



Insight on Exogenous Calcium/Magnesium in Weakening Pyrite Floatability with Prolonged Pre-Oxidation: Localized and Concomitant Secondary Minerals and Their Depression Characteristics

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Abstract: In this study, we investigated the localized and concomitant precipitation of calcium (Ca)/magnesium (Mg)-bearing species and iron oxides/oxyhydroxides, and their depression characteristics to the pyrite floatability in floation process at pH 9 and pH 10.5 with prolonged pre-oxidation. Contrary to the depression characteristics at pH 9, the incipient (within aeration times of 30 min) depression of pyrite floatability in Ca/Mg-bearing solutions was more obvious at pH 10.5, while the subsequent decline was only slightly when the pre-oxidation time was expanded to 120 min and 360 min. The competitive adsorption among Ca/Mg-bearing species and potassium amyl xanthate $(PAX, C_6H_{11}OS_2K, collector)$ at specific sites onto the pyrite surface was demonstrated by the regularly decreased zeta potential of the pyrite surface pretreated in Ca/Mg-bearing solutions. Further scanning electron microscopy-energy dispersive spectrometry demonstrated the concomitant secondary Ca/Mg/Fe-bearing precipitates on the pyrite surface. X-Ray photoelectron spectroscopy suggested strong reprecipitation of iron oxides/oxyhydroxides on the pyrite surface via acid-base complexation among Ca/Mg hydroxy species and iron hydroxy species. Incipient occupation efficiency of specific reaction sites by Ca/Mg-bearing species, which were mainly controlled by the metastable distribution of Ca/Mg hydroxy species and their electrostatic affinity with pyrite surface, was the crucial factor that influenced the competitive adsorption of xanthate and pyrite floatability. More obvious incipient depression at pH 10.5 rather than at pH 9 contributed to more effective Ca/Mg-bearing species and their higher affinity to pyrite surface at pH 10.5. The localized and concomitant precipitation of secondary Ca/Mg/Fe-bearing species leads to a slightly increased hydrophilic coverage upon the pyrite surface, thus a slowly decreased pyrite floatability with increasing pre-oxidation time.

Keywords: pyrite; calcium; magnesium; flotation depression; specific adsorption; coaggregation

1. Introduction

Pyrite (FeS₂) commonly acts as fine gangue mineral during pyrite–chalcopyrite separation in view of its low economic significance and abundance in most copper ores [1–4]. Traditionally, to reduce sulfur pollution in hydrometallurgy processes through effective pyrite removal, lime was utilized as a cost-effective pulp modifier to alleviate pyrite recovery by forming surface hydrophilic Ca-bearing minerals on pyrite [5–7]. Additionally, the surface dissolution of clay minerals such as serpentine, talc, calcite and dolomite also release Ca²⁺ and Mg²⁺ into flotation systems, which easily form the Ca/Mg hydroxy species/carbonates when pH is over 8 [8–10]. Similar to the influence of Ca-bearing minerals on pyrite flotation in alkaline conditions, Mg²⁺ can also deteriorate the pyrite floatation



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). recovery because hydrophilic MgOH⁺ and Mg(OH)₂ precipitate attach onto the pyrite surface [11,12]. However, some researchers have observed that the Ca/Mg-bearing minerals and iron oxides on oxidized pyrite occur as colloidal aggregates, but still had strong depression effects on pyrite although the bulk of pyrite surface was pristine [12–14]. Using Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS), John et al. [14] and Mermillod-Blondin et al. [15] found that Ca-bearing minerals stabilized the Fe-bearing species in alkaline conditions regulated by lime. They suggested that the Ca-bearing minerals precipitated more stably on the surface ferrous/ferric sulfates substrate via a "cementation effect" and showed a synergistic relationship with the reprecipitation of Fe-bearing species. Recent investigations of pre-oxidation treatments of pyrite considered important factors such as prolonged oxidation treatment with various oxidizing agents, and pulp chemistry including dissolved oxygen (DO), redox potential (Eh), and pH [16–18]. In view of the fact that the contact time of sulfide minerals with coexisting Ca^{2+} and Mg^{2+} will be amplified with multiple stage flotation, closed water circuits, and tailings recycling in flotation plants, the time-related interaction among Ca/Mg species and sulfide minerals should also be systematically examined [8,19,20]. However, the effect of pyrite floatability with exogenous Ca/Mg in an alkaline environment is still unclear. Especially, the time-related depression characteristic of Ca/Mg-bearing species on pyrite surface should be discussed alongside their adsorption/precipitation behavior, subsequent influence to pyrite oxidative dissolution and the distribution of hydrophilic species on the pyrite surface.

Xanthate-derived collectors are extensively used for metal sulfides flotation because of their low cost [21,22]. Furthermore, xanthate activates the floatation of metal sulfides via forming hydrophobic dixanthogen on the particle surface where the metal xanthate and metal hydroxy xanthate are suggested as intermediates based on FTIR and pH-Eh calculation of a metal-xanthate system [13,23-25]. Interestingly, with the aid of timeof-flight secondary ion mass spectrometry (ToF-SIMS), researchers have observed heterogeneous oxidation coupling with the non-uniform adsorption of collectors on metal sulfides surface [26–28]. It was also reported that the surface of high-iron sphalerite loaded with CaOH⁺ and iron hydroxides could inhibit xanthate adsorption, based on zeta potential and ToF-SIMS analysis [29]. The aforementioned results suggested that the dotted adsorption/precipitation of Ca/Mg-bearing species may still strongly influence xanthate/dixanthogen adsorption behavior on the pyrite surface. Meanwhile, the potential localized distribution of Ca/Mg-bearing minerals and its effects on the distribution of secondary iron-bearing precipitates are also important, which may directly relate to collector adsorption behavior and pyrite floatability in view of the prolonged pre-oxidation of pyrite with added Ca/Mg. Nevertheless, there remains a lack of studies combing the localized co-aggregation characteristics of secondary hydrophilic minerals with time-related variation of pyrite floatability, especially for evaluating the crucial factor of influencing pyrite floatability. Meanwhile, the incipient adsorption Ca/Mg-bearing species on the pyrite surface, which is suggested to be highly associated with pH and electrostatic interaction, should also be meticulously discussed.

This study investigated the time-related effect of exogenous Ca/Mg on pyrite floatability with prolonged pre-oxidation time in consideration of localized coprecipitation of secondary minerals and its depression characteristics to pyrite flotation. To analyze the interaction among the adsorption/precipitation of Ca/Mg-bearing species and xanthate onto pyrite surface, a time-related single-mineral floatability test and zeta potential analysis were established. SEM-EDS and XPS analysis were applied to investigate the surface morphology, secondary minerals distribution and chemical compositions of differently treated pyrite samples after prolonged pre-oxidation at pH 9 and 10.5. The effect of Ca/Mgbearing precipitates on pyrite oxidation and in-situ reprecipitation characteristic of iron oxides/oxyhydroxides was quantitively analyzed via extraction tests using ethylenediaminetetraacetic acid (EDTA) [30,31]. Such an investigation would benefit to evaluate the effect of localized coprecipitation of secondary minerals on pyrite floatability with prolonged pre-oxidation in view of multiple-stage flotation of mixed metal sulfides and cyclic utilization of process water, and provide an insight of combining surface morphology, chemical adsorption/complexation with floatability researches. The study will benefit the optimization of the industrial flotation process from a lab-scale research perspective.

2. Materials and Methods

2.1. Materials and Reagents

Pyrite samples were obtained from Hanaoka Mine, Akita Prefecture, Japan. X-ray diffraction analysis (XRD; Smart lab, Rigaku Corporation, Tokyo, Japan) reflected the existence of pyrite (Figure S1), and X-ray fluorescence analysis (XRF; ZSX Primus2, Rigaku Corporation, Tokyo, Japan) indicated pyrite samples were around 95% purity with minor amounts of Si, Ca and Al-bearing gangues (Table S1). Anhydrous CaCl₂ and MgCl₂, 1 M HCl, 1 M NaOH, and 50% (*w*/*v*) NaOH were used for electrolyte and pH adjustment. EDTA solution was used for iron (oxy)hydroxides extraction and 4-methyl-2-pentanol was used as a foaming agent in floatability tests. These reagents were all analytical grade and purchased from Wako Pure Chemical Industries (Osaka, Japan). Potassium amyl xanthate (PAX; >97% purity) was purchased from Tokyo Chemical Industry (Tokyo, Japan). Standard solution of Ca²⁺/Mg²⁺ (1000 ppm) was prepared by thoroughly mixing 2.770 g of anhydrous CaCl₂ or 3.917 g of anhydrous MgCl₂ with 1 L of deionized water in a 1-L volumetric flask, respectively.

2.2. Pretreatment of Pyrite

The pyrite samples were sieved to 106–150 µm after crushing and grinding in a jaw crusher and ball mill. Before the experiments, the surface impurities of pyrite were removed based on methods described in previous reports with slight changes [32]. Pyrite samples of approximately 3 g were rinsed with 50 mL 6 M HCl (previously heated to 70 °C) for 10 min at room temperature and then with 1:1 acetone-water (v/v) for 2 min at room temperature. The solid residue was subsequently freeze-dried under vacuum for 12 h and encapsulated in oxygen-free conditions before each experiment.

2.3. Pyrite Pre-Oxidation and Floatability Experiment

Each pyrite pre-oxidation experiment was performed by mixing 0.5 g of clean pyrite sample with 100 mL of prepared solution in a 250-mL plastic beaker with magnetic stirring at 700 rpm at 25 °C under atmospheric conditions. Herein, the Ca/Mg-free solutions consisted of 0.05 M NaCl, which was attained by mixing 5 mL of HCl and 5 mL of NaOH in a 100-mL volumetric flask then was replenished until 100 mL with deionized water. The Ca/Mg-bearing solution used 0.025 M (100 ppm) Ca²⁺ or 0.041 M (100 ppm) Mg²⁺ provided by 1000 ppm Ca²⁺/Mg²⁺ standard solution in addition to the steps to prepare the Ca/Mg-free solution. Before the experiments, the pH of each prepared solution was rapidly adjusted to the specified value by the addition of HCl and NaOH solution with 3 min of conditioning. The pH of each reaction system was maintained within \pm 0.2 of the initial pH values during the entire reaction process. After oxidation, each suspension was filtered on 0.1-µm mixed cellulose filter paper and the solid residue was freeze-dried before surface characterization test.

The floatability tests were performed using a 100-mL Hallimond tube. Each 100 mL of the pyrite suspensions after pre-oxidizing for selected time was used as the floatation feed, 0.1 mL of 0.025 M PAX solution was directly added into each suspension after pre-oxidation followed by 10 μ L of 4-methyl-2-pentanol with 3 and 1 min of conditioning, respectively, at the same stirring speed. Each mixture was transferred into the Hallimond tube with gas purging (gas content: 79 v/v% of N₂ and 21 v/v% of O₂, gas flow rate: 0.2 L·min⁻¹). The flotation time was fixed at 2 min and the recovery of the concentrate was calculated according to Equation (1):

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$$R = \frac{m_1}{m_0} \tag{1}$$

where *R* is the concentrate recovery (%); m_1 is the dry weight of froth product (g), and m_0 is the initial pyrite mass. Each floatability test was performed three times.

2.4. Surface Characterization of Pyrite

The zeta potential of the pyrite surface was measured using a zeta potential analyzer (Nano ZEN 2600, Malvern Instruments, Malvern, Worcestershire, UK). Each zeta potential measurement was performed by mixing 1 g of cleaned pyrite sample with 100 mL of Ca/Mg-bearing or Ca/Mg-free solution at selected pH at 25 °C for 30 min with stirring. To determine the influence of PAX adsorption on the surface electro properties of pyrite, 1 mL of 0.025 M PAX solution was added into each suspension after stirring for 27 min then stirred for another 3 min. The pH of the reaction was maintained within \pm 0.2 of the selected pH conditions. After reaction, about 3 mL of suspension was rapidly collected by syringe then injected into a quartz tube for zeta potential measurement. The test of each condition was performed three times.

A thermal field emission scanning electron microscope (FE-SEM; JSM-6500F, JEOL, Tokyo, Japan) equipped with an energy dispersive spectrometer (EDS; JED-2300F, JEOL, Tokyo, Japan) was used to investigate the morphology and elemental distribution of pyrite surface. The accelerating voltage of the scanning electron microscope was set to 15 kV using a secondary electron model.

The surface chemical compounds of pyrite samples were analyzed by XPS (JPS-9010, JEOL, Tokyo, Japan) using monochromatic Al K α X-rays (1486.6 eV) operated at 600 W, where the standard C1s binding energy of 284.8 eV was utilized to calibrate each spectrum.

Each EDTA extraction test was conducted by blending 0.5 g oxidized pyrite sample and 40 mL of 0.2 M EDTA solution in an enclosed 50-mL plastic jar with the pH maintained at pH 7.5 \pm 0.2. After agitation at 300 rpm for 1 h, each suspension was filtered on 0.1-µm mixed cellulose filter paper and the extractable Fe in the filtrate was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES; Agilent 5100; Agilent, Santa Clara, CA, USA). The test of each condition was performed three times.

3. Results and Discussion

3.1. Floatability of Pyrite

The floatability of pyrite samples after different pre-oxidation treatments is summarized in Figure 1. In Ca/Mg-free solution, the pyrite flotation recovery slightly declined from 78.0% at pH 9 to 73.7% at pH 10.5 with 30 min of conditioning, decreased to 76.7% and 69.6% within 120 min of conditioning, and was reduced to 75.1% and 67.0% with 360 min of conditioning at pH 9 and pH 10.5, respectively. This may be due to the insufficient accumulation of hydrophilic species on the pyrite surface. However, when pyrite was oxidized in Ca-bearing solution, the pyrite recovery was sharply reduced from 77.5% after 30 min to 56.3% after 360 min of conditioning at pH 9. In addition, it decreased less markedly from 55.8% after 30 min to 47.3% after 360 min of conditioning at pH 10.5. Similarly, in the Mg-bearing solution, the pyrite recovery decreased substantially from 66.6% after 30 min to 46.1% after 360 min of conditioning at pH 9, while it decreased sharply to 30.1% after initial 30 min and slightly decreased to 28.0% after 360 min of conditioning. Notably, the pH-related pyrite depression was faint with 30 min of conditioning at pH 9 but was remarkably enhanced with same conditioning time at pH 10.5 in Ca/Mg-bearing solutions. It was apparent that incipient adsorption status was crucial to the depression of pyrite, which may be associated with the more stable adsorption of positively-charged Ca/Mg hydroxy species like CaOH⁺ and Mg(OH)₂ at pH 10.5 rather than pH 9 considering the stronger surface electronegativity of pyrite at higher pH [12,33]. Meanwhile, the further precipitation of Ca/Mg-bearing species may favor these pre-occupied sites and show a weak time-related passivation effect to pyrite floatability. The faint depression at pH 9 during initial 30 min may be caused by the weak initial occupation of these specific sites on the pyrite surface, while it was gradually enhanced when enlarging the pre-oxidation time as shown in Figure 1.



Figure 1. Floatability of pyrite after reaction in Ca/Mg-free solution and Ca/Mg-bearing solution at pH 9 and pH 10.5 with aeration times of 30 min, 120 min, and 360 min. The values and error bars show the mean values and ranges of duplicates.

3.2. Electrostatic Properties of Pyrite Surface

Pyrite floatability results in Figure 1 suggested the incipient solution conditions (especially the pH variation and Ca/Mg existence) rather than pre-oxidation time, showed a stronger influence determining the ceiling of pyrite floatability. Thus, the adsorption behavior of Ca/Mg-bearing species in incipient 30 min may play a vital role in influencing pyrite floatability, while the xanthate adsorption is suggested to be influenced and could be reflected by the zeta potential analysis of pyrite surface as shown in Figure 2 [29,34]. Herein, the pyrite surface showed a zeta potential of -31.8 mV at pH 9 and -34.4 mV at pH 10.5 in Ca/Mg-free solution after 30 min of conditioning. In Ca-bearing solution, pyrite surface showed a zeta potential of -2.82 mV at pH 9 and -1.36 mV at pH 10.5 after 30 min of conditioning. Meanwhile, pyrite surface showed a zeta potential of -9.89 mV at pH 9 and 12.9 mV at pH 10.5 after 30 min of conditioning in Mg-bearing solution. The pyrite surfaces exhibited large divergence of zeta potential in Ca/Mg-free solutions with and without PAX conditioning, which were 19.8 mV at pH 9 and 8.80 mV at pH 10.5, respectively. However, after conditioning in all Ca/Mg-bearing solutions, pyrite surface showed close and slight divergence of zeta potential around 4–5 mV with and without PAX conditioning regardless of pH conditions or ionic environment. Although the surface electrostatic repulsion of pyrite to xanthate anions was weakened by the pre-adsorbed Ca/Mg-bearing species as reflected in Figure 2, it indicates that PAX adsorption may be preferred on the same specific adsorption sites of Ca/Mg-bearing species on the pyrite surface.



Figure 2. Zeta potentials of pyrite surfaces after reaction in Ca/Mg-free solution and Ca/Mg-bearing solution at pH 9 and pH 10.5 with aeration time of 30 min. PAX, potassium amyl xanthate.

3.3. Equilibrium Calculation of Ca/Mg-Bearing Species

The metastable species distribution of the Ca/Mg-H₂O system in equilibrium with air atmosphere at 25 °C was calculated by Visual MINTEQ ver. 3.1 software (KTH, Stockholm, Sweden) (pH-log C diagrams showed in Figure 3). The initial solutions were CO_2 free, but during the entire reaction under air atmosphere, the continuous dissolution of CO_2 into solutions during prolonged reaction process should be considered. Especially, in alkaline and Ca-bearing conditions, the formation of hydrophilic CaCO₃ and its precipitation on the pyrite surface can depress pyrite flotation [6]. The CO_2 partial pressure used in related thermodynamic calculations was fixed at 3.8×10^{-4} atm until the gas-liquid dissolution equilibrium of CO₂ at selected aqueous conditions [6,11]. The calculation results (Figure 3) were consistent with the results reported in previous research, while $CaCO_3$ and $Mg(OH)_2$ were calculated as the main Ca/Mg-bearing species when the pH was higher than 8.4 and 9.9, respectively [6,11,35]. Previously, Zhang et al. [36] reported the zeta potential of synthetic CaCO₃ with a CaCl₂: Na₂CO₃ ratio of 2:1 was around 10 mV at pH 9 and 8 mV at pH 10.5, meanwhile, that of Mg(OH)₂ with a MgCl₂: NaOH ratio of 1:2 was around -10 mV at pH 9 and 10 mV at pH 10.5. Thus, the charge inversion of pyrite surface in Mgbearing solutions from pH 9 to 10.5 (Figure 2) can be ascribed as the vigorous adsorption of positive-charged Mg(OH)₂ on the pyrite surface [12]. Meanwhile, CaCO₃ dominates the Ca-bearing species when pH is over 8 with limited CaOH⁺ (lower than 10^{-8} M), while MgOH⁺ shows a concentration over 10⁻⁵ M when pH is over 9 and almost precipitates as $Mg(OH)_2$ when pH is over 9.9 (Figure 3). The pyrite surface in Ca-bearing solution was still negatively-charged at pH 9 and pH 10.5 without an evident charge inversion. It could be suggested that the incipient adsorption status of these hydrophilic Ca/Mgbearing species depends on pH conditions, which are crucial to limiting the ceiling of pyrite depression as reflected in Figures 1 and 3. In alkaline conditions, a higher pH leads to a stronger surface electronegativity of pyrite and benefits the adsorption of positively charged Ca/Mg-bearing species herein [33,37,38]. Moreover, the more prominent depression of pyrite in Mg-bearing solution than in Ca-bearing solution at pH 10.5 may be ascribed to the more rapid and vigorous precipitation of Mg(OH)₂ (K_{sp} = $1.2 \times 10^{-11} \text{ mol}^2 \cdot \text{L}^{-2}$) than CaCO₃ (K_{sp} = 6.7×10^{-7} mol²·L⁻²) on the hydroxylated metal sulfide surface via acid-base complexation among metal hydroxy species [11,12,39,40]. The alleviation of

pyrite surface electronegativity in Ca/Mg-bearing solutions is suggested to decrease the electrostatic repulsion among pyrite surface and negative-charged species in solutions [12,38]. Thus, the dissociative species like $Fe(OH)_3$ and $Fe(OH)_4^-$ are expected to preferentially precipitate at Ca/Mg-loaded area of pyrite surface, which will be further discussed in the later section [22].



Figure 3. Metastable distribution of Ca-bearing species (**a**) and Mg-bearing species (**b**) in aqueous and aeration conditions with fixed CO₂ partial pressure of 3.8×10^{-4} atm at 25 °C.

3.4. Morphology and Chemical Characterization of Secondary Minerals on the Pyrite Surface

To verify our conjecture of specific adsorption/precipitation characteristics of secondary hydrophilic minerals on the pyrite surface and their effect on pyrite depression, the FE-SEM-EDS analysis results are compiled and summarized in Figure 4 and Table 1. The EDS elements mapping and point analysis were proved available to schematically distinguish the distribution characteristics of secondary minerals on the pyrite surface, as they are the main source of surface oxygen element [41]. Moreover, the localized distribution of hydrophilic species means a weaker hydrophilic modification than their uniform coverage on the pyrite surface when involved in the prolonged surface precipitation of secondary hydrophilic minerals herein [12,18]. When pyrite oxidized in Ca/Mg-free solution for 360 min (Figure 4a), unoxidized areas appeared to dominate the bulk of the pyrite particle surface with sparse and patched iron oxides/oxyhydroxides. Meanwhile, when pyrite oxidized in Ca/Mg-bearing solution for 360 min, Ca/Mg-bearing aggregates with closely concomitant oxygen suggested a strong affinity between Ca/Mg-bearing minerals and iron oxides/oxyhydroxides on oxidized pyrite surfaces, which was supported by the EDS mapping results in Figure 4b,c. Further EDS point analysis results (Table 1) indicated that the pristine area without slime coating on the pyrite surface showed a negligible presence of oxygen, which was consistent with a previous report [41]. When continuously contacting with Ca/Mg-bearing species, the pyrite surface is oxidatively-dissolved and stabilizes Ca/Mg-bearing species simultaneously from the bulk solution. The region of higher surface energy caused by the localized cleavage, atomic defects, and chemical bonding breakage plays a vital role in both of aforementioned processes as discussed in previous researches [24,41,42]. It could be found in Figure 4 that the adsorbed Ca/Mg-bearing species not only promotes their steady precipitation from bulk solution and forms the stable "skeleton" of Ca/Mg-bearing minerals [15], but benefits to the reprecipitation of dissolved iron hydroxy species as iron oxides/oxyhydroxides [6]. The surface adsorption/reprecipitation mechanism can be first elaborated by the "surface hydrolysis + species precipitation" or a "cementation" effect [14,42]. The hydroxylated pyrite surface shows as the localized distribution of Fe hydroxy groups (Fe-OH) [37]. The immigration of Ca/Mg-bearing species like $CaCO_3$, $CaOH^+$, $MgOH^+$, and $Mg(OH)_2$ to pyrite surface was promoted by electrostatic interaction. Subsequently, the continuous precipitation of aforementioned Ca/Mg-bearing species via acid-base complexation could easily combine with dissolved iron hydroxy species such as amorphous ferrihydrite and $Fe(OH)_4^-$ in such high alkaline conditions likewise [43–46].

The XPS spectra of pyrite surface after 360 min of pre-oxidation in selected aqueous conditions are shown in Figure 5. The existence of CaCO₃ at 351.2 eV and 347.6 eV was confirmed in Figure 5a, while the prominent Mg-OH peak (49.4 eV) was observed at both pH 9 and 10.5 in Figure 5b [7,47]. Figure 5c–e shows the Fe (II)-S peak at 706.7 eV and the surface defect peak at 708.1 eV. Here, the satellite peaks of Fe (III)-O/OH distributed from 709.0 to 714.0 eV indicated the accumulation of secondary iron-bearing minerals on the pyrite surface [6,48-51]. Generally, the formation of iron oxides/oxyhydroxides from pyrite oxidation occurs through a process of "surface oxidative dissolution, combination with hydroxy ions, reprecipitation, and recrystallization" in alkaline conditions, where the surface Fe(II) of pyrite oxidatively dissolves and combines with OH⁻ as amorphous ferrihydrite, $Fe(OH)_3$, and $Fe(OH)_4^-$ in highly alkaline conditions before being reprecipitated as ferric (oxy)hydroxides after further structural rearrangement and dehydration [22,45,52]. On the other hand, the apparent accumulation of Ca/Mg-bearing minerals on the pyrite surface provides an abundance of Ca/Mg hydroxy groups, which can stabilize more amorphous ferrihydrite, $Fe(OH)_3$, and $Fe(OH)_4^-$ from the bulk solution to the adjacent area of Ca/Mg-bearing precipitates as reflected in Figure 5c–e.





Figure 4. SEM images and EDS mapping results of pyrite surface oxidized in Ca/Mg-free solution (a), 0.025 M Ca solution (b) and 0.041 M Mg solution (c). Conditions: 360 min of aeration time, pH 10.5. EDS mapping results of (a-1) Fe element, (a-2) S element, (a-3) O element on Ca/Mg-free oxidized pyrite surface; (b-1) Fe element, (b-2) S element, (b-3) Ca element, (b-4) O element on Ca-loaded oxidized pyrite surface; (c-1) Fe element, (c-2) S element, (c-3) Mg element, (c-4) O element on Mg-loaded oxidized pyrite surface. "+" as the sites of EDS points analysis, number "1–7" represents each EDS point analysis.



Figure 5. XPS spectra of Ca 2p (a), Mg 2p (b) and Fe 2p3/2 (c–e) after 360 min of aeration.

Points	Atomic Ratio (%)							
	Ca	Mg	Fe	>S	0	Si	С	
1	1.55		8.81	14.63	7.12		67.88	
2			20.69	30.29			48.52	
3			20.26	29.33			50.41	
4	10.27		3.97	7.39	19.56		58.80	
5			22.21	31.34			46.25	
6		1.29	15.71	22.46	5.34		55.19	
7		3.11	10.42	13.52	14.13	1.81	57.02	

Table 1. EDS points analysis of oxidized pyrite surface.

Meanwhile, Table 2 shows the Fe extracted by EDTA solution from oxidized pyrite quantitatively verifies the stronger accumulation of extractable Fe in Ca/Mg-bearing solutions rather than in Ca/Mg-free solutions at both pH 9 and 10.5, which supports the atomic ratio of Fe(III)-O/OH in Table S4. Notably, more Fe was obtained from pyrite samples that had been oxidized in Mg-bearing solution than from samples oxidized in Ca-bearing solution after 360 min of conditioning at pH 9 and 10.5. This phenomenon could be explained as the more apparent adsorption of Mg(OH)₂ than CaCO₃ on the pyrite surface as suggested by zeta potential results, and likely, provided more acid–base reaction sites and was more beneficial to the reprecipitation of ferric hydroxy species from bulk solution. Consequently, even the surface accumulation of secondary hydrophilic minerals was enhanced during the prolonged pre-condition process; it could be explained that the localized distribution and obvious concomitant relationship among these secondary Ca/Mg/Fe-bearing minerals, was attributed to cause the faint decline of pyrite floatability from the incipient 30 min to a prolonged 360 min of pre-oxidation.

Table 2. Concentration of surface extracted-Fe (μ mol·g⁻¹ pyrite) after 360 min aeration of pyrite in selected conditions.

pН	Ca/Mg-Free	Ca-Bearing	Mg-Bearing
9	2.77	5.18	11.9
10.5	5.93	6.98	19.7

3.5. Relationship among Secondary Minerals Accumulation, Xanthate Adsorption and Time-Related Pyrite Depression

The precipitation characteristics of secondary minerals during prolonged pre-oxidation process and their effect on subsequent xanthate adsorption and pyrite floatability, are elaborated in Figure 6. Pyrite exhibits a heterogeneous reactivity to its surface hydrolysis, oxidation and substance adsorption due to the high surface energy caused by localized cleavage, atomic defects, and chemical bonding breakage [24]. These active sites can be more easily oxidized and hydroxylated then occupied by secondary hydrophilic minerals as the bulk of pyrite surface is less sensitive to the surface reactions [22,28,52,53]. Although the adsorption of Ca/Mg-bearing species in alkaline conditions elevated the pyrite surface electro positivity as shown in Figure 2, the adsorption of xanthate anions was still weakened instead. It could be explained as xanthate anions favor the transport from bulk solution then are aggregated near high physiochemically active sites to form hydrophobic dixanthogen, while these hydroxylated sites have been partially occupied by loaded Ca/Mg hydroxy species. Hence, it can be inferred that the pyrite floatability could still be controlled by the colloidal secondary hydrophilic precipitates where even the bulk of pyrite surface is noble.

- active sites
- of amyl xanthate (blue line as alkyl chain, yellow bottom as hydrophilic part)
- 🎸 di-xanthogen
- dissolved iron (hydroxy-) species
- ferric amyl (hydroxy-)xanthate
- Ca/Mg-bearing species: CaOH⁺, surface hydrolyzed CaCO₃, MgOH⁺, Mg(OH)₂

(Xanthate adsorption on pristine pyrite surface)



(Pre-oxidation in Ca/Mg-free solutions: weaker pyrite depression)



(Pre-oxidation in Ca/Mg-bearing solutions: stronger incipient pyrite depression and subsequent its slight enhancement)



Figure 6. Influence of surface adsorption/precipitation of Ca/Mg-bearing species on pyrite flotation depression.

In Ca/Mg-free solution, the weak depression effect on pyrite floatability alongside a faint decline with ever-increased pre-oxidation time, may be due to the insufficient accumulation of hydrophilic iron oxides/oxyhydroxides without the synergistic immobilization by Ca/Mg-bearing precipitates on the pyrite surface. From Ca/Mg species distribution calculation (Figure 3) and XPS analysis results (Figure 5a,b), the existence of $CaCO_3$ and $Mg(OH)_2$ as two of dominant Ca/Mg-bearing species on the pyrite surface was confirmed, respectively. Apart from the Ca/Mg hydroxy species, the accumulation of CaCO₃ on the pyrite surface is also suggested to enhance the pyrite surface hydrophilicity then inhibit pyrite flotation [6,11]. At the incipient stage of pyrite pre-oxidation, it could be suggested the CaOH⁺ and MgOH⁺ first rapidly occupy the active sites on the pyrite surface, and depress the xanthate collector adsorption [24,29]. When enlarging the pre-oxidation time in alkaline conditions, the dominant Ca-bearing species (CaCO₃) and Mg-bearing $(Mg(OH)_2)$ favor the continuous coaggregation upon these Ca/Mg pre-loaded sites on the negative pyrite surface alongside the nucleation herein, further increasing the pyrite surface hydrophilicity [9,14,15,42,46]. The specific accumulation of secondary hydrophilic Ca/Mg/Fe-bearing minerals leads to a slightly increased hydrophilic coverage upon the pyrite surface, thus a slowly decreased pyrite floatability with increasing preoxidation time. Furthermore, a higher pH (10.5) means a higher surface negative charge and weaker repulsion to the adsorption of positive-charged CaOH⁺, CaCO₃ and Mg(OH)₂ on the pyrite surface. Meanwhile, the lower K_{sp} of $Mg(OH)_2$ than of CaCO₃ means a more stable existence of the former and its more rapid precipitation on pyrite surface [12,39]. Thus, the former performed a stronger depression effect than the latter while the surface accumulation of Mg-bearing species is more advantageous than that of Ca-bearing species throughout the selected reaction conditions.

4. Conclusions

In this study, the precipitation characteristics of secondary minerals during prolonged pre-oxidation (30, 120, and 360 min) process and its time-related depression characteristics to pyrite floatability were investigated. In Ca/Mg-bearing solutions, the higher pH (10.5) led to a more negative pyrite surface, stronger surface hydroxylation and Ca/Mg precipitation, which all benefit the incipient depression of pyrite within 30 min whereas a slight decline of pyrite floatability occurred when enlarging the conditioning time to 120 min and 360 min. Zeta potential analysis suggested that xanthate adsorption occur preferentially at specific reaction sites of Ca/Mg adsorption/precipitation on the pyrite surface, considering its affinity to these hydroxylated highly reactive sites. Surface characterization analysis reflected the contaminant precipitation of secondary minerals together with the promotion of iron oxyhydroxides immobilization by hydroxylated Ca/Mg-bearing minerals. By aforementioned analysis, the incipient 30 min of Ca/Mg adsorption status determined the ceiling of pyrite floatability, which was mainly controlled by pH conditions, and consequent metastable distribution of Ca/Mg-bearing species and their electrostatic interaction with the pyrite surfaces. The xanthate adsorption was initially limited especially at pH 10.5 due to its competitive adsorption with coexisting Ca/Mg-bearing species on the pyrite surface, as reflected by zeta potential analysis. The subsequent co-precipitation of Ca/Mg/Fe-bearing species preferentially happens at these Ca/Mg-loaded area on the pyrite surface. Thus, even the pre-oxidation time is prolonged, and the continuously localized precipitation of secondary Ca/Mg/Fe-bearing minerals on the pyrite surface led to a slight enhancement to pyrite depression. This study helps to determine the significant indexes that strongly influence the pyrite floatability considering the utilization of process water and pre-oxidation treatment, and clarify related mechanisms combining with a series of surface analysis methods (Zeta potentials, SEM-EDS and XPS). To explore the optimal conditions that realize the high-effective pyrite depression in multi-index flotation systems, this study provides some beneficial results from a lab-scale research.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/ 10.3390/min12020115/s1, Figure S1: The XRD pattern of pyrite samples, Table S1: The XRF results of pyrite samples, Table S2: Floatability of pyrite after reaction in Ca/Mg-free solution and Ca/Mgbearing solution at pH 9 and pH 10.5 with aeration time of 30 min, 120 min, and 360 min, Table S3: Zeta potentials of pyrite surfaces after reaction in Ca/Mg-free solution and Ca/Mg-bearing solution at pH 9 and pH 10.5 with aeration time of 30 min, before PAX condition of 3 min, Table S4: Zeta potentials of pyrite surfaces after reaction in Ca/Mg-free solution and Ca/Mg-bearing solution at pH 9 and pH 10.5 with aeration time of 30 min, after PAX condition of 3 min, Table S5: Binding energies and atomic ratios of Fe 2p3/2 species after pyrite oxidizing in selected conditions

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