The Influence of Common Monovalent and Divalent Chlorides on Chalcopyrite Flotation

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Abstract: Much attention has been paid to the flotation of chalcopyrite using saline seawater. However, the influence of salt ions on mineral flotation is complex, and different salts may play various roles—either beneficial or detrimental. This study investigated the effects of common chlorides (Cl^-) of Na^+, K^+, Mg^{2+}, and Ca^{2+} in seawater on chalcopyrite floatability. The presence of Na^+, K^+, and Ca^{2+} resulted in greater chalcopyrite recovery, with this effect being more pronounced for the monovalent cations. In contrast, the addition of Mg^{2+} resulted in decreased chalcopyrite flotation efficiency. Contact angle measurements showed that the presence of monovalent cations increased the hydrophobicity of the chalcopyrite surface, while the presence of divalent cations reduced its hydrophobicity, depending on the concentration. Zeta potential, pulp species, and X-ray photoelectron spectroscopy (XPS) cross-confirmed the precipitation of $Mg(OH)_2$ on the chalcopyrite surface when Mg concentration was 10^{-2} M and pulp pH was 10.

Keywords: chalcopyrite; flotation; chlorides; zeta potential; contact angle

1. Introduction

Chalcopyrite ($CuFeS_2$) comprises nearly 70% of the Earth's copper resources, and is the most important and abundant cupriferous mineral [1,2]. Chalcopyrite is typically processed pyrometallurgically subsequent to its separation from gangue minerals by flotation which is a water-intensive process based on the different natural or induced surface properties of the valuable and gangue minerals [3–5]. However, due to the scarcity of fresh water and stringent environmental regulations regarding the quality of discharged water, many flotation plants have to use recycled water or sea water—both of which contain a high concentration of electrolytes [6–8]. For instance, Las Luces—a copper–molybdenum plant in Chile—utilizes seawater mixed with tailings dam water for ore grinding and flotation [9]. Batu Hijau Concentrator in America (Newmont, operating from 2000) uses sea water to process gold-rich porphyry copper ore [10]. Inevitably, the application of highly saline slurries results in challenging flotation process control issues, frequently associated with the maintenance of grade and recovery while minimizing the dosage of reagents.

The presence of salt ions in the flotation slurry increases the complexity of pulp aqueous environment by affecting the structure of the water surrounding mineral particles [11–14], particle surface properties [15–17], and bubble properties [18–21]—all of which influence the mineral–bubble interaction and flotation efficiency [6].

In the flotation process, frothers are normally employed to inhibit bubble coalescence, stabilize the froth by dispersing air [22], and provide adequate frothing characteristics [23,24]. The presence of inorganic salts leads to more complex bubble coalescence, as inorganic ions—similar to frothers—can stabilize foams against coalescence and reduce bubble size [19,25]. The effects of salts on both floatability and frothability have been examined for copper ores [3,19,21,22,26–30]. However, the effects of frothing characteristics of specific chloride salts on chalcopyrite flotation remain unclear.

Suyantara et al. [27] found that the hydrophobic chalcopyrite surfaces became hydrophilic in 10^{-2} M $MgCl_2$ solution at high pH due to the precipitation of $Mg(OH)_2$ onto the mineral surfaces. Hirajima et al. [3] reported that high concentrations of divalent cations (i.e., Ca^{2+} and Mg^{2+}) reduced chalcopyrite floatability at pH greater than 9, owing to the surface adsorption of $Mg(OH)_2$ and $CaCO_3$ precipitates, thereby reducing surface hydrophobicity. In addition, Ramos et al. [22] investigated copper ores flotation in sea water (major cations include 0.6 M Na^+, 1300 ppm Mg^{2+}, and 400 ppm Ca^{2+}) and observed that chalcopyrite floatability was slightly reduced in sea water as compared to fresh water under alkaline conditions. However, the effects of each cation at different concentrations were not examined. Copper flotation recoveries using distilled water and seawater were found to be similar in lab-scale studies by Aral et al. [30] and Corin et al. [21], but deteriorated at greater ionic strengths. Jeldres et al. [29] studied the impact of seawater ions on the flotation of copper-molybdenum sulfides. By adding CaO-Na_2CO_3 mixtures, a significant portion of the divalent ions—Ca^{2+} and Mg^{2+}—was removed and the flotation showed rapid increase in both chalcopyrite and molybdenite recovery.

In contrast to the examination of divalent cations, the specific effects of monovalent cations on chalcopyrite floatability have not attracted much attention. In order to utilize seawater or high salt concentration solutions containing both monovalent (e.g., Na^+, K^+) and divalent (e.g., Ca^{2+}, Mg^{2+}) cations, it is important and necessary to understand the effects of these cations on chalcopyrite floatability. In the present study, we focused on the effects on chalcopyrite flotation of four seawater-containing chloride salts (Na^+, K^+, Mg^{2+}, and Ca^{2+}) in a laboratory-scale mechanical flotation cell. The zeta potential, contact angle, pulp species of these salt ions on chalcopyrite, as well as the surface species were studied to further reveal changes in the chalcopyrite flotation processes in the presence of differing cations.

2. Materials and Methods

2.1. Materials

Chalcopyrite samples used in this study were purchased from GEO discoveries, Australia. Prior to wet sieving, the chalcopyrite was crushed and ball milled. The clinging fines were removed from the resulting samples via sonication. The samples were then dried in a vacuum oven at 30 °C for 24 h. Subsequently, the dried powder samples were transferred into plastic tubes which were sealed after being filled with N_2 gas to minimize surface oxidation by air. All the samples were stored in a freezer prior to flotation and related measurements. The X-ray powder diffraction indicated that the majority of the sample was well-crystallized chalcopyrite.

Analytical-grade collector (sodium butyl xanthate) was used, and technical grade terpenic oil was used as the frother. NaOH and HCl were used for solution pH adjustment. Millipore® (Billerica, MA, USA) ultrapure water with a resistivity of 18.2 MΩ·cm was employed in all measurements except flotation experiments using distilled water.

2.2. Flotation Experiments

All chalcopyrite flotation tests were conducted using a hanging trough-type flotation machine (XFGII5–35g, Wuhan Exploration Machinery Factory, Wuhan, China) at 1200 rpm with an airflow rate of 80 mL·min^{-1}. Chalcopyrite powder (2 g) with a particle size of 38–75 μm was suspended in 25 mL of solution containing chloride salts (NaCl, KCl, $CaCl_2$, and $MgCl_2$) at various concentrations. The pulp pH was adjusted to 10 within 3 min using NaOH, followed by the addition of butyl xanthate

collector within 1 min. Thereafter, terpenic oil was added and mixed for 1 min prior to froth collection at 1, 3, 5, and 8 min. Both the floated and unrecovered fractions were collected and air dried at 70 °C for 2 h prior to weighing.

2.3. Zeta Potential Measurements

Chalcopyrite samples (0.5 g, -38 μm) were placed into 50 mL NaCl, KCl, CaCl$_2$, and MgCl$_2$ solutions at various concentrations. During stirring for 3 min, the solution pH was adjusted to designed value ranging from 2 to 10 using NaOH and HCl. The agitated suspension was then sampled for zeta potential measurements (Zetasizer Nano-zs90, Malvern Co., Ltd., Malvern, UK). The results presented were the average of three independent measurements, with a typical variation of ± 5 mV.

2.4. Contact Angle Measurements

Chalcopyrite slab samples were progressively polished using 600, 1000, and 5000 mesh metallographic abrasive papers, providing a flat surface. Ethanol was applied to clean the surface, which was subsequently carefully dried using filter papers. Prior to contact angle measurements, each chalcopyrite slab was treated for 3 min in a solution containing the same salt concentrations as for flotation. This was then followed by butyl xanthate addition into the solution to react with the slab sample for 0, 1, 3, 5, and 8 min, respectively. All the measurements were repeated at least three times, and the average values are reported herein. The sessile drop technique (JC2000C1, Shanghai Zhongchen Digital Technology Company, Shanghai, China) was applied to measure contact angles of chalcopyrite surface. After a drop (0.25 μL) of Millipore® ultrapure water being placed onto the chalcopyrite slab surface through a microliter syringe, the profile of contact angle was imaged within 30 s and processed using JC2000D software.

2.5. X-ray Photoelectron Spectroscopy (XPS) Analysis

The X-ray photoelectron spectroscopy was conducted using ESCALAB 250Xi (Thermo Fisher Scientific Inc., Waltham, MA, USA) equipped with an Al Kα monochromatic X-ray source. The survey spectra were collected from 1350 to 0 eV with a pass energy of 30 eV and a step size of 0.1 eV. The spectra and surface atomic ratios were obtained and calculated through Thermo Avantage software using Shirley method [31] for background corrections. The binding energy of C 1s at 284.8 eV was used as an internal standard for calibration [32].

3. Results and Discussion

3.1. Effects of Reagent Dosages

Figure 1a shows the chalcopyrite recovery on addition of various amounts of terpenic oil (frother) and 30 ppm butyl xanthate (collector). The cumulative recovery of chalcopyrite increased significantly when the frother dosage was increased from 5 to 10 ppm. However, when terpenic oil was further increased to 15 ppm, the cumulative recovery did not increase significantly. However, a more significant increase was observed at a lower frother concentration of 5 ppm between 1 and 8 min flotation time, as compared to that over the same time period at 10 and 15 ppm frother. Therefore, 10 ppm was selected as the optimal frother dosage for further flotation experiment, with an approximately 80% recovery after 8 min.

Figure 1b shows the effects of collector dosage, with a frother dosage of 10 ppm. The cumulative recovery of chalcopyrite increased significantly with increasing butyl xanthate concentration from 20 to 30 ppm. However, no significant increase was observed on further collector dosage increasing to 50 ppm. Therefore, the collector dosage of 30 ppm was applied for further study.
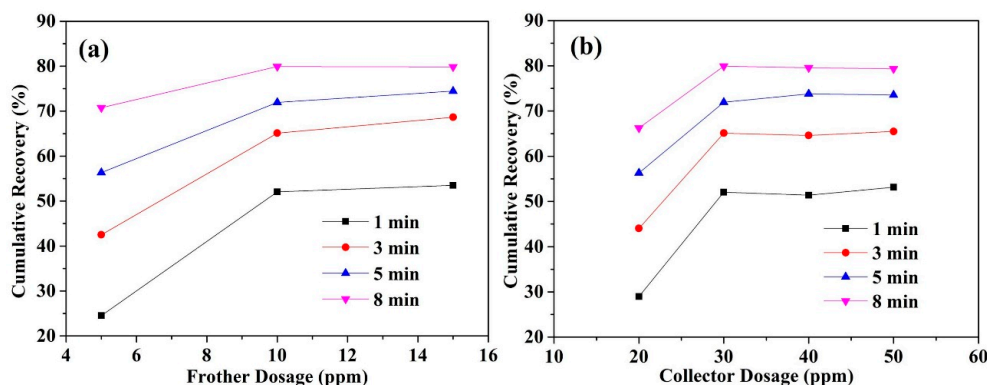
Figure 1. The effects of (**a**) frother and (**b**) collector on chalcopyrite recovery.

3.2. Effects of Salts

Figure 2 shows the effects of typical soluble chloride salts on chalcopyrite flotation. As the pulp was adjusted to pH 10 using NaOH, approximately 10^{-4} M Na$^+$ was added to the slurry, which was present as a background Na$^+$ concentration. Therefore, the effect of Na$^+$ was limited to the addition of 10^{-2} and 10^{-1} M to negate the Na$^+$ background effects. It is observed that the addition of NaCl, KCl, and CaCl$_2$ resulted in greater chalcopyrite recovery (Figure 2a–c). In contrast, the presence of MgCl$_2$ decreased chalcopyrite flotation recovery, especially at a high concentration of 10^{-2} M (Figure 2d).
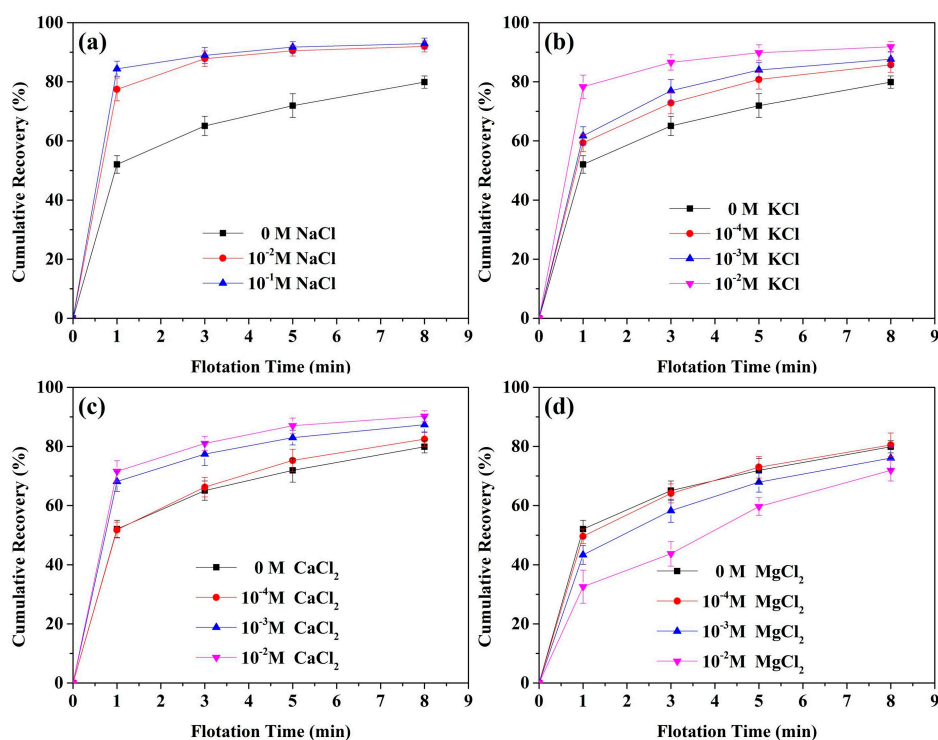

Figure 2. The effects of salts on chalcopyrite recovery: (**a**) NaCl; (**b**) KCl; (**c**) CaCl$_2$; and (**d**) MgCl$_2$.

Specifically, the chalcopyrite recovery increased rapidly within the first 1 min, from 52% (0 M Na$^+$) to 77% and 84%, with an increase in Na$^+$ concentration from 10^{-2} and 10^{-1} M, respectively (Figure 2a). Three minutes later, no significant difference in chalcopyrite recovery was observed due to increased Na$^+$ concentration, eventually achieving an approximately 92% recovery at 8 min, but still significantly greater than that without Na$^+$ addition. The cumulative recovery of chalcopyrite gradually increased when KCl concentration was increased from 10^{-4} to 10^{-2} M (Figure 2b). It should be noted

that the addition of 10^{-2} M KCl had an almost equivalent effect to NaCl at the same concentration. These results indicated that the presence of monovalent cations is beneficial to chalcopyrite flotation at the concentration range examined.

Ca^{2+} addition was observed to be beneficial (Figure 2c), while Mg^{2+} was detrimental (Figure 2d) to chalcopyrite flotation. Chalcopyrite recovery was not significantly improved in the presence of 10^{-4} M Ca^{2+} solution, but apparently greater chalcopyrite recovery was obtained on increased Ca^{2+} concentration to 10^{-3} M, with a further slight increase in chalcopyrite recovery at 10^{-2} M Ca^{2+}. The recovery within the first minute in 10^{-2} M $CaCl_2$ solution was only 71.6% as compared to 77% in 10^{-2} M NaCl and KCl solutions, indicating that monovalent cations had a more positive effect on chalcopyrite flotation. $CaCl_2$ was reported to have negligible effects by Nagaraj and Farinato [33], while Hirajima et al. [3] reported the effects to be negative. Such contrasting results are likely due to the differences in pulp density and flotation reagents influencing the mineral floatability by changing the frothability of seawater solutions [22], e.g., Nagaraj and Farinato [33] used a very high pulp density (35 wt·%) with added sodium diisobutyl dithiophosphate as the collector, while Hirajima et al. [3] used a very low pulp density (0.03 wt %) using a Hallimond tube.

Although chalcopyrite recovery was not significantly reduced in the presence of 10^{-4} M Mg^{2+}, this effect increased on increasing Mg^{2+} concentration to 10^{-2} M (Figure 2d). Detrimental effects of $MgCl_2$ on chalcopyrite floatability at high pH has been reported by Hirajima et al. [3] and Nagaraj and Farinato [33].

3.3. Contact Angle

Figure 3 shows the contact angles for chalcopyrite surfaces treated with various salt solutions for different exposure time from 1 to 8 min. It was found that the contact angle of freshly polished chalcopyrite immersed in pH 10 solution was approximately 62°, close to the value reported by Hirajima et al. [3]. The eventual contact angle (exposure time of 8 min) of the chalcopyrite treated in solution containing either KCl or NaCl was around 90°, indicating successful adsorption of butyl xanthate onto the chalcopyrite surfaces. Specifically, the addition of these two monovalent salts had a positive effect on the adsorption of collector onto mineral surface before 3 min, which further increased the contact angle of the chalcopyrite surface, indicating that the process of collector absorption on the chalcopyrite surface was achievable during this short period. These results are in accordance with the chalcopyrite flotation (Figure 2a,b), confirming that NaCl and KCl can promote chalcopyrite floatability by increasing xanthate adsorption on chalcopyrite surface within a shorter time compared to the pulp without salts, further illustrating that NaCl and KCl were beneficial to improving chalcopyrite flotation rate, especially within 3 min. The above positive roles of cations in increasing mineral flotation recovery may be attributed to the lower stability of hydration layer on samples in solutions with higher ionic strength. Blake and Kitchener [34] reported that the stable films of hydration layer were reduced when KCl concentration was gradually increased. Laskowski [35] conducted coal flotation using inorganic salts (NaCl and KCl) and proposed that the electrical double layer around the particles was compressed, resulting in the opening of hydrophobic surface sites which may attract bubbles by hydrophobic bonding. In addition, these studies suggested that the addition of salt decreased the energy barrier in wetting film rupture by compressing the electrostatic double-layer force, which is beneficial to the mineral flotation.

Figure 3c,d showed the contact angle of chalcopyrite treated in $CaCl_2$ and $MgCl_2$ solution. It was observed that the contact angles increased slightly on the addition of 10^{-4} M $CaCl_2$ with a slightly negative effect on increased $CaCl_2$ concentration (10^{-3}–10^{-2} M), suggesting that $CaCl_2$ had an insignificant impact on chalcopyrite wettability. However, Figure 3d indicated that the contact angle of chalcopyrite was greatly decreased with increasing $MgCl_2$ concentration, although a low concentration (10^{-4} M) had unapparent effect, indicating that the presence of $MgCl_2$ depressed the adsorption of collector on chalcopyrite. Increased surface wettability stabilizes the liquid layer on the surface and lengthens the induction time (i.e., the time required for bubbles to remove the intervening

liquid layer on particle surfaces and form bubble-particle attachments), resulting in poor mineral flotability [3]. Suyantara et al. [27] demonstrated that the induction time was longer on chalcopyrite and molybdenite surfaces in a 10^{-2} M MgCl$_2$ solution at high pH values, due to the adsorption of Mg(OH)$_2$ precipitation and decreased surface hydrophobicity.

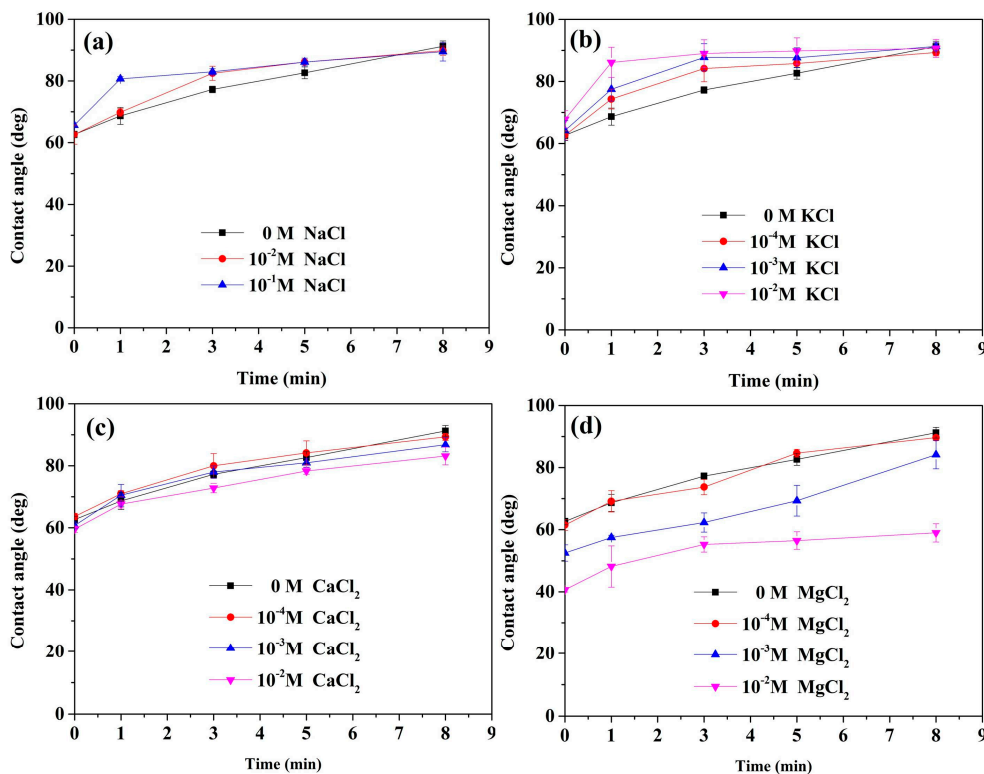**Figure 3.** Contact angle of chalcopyrite surface exposed to collectors for various times in (**a**) NaCl; (**b**) KCl; (**c**) CaCl$_2$; and (**d**) MgCl$_2$ solution. Each measurement was finished within 30 s.

3.4. Zeta Potential

Figure 4 shows the zeta potentials of chalcopyrite in the presence of NaCl, KCl, CaCl$_2$, and MgCl$_2$. The overall zeta potentials were gradually decreased to more negative values with increased pH. More importantly, the zeta potential became less negative on increasing salt concentration, indicating a decrease in the electrostatic repulsion between solid surfaces at high salt concentrations. For instance, when NaCl concentration was 10^{-1} M (Figure 4a), the zeta potential was significantly increased at all pH examined. In contrast, the zeta potentials in KCl solution remained in a relatively narrow range across all pH values (Figure 4b), especially at pH 10 which was used for the flotation experiment. This indicates that KCl had no significant effect on the zeta potential of chalcopyrite.

A similar change in the zeta potential as for NaCl addition was observed in CaCl$_2$ solution (Figure 4c); i.e., it increased with increased CaCl$_2$ concentration, although no further increment was observed when CaCl$_2$ was in the range of 10^{-3}–10^{-2} M, indicating that the effect of CaCl$_2$ on zeta potential achieved a plateau at this concentration range. Therefore, the increase in the floatability of chalcopyrite in CaCl$_2$ solution (Figure 2c) was mainly attributed to changed zeta potential (Figure 4c), rather than wettability (Figure 3c). In contrast to the zeta potential trends observed for other chloride salts, the zeta potentials became positive values in 10^{-3} and 10^{-2} M MgCl$_2$ solutions at pH 10. Therefore, the poor floatability of chalcopyrite at pH 10 in the presence of MgCl$_2$ was largely due to the adsorption of Mg(OH)$_2$ precipitation [3], which reversed the zeta potential of the chalcopyrite surface and reduced the hydrophobicity (10^{-2} M vs. 0 M, Figure 3d). The Mg(OH)$_2$ precipitation will be verified in Sections 3.5 and 3.6 through solution speciation calculation and XPS analysis.
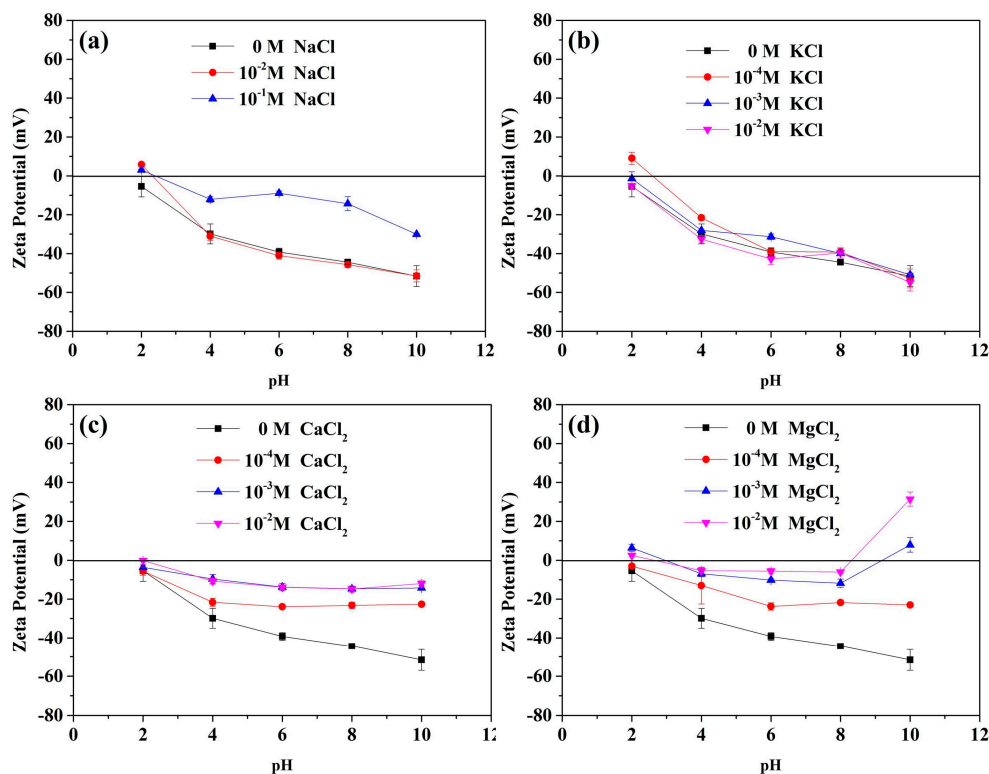
Figure 4. Zeta potential of chalcopyrite in (**a**) NaCl; (**b**) KCl; (**c**) CaCl$_2$; and (**d**) MgCl$_2$ solutions at various concentrations and pH.

3.5. Solution Species

Various chalcopyrite flotation behaviors due to the presence of different salts can be further explained by the solution species diagrams shown in Figure 5. No Ca precipitation was expected at pH below 10 when its concentration was increased from 10^{-4} to 10^{-2} M. However, the precipitation pH for Mg(OH)$_2$ was reduced from 10.6 to 9.6 when Mg^{2+} concentration was increased from 10^{-4} to 10^{-2} M, respectively, similar to that observed by Li and Somasundaran [36]. This further confirms the precipitation of Mg(OH)$_2$ in the flotation system when the pH of the pulp in the presence of 10^{-2} M Mg^{2+} was controlled at 10. Ramos et al. [22] reported that the charge of the bubble should be considered during flotation process, especially when cationic hydroxyl complexes were formed in the pulp. It was reported that the magnesium hydroxyl complexes and hydroxide formed were affinity approaching the liquid/gas interface, resulting in positively charged bubbles [36]. Similarly, magnesium hydroxyl complexes and hydroxide precipitated on chalcopyrite surface results in a positively-charged mineral surface, strongly influencing the flotation process, consistent with the observation shown in Figure 4d.

Therefore, the decrease in chalcopyrite flotability may be attributed to the increase of mineral surface wettability due to precipitation occurring at high Mg^{2+} concentrations and pH. In other words, the presence of a certain amount of Mg^{2+} is detrimental to chalcopyrite flotation, while the beneficial pH for chalcopyrite flotation should be controlled lower than the critical value when Mg^{2+} is present. This is also consistent with the flotation results shown in Figure 2 and the contact angle shown in Figure 3, where 10^{-4} Mg^{2+} had a slight influence while 10^{-2} M Mg^{2+} significantly affected chalcopyrite recovery and contact angle at pH 10.
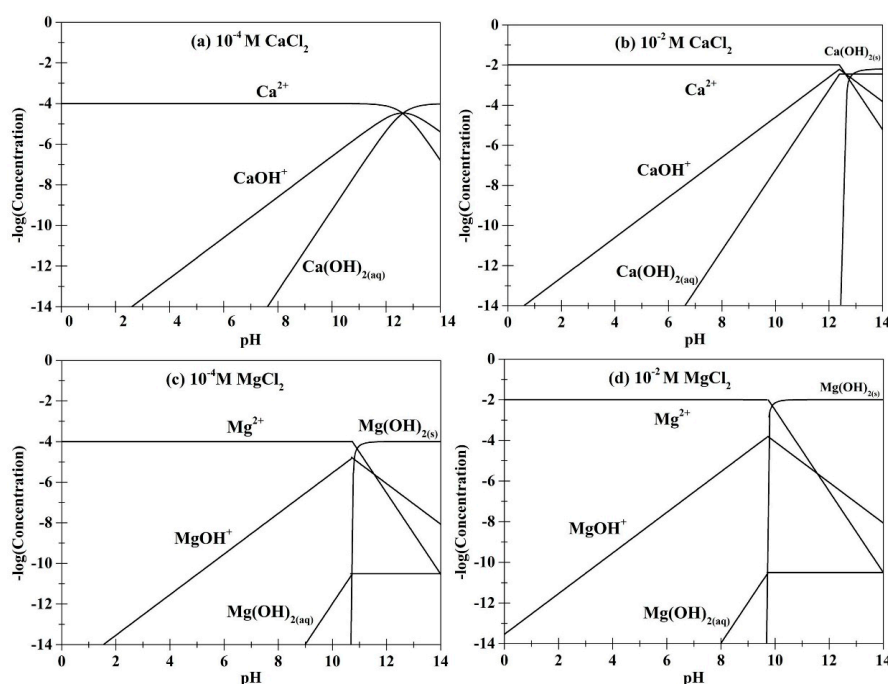
Figure 5. Ca and Mg species at 10^{-2} and 10^{-4} M.

3.6. XPS Measurements

The chalcopyrite samples floated from the pulp in the presence of 10^{-4} and 10^{-2} M Mg^{2+} were collected and dried for XPS analysis. Figure 6 shows the survey of these two chalcopyrite surfaces.
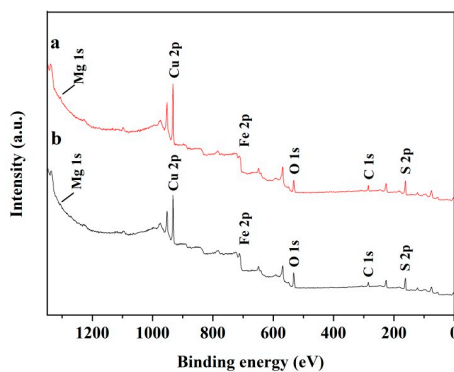

Figure 6. X-ray photoelectron spectroscopy (XPS) survey spectra of chalcopyrite surface in the presence of (**a**) 10^{-2} M and (**b**) 10^{-4} M Mg^{2+}.

Table 1 shows that the elemental composition of the chalcopyrite surfaces. It is obvious that the Mg on the chalcopyrite surface floated with 10^{-2} M $MgCl_2$ was 2 at %, while less than 1 at % Mg was observed on the chalcopyrite surface floated with 10^{-4} M $MgCl_2$ during the flotation process, further confirming the precipitation of $Mg(OH)_2$ in the presence of 10^{-2} M $MgCl_2$.

Table 1. Elemental composition of floated chalcopyrite surface.

$MgCl_2$ Concentration (M)	at %				
	Cu 2*p*	S 2*p*	Fe 2*p*	O 1*s*	Mg 1*s*
10^{-2}	24	38	6	30	2
10^{-4}	21	35	8	36	<1

4. Conclusions

The effects of four salts—NaCl, KCl, CaCl$_2$ and MgCl$_2$—at pH 10 on chalcopyrite flotability were investigated. Both NaCl and KCl were found to be beneficial to the recovery of chalcopyrite, suggesting that monovalent cations improve the flotation response of chalcopyrite, possibly due to lower energy barrier and stability of hydration layer on chalcopyrite surface through compressing the electrostatic double-layer force.

In contrast, the addition of the divalent salts CaCl$_2$ and MgCl$_2$ showed only a slightly beneficial effect and a negative effect, respectively. The effects of CaCl$_2$ may be due to the decreased electrostatic repulsion between solid surfaces at pH 10. The depression caused by MgCl$_2$ at high concentrations was mainly due to the adsorption of Mg(OH)$_2$ precipitates on the chalcopyrite surfaces, reducing chalcopyrite surface hydrophobicity.

Author Contributions: Yubiao Li designed the experiment and wrote the manuscript while Wanqing Li run the experiment and collected all the data. Qing Xiao involved in the discussion of the results and approved reading the manuscript. Nan He and Zijie Ren analysed data. Clement Lartey and Andrea R. Gerson reviewed and edited the manuscript.

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

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