolomite without Ca^{2+} has not been observed over the entire pH studied, it can be seen that the IEP value shifted from 10 to 11.25, with the addition of Ca^{2+} at concentrations from 2.5×10^{-4} to 2.5×10^{-3} M. The IEP was reported at pH 6.0 based on the species distribution of dolomite [31], and pH 6.2 as obtained by measurement [32].

In contrast to the zeta potential of -20.93 mV charged on the surface of apatite at pH 4.6 and much more negative above pH 10.8 in the absence of calcium ions, it is interesting to note that the minimum value of the zeta potential of dolomite was just -17.47 mV at pH 11.7. Therefore, it can be inferred that there is a higher concentration of metal cations on the surface of dolomite than that of apatite, which is likely responsible for their different flotation behaviors in the anionic flotation.
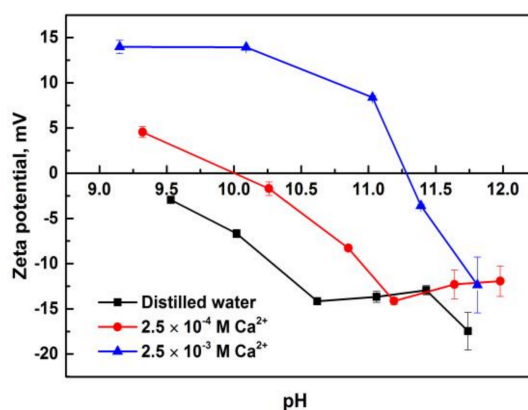

Figure 7. Zeta potential of dolomite as a function of pH in the absence and presence of calcium ions.

Figure 8 shows the zeta potential of quartz as a function of pH in the absence and presence of calcium ions. The IEP of quartz in distilled water was observed around pH = 2, which was in good agreement with results reported by other researchers [33–35]. It can be seen that the IEP values did not change with the increase of calcium ion concentration, but the quartz surface was less negatively charged in the presence of Ca^{2+} above pH 3.4. Meanwhile, an obvious variation of zeta potential was observed under the pH conditions from 8 to 12.
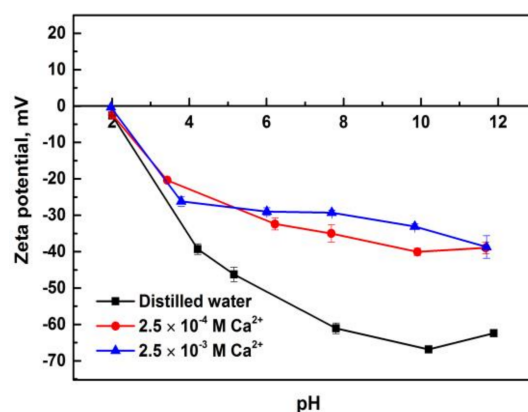

Figure 8. Zeta potential of quartz as a function of pH in the absence and presence of calcium ions.

According to the species distribution diagram shown in Figure 5, calcium ions existed as free ions below pH 12, while the concentration of $Ca(OH)^{+}$ was up to 6.3×10^{-7} M at pH 9, and at a maximum of 8.5×10^{-4} M at pH 12.6. There was no flotation response of quartz observed in Figure 4a under the pH of 9, even though the zeta potential became less negative in the presence of calcium ions. This was

caused by the compression of the electric double layer. In this case, the Ca^{2+} ions were mobile in the diffuse layer and not adsorbed in the Stern plane and fixed on the solid surfaces [23]. Therefore, they could not help quartz to adsorb carboxylates. Hence the activation mechanism of quartz was likely related to the chemisorbed $Ca(OH)^+$ on the surface or surface precipitation.

3.4. XPS Analyses and High-Resolution Spectra of Pure Minerals

To further directly investigate the effect of Ca^{2+} on the flotation behaviors of different minerals, the atomic percent of elements for the surfaces of apatite, dolomite, and quartz in various conditions was determined by XPS [36]. The results presented in Tables 2 and 3 indicated that the atomic percent of calcium slightly increased when apatite and dolomite were conditioned in a 2.5×10^{-3} M Ca^{2+} solution at neutral pH. After the flotation, using cottonseed oil soap as a collector, the carbon concentration apparently increased with a decrease of the oxygen and calcium concentrations, suggesting the adsorption of collector on the mineral surfaces. Moreover, the magnitude of adsorption was enhanced in the presence of calcium ions.

As shown in Table 4, the increase of calcium concentrations and the corresponding decrease of silicon concentrations were observed for quartz surfaces in the presence of calcium ions. After the interaction between activated quartz and collector, the carbon concentration drastically increased from 14.50% to 53.96%, indicating the significant adsorption of collector on the quartz surfaces. Additionally, a further increase of the calcium concentration proved that the collector reacted with free calcium ions in the pulp and precipitate on quartz surfaces.

Table 2. Atomic percent of elements for apatite surfaces in various conditions (pH = 7.0).

Sample	Elements (Atomic %)				
	O1s	C1s	Ca2p	P2p	F1s
Apatite	45.89	24.95	15.30	10.13	3.73
Apatite + Ca^{2+}	45.01	25.43	15.82	9.90	3.84
Apatite + collector	41.19	33.35	13.21	9.65	2.60
Apatite + Ca^{2+} + collector	38.62	36.07	13.22	8.89	3.20

Table 3. Atomic percent of elements for dolomite surfaces in various conditions (pH = 7.0).

Sample	Elements (Atomic %)			
	O1s	C1s	Ca2p	Mg1s
Dolomite	51.66	34.14	9.26	4.94
Dolomite + Ca^{2+}	50.27	36.45	9.48	3.80
Dolomite + collector	44.87	43.51	8.55	3.07
Dolomite + Ca^{2+} + collector	43.64	45.29	8.50	2.57

Table 4. Atomic percent of elements for quartz surfaces in various conditions (pH = 11.0).

Sample	Elements (Atomic %)			
	O1s	C1s	Ca2p	Si2p
quartz	55.04	14.16	-	30.80
quartz + Ca^{2+}	57.78	14.50	0.17	27.55
quartz + Ca^{2+} + collector	29.38	53.96	1.48	15.18

The C1s spectra of samples shown in Figure 9 can be fitted with four component binding energies of C1s at around 284.87 eV, 285.85 eV, 288.65 eV and 289.85 eV that originated from the carbon atoms in functional groups of C–C/C–H, C–O, C=O and O–C=O, respectively [36–38]. In the absence of

collector in solution, the binding energy at around 284.80 eV for apatite, dolomite, and quartz can be attributed to adventitious carbon contamination.
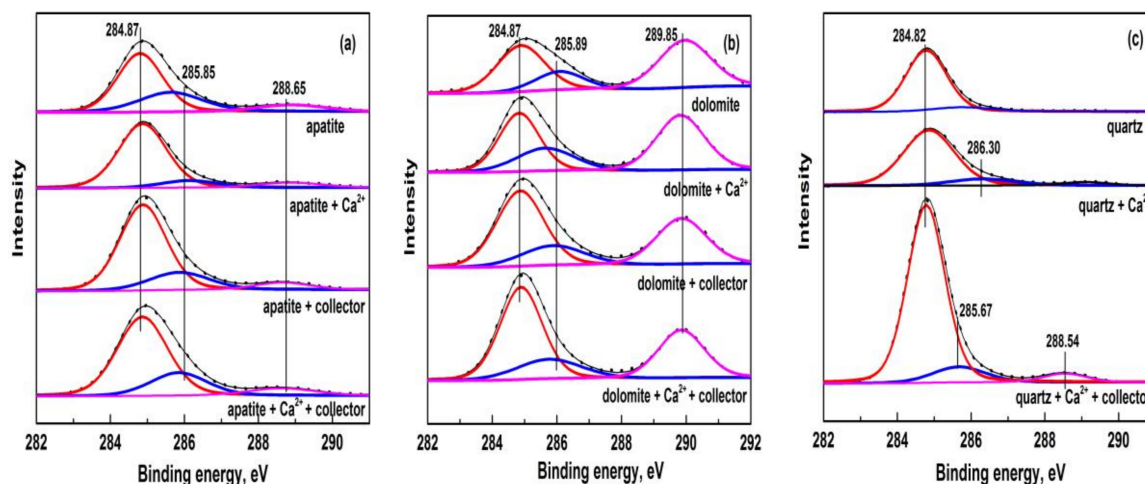

Figure 9. High resolution C1*s* spectra of (**a**) apatite; (**b**) dolomite; (**c**) quartz in the absence and presence of 2.5×10^{-3} M Ca^{2+} and 60 mg/L cottonseed oil soap.

According to the results shown in Figure 9a and Table S1, calcium ions can enhance the intensity and area of binding energy positioned at 285.85 eV and 288.65 eV for the apatite, suggesting an increased adsorption of C–O and C=O sourced from fatty acid soap. However, there were no apparent changes to be observed from the C1*s* spectra of dolomite in the absence and presence of Ca^{2+} using anionic collector (Figure 9b, Table S2). The intensity and area of binding energy at 284.82 eV exhibited a significant increase on the surface of quartz being floated, and that of higher binding energies at 285.67 eV and 288.54 eV concurrently increased (Figure 9c, Table S3). On the other hand, the peak was observed to shift towards the lower binding energy from 286.30 to 285.67 eV in the presence of calcium ions and collector, indicating the chemisorption of reagent on the activated quartz surface [39]. These results can be well explained by the different effects of Ca^{2+} on the flotation behavior of apatite, dolomite and quartz at a concentration of 2.5×10^{-3} M.

4. Conclusions

1. The flotation behaviors of apatite, dolomite, and quartz, in the presence of metal ions, were investigated through micro-flotation tests. The beneficial effect of Ca^{2+} and Mg^{2+} with an appropriate concentration on anionic flotation of apatite was confirmed, and was proved negligible on that of dolomite. Excessive amounts of Ca^{2+} can reduce the floatability of apatite and dolomite at neutral pH. Both Al^{3+} and Fe^{3+} exhibited a depression effect on these calcium-bearing minerals. Quartz can be activated by metal ions, and its floatability varied under different pH conditions and metal ion species.

2. Solution chemistry and zeta potential measurement indicate that the influence of metal ions on the flotation of apatite, dolomite and quartz are attributed to the adsorption of various hydrolysis species of metal ions on the mineral surfaces. It was inferred that Ca^{2+} and Mg^{2+} were mainly adsorbed on the apatite and dolomite surface in the form of divalent ions while $Ca(OH)^+$ and $Mg(OH)^+$ were responsible for the activation of quartz.

3. Various adsorption characteristics of collector on apatite, dolomite, and quartz surfaces in the absence and presence of calcium ions were revealed by XPS analyses, which was in agreement with the flotation results of these minerals under the same ionic concentration.

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