

Article



Control of the Redox Potential by Microcontroller Technology: Researching the Leaching of Chalcopyrite

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Abstract: The leaching of chalcopyrite under different redox potentials was studied with a redox potential controlling device based on microcontroller technology. The leaching test was carried out in a 500 mL flask with 4 g pure chalcopyrite and 200 mL sulfuric acid. The additional total Fe concentration was 0.1 mol/kg, and the initial pH was 0.7. Chalcopyrite leaching tests with initial redox potential of 400 mV and 600 mV (vs. Ag/AgCl, the same below) and controlled redox potential of 350 mV, 400 mV, 450 mV, 500 mV, and 600 mV were carried out at a temperature of 60 °C and a stirring speed of 300 rpm. The results showed that the dissolution of chalcopyrite could not be hindered until the granular intermediates (S⁰ and S_n²⁻) accumulated to a certain amount on the chalcopyrite surface. The main passivating species in chalcopyrite dissolution may be iron-deficient polysulfides. At 400 mV, the chalcopyrite, and the chalcopyrite was rapidly oxidized with Cu leaching rate reaching up to 32% in 7 h, while it was only 15% in the other experimental groups. However, at 450–500 mV, pyrite was oxidized and the galvanic effect between chalcopyrite and pyrite was destroyed, leading to a significant decrease in Cu leaching rate. When the redox potential was 600 mV, the dissolution of metal-deficient polysulfides was promoted; thus, the passivation was weakened.

Keywords: redox potential control; chalcopyrite; microcontroller; iron-deficient polysulfides

1. Introduction

Chalcopyrite (CuFeS₂) is the most abundant copper-bearing mineral in the earth's crust, accounting for more than 70% of the global copper reserves [1]. The processes to extract copper from chalcopyrite include flotation, pyrometallurgy, and electrorefining. However, with the development of chemical and biological leaching for sulfide ores, hydrometallurgy has gradually become a promising technology to extract copper directly from low-grade ores and flotation concentrates. Compared with traditional processes, hydrometallurgical processes are more environmentally friendly. However, the chalcopyrite leaching process has not been widely adopted due to its low recovery rate and slow leaching rate. Therefore, research on the chalcopyrite leaching mechanism and improving the chalcopyrite leaching rate have always been the focus of hydrometallurgy.

Many researchers have observed a passive layer during chalcopyrite leaching. However, there is still disagreement about the composition of the passive layer. The reported possible passivating species mainly consist of polysulfide (S_n^{2-}) elemental sulfur (S^0) and insoluble sulfate (SO_4^{2-}). Linge [2] found that more iron than copper dissolved from the lattice during the initial stage of chalcopyrite leaching, producing metal-deficient polysulfide of the chalcopyrite surface. Yang [3] analyzed the leaching process of chalcopyrite by XANES, and found that the polysulfides generated on the surface of chalcopyrite in the initial stage were CuS_n -like species. With further Cu leaching, CuS_n -like species were transformed into S_n -like species. The slow oxidation rate of S_n -like species was the reason for the passivation. Dutrizac [4] found that the chalcopyrite surface produced approximately



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Copyright: © 2021 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/). 94% elemental sulfur and 6% sulfate in the sulfuric acid solution at 95 °C, and believed that elemental sulfur was the main passivating species of chalcopyrite in the ferric sulphate system. Klauber [5] believed that the reactivity of polysulfide was strong, and it could be oxidized to elemental sulfur by oxygen; the elemental sulfur could cause the passivation of chalcopyrite, but it was easy to peel off from chalcopyrite surface, and jarosite should be the main passivating species.

The passive layer can be dissolved at high redox potential, except jarosite. The effects of oxidants on chalcopyrite leaching have extensively been studied; for example, dichromate [6], permanganate [7], MnO₂ [8], chlorate [9], nitrate [10], hydrogen peroxide [11], etc. The results showed that the oxidants could observably promote the dissolution of chalcopyrite, even under mild conditions. Antonijevic [12] reported that the chalcopyrite leaching conformed to the shrinking core model with the presence of hydrogen peroxide. The chemical reaction was the controlling step and increasing the concentration of hydrogen peroxide could significantly accelerate the chalcopyrite dissolution rate. Toro [13] found that chalcopyrite can dissolve rapidly at room temperature when working at 4:1 ratio of oxidizing agent (MnO₂): chalcopyrite in chlorinated acid medium.

The rest potential of pyrite is higher than chalcopyrite, therefore pyrite is more stable than chalcopyrite [14]. GalvanoxTM process increases the reduction site of Fe³⁺ to Fe²⁺ by adding insoluble pyrite, and alleviates the negative impact of passive layer on chalcopyrite dissolution [15]. An appropriate amount of Ag⁺ can improve the electrical conductivity of the sulfur layer on the surface of chalcopyrite, and further strengthen the galvanic effect between pyrite and chalcopyrite [16]. In addition, Zhao [17] believed that Fe²⁺ generated by the pyrite oxidation could reduce the redox potential to the range of promoting the chalcopyrite dissolution. A technique developed by Dixon [18] showed that the recovery of copper can reach 98% or more in just 4 h retention time when the ratio of pyrite:chalcopyrite is 2:1, the solution redox potential is controlled at 470 mV (vs. Ag/AgCl, the same below), and the atmosphere temperature is 80 °C.

The elements Cu, Fe and S in chalcopyrite have multiple valence states, which is the reason for the diversity of intermediate products. The redox potential determines the oxidation degree of chalcopyrite, which in turn determines the type of intermediate products [19]. Chalcopyrite dissolution consists of two stages, the chemical reaction control stage with a trace of surface products, and the diffusion control stage with a mass of surface products. Iron ions can promote the rate of chemical reaction stage, thus accelerating the transformation from chemical reaction control to diffusion control [20]. Chalcopyrite leaching and electrochemical studies show that at a low redox potential of 400-420 mV, chalcopyrite is actively dissolved, and less affected by the surface product layer. Chalcopyrite is reduced by Fe^{2+} and Cu^{2+} to Cu_2S at low redox potential [21]. In ferric sulfate solution, Cu₂S is more readily dissolved than chalcopyrite. Ahmadi [22] studied the electrochemical bioleaching of chalcopyrite and indicated that the copper leaching rate under the redox potential controlled at 400-425 mV was 35% higher than that under the natural redox potential. Kametani [23] found that the chalcopyrite leaching was promoted when the redox potential of the solution was 400-430 mV. However, when the potential was higher than 450 mV, chalcopyrite leaching was significantly inhibited. Because pyrite began to be oxidized to sulfate, the jarosite layer played a passivation role on the surface of chalcopyrite [7].

In conclusion, different redox potentials and the types of intermediate products significantly affect the process of chalcopyrite leaching. The purpose of this study was to develop a redox potential controlling device using microcontroller technology and evaluate the effect of redox potential on the leaching of chalcopyrite. The leaching mechanism of chalcopyrite was deduced by XRD, XPS, and SEM-EDS detection of the leaching residue. The device used in this study controlled the redox potential of the solution through feedback control, which can reduce the unnecessary use of an oxidizer, so it can provide a reference for the development of the new process of chalcopyrite leaching.

2. Materials and Methods

2.1. Minerals

All chalcopyrite used in this study was from Hunan Province, China. X-ray diffraction (XRD) analysis (Figure 1) showed that the chalcopyrite was of high purity with only a small amount of quartz and pyrite. The chemical composition of the ore sample, as shown in Table 1, indicated that the chalcopyrite contained 33.85% Cu, 29.75% Fe and 51.58% S. The presence of pyrite and Ag is conducive to chalcopyrite oxidation leaching due to the galvanic effect between pyrite and chalcopyrite and the activation effect of Ag by improving the electrical conductivity of the sulfur layer on the chalcopyrite surface. The mineral particles were ground to particles of $-74 \,\mu\text{m}$ using a ceramic ball mill (Changsha Tencan powder technology Co. Ltd., Changsha, China).



Figure 1. X-ray diffractogram pattern of the ore of chalcopyrite.

Table 1. Chemical composition of the ore.

Element.	0	Al	Si	S	К	Ca	Fe	Cu	Ag
Wt. %	0.14	0.025	0.098	34.16	0.009	0.01	29.75	33.85	0.022

2.2. Apparatus

The reaction apparatus used in this experiment, as shown in Figure 2, consisted of a 500 mL four-hole boiling flask, a stirrer, a water bath, and a redox potential controlling device.

The microcontroller system was used to collect the real-time redox potential data of the solution and controlled the release of redox potential regulators by the peristaltic pump. The detailed working process is as follows: collecting the voltage data of the redox potential composite electrode (vs. Ag/AgCl) through a microcontroller, and then sending a control signal to the peristaltic pump after comparing with the set threshold value. If the redox potential of the solution was higher than the threshold value, the reducing agent was added; otherwise, the oxidizing agent was added. Real-time volume of the redox potential regulator was obtained by using graduated container. The computer was only used to easily read real-time redox potential data.

The division value of the redox potential control device was 0.6 mV. The model of microcontroller was STC15F2K60S2 and used an ADS1015 analog to digital converter (ADC).



Figure 2. Schematic diagram of the redox potential controlling device: (1) host computer, (2) microcontroller, (3) analog to digital converter (ADC), (4) redox potential composite electrode, (5) stirrer, (6) four-hole boiling flask, (7) water bath heater, (8) peristaltic pump, (9) rubber tube, (10) redox potential regulator.

2.3. Procedures

Solutions with different redox potentials were prepared by adding redox regulators to sulfuric acid solutions with a pH of 0.7 and a total Fe concentration of 0.1 mol/kg. The redox potential regulators were H_2O_2 (3 wt.%) as the oxidant and ascorbic acid (8 wt.%) as the reductant.

All leaching tests were carried out at a stirring speed of 300 rpm, a pulp concentration of 2% (200 mL leaching solution and 4 g ore), and a temperature of 60 $^{\circ}$ C. During the test, the redox potential of the solution was controlled by the redox potential controlling device, and data were recorded every 10 s.

The initial pH of the leaching solution was measured using a glass electrode. During the leaching test, the solution was regularly sampled, 50 μ L each time, to measure the concentration of Cu²⁺ and Fe by inductively coupled plasma atomic emission spectrometry (ICP-AES, Agilent 720ES). The sampling loss was compensated by adding equal volumes of acid. After filtration, washing and vacuum drying, the residue underwent XRD, SEM-EDS, and XPS.

2.4. Surface Analysis

The S speciation transformations on the chalcopyrite surfaces were analyzed by X-ray photoelectron spectroscopy (XPS), which was carried out using the EscaLab Xi+ model, and the spectra were recorded with a constant pass energy of 20 eV and 0.1 eV/step using an Al K α X-ray source. The obtained XPS spectra were fitted by using Thermo Avantage 5.52 software. During the fitting process, the binding energies of the spectra were calibrated by the C 1s level at 284.8 eV, the background was achieved by using the Shirley method, and the spectrum was fitted by the Gauss–Lorentz line (SGL) function.

The phase compositions of chalcopyrite were analyzed by X-ray diffraction (XRD, Advance D8/Bruker). Jade6 software was used to analyze the XRD patterns. The microstructure of the pyrite was studied in a scanning electron microscope (SEM, JSM-6490LV/JEOL) equipped with an energy dispersive spectrometer (EDS, Nepture XM 4/EDAX).

3. Experimental Results

3.1. Leaching under Different Initial Redox Potentials

This study first investigated the leaching of chalcopyrite under initial redox potentials of 600 mV and 400 mV. Only the initial redox potentials were set to different values, and the redox potentials were not fixed in the test process. Figure 3b shows the change in

redox potential with time during the experiment. As shown in Figure 3a, the Cu leaching rate of the experimental group with an initial redox potential of 400 mV at 23.5 h was 3.47-fold greater than that of the experimental group with initial redox potential of 600 mV. Therefore, a lower redox potential is more conducive to the leaching of chalcopyrite.



Figure 3. Cu leaching rate (**a**) and real-time redox potential data of the leaching solution (**b**), with initial redox potentials of 400 mV and 600 mV, respectively; the redox potential was not fixed in the test process.

In the experimental group with an initial redox potential of 600 mV, the redox potential of the solution dropped sharply within the first few minutes after adding the chalcopyrite, and then decreased slowly to 455 mV at 23.5 h, as shown in Figure 3b. The reason for the decrease in redox potential was that Fe^{3+} was consumed as chalcopyrite was being oxidized. The reasons for the sharp drop of redox potential in the initial stage were the rapid reaction of the fine particles and the surface reconstruction of the ore. In the experimental group with an initial redox potential of 400 mV, the potential of the solution began to rise slowly around 5 h, and began to rise rapidly after 16 h, reaching 449 mV at 23.2 h. At the initial stage, the minerals were oxidized, but at the later stage, Fe^{2+} was oxidized and the minerals or intermediate products were reduced. The same experimental phenomenon was observed by Cordoba [24] and Third [25]. Therefore, the leaching mechanism of chalcopyrite is different under different redox potentials.

3.2. Controlled Redox Potential Leaching

The redox potential controlling device, shown in Figure 2, was used to perform the leaching test of chalcopyrite at the redox potentials of 350 mV, 400 mV, 450 mV, 500 mV, and 600 mV. As shown in Figure 4, the redox potential was precisely controlled. When the target redox potential was 450 mV, 500 mV, and 600 mV, the ore sample was oxidized, resulting in a decreasing trend of the redox potential. Oxidizer was added to maintain the redox potential to the target value.

When the target redox potential was 400 mV and 350 mV, the redox potential showed a decreasing trend in the first five hours, and oxidant was added; however, after about 5 h, the redox potential showed an increased trend, and reductant was added.



Figure 4. Real-time redox potential data with the redox potential controlling device.

Figure 5 shows the test results of the redox potential fixed at 350 mV, 400 mV, 450mV, 500mV and 600 mV. At the redox potential of 400 mV, the leaching rates of Cu and Fe were the same (Figure 5b). However, at the lower potential of 350 mV and the higher potentials of 450 mV, 500 mV and 600 mV, the leaching rate of Fe was higher than Cu. In all the leaching tests, chalcopyrite was leaching at a faster rate at the beginning and then gradually slowed down. At the redox potential of 400 mV, chalcopyrite was leached at a faster rate before 7 h; however, after 7 h, the inhibition was more obvious, and the leaching almost stopped. The Cu leaching rate reached 32% at 7 h, and only 15% in the other experimental groups. However, at 23.5 h, the Cu leaching rate was only 37%.

Figure 5f shows that the leaching of Cu was faster when the redox potential was maintained at 400 mV, which was identical with previous experimental results [24,26–28]. When the redox potential was between 400 mV and 500 mV, the leaching of Cu decreased. When the redox potential was over 500 mV, Cu leaching increased again. This experimental result is consistent with the activation, passivation, and over-passivation phenomenon in the presence of a passivating substance. The activation potential is 400 mV, the passivation potential ranges from 400 to 500 mV, and the over-passivation potential is above 500 mV.



Figure 5. Cont.



Figure 5. In the controlled redox potential test process, the redox potentials (**a**–**e**) were fixed at 350 mV, 400 mV, 450 mV, 500 mV and 600 mV, respectively, showing the Cu and Fe leaching rates at different times; (**f**) Cu leaching rate at different redox potentials.

3.3. Analysis of Chalcopyrite Leaching Residue

According to the above leaching test results, chalcopyrite undergoes oxidation reaction at high redox potential, but at low redox potential, there was a reduction reaction causing the increase in redox potential. Therefore, the leaching mechanism of chalcopyrite is different at various redox potentials. Different intermediate products may be produced, such as polysulfide, elemental sulfur, and jarosite. To further study the leaching mechanism of chalcopyrite at various redox potential, the leaching residues with redox potentials fixed at 400 mV and 600 mV were analyzed.

3.3.1. XPS Analysis

The S speciation transformations on the chalcopyrite surfaces were analyzed by X-ray photoelectron spectroscopy (XPS), as shown in Table 2. Due to spin-orbit splitting, S 2p peak presents a S $2p_{3/2}$ and S $2p_{1/2}$ doublet. The S 2p spectra were fitted on the Thermo ScientificTM Avantage software. The area ratio of the two peaks fitted was 2:1, and the energy difference of the two peaks was 1.2 eV. Figures 6d and 7c show the fitting results of S 2p peaks. The S $2p_{2/3}$ peaks were found to be 161.36 eV (full width at half maximum, FWHM = 0.84), 162.41 eV (FWHM = 0.84), 163.41 eV (FWHM = 0.84), 164.2 eV (FWHM = 0.84), and 168.9 eV (FWHM = 1.48), respectively. These peaks are attributed to monosulfide (S²⁻), disulfide (S₂²⁻), polysulfide (S_n²⁻), elemental sulfur (S⁰), and sulfate (SO₄²⁻) [29]. According to the fitting results in Figures 6d and 7c and the S species on the ore sample surface as shown in Table 2, S²⁻, S₂²⁻, S_n²⁻, S⁰, and SO₄²⁻ were the major species of S on the leaching residue surface. According to the S distribution on the surface of

the ore sample, the oxidation of chalcopyrite was complex with multiple steps. According to the number of electrons obtained, the oxidation of S^{2-} proceeds in the following process:

$$S^{2-} \rightarrow S^{2-}_2 \rightarrow S^{2-}_n \rightarrow S^0 \rightarrow SO^{2-}_4 \tag{1}$$

Whether it was a low or a high redox potential, the leaching residue contained S^{2-} , S_2^{2-} , S_n^{2-} and S^0 after 23.5 h of leaching. Due to the presence of jarosite deposition at high redox potential, 10.84% of the sulfur existed in the sulfate. However, sulfate was not detected in the low redox potential group.

Table 2. XPS test results of the leaching residue.

From and in a set of Conserve	Percentage (%)					
Experimental Group	S ² -	S_2^{2-}	S_n^{2-}	S ⁰	SO_4^{2-}	
400 mV	62.24	15.68	13.76	8.32	0	
600 mV	56.10	13.19	12.23	7.65	10.84	



Figure 6. In the experimental group with redox potential of 400 mV, solid-phase SEM image at 12 h of chalcopyrite leaching (**a**), and solid-phase SEM image (**b**), XRD image (**c**), and XPS image (**d**) at 23.5 h of chalcopyrite leaching. (A and B in the figures are EDS detection areas).



Figure 7. For the experimental group with a redox potential of 600 mV, solid phase SEM image (**a**), XRD image (**b**), and XPS image (**c**) at 23.5 h of chalcopyrite leaching. (C and D in the figure are EDS detection areas).

3.3.2. XRD and SEM-EDS Analysis

In the experimental group with redox potential fixed at 400 mV, Cu leaching rate was significantly different in the initial and later stages. Therefore, leaching residue at 12 h and 23.5 h were selected for SEM detection as shown in Figure 6a,b, and area A of the chalcopyrite surface and area B of the particles on the ore surface were selected for EDS detection.

According to the SEM results, many granular intermediate products were generated and attached to the chalcopyrite surface, and the intermediate products increased over time. At 23.5 h, mineral particles were almost completely covered by particles formed by intermediate products (Figure 6b), and the chalcopyrite leaching was inhibited at this time, as shown in Figure 5b. Therefore, after leaching for a period of time, the covering of a large number of intermediate products had a significant negative effect on chalcopyrite leaching.

The EDS detection depth is $1-2 \mu m$, and the particle size formed by the intermediate was $2 \mu m$ on average; thus, EDS detection could be used as the basis to judge the elements contained in the intermediate products. The results (Table 3) show that the particles formed by the intermediate products not only contain a large amount of S, but also Cu and Fe. The area A that is not covered by the intermediate is still the intrinsic chalcopyrite.

The XRD result shows that the newly formed phase was elemental sulfur. In addition, pyrite was nonreactive at low redox potential. With the leaching of chalcopyrite, the characteristic peak of pyrite in the ore sample, as shown in Figure 6c, becomes more apparent.

Detecting Area	Percentage %					
Dettetting Mea —	Cu	Fe	S			
400 mV—A	26.51	25.33	48.16			
400 mV—B	20.18	16.45	63.37			
600 mV—C	27.02	26.69	46.29			
600 mV—D	18.46	21.66	59.88			

Table 3. EDS results of the leaching residue.

The surface morphology of chalcopyrite at a redox potential of 600 mV (Figure 7a) was significantly different from that at a redox potential of 400 mV (Figure 6a,b). At high redox potential, intermediate products such as polysulfide and elemental sulfur were oxidized to sulfate, so the particles formed by the intermediate products on the ore surface were significantly reduced. However, crystals with particle size less than 1 μ m were formed in large quantities, which not only existed in intermediate particles, but also densely distributed on the mineral surface.

The XRD result (Figure 7b) shows that the newly produced phases included sulfur elemental and hydroniumjarosite $(H_3OFe_3(SO_4)_2(OH)_6)$ at the redox potential of 600 mV. EDS results show that the Fe content in area D was higher than that in area B, and the sulfate detected by XPS indicates that the newly formed crystal could be hydroniumjarosite detected by XRD. Although a large amount of hydroniumjarosite was attached to the mineral particles, there was still a partially uncovered surface, such as area C.

4. Mechanism of Chalcopyrite Leaching

At 600 mV, the microstructure of the leaching residues showed that most of the surface of chalcopyrite particles was still uncovered by elemental sulfur and jarosite. Therefore, elemental sulfur and jarosite may not be the main cause of chalcopyrite passivation.

When the redox potential of the solution was higher than 450 mV, the Fe element dissolved prior to Cu at the beginning of dissolution process, and then the presence of polysulfide (S_2^{2-} and S_n^{2-}) on the surface of chalcopyrite. Therefore, the chalcopyrite passivation may be caused by the formation of metal-deficient polysulfides on the chalcopyrite surface due to the preferential leaching of Fe. Linge [2] obtained the same conclusion when studying the electrochemical dissolution mechanism of chalcopyrite by a potentiometric titration technique. The thickness of a metal-deficient polysulfide passivation film on the chalcopyrite surface is less than 1 μ m [30]. Therefore, it was difficult to identify metal-deficient polysulfides on the chalcopyrite surface by SEM. However, when the redox potential reached 600 mV, the dissolution of chalcopyrite was accelerated. The possible reason is that some of the polysulfides on the mineral surface were oxidized and dissolved under high potential; thus, the passivation was weakened.

At 400 mV, elements Fe and Cu were leached simultaneously. Passivation of polysulfides appeared to have been overcome; however, XPS results showed that polysulfide films still existed.

The Pourbaix diagram of chalcopyrite drawn by HSC Chemistry 6 software, as shown in Figure 8. There was a deviation between ion activity and concentration in the actual solution; therefore, Figure 8 is only for qualitative analysis. The upper boundary of chalcopyrite stability region is connected with CuS and FeS₂. At a redox potential of 400 mV, Cordoba [23] found a presence of CuS in the chalcopyrite leaching process. Therefore, at low pH, 400 mV may be the stable redox potential for the polysulfide and elemental sulfur produced by the oxidation of chalcopyrite. In this study, the XRD result of the leaching residue showed that the pyrite was not oxidized and stable at 400 mV. Therefore, 400 mV could also be the stable potential for pyrite. Kametani [23] reported that pyrite began to oxidize at 450 mV (vs. SCE, saturated calomel electrode).



Figure 8. Pourbaix diagram of chalcopyrite (black solid line) and pyrite (red dashed line). (SHE stands for standard hydrogen electrode).

At a potential of 400 mV, the galvanic effect between pyrite and chalcopyrite may be the reason for the rapid dissolution of chalcopyrite over the passivation of polysulfide. The success of GalvanoxTM processes also demonstrates the important role of pyrite in overcoming the surface passivation of chalcopyrite [18]. At high potential, pyrite was oxidized to destroy the galvanic effect, so the copper leaching rate decreased significantly. At 400 mV, the dissolution of chalcopyrite could not be hindered until the granular intermediates including elemental sulfur and polysulfides accumulated to a certain amount on the chalcopyrite surface, as shown in Figure 7b.

The dissolution of chalcopyrite produces elemental sulfur, and 400 mV is the stable redox potential of CuS and FeS₂. Therefore, it is speculated that when chalcopyrite was leaching at 400 mV, the reason for the increasing tendency of redox potential in the later period may be caused by the formation of CuS and FeS₂ by Fe²⁺, Cu²⁺ and elemental sulfur:

$$2S^0 + 3Fe^{2+} = FeS_2 + 2Fe^{3+}$$
(2)

$$S^{0} + Cu^{2+} + 2Fe^{2+} = CuS + 2Fe^{3+}$$
(3)

When the redox potential was fixed at 350 mV, almost all Fe in the solution existed as Fe²⁺. Even though pyrite was stable, chalcopyrite was leached slowly under the action of ferrous and sulfuric acid because of the weak oxidation capacity of the solution. Hiroyoshi [31] believed that Fe²⁺ would inhibit the chalcopyrite leaching, but in the presence of a large amount of Cu²⁺, Fe²⁺ could reduce chalcopyrite to Cu₂S:

$$CuFeS_2 + 3Cu^{2+} + 3Fe^{2+} = 2Cu_2S + 4Fe^{3+}$$
(4)

This reaction also revealed the reason why the solution redox potential had an upward trend in the later stage, when the redox potential was fixed at 350 mV.

5. Conclusions

In this paper, chalcopyrite leaching tests were carried out with a redox potential controlling device based on microcontroller technology. The effect of redox potential on chalcopyrite leaching at 60 °C was studied. The preferential dissolution of Fe led to the formation of Fe-deficient polysulfides on the surface of chalcopyrite, which hindered the diffusion of ions from the chalcopyrite/passivation film interface to passivation film/solution interface, thus resulting in passivation. At 400 mV, due to the presence of pyrite contained in the raw ore or produced by chalcopyrite oxidation, the galvanic effect between chalcopyrite and pyrite overcame the passivation of chalcopyrite by metal-deficient polysulfides. When the redox potential of the solution was increased, the pyrite was oxidized and the galvanic effect between chalcopyrite and pyrite was destroyed, so the Cu leaching was decreased. However, with the continuous increase in potential, the dissolution of polysul-

fide was increased, and the Cu leaching was increased again. The possible reason is that some of the polysulfides on the mineral surface were oxidized and dissolved under high potential, thus the passivation was weakened.

At 400 mV, the granular intermediate produced on the chalcopyrite surface did not inhibit the chalcopyrite leaching at the initial stage. However, the dissolution of chalcopyrite was significantly inhibited when the mineral particles were almost completely covered by intermediate products due to the continuous accumulation of intermediate products. In this study, there was not enough evidence to suggest that surface jarosite was the main cause of chalcopyrite passivation.

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