

Article

Oxidative Depression of Arsenopyrite by Using Calcium Hypochlorite and Sodium Humate

Shangyong Lin ^{1,2}, Runqing Liu ^{1,2,*}, Yongjie Bu ^{1,2}, Chen Wang ^{1,2}, Li Wang ^{1,2}, Wei Sun ^{1,2} and Yuehua Hu ^{1,2}

¹ School of Mineral Processing and Bioengineering, Central South University, Changsha 410083, China; linshangyong@csu.edu.cn (S.L.); yongjie_bu@csu.edu.cn (Y.B.); 165611065@csu.edu.cn (C.W.); li_wang@csu.edu.cn (L.W.); sunmenghu@csu.edu.cn (W.S.); hyh@csu.edu.cn (Y.H.)

² Key Laboratory of Hunan Province for Clean and Efficient Utilization of Strategic Calcium-Containing Mineral Resources, Central South University, Changsha 410083, China

* Correspondence: liurunqing@126.com; Tel.: +86-731-88836873

Received: 30 August 2018; Accepted: 15 October 2018; Published: 18 October 2018



Abstract: During smelting, arsenic in copper concentrates affects the product quality and causes environmental pollution. Removing arsenic minerals from copper concentrates requires environmental-friendly and cost-effective depressants for flotation separation. $\text{Ca}(\text{ClO})_2$ was combined with sodium humate (SH) to improve the flotation separation of chalcopyrite from arsenopyrite. Results of single-mineral flotation indicated that combined $\text{Ca}(\text{ClO})_2$ and SH significantly inhibited arsenopyrite and exerted a negligible effect on chalcopyrite. The arsenic content in copper concentrates significantly decreased from 63% to 11% in the absence of a depressant and in the presence of $\text{Ca}(\text{ClO})_2$ and SH, as proven by the mixed-mineral flotation results. SH can adsorb on both mineral surfaces as indicated by the zeta potential measurements and Fourier transform infrared spectroscopy. However, the presence of $\text{Ca}(\text{ClO})_2$ increased the adsorption of arsenopyrite compared with chalcopyrite. The arsenopyrite floatability depressed with the $\text{Ca}(\text{ClO})_2$ oxidation and subsequent SH adsorption, as verified by X-ray photoelectron spectroscopy. Results of flotation tests confirmed that the chalcopyrite surface was slightly oxidized, but it remained hydrophobic. The combination of depressants has the potential for industrial application.

Keywords: chalcopyrite; arsenopyrite; calcium hypochlorite; oxidation; sodium humate

1. Introduction

In natural environments, arsenic is a toxic element that is widely distributed [1]. The most abundant arsenic-containing mineral is arsenopyrite, which is also present in many mineral concentrates, such as copper [2,3]. In final copper products, high arsenic content is undesirable due to its high risks [4,5]. Flotation is one method of arsenic removal. Sulfide-ore-bulk flotation followed by selective copper flotation with the addition of arsenic sulfide depressants can also separate copper and arsenic ores via conventional flotation [6]. Flotation of arsenic separation from non-arsenic copper minerals routinely uses the mixture of sodium cyanide, lime, sodium hydrosulfide, sodium sulfite, and magnesium–ammonium [6–9]. However, environmental friendliness and technical and cost effectiveness are some factors that limit the industrial applications of most depressants. For example, a well-known arsenopyrite depressant is sodium cyanide [7]. However, its toxicity limits its application [10]. Lime can also be used as a depressant but usually requires large dosages [8]. Addition of a great amount of lime not only decreases chalcopyrite flotation rate and recovery but also increases plant operation costs [11].

In arsenopyrite depression, many new separation technologies were proposed to produce high-quality copper concentrates with low arsenic content. Changing the pulp pH [12], controlling the pulp potential [12,13], and developing a new selective collector or depressant are some of these technologies [14,15]. Potential-controlled flotation technology is the most successful approach [16]. Worldwide, this technology has been developed and employed in many copper, lead, and zinc sulfide mines [17]. However, controlling potential of pulp during flotation involves many factors [18]. Thus, obtaining high separation efficiency via the potential-controlled flotation is difficult.

Previous studies focused on using high-molecular-weight organic compounds to improve separation efficiency. Sodium humate (SH) is a cost-effective and environmental-friendly humic substance and is also a polymer with a high molecular weight ranging from 2 kDa to 1300 kDa [19]. The SH molecule structure is complex because of the presence of the carboxyl, phenolic hydroxyl, methoxy, and quinolyl groups [20]. This complex structure gives SH its hydrophilic characteristics and allows it to combine with heavy metals; this complex structure also adsorbs on mineral surfaces [21,22]. Recently, chalcopyrite and pyrite separation at Dexing Copper Mine successfully used SH as a pyrite depressant [23]. SH revealed a depressing effect on arsenopyrite but with a negligible effect on chalcopyrite [24,25]. However, the optimal separation between the chalcopyrite and arsenopyrite cannot be achieved by utilizing SH alone.

The arsenopyrite depression can be improved by oxidizing agents, such as hydrogen peroxide, potassium permanganate, and manganese dioxide [26–29]. The formation of a layer of oxidation products on the arsenopyrite surface caused the oxidation depression mechanism [30]. However, in mineral processing industries, high cost limits their use. Calcium hypochlorite ($\text{Ca}(\text{ClO})_2$) is an inexpensive and readily available oxidant; it is widely used in the industry [31]. We hypothesized that $\text{Ca}(\text{ClO})_2$ exhibits the same adverse effect on arsenopyrite and improves the SH depression performance by its addition to achieve selective flotation of chalcopyrite and arsenopyrite. To confirm this hypothesis, we employed $\text{Ca}(\text{ClO})_2$ to condition the arsenopyrite and to enhance the SH depression effect under mild alkaline conditions. The depression mechanisms were examined via Fourier transform infrared spectroscopy (FTIR), microflotation, zeta potential measurements, and X-ray photoelectron spectroscopy (XPS).

2. Materials and Methods

2.1. Materials

2.1.1. Minerals

Natural arsenopyrite and chalcopyrite specimens were provided from Guangdong and Yunnan Provinces in China, respectively. Dry grinding and then screening were used for the samples to collect the $-74\ \mu\text{m}$ to $38\ \mu\text{m}$ particle size fraction for flotation tests. The purities of chalcopyrite and arsenopyrite samples were 96% and 95%, respectively, as shown by mineralogical compositions. These samples were of high purity, as confirmed by X-ray diffraction analysis (Figure 1). A polyethylene bag was used to seal all the samples. Then, these samples were stored in a freezer to reduce the surface oxidation.

2.1.2. Reagents

For flotation tests, chemically pure sodium n-butyl xanthate (SBX, supplied by Aladdin Industrial, Shanghai, China) was the collector, SH (chemically pure, procured from Aladdin Industrial, Shanghai, China) was the depressant, $\text{Ca}(\text{ClO})_2$ (chemically pure, obtained from Kermel Company, Tianjin, China) was the oxidizing agent, and terpinol (chemically pure, purchased from Xilong Science, Guangzhou, Guangdong, China) was the frother. Analytical grade sodium hydroxide (NaOH) obtained from Xilong Science, Guangzhou, Guangdong, China and analytical grade hydrochloric acid (HCl), purchased from Zhuzhou Chemical Reagent, Zhuzhou, Hunan, China, were used to adjust the solution pH.

Throughout the experiment, ultrapure water with $18.2 \text{ M}\Omega\cdot\text{cm}^{-1}$ resistivity was used. Before each experiment, a fresh solution of each reagent was prepared in ultrapure water.

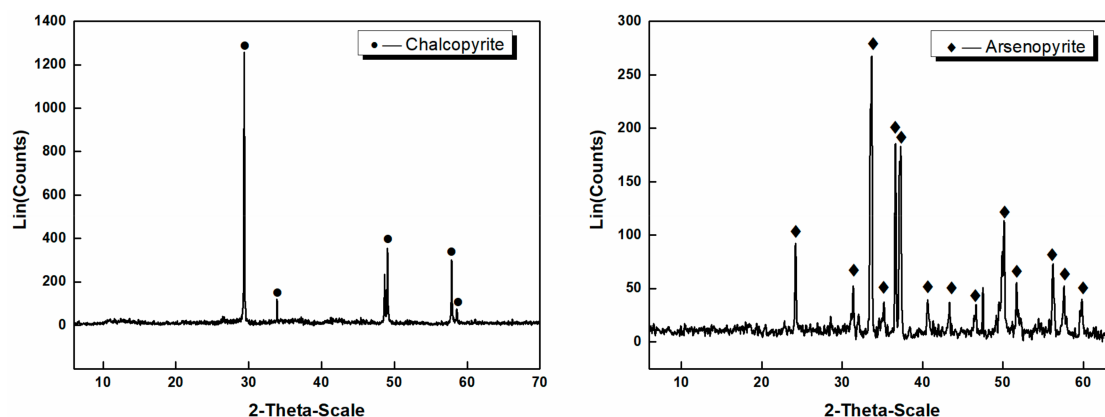


Figure 1. Chalcopyrite (CuFeS_2) and arsenopyrite (FeAsS) samples showing patterns of X-ray diffraction.

2.2. Methods

2.2.1. Flotation Study

An XFG flotation machine with a 40 mL, plexiglass cell was used for single-mineral flotation tests. The agitation speed was fixed at 1650 rpm. Chalcopyrite/arsenopyrite of 2 g was prepared before each test. In addition, an ultrasonic cleaner was used to clean the mineral sample for 5 min to remove the surface oxides. NaOH or HCl was utilized to adjust the mineral slurry pH value to the target value. Then, the reagents (oxidant, collector, depressant, and frother) were sequentially added, and the suspensions were conditioned for 2, 2, 3, and 1 min after the addition of each reagent. Flotation was performed for 4 min after the conditioning step. Subsequently, the froth and tailing fractions were collected and filtered separately, dried in a vacuum oven, and then weighed. The following equation was used to calculate the recovery of single-mineral flotation:

$$\varepsilon = \frac{m_1}{m_1 + m_2}$$

where ε represents the recovery; m_1 is the weight of solids in the froth; and m_2 indicates the weight of solids in the tailings.

Pure chalcopyrite and arsenopyrite with a mass ratio of 1:1 composed the sample during flotation of the artificially mixed mineral. The procedure of flotation was similar to that of single-mineral flotation. For mixed-mineral flotation, the recovery rates of each mineral were calculated from the X-ray fluorescence analysis results of copper and arsenic in the concentrates and tailings. The average of three measurements was obtained for each experiment. All tests were implemented in duplicate at ambient temperature.

2.2.2. Zeta Potential Measurement

A zeta potential analyzer (Malvern Zeta Sizer Nano Series, Malvern Panalytical Ltd., Great Malvern, UK) was used for zeta potential measurements. Approximately 0.02 g of fresh chalcopyrite/arsenopyrite sample was dispersed in 100 mL of $1.0 \times 10^{-3} \text{ M}$ KNO_3 electrolyte solution. The pH adjustments were made using dilute NaOH or HCl solutions. After pH stabilization, the supernatant was transferred to the zeta potential analyzer. Then, the potential was automatically measured. The existing electrophoresis-based technique resulted in a particle size of less than $5 \mu\text{m}$ of the sample. All zeta potential experiments were conducted at ambient temperature, open to atmosphere. The average of three independent measurements was the data obtained.

2.2.3. FTIR Spectroscopic Measurements

An infrared spectrophotometer (type NEXUS-670, Thermo Nicolet Co., New York, NY, USA) was used for FTIR spectral analyses. The experimental procedure for chalcopyrite/arsenopyrite samples (100% passing 5 μm) was performed similar to that of previously described [32]. At the desired reagent concentrations and corresponding pH, a chalcopyrite/arsenopyrite sample (2 g) was placed into a 50 mL aqueous solution. Subsequently, the suspension was stirred and then settled for 30 and 15 min, respectively. Finally, the suspension was filtered and washed thrice with ultrapure water. A vacuum oven was used to dry the treated sample. The pellets for FTIR spectroscopy were prepared by mixing 1 mg of the treated sample, and then, testing was performed with 100 mg of purified fine potassium bromide salt (KBr, potassium bromide, spectroscopic grade, supplied by Shanghai Chemical Reagent, Shanghai, China).

2.2.4. X-ray Photoelectron Spectroscopy

A K-Alpha 1063 spectrometer (Thermo Scientific Co., Waltham, MA, USA) at ambient temperature was employed to achieve the XPS results of the treated and untreated samples. Al K α X-ray source operated at 12 kV and 6 mA was used during the experiment. The pressure was 1.0×10^{-12} Pa in the analytical chamber during time analysis. To compensate for the surface charging effects, all binding energy calibrations were based on the C 1s peak at 284.8 eV. A pass energy of 100 eV and a step of 1 eV were used to collect the survey spectra. A pass energy of 30 eV and a step size of 0.1 eV were utilized to scan the various elemental regions. Ten sweeps at 100 ms dwell time for S 2p and 20 sweeps at 100 ms dwell for Fe 2p were also used. XPS Peak 4.1 software was used to analyze the data from the XPS tests.

3. Results and Discussion

3.1. Microflotation of Pure Mineral

For microflotation tests, SBX was used as collector, and terpinenol was used as frother. The effects of depressant dosage and pulp pH on the flotation recoveries of chalcopyrite and arsenopyrite were investigated. Results are presented in Figures 2–5.

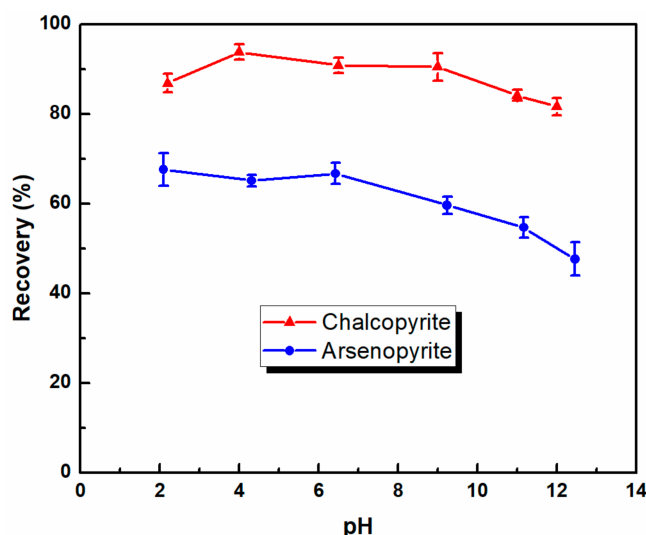


Figure 2. Flotation recovery of chalcopyrite and arsenopyrite as a pH function in the absence of sodium humate (SH) and $\text{Ca}(\text{ClO})_2$ ($C_{\text{SBX}} = 1.0 \times 10^{-4}$ mol/L, 2#oil = 15 mg/L).

Figure 2 displays the effect of pH on the flotation recovery of arsenopyrite and chalcopyrite in the absence of depressants. At approximately 90%, the flotation recovery of chalcopyrite remained in the pH range of 2–9 and then slightly decreased at pH values greater than 9. Arsenopyrite recovery

decreased with increasing pH, but it was maintained at >60% at pH values less than 9. Both chalcopyrite and arsenopyrite exhibited good floatability. The flotation separation between the chalcopyrite and arsenopyrite was hardly achieved in the absence of the depressant. pH 9 is the optimum pH for separating chalcopyrite from arsenopyrite.

Chalcopyrite recovery remained relatively constant at approximately 90% in the SH presence (Figure 3). Meanwhile, with the increasing SH dosage, the flotation recovery of arsenopyrite gradually decreased from 60% to 42%. Similarly, the arsenopyrite recovery continuously reduced to 40%, and that of chalcopyrite slightly decreased with the addition of $\text{Ca}(\text{ClO})_2$ (Figure 4). Combined results presented in Figures 3 and 4 indicated that SH and $\text{Ca}(\text{ClO})_2$ negatively affected arsenopyrite. However, single SH or $\text{Ca}(\text{ClO})_2$ can obtain satisfactory separation results in a difficult manner.

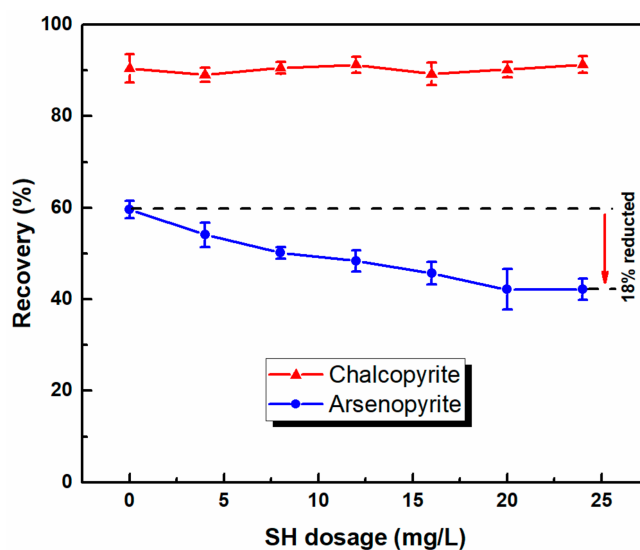


Figure 3. Flotation recovery of chalcopyrite and arsenopyrite as an SH dosage function ($C_{\text{SBX}} = 1.0 \times 10^{-4}$ mol/L, 2#oil = 15 mg/L and pH 9).

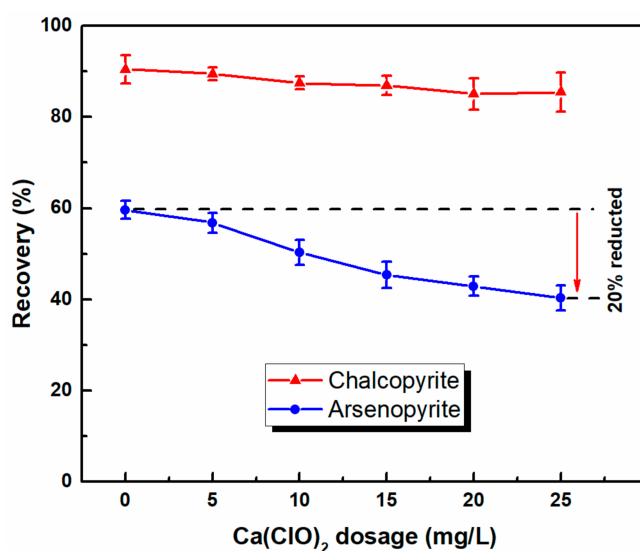


Figure 4. Flotation recovery of chalcopyrite and arsenopyrite as a $\text{Ca}(\text{ClO})_2$ dosage function ($C_{\text{SBX}} = 1.0 \times 10^{-4}$ mol/L, 2#oil = 15 mg/L and pH 9).

The use of only a single depressant cannot achieve a favorable separation performance. Therefore, $\text{Ca}(\text{ClO})_2$ and SH were combined. In addition, their synergistic depression effect on chalcopyrite and arsenopyrite separation was investigated. Figure 5 shows that the arsenopyrite depression was

enhanced to the pulp by $\text{Ca}(\text{ClO})_2$ addition. The arsenopyrite recovery decreased from 42% to below 10% with the increasing $\text{Ca}(\text{ClO})_2$ dosage in the presence of 20 mg/L SH, whereas that of chalcopyrite remained high. The use of SH and $\text{Ca}(\text{ClO})_2$ application as depressants possibly caused satisfactory separation of chalcopyrite and arsenopyrite.

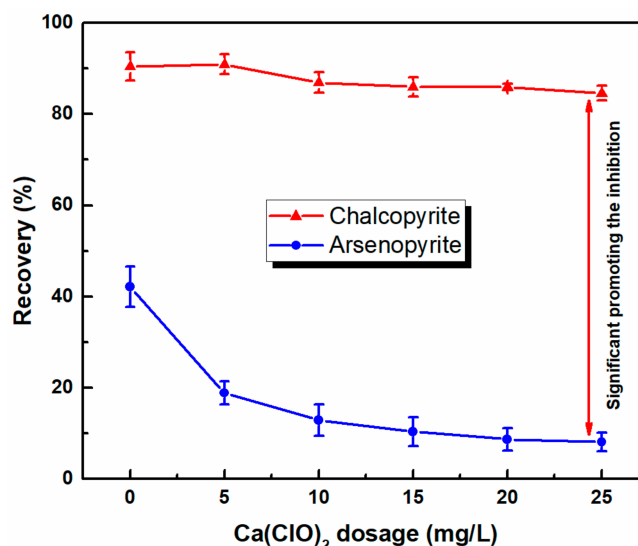


Figure 5. Flotation recovery of chalcopyrite and arsenopyrite as a $\text{Ca}(\text{ClO})_2$ dosage function in the presence of 20 mg/L SH. ($C_{\text{SBX}} = 1.0 \times 10^{-4}$ mol/L, 2#oil = 15 mg/L and pH 9).

3.2. Flotation Separation of Mixed Minerals

The effect of the combined depressant on the flotation of chalcopyrite and arsenopyrite was studied via an artificially mixed mineral flotation test. The process was similar to that in the single-mineral flotation experiment. The reagents $\text{Ca}(\text{ClO})_2$, SH, SBX, and 2#oil were sequentially added at dosages of 25 mg/L, 20 mg/L, 1.0×10^{-4} mol/L, and 15 mg/L, respectively. The artificially mixed-mineral flotation test was also conducted using tap water to simulate actual flotation. Table 1 shows the flotation results for the chalcopyrite and arsenopyrite mixtures (mass ratio of 1:1).

Table 1. Results of separation of chalcopyrite and arsenopyrite mixture samples.

Water	Depressant	Product	Yield (%)	Grade (%)		Recovery (%)	
				Cu	As	Cu	As
Ultrapure water	No depressant	Cu Concentrate	72.89	25.93	14.32	90.93	63.40
		As Concentrate	27.11	6.96	22.23	9.07	36.60
		Feed	100.0	20.79	16.46	100.0	100.0
Ultrapure water	Combination of SH and $\text{Ca}(\text{ClO})_2$	Cu Concentrate	52.87	34.55	3.54	88.51	11.45
		As Concentrate	47.13	5.03	30.72	11.49	88.55
		Feed	100.0	20.64	16.35	100.0	100.0
Tap water	No depressant	Cu Concentrate	72.12	26.07	14.67	90.88	62.98
		As Concentrate	27.88	6.77	22.31	9.12	37.02
		Feed	100.0	20.69	16.80	100.0	100.0
Tap water	Combination of SH and $\text{Ca}(\text{ClO})_2$	Cu Concentrate	51.34	34.98	3.89	87.80	11.99
		As Concentrate	48.66	5.13	30.12	12.20	88.01
		Feed	100.0	20.46	16.65	100.0	100.0

The experimental results obtained after using tap water displayed the same tendency as those obtained after using ultrapure water, as shown in Table 1. In the absence of depressant, approximately 90% of chalcopyrite and 63% of arsenopyrite were recovered. The arsenopyrite recovery sharply

decreased to approximately 12% in copper concentrate via the $\text{Ca}(\text{ClO})_2$ oxidation pretreatment and SH depression, whereas that of chalcopyrite slightly decreased to 88%. The combination of $\text{Ca}(\text{ClO})_2$ and SH as the depressant can achieve the selective separation of chalcopyrite from arsenopyrite.

3.3. Zeta Potential

Figures 6 and 7 show the zeta potentials of chalcopyrite and arsenopyrite as a pH function in the absence and presence of various reagents, respectively. Before the addition of each reagent, the zeta potentials of chalcopyrite and arsenopyrite at low pH values were positive, decreased to zero, and became negative with increasing pH. The isoelectric point (IEP) of chalcopyrite occurred at pH 2.7, in accordance with the test data plotted in the figures. This value was close to the value reported by Rath et al. [33]. The arsenopyrite IEP occurred at pH 2.5 [4].

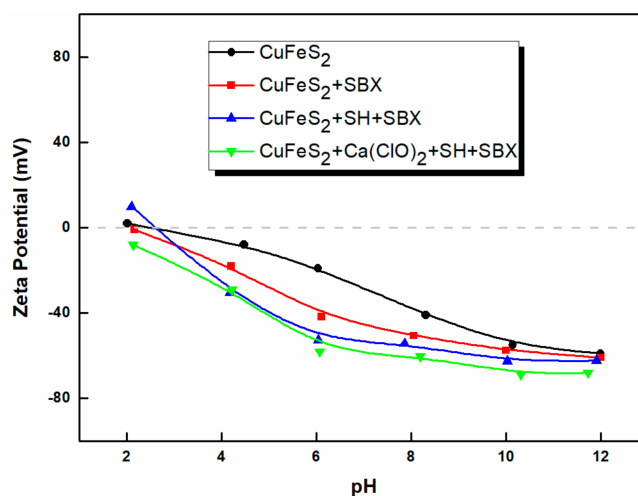


Figure 6. Zeta potential of chalcopyrite (CuFeS_2) with and without SBX (1.0×10^{-4} mol/L), SH (20 mg/L), and $\text{Ca}(\text{ClO})_2$ (20 mg/L).

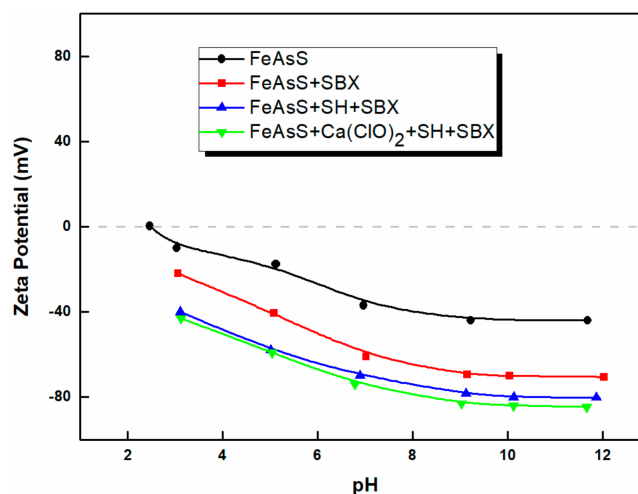


Figure 7. Zeta potential of arsenopyrite (FeAsS) with and without SBX (1.0×10^{-4} mol/L), SH (20 mg/L), and $\text{Ca}(\text{ClO})_2$ (20 mg/L).

After the addition of SBX, the zeta potential of chalcopyrite became more negative throughout the experimental pH range. This outcome was attributed to the increase in xanthate ion sorption [34]. The decline of the zeta potential of chalcopyrite in the presence of SBX and SH was minimal. SH did not strongly interact with chalcopyrite surfaces. This electrokinetic behavior of chalcopyrite correlated well with the industrial flotation results [34,35]. After the addition of $\text{Ca}(\text{ClO})_2$, the zeta potential

of chalcopyrite became slightly negative when the pH value exceeded 5, thereby suggesting that $\text{Ca}(\text{ClO})_2$ interacted weakly with chalcopyrite.

Figure 7 shows that SBX rendered the zeta potential of arsenopyrite more negatively. When xanthate ions were oxidized to dixanthogen on the arsenopyrite surface, negative zeta potential increased [36]. With SH, the zeta potential of arsenopyrite decreased sharply over the entire pH range. This significant decrement was related to the adsorption of SH, which possessed a molecular structure containing carboxylic acid functional groups [37]. After adding the $\text{Ca}(\text{ClO})_2$, the zeta potential of arsenopyrite become more negative at pH values higher than 5, thereby indicating that $\text{Ca}(\text{ClO})_2$ was strongly adsorbed on arsenopyrite.

3.4. FTIR Spectra of Chalcopyrite and Arsenopyrite

The FTIR spectra of chalcopyrite before and after treatment with reagents obtained in the wavenumber range of $4000\text{--}400\text{ cm}^{-1}$ are presented in Figure 8. Compared with the infrared spectrum of native chalcopyrite (Spectrum [a]), Spectrum (b) exhibited weak peaks at 2960.04 and 1711.39 cm^{-1} . The peak at 2960.04 cm^{-1} belonged to the asymmetrical stretching vibrations of alkyl group $-\text{CH}_3$ (inset A of Figure 8). The peak at approximately 1711.39 cm^{-1} (inset B of Figure 8) was assigned to the stretching vibrations of the $\text{C}=\text{O}$ group. Absorption occurred when SH interacted with chalcopyrite. Compared with spectra (a) and (c) between 1200 and 800 cm^{-1} (inset B of Figure 8), several characteristic peaks occurred at around 1197.42 , 1093 , and 1018.16 cm^{-1} . According to a literature [38], these peaks are the characteristic peaks of cupric xanthate. The peaks at 1197.42 and 1093 cm^{-1} corresponded to the $\text{C}-\text{O}-\text{C}$ asymmetric and symmetric stretching vibrations [38]. Meanwhile, the peak at 1018.16 cm^{-1} was attributed to the $\text{C}=\text{S}$ stretching vibration [39]. With $\text{Ca}(\text{ClO})_2$, SH, and SBX (Spectrum [d]), the characteristic peaks of SBX and SH coexisted, thereby suggesting that SBX and SH were adsorbed simultaneously on the chalcopyrite surface. The interaction between chalcopyrite and SBX or SH slightly affected $\text{Ca}(\text{ClO})_2$. This finding was consistent with the flotation results.

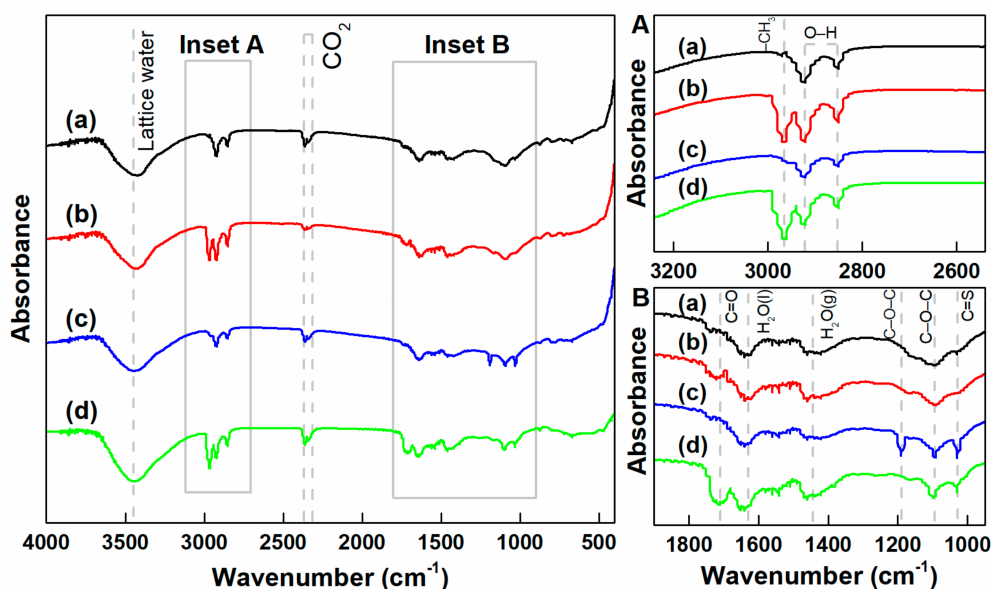


Figure 8. FTIR spectra of chalcopyrite before and after conditioning in the aqueous solutions of reagents: (a) Chalcopyrite; (b) Chalcopyrite + SH; (c) Chalcopyrite + SBX; and (d) Chalcopyrite + $\text{Ca}(\text{ClO})_2$ + SH + SBX.

Figure 9 shows the FTIR spectra of arsenopyrite before and after interacting with the reagent(s). After treatment with SH (Spectrum [b], inset A), the characteristic absorption band of $\text{C}-\text{O}-\text{C}$ (symmetrical stretching vibration) was at approximately 1021.48 cm^{-1} , and the weak $\text{C}-\text{S}$ peaks occurred at 667.08 and 600.88 cm^{-1} . All these characteristic peaks can be ascribed to the adsorption of

SH on the arsenopyrite surface. The symmetrical stretching vibration of $(\text{CH}_3)_2\text{CHR}$ at 1121.50 cm^{-1} belonged to butyl xanthate (Spectrum [c], inset A), thereby indicating that SBX was adsorbed on the arsenopyrite surface. Stable adsorption of dioxanthogen at the arsenopyrite/aqueous solution interface causes the arsenopyrite to float well [40]. With $\text{Ca}(\text{ClO})_2$, no new characteristic peaks in Spectrum (d) were observed compared with those in Spectra (b) and (c). Given that C–O–C peak intensity remarkably increased (1021.48 cm^{-1}), this peak belonged to the SH. Thus, with $\text{Ca}(\text{ClO})_2$, SH exhibited strong adsorption on the arsenopyrite surface. The observations of FTIR studies supported the result that arsenopyrite flotation was depressed with the addition of $\text{Ca}(\text{ClO})_2$.

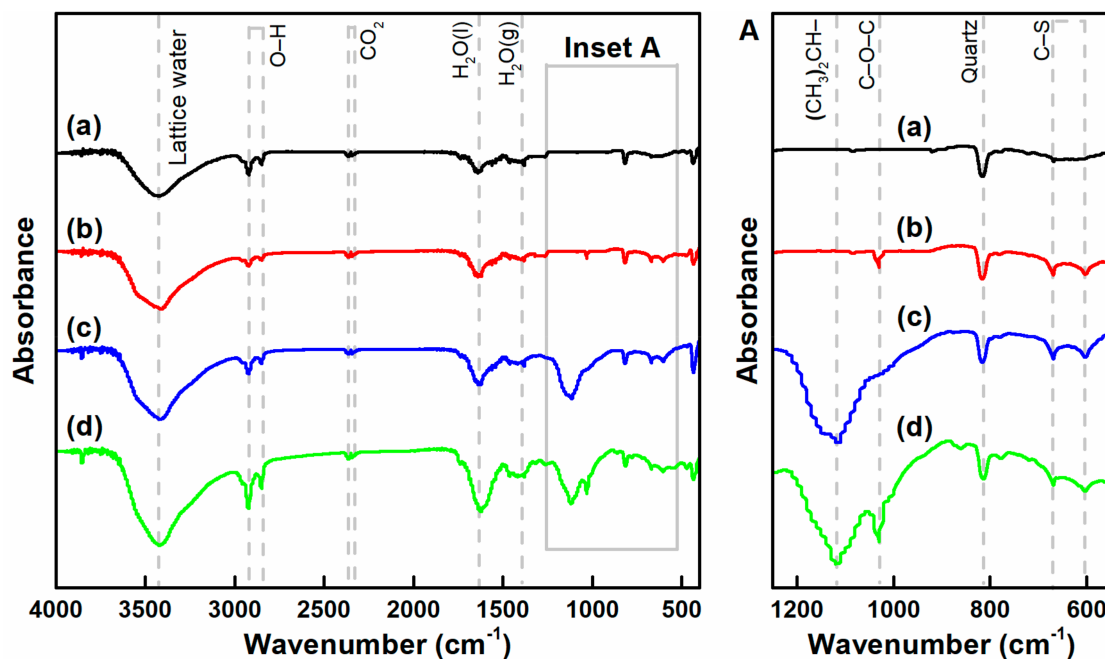


Figure 9. FTIR spectra of arsenopyrite before and after conditioning in the aqueous solutions of reagents: (a) Arsenopyrite; (b) Arsenopyrite + SH; (c) Arsenopyrite + SBX; and (d) Arsenopyrite + $\text{Ca}(\text{ClO})_2$ + SH + SBX.

3.5. XPS Study

To further elucidate the changes in the XPS spectra during interaction, we deconvoluted the spectra into individual components. Figure 10 shows the XPS spectrum of chalcopyrite from representative samples, namely, (A) Cu 2p, (B) Fe 2p, and (C) S 2p. Figure 11 shows the XPS spectrum of arsenopyrite from representative samples, namely, (A) As 3d, (B) Fe 2p, and (C) S 2p.

As illustrated in Figure 10A, the Cu 2p spectra were similar with or without conditioning with the flotation reagents. The binding energy peak of Cu 2p spectra at around 932.4 eV corresponded to Cu(I) in the sulfide lattice [41]. The remaining binding energy peak was assigned to the Cu $2p_{1/2}$ doublet due to the spin-orbit splitting (same FWHM, a 2:1 peak area ratio for Cu $2p_{3/2}$ and Cu $2p_{1/2}$). With the presence of cupric, a satellite peak subsequently appears around the binding energy of 942 eV [42]. Clearly, Figure 10A shows no evidence for the occurrence of such a satellite peak. The divalent state of Cu(II) was not found. Thus, SH and $\text{Ca}(\text{ClO})_2$ were not affected by the formation of cuprous xanthate on the chalcopyrite surface [43].

The Fe 2p spectra (Figure 10B) of the original chalcopyrite showed a low binding energy peak at around 708 eV arising from fully coordinated iron in bulk chalcopyrite, together with a broad peak at 712 eV representing Fe(III)–O species [44,45]. After treatment with $\text{Ca}(\text{ClO})_2$, the Fe(III)–S peak area remarkably declined and the peak shifted to higher binding energy (ca. 712 eV), conforming to the O 1s data reported in Figure 10D. These findings proved that the iron element of chalcopyrite was comparatively sensitive to oxidation, and the Fe(III) oxygen-containing species are the main oxidation

products on the surface of chalcopyrite. From Figure 10, it can be found that there was negligible difference on the trend of Fe 2*p* spectra with or without the addition of SBX or SH. Similar results were observed under mixed reagents condition.

The S 2*p* spectra (Figure 10C) of untreated chalcopyrite consisted of three major doublets. The binding energy peak centered at 161.5 eV was attributed to the monosulfide (S^{2-}) [46], the peak located at 162.5 eV conformed to disulfide (S_2^{2-}) [47], and the one at 169.0 eV matched the sulfate species [44]. In addition to the three S 2*p* doublets, another broad peak (FWHM = 2.3) was observed at 164.6 eV, which was previously related to energy loss [48,49]. Under the condition of SH, SBX, and mixed reagents, the proportion of S^{2-} remained at approximately 40%, whereas that of S_2^{2-} nearly remained unchanged at approximately 32%. With SH, the proportion of SO_4^{2-} slightly decreased, whereas that of SO_4^{2-} was unchanged. Meanwhile, with $Ca(ClO)_2$, the S^{2-} content decreased to 28%; conversely, the S_2^{2-} and SO_4^{2-} increased to 39% and 16%, respectively. In the presence of SH, the content of every component on the S 2*p* spectra was negligibly different, indicating that the adsorption of SH can reduce the oxidation of chalcopyrite surface caused by $Ca(ClO)_2$.

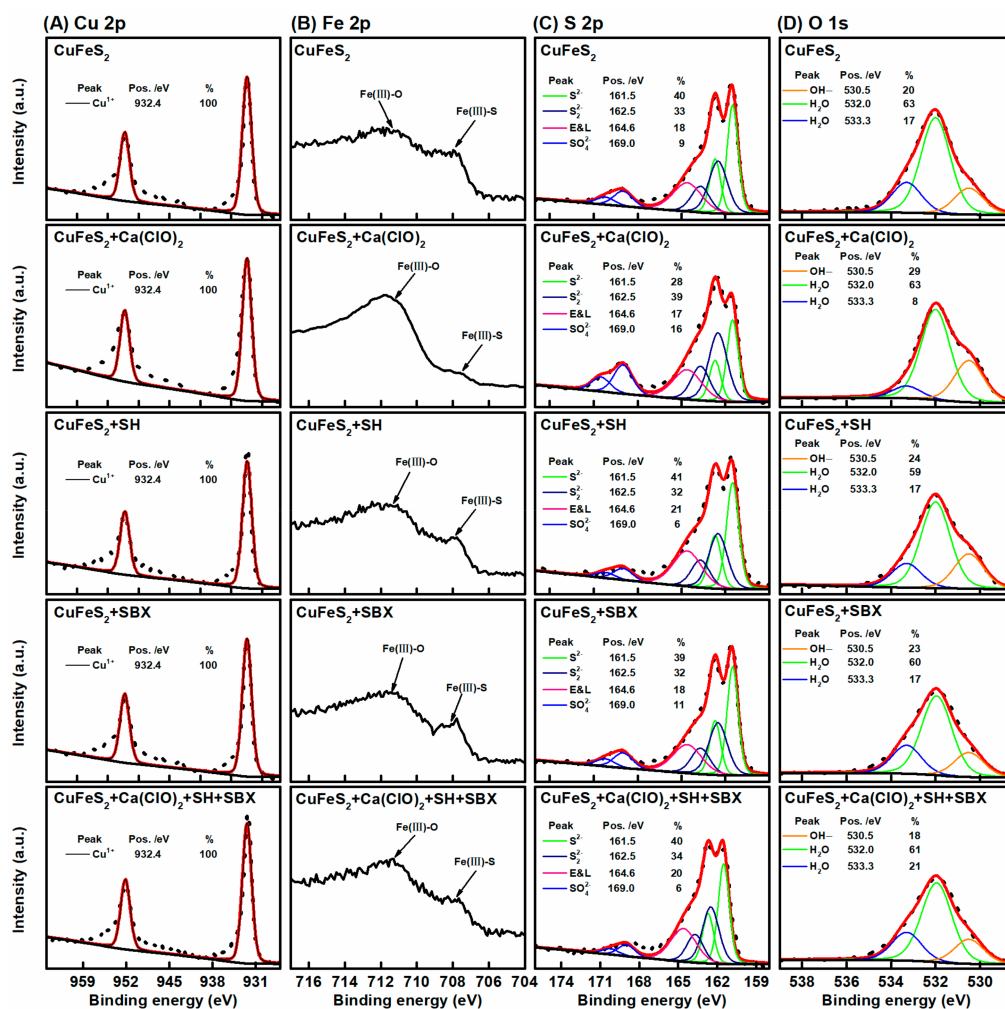


Figure 10. Normalized X-ray photoelectron spectroscopy (XPS) spectra of chalcopyrite for various treated samples: (A) Cu 2*p* peaks, (B) Fe 2*p* peaks, (C) S 2*p*, and (D) O 1s. Dots represent the experimental spectrum, heavy red solid lines indicate the best fit curve, and the individual XPS peaks are shown as thin solid lines in different colors corresponding to their doublets.

As depicted in Figure 11A (As 3*d* peaks), the As 3*d* spectra were fitted with three doublets. Each doublet consisted of two peaks, namely, As 3*d*_{5/2} and As 3*d*_{3/2}. The As 3*d*_{3/2} peak was higher than 3*d*_{5/2} peak at 0.7 eV, whereas the FWHM values were the same. However, the area of the

$3d_{3/2}$ peak was two-thirds that of the $3d_{5/2}$ peak. Untreated arsenopyrite had a high-intensity peak at 41.5 eV that can be assigned to arsenic in the sulfarsenide lattice [50]. The peak located at 44.1 eV corresponded to As(III)–O bonding [51], and the peak at approximately 45.4 eV was assigned to As(V)–O bonding [52]. Compared with that of the original arsenopyrite, the As 3d spectrum of arsenopyrite did not evidently interact with SH, similar to the outcome with SBX. After the $\text{Ca}(\text{ClO})_2$ treatment, the binding energy of sulfarsenide from arsenopyrite at 44.1 eV shifted to 44.2 eV. Additionally, As(III)–O and As(V)–O increased, and sulfarsenide declined. Therefore, $\text{Ca}(\text{ClO})_2$ can oxidize the As element on the arsenopyrite surface, similar to the results of arsenic under mixed reagent conditions.

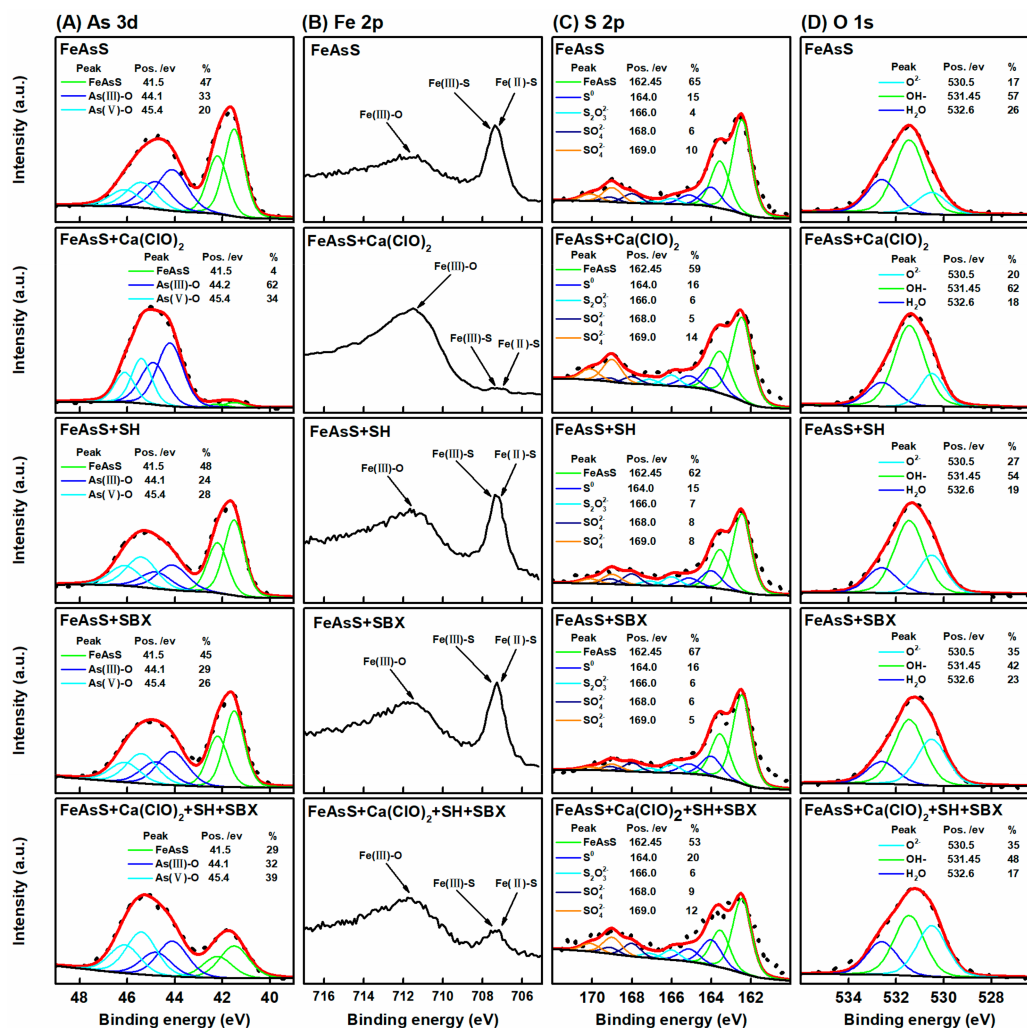


Figure 11. Normalized XPS spectra of arsenopyrite for various treated samples: (A) As 3d peaks, (B) Fe 2p peaks, (C) S 2p, and (D) O 1s. Dots represent the experimental spectrum, heavy red solid lines indicate the best fit curve, and the individual XPS peaks are shown by thin solid lines in different colors corresponding to their doublets.

The Fe 2p spectra (Figure 11B) of the original arsenopyrite demonstrated intense and narrow peaks located at 707.3, thereby corresponding to FeAsS, according to the literature [51,52]. A low-intensity broad peak appeared that extended from approximately 709 eV to 715 eV; this peak was ascribed to Fe(III)–O oxidation products [53]. After $\text{Ca}(\text{ClO})_2$ treatment, the region of Fe 2p peaks ranging from 700 eV to 709 eV decreased by a large margin, and the proportion of iron oxidation products increased. A similar phenomenon was also observed under mixed reagent conditions. By contrast, the proportion

of iron species in SBX and SH condition slightly varied. Therefore, the arsenopyrite surface was oxidized with the formation of a layer of iron oxidation products in the presence of $\text{Ca}(\text{ClO})_2$.

Figure 11C shows the S 2p spectra of arsenopyrite before and after treatment with reagents. The best fit to the S 2p spectrum of the untreated sample generated five peaks. Each doublet constituted two peaks, namely, S $2p_{3/2}$ and S $2p_{1/2}$, which were separated by 1.1–1.2 eV. The S $2p_{1/2}$ peak that resulted from spin-orbit splitting was controlled to the same FWHM (same shape) and to be half the area of the S $2p_{3/2}$ peak. The peaks at 162.45 and 164.0 eV corresponded to the un-oxidized arsenopyrite [53] and sulfur formation [50], respectively. Moreover, the thiosulfate peak was located at 166.0 eV, and sulfate peaks occurred at 168.0 and 169.0 eV. Compared with the untreated arsenopyrite, the amount of sulfur species with higher binding energy increased upon exposure to $\text{Ca}(\text{ClO})_2$, along with a slight decrease in sulfur in the sulfarsenide lattice. The main component of O 1s spectra was located at 531.45 eV, which corresponded to hydroxyl oxygen (OH^-). A lower component was at 530.5 eV, which was due to the presence of lattice oxygen (O^{2-}). A peak at 532.6 eV corresponded to water (H_2O) [52].

The XPS analyses can be summarized as follows. With $\text{Ca}(\text{ClO})_2$, the chalcopyrite surface was mildly oxidized with the formation of iron oxidation products. However, under mixed reagent conditions, the hydrophobicity of chalcopyrite surface was hardly affected. Conversely, the $\text{Ca}(\text{ClO})_2$ treatment on arsenopyrite resulted in the formation of hydrophilic oxidation films containing arsenate, ferric hydroxide, and some sulfates. Considering the persistent iron hydroxide deposited on the arsenopyrite surface, arsenopyrite became hydrophilic [54]. Furthermore, the hydrophilic oxidation film caused by $\text{Ca}(\text{ClO})_2$ enhanced SH adsorption on the arsenopyrite surfaces and strengthened the depression of arsenopyrite. This finding is consistent with the observations in Section 3.4.

4. Conclusions

In this study, the flotation of chalcopyrite and arsenopyrite was observed by microflotation tests and the interaction mechanism was studied by zeta potential measurements, FTIR, and XPS. The main conclusions were as follows:

- (1) Microflotation tests showed that chalcopyrite can be selectively separated from arsenopyrite by selective flotation using the combined depressants of $\text{Ca}(\text{ClO})_2$ and SH in a low alkaline system. With the use of combined depressants, the recovery of arsenic in copper concentrates sharply decreased from 63% to 11%; that of chalcopyrite also slightly decreased.
- (2) The measurements of zeta potential and FTIR spectra revealed that SH adsorption on the arsenopyrite surface was stronger than that on the chalcopyrite surface. SH adsorption on arsenopyrite was enhanced with $\text{Ca}(\text{ClO})_2$.
- (3) XPS analysis demonstrated that SH unremarkably affected the chalcopyrite and arsenopyrite, whereas $\text{Ca}(\text{ClO})_2$ simultaneously oxidized the surfaces of chalcopyrite and arsenopyrite. However, oxidation was stronger on arsenopyrite than on chalcopyrite. The oxidation products caused by $\text{Ca}(\text{ClO})_2$ not only reduced the hydrophobicity of the arsenopyrite surface but also caused SH adsorption.

Author Contributions: The experiments were formulated and designed by Y.H. and W.S. and performed by S.L. and C.W. Data were analyzed by R.L. and S.L.; reagents/materials/analysis tools were contributed by Y.B. and L.W. The paper was written by S.L. and R.L.

Funding: This research was funded by the National Natural Science Foundation of China (No. 51104179), the Fundamental Research Funds for the Central Universities of Central South University (No. 2018zzts223), and the Key Laboratory of Hunan Province for Clean and Efficient Utilization of Strategic Calcium-containing Mineral Resources (No. 2018TP1002).

Acknowledgments: We are grateful to Central South University for providing us with the experimental platform. We thank Mercy. Liu for her help in the field work.

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

References

1. Wang, J.S. Arsenic in drinking water—A global environmental problem. *J. Chem. Educ.* **2004**, *81*, 207–213. [\[CrossRef\]](#)
2. Chandraprabha, M.N.; Natarajan, K.A.; Somasundaran, P. Selective separation of pyrite from chalcopyrite and arsenopyrite by biomodulation using acidithiobacillus ferrooxidans. *Int. J. Miner. Process.* **2005**, *75*, 113–122. [\[CrossRef\]](#)
3. Long, G.; Peng, Y.; Bradshaw, D. Flotation separation of copper sulphides from arsenic minerals at rosebery copper concentrator. *Miner. Eng.* **2014**, *66–68*, 207–214. [\[CrossRef\]](#)
4. López Valdivieso, A.; Ojeda Escamilla, C.; Song, S.; Baez, I.L.; Martínez, I.G. Adsorption of isopropyl xanthate ions onto arsenopyrite and its effect on flotation. *Int. J. Miner. Process.* **2003**, *69*, 175–184. [\[CrossRef\]](#)
5. Long, G.; Peng, Y.; Bradshaw, D. A review of copper–arsenic mineral removal from copper concentrates. *Miner. Eng.* **2012**, *36–38*, 179–186. [\[CrossRef\]](#)
6. Smith, L.K.; Bruckard, W.J. The separation of arsenic from copper in a northparkes copper–gold ore using controlled-potential flotation. *Int. J. Miner. Process.* **2007**, *84*, 15–24. [\[CrossRef\]](#)
7. You, K.-S.; Kim, H.-S.; Ahn, J.-W.; Lee, S. Arsenic rejection from lead concentrate using aluminosulfate. *Int. J. Miner. Process.* **2013**, *125*, 118–121. [\[CrossRef\]](#)
8. Matveeva, T.N.; Gromova, N.K.; Lantsova, L.B. Effect of tannin on compound collector adsorption and stibnite and arsenopyrite flotation from complex ore. *J. Min. Sci.* **2018**, *53*, 1108–1115. [\[CrossRef\]](#)
9. Tapley, B.; Yan, D. The selective flotation of arsenopyrite from pyrite. *Miner. Eng.* **2003**, *16*, 1217–1220. [\[CrossRef\]](#)
10. Lopez Valdivieso, A.; Orozco, L. The flotation column to control arsenic, zinc and insoluble in lead concentrates. *GEOMIMET XXI Epoca* **1994**, *187*, 33–45.
11. Mu, Y.; Peng, Y.; Lauten, R.A. The depression of pyrite in selective flotation by different reagent systems—A literature review. *Miner. Eng.* **2016**, *96–97*, 143–156. [\[CrossRef\]](#)
12. López Valdivieso, A.; Sánchez López, A.A.; Ojeda Escamilla, C.; Fuerstenau, M.C. Flotation and depression control of arsenopyrite through pH and pulp redox potential using xanthate as the collector. *Int. J. Miner. Process.* **2006**, *81*, 27–34. [\[CrossRef\]](#)
13. Bruckard, W.J.; Kyriakidis, I.; Woodcock, J.T. The flotation of metallic arsenic as a function of pH and pulp potential—A single mineral study. *Int. J. Miner. Process.* **2007**, *84*, 25–32. [\[CrossRef\]](#)
14. Sirkeci, A.A. The flotation separation of pyrite from arsenopyrite using hexyl thioethylamine as collector. *Int. J. Miner. Process.* **2000**, *60*, 263–276. [\[CrossRef\]](#)
15. Chen, J.; Chen, Y.; Wei, Z.; Liu, F. Bulk flotation of auriferous pyrite and arsenopyrite by using tertiary dodecyl mercaptan as collector in weak alkaline pulp. *Miner. Eng.* **2010**, *23*, 1070–1072. [\[CrossRef\]](#)
16. Chimonyo, W.; Corin, K.C.; Wiese, J.G.; O'Connor, C.T. Redox potential control during flotation of a sulphide mineral ore. *Miner. Eng.* **2017**, *110*, 57–64. [\[CrossRef\]](#)
17. Hu, Y.; Sun, W.; Wang, D. Electrochemistry of flotation of sulphide minerals. In *Electrochemistry of Flotation of Sulphide Minerals*; Springer: Berlin/Heidelberg, Germany, 2009; pp. 142–166.
18. Ruonal, M.; Heimala, S.; Jounela, S.; Ruonal, M.; Heimala, S.; Jounela, S. Different aspects of using electrochemical potential measurements in mineral processing. *Int. J. Miner. Process.* **1997**, *51*, 97–110. [\[CrossRef\]](#)
19. Wang, D.; Jiao, F.; Qin, W.; Wang, X. Effect of surface oxidation on the flotation separation of chalcopyrite and galena using sodium humate as depressant. *Sep. Sci. Technol.* **2017**, *53*, 961–972. [\[CrossRef\]](#)
20. Ai, G.; Liu, C.; Zhang, W. Utilization of sodium humate as selective depressants for calcite on the flotation of scheelite. *Sep. Sci. Technol.* **2018**, *53*, 2136–2143. [\[CrossRef\]](#)
21. Zhang, J.; Wang, A. Adsorption of Pb(II) from aqueous solution by chitosan-g-poly(acrylic acid)/attapulgit/sodium humate composite hydrogels. *J. Chem. Eng. Data* **2010**, *55*, 2379–2384. [\[CrossRef\]](#)
22. González, M.A.; Pavlovic, I.; Rojas-Delgado, R.; Barriga, C. Removal of Cu²⁺, Pb²⁺ and Cd²⁺ by layered double hydroxide–humate hybrid. Sorbate and sorbent comparative studies. *Chem. Eng. J.* **2014**, *254*, 605–611. [\[CrossRef\]](#)
23. Chen, J.; Li, Y.; Chen, Y. Cu–S flotation separation via the combination of sodium humate and lime in a low pH medium. *Miner. Eng.* **2011**, *24*, 58–63. [\[CrossRef\]](#)
24. Qin, D. *Research on Flotation Separation of Chalcopyrite and Pyrite Arsenopyrite*; Central South University: Changsha, China, 2014. (In Chinese)

25. Zeng, K. *Study on the Flotation Behavior and Separation of Sulfur-Arsenic Mineral*; Central South University: Changsha, China, 2010. (In Chinese)
26. Fuerstenau, M.C.; Gaudin, A.M. *Flotation: A.M. Gaudin Memorial Volume*; American Institute of Mining, Metallurgical, and Petroleum Engineers: New York, NY, USA, 1976.
27. Vreugde, M.J.A. Flotation Characteristics of Arsenopyrite. Ph.D. Thesis, University of British Columbia, Vancouver, BC, Canada, 1982.
28. Beattie, M.J.V.; Poling, G.W. Flotation depression of arsenopyrite through use of oxidizing agents. In *Mineral Processing and Extractive Metallurgy*; Institution of Mining and Metallurgy Transactions: Vancouver, BC, Canada, 1987.
29. Li, G.; Zhang, H. The chemical principles of flotation, activation and depression of arsenopyrite. *Process. Complex Ores* **1989**, 61–70. [[CrossRef](#)]
30. Ma, X.; Bruckard, W.J. Rejection of arsenic minerals in sulfide flotation—A literature review. *Int. J. Miner. Process.* **2009**, 93, 89–94. [[CrossRef](#)]
31. Yigit, O.; Soyuncu, S.; Eray, O.; Enver, S. Inhalational and dermal injury due to explosion of calcium hypochlorite. *Cutan. Ocul. Toxicol.* **2009**, 28, 37–40. [[CrossRef](#)] [[PubMed](#)]
32. Reyes-Bozo, L.; Escudey, M.; Vyhmeister, E.; Higuera, P.; Godoy-Faúndez, A.; Salazar, J.L.; Valdés-González, H.; Wolf-Sepúlveda, G.; Herrera-Urbina, R. Adsorption of biosolids and their main components on chalcopryrite, molybdenite and pyrite: Zeta potential and ftir spectroscopy studies. *Miner. Eng.* **2015**, 78, 128–135. [[CrossRef](#)]
33. Rath, R.K.; Subramanian, S.; Sivanandam, V.; Pradeep, T. Studies on the interaction of guar gum with chalcopryrite. *Can. Metall. Q.* **2001**, 40, 1–11. [[CrossRef](#)]
34. Liu, R.-Z.; Qin, W.-Q.; Jiao, F.; Wang, X.-J.; Pei, B.; Yang, Y.-J.; Lai, C.-H. Flotation separation of chalcopryrite from galena by sodium humate and ammonium persulfate. *Trans. Nonferr. Met. Soc. China* **2016**, 26, 265–271. [[CrossRef](#)]
35. Chen, J.; Feng, Q.; Ou, L. The Flotation Separation of Chalcopryrite-Pyrite in the Presence of Sodium Humate. *Front. Sep. Sci. Technol.* **2004**, 1019–1028. [[CrossRef](#)]
36. Park, K.; Choi, J.; Gomez-Flores, A.; Kim, H. Flotation behavior of arsenopyrite and pyrite, and their selective separation. *Mater. Trans.* **2015**, 56, 435–440. [[CrossRef](#)]
37. Pandey, A.K.; Pandey, S.D.; Misra, V. Stability constants of metal-humic acid complexes and its role in environmental detoxification. *Ecotoxicol. Environ. Saf.* **2000**, 47, 195–200. [[CrossRef](#)] [[PubMed](#)]
38. Zhang, Y.; Cao, Z.; Cao, Y.; Sun, C. FTIR studies of xanthate adsorption on chalcopryrite, pentlandite and pyrite surfaces. *J. Mol. Struct.* **2013**, 1048, 434–440. [[CrossRef](#)]
39. Mielczarski, J.A.; Mielczarski, E.; Zachwieja, J.; Cases, J.M. In situ and ex situ infrared studies of nature and structure of thiol monolayers adsorbed on cuprous sulfide at controlled potential. *Langmuir* **1995**, 11, 2787–2799. [[CrossRef](#)]
40. Allison, S.A.; Goold, L.A.; Nicol, M.J.; Granville, A. A determination of the products of reaction between various sulfide minerals and aqueous xanthate solution, and a correlation of the products with electrode rest potentials. *Metall. Trans.* **1972**, 3, 2613–2618. [[CrossRef](#)]
41. Brion, D. Etude par spectroscopie de photoelectrons de la degradation superficielle de FeS₂, CuFeS₂, ZnS et PbS a l'air et dans l'eau. *Appl. Surf. Sci.* **1980**, 5, 133–152. [[CrossRef](#)]
42. Ghahremaninezhad, A.; Dixon, D.G.; Asselin, E. Electrochemical and XPS analysis of chalcopryrite (CuFeS₂) dissolution in sulfuric acid solution. *Electrochim. Acta* **2013**, 87, 97–112. [[CrossRef](#)]
43. Kalgowda, Y.; Chan, Y.-L.; Wei, D.-H.; Harmer, S.L. X-PEEM, XPS and ToF-SIMS characterisation of xanthate induced chalcopryrite flotation: Effect of pulp potential. *Surf. Sci.* **2015**, 635, 70–77. [[CrossRef](#)]
44. Buckley, A.N.; Woods, R. An X-ray photoelectron spectroscopic study of the oxidation of chalcopryrite. *Aust. J. Chem.* **1984**, 37, 401–414. [[CrossRef](#)]
45. McIntyre, N.S.; Zetaruk, D.G. X-ray photoelectron spectroscopic studies of iron oxides. *Anal. Chem.* **1977**, 49, 1521–1529. [[CrossRef](#)]
46. Harmer, S.L.; Pratt, A.R.; Nesbitt, W.H.; Fleet, M.E. Sulfur species at chalcopryrite (CuFeS₂) fracture surfaces. *Am. Mineral.* **2004**, 89, 1026–1032. [[CrossRef](#)]
47. Klauber, C.; Parker, A.; Bronswijk, W.V.; Watling, H. Sulphur speciation of leached chalcopryrite surfaces as determined by X-ray photoelectron spectroscopy. *Int. J. Miner. Process.* **2001**, 62, 65–94. [[CrossRef](#)]

48. Chen, X.; Peng, Y. The effect of regrind mills on the separation of chalcopyrite from pyrite in cleaner flotation. *Miner. Eng.* **2015**, *83*, 33–43. [[CrossRef](#)]
49. Acres, R.G.; Harmer, S.L.; Beattie, D.A. Synchrotron XPS, NEXAFS, and ToF-SIMS studies of solution exposed chalcopyrite and heterogeneous chalcopyrite with pyrite. *Miner. Eng.* **2010**, *23*, 928–936. [[CrossRef](#)]
50. Costa, M.C.; Rego, A.M.B.D.; Abrantes, L.M. Characterization of a natural and an electro-oxidized arsenopyrite: A study on electrochemical and X-ray photoelectron spectroscopy. *Int. J. Miner. Process.* **2002**, *65*, 83–108. [[CrossRef](#)]
51. Buckley, A.N.; Walker, G.W. The surface composition of arsenopyrite exposed to oxidizing environments. *Appl. Surf. Sci.* **1988**, *35*, 227–240. [[CrossRef](#)]
52. Nesbitt, H.W.; Muir, I.J.; Prarr, A.R. Oxidation of arsenopyrite by air and air-saturated, distilled water, and implications for mechanism of oxidation. *Geochim. Cosmochim. Acta* **1995**, *59*, 1773–1786. [[CrossRef](#)]
53. Pratt, A.R.; McIntyre, N.S.; Splinter, S.J. Deconvolution of pyrite marcasite and arsenopyrite XPS spectra using the maximum entropy method. *Surf. Sci.* **1998**, *396*, 266–272. [[CrossRef](#)]
54. Beattie, M.J.V.; Poling, G.W. A study of the surface oxidation of arsenopyrite using cyclic voltammetry. *Int. J. Miner. Process.* **1987**, *20*, 87–108. [[CrossRef](#)]



© 2018 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 (<http://creativecommons.org/licenses/by/4.0/>).