Int. J. Electrochem. Sci., 8 **(2013)** 12590 - 12599

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Investigation of Interface Reactions and Electrochemical Behaviors of Chalcopyrite Dissolution in Different Leaching Mediums

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Received: 18 August 2013 / *Accepted:* 30 September 2013 / *Published:* 20 October 2013

In this work, a comparative study on the electrochemical behavior of massive chalcopyrite electrode in different leaching mediums was carried out to investigate the different interface reactions. The results showed that the dissolution process of chalcopyrite in sulfuric acid solution system involves series of complex oxidation and reduction reactions, containing several intermediate species. The corresponding interface reactions were discussed in details according to some other researches. The results also revealed that the pH values, the addition of *Acidithiobacillus ferrooxidans* (*A.f*) and *Acidithiobacillus caldus* (*A.c*) do not change the interface reactions of chalcopyrite dissolution. But a lower pH value and the presence of the two strains of bacteria could significantly accelerate the oxidation rate of chalcopyrite. Additionally, low pH value and the presence of *Acidithiobacillus ferrooxidans* (*A.f*) made chalcopyrite prone to be reduced to bornite or talnakhite, thus resulting in a higher copper leaching rate.

Keywords: Chalcopyrite ($CuFeS_2$); Interface reactions; Electrochemical behavior

1. INTRODUCTION

Chalcopyrite is an extremely important copper mineral, and is also the most abundant copper bearing mineral in the world. It is known to be recalcitrant to conventional hydrometallurgical processing. Bioleaching has been applied successfully to the extraction of copper from secondary copper sulphides, while both the chemical leaching rate and bioleaching rate of chalcopyrite are still too low, which was mainly due to the reasons that the detailed dissolution process and intermediate products are not explicit enough [1-5].

It is commonly known that the bioleaching process of chalcopyrite often consist of series of oxidation-reduction reactions concerning electron exchange, it could be described as an electrochemical dissolution or electrochemical corrosion process, which contain complex interface reactions. Therefore, numerous electrochemical studies have been carried out to determine the interface reactions of copper sulfide minerals dissolution process, especially in the presence of bacteria. Most of the studies showed that series of intermediate species could be formed during the oxidation and reduction process of chalcopyrite, such as covellite, bornite, chalcocite, talnakhite and some other compounds. However, the mechanism of different pH values and different bacteria on chalcopyrite bioleaching is still not explicit enough [6-11]. Cyclic voltammetry test is a kind of widely used electrochemical method for studying the electrochemical reactions, it provides rapid and reasonably accurate determination for interface reaction parameters [12-14].

Therefore, the aim of present work is to discuss the detailed interface reactions of chalcopyrite dissolution in the presence of different pH values and different bioleaching bacteria. The bacteria involve *Acidithiobacillus ferrooxidans* (*A.f*) and *Acidithiobacillus caldus* (*A.c*), which were iron-sulfur oxidizing strain and sulfur oxidizing strain, respectively. This work will help to obtain a deeper knowledge about the interface reactions of chalcopyrite dissolution in the presence of different mediums.

2. MATERIALS AND METHODS

2.1 Massive chalcopyrite electrodes

Chalcopyrite electrodes used in this study was prepared from natural chalcopyrite obtained from Meizhou of Guangdong Province in China. X-ray diffraction analysis showed a pure and homogeneous phase. Samples were cut so as to obtain working surface of approximately 1.0 cm^2, with no visible imperfections. The specimens were mounted in an epoxy resin and were connected to a copper wire by graphite paint on the back face. The electrodes were polished using 600-grit silicon carbide paper to obtain smooth surface before electrochemical measurements.

2.2 Bacterial cultures

The bacteria used was obtained from the Key Lab of Biohydrometallurgy of Ministry of Education, Central South University, Changsha, China, bacteria was cultured in 250 mL shake flasks using an orbital incubator with a stirring speed of 200 r/min at 30℃. The 9K medium used for cell cultivation consisted of the following components: $(NH_4)_2SO_4$ (3.0 g/L), $MgSO_4{\cdot}7H_2O$ (0.5 g/L), K_2HPO_4 (0.5 g/L), KCl (0.1 g/L), $Ca(NO_3)_2$ (0.01 g/L). All the bacterial cultures were sub-cultured into basal salts medium supplemented with 5 g of chalcopyrite.

2.3 Electrochemical measurements

For the cyclic voltammograms test, a conventional three-electrode system consisted of working electrode, graphite rod as counter electrode and Ag/AgCl (3.0 M KCl) electrode as reference electrode. The electrolyte used was composed of the following compositions: 3.0 g/L $(NH_4)_2\cdot SO_4$, 0.1 g/L KCl, 0.5 g/L K_2HPO_4, 0.5 g/L $MgSO_4$/L and 0.01 g/L Ca $(NO_3)_2$, the pH value of solution was adjusted to by H_2SO_4. The electrochemical measurement was conducted on a Princeton Model 283 potentiostat (EG&G of Princeton Applied Research) coupled to a personal computer, cyclic voltammogram tests were carried out at a sweep rate of 20 mV/s.

2.4 Analytical techniques/SEM-EDX analysis

Scanning electron microscopy (SEM) and Energy Dispersive X-ray Analysis (EDX) (JSM-6360LV) were utilized to observe the surface image and chemical compositions of chalcopyrite electrode surface after electrochemical measurement.

3. RESULTS AND DISCUSSIONS

3.1 Interface reactions of chalcopyrite dissolution

Cyclic voltammetry tests were carried out to investigate the oxidative and reductive reactions during the dissolution of chalcopyrite. Fig.1 showed the results of cyclic voltammetry of massive chalcopyrite electrodes in the 9K electrolyte of three different pH values adjusted by 4mol/L H_2SO_4, and all three were conducted in the absence of bacteria.

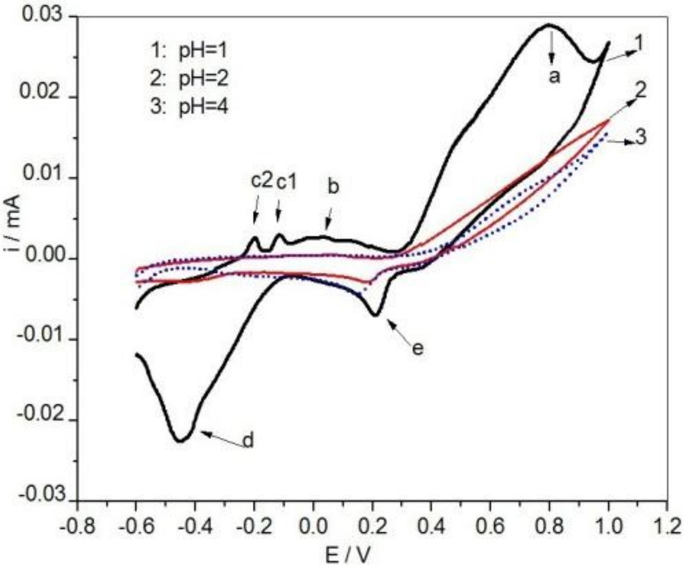

Figure 1. Cyclic voltammograms of massive chalcopyrite electrode in 9K medium of different pH values (pH=1,2,3). Sweep rate = 20 mv/s; Reference electrode: Ag/AgCl electrode (3 mol/L KCl)

In the anodic scan from -0.6 V, four distinct anodic peaks were observed, including peak c2, peak c1, peak b and peak a. There were few reports on the peak c2 and peak c1, even though the two peaks always exist during the dissolution of chalcopyrite, as well as the dissolution of chalcocite and bornite[15-17]. When the potential was more negative than −0.5 V vs. SHE, chalcopyrite could be reduced to elemental copper as shown in Eq. (1)[18, 19]. Based on this chemical reaction, peak c2 was considered as the oxidation of elemental copper to chalcocite shown as Eq.(2), and series of anodic peaks around peak b were considered as the further oxidation of formed chalcocite to Cu-S intermediate species shown as Eq.(3).

$$CuFeS_2 + 4H^+ + 2e^- \rightarrow Cu^0 + 2H_2S + Fe^{2+} \qquad (1)$$

$$2Cu + H_2S \rightarrow Cu_2S + 2H^+ + 2e^- \qquad (2)$$

$$Cu_2S \rightarrow Cu_{2-x_1}S + x_1Cu^{2+} + 2x_1e^- \qquad (3)$$

Peak c1 might be associated with the oxidation of hydrogen sulfide produced during reaction (1) to elemental sulfur shown as Eq.(4)[18, 20, 21].

$$H_2S \rightarrow S^0 + 2H^+ + 2e^- \qquad (4)$$

For the prewave (a), which has been reported by Biegler, et al[22] and Parker, et al[23], it is a region of selective dissolution of elements from the crystal lattice of chalcopyrite to form covellite according to Eq. (5):

$$CuFeS_2 \rightarrow 0.75CuS + 0.25Cu^{2+} + Fe^{2+} + 1.25S^0 + 2.5e \qquad (5)$$

More studies[24, 25] proposed it as the formation of nonstoichiometric sulfides shown as Eq. (6).

$$CuFeS_2 \rightarrow xCu^{2+} + yFe^{2+} + Cu_{1-x}Fe_{1-y}S_{2-z} + zS^0 + 2(x+y)e^- \qquad (6)$$

And the electrochemical reaction of Eq.(7), which is the oxidation of chalcocite to a series of covellite (CuS), also belongs to this range of potentials.

$$Cu_2S \rightarrow CuS + Cu^{2+} + 2e^- \qquad (7)$$

When potential value was more than 0.6 V, covellite (CuS) could be oxidized directly to cupric ions according to Eq. (8):

$$CuS + 8H_2O \rightarrow Cu^{2+} + 2SO_4^{2-} + 16H^+ + 14e^- \qquad (8)$$

When at the potential values more than 0.7 V (vs. Ag/AgCl), some studies considered this region as the oxidation of ferrous iron to ferric iron and the oxidation of sulphur to sulphuric acid[26, 27]. However, Lopez-Juarez et al[28] found that a large amount of S^0 was still existed on the chalcopyrite surface, and gave a favor on the oxidation of iron. Therefore, the reaction of peak a might be shown as Eq.(9).

$$CuFeS_2 \rightarrow 2S^0 + Cu^{2+} + Fe^{3+} + 5e^- \qquad (9)$$

In the reverse scan towards negative direction, an obvious peak e occurred around the potential value of 0.2 V, this might be mainly attributed to the reduction of Fe^{2+}、Cu^{2+} and S^0 according to the reactions from Eq.(10) to Eq.(13), which is consistent with the results of some other researchers[17, 29, 30].

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (10)$$

$$Cu^{2+} + S^0 + 2e^- \rightarrow CuS \qquad (11)$$

$$Cu^{2+} + 2e^- \rightarrow Cu^0 \qquad (12)$$

$$Cu_2 + CuS \rightarrow Cu_2S \qquad (13)$$

For the prewave of peak d, which was between -0.2 V and -0.5 V approximately. Lu, et al[17] attributed it to the reduction process of remnant chalcopyrite to intermediate copper sulfide phase such as talnakhite ($Cu_9Fe_8S_{16}$), mooihoekite ($Cu_9Fe_9S_{16}$) and bornite (Cu_5FeS_4) shown as Eq.(14) and Eq.(15).

$$9CuFeS_2 + 4H^+ + 2e^- \rightarrow Cu_9FeS_{16} + Fe^{2+} + 2H_2S \qquad (14)$$

$$5CuFeS_2 + 12H^+ + 4e^- \rightarrow Cu_5FeS_4 + 4Fe^{2+} + 6H_2S \qquad (15)$$

When at the potentials more negative than peak d, some researchers [26, 27, 29] attributed it to the reduction of covellite and chalcopyrite to chalcocite shown as Eq.(16) and Eq.(17).

$$2CuS + 2H^+ + 2e^- \rightarrow Cu_2S + H_2S \qquad (16)$$

$$2CuFeS_2 + 6H^+ + 2e^- \rightarrow Cu_2S + 2Fe^{2+} + 3H_2S \qquad (17)$$

Velasquez et al[15] considered it as the reduction of chalcocite to elemental copper shown as Eq.(18), which is an inverse reaction of peak c2.

$$Cu_2S + H^+ + 2e^- \rightarrow 2Cu + HS^- \qquad (18)$$

3.2 Comparison of interface reactions in different leaching mediums

The analytical results of Fig.1 showed that pH values do not change the interface reactions of chalcopyrite dissolution. However, the current density of anodic peaks increased significantly with the decrease of pH value, indicating that a lower pH value could accelerate the oxidative rate during chalcopyrite dissolution. The significantly higher cathodic current density of peak d revealed that chalcopyrite was prone to be reduced to bornite or talnakhite, which was considered as the rate-limiting step during chalcopyrite dissolution, thus accelerating the dissolution rate of chalcopyrite[18, 31].

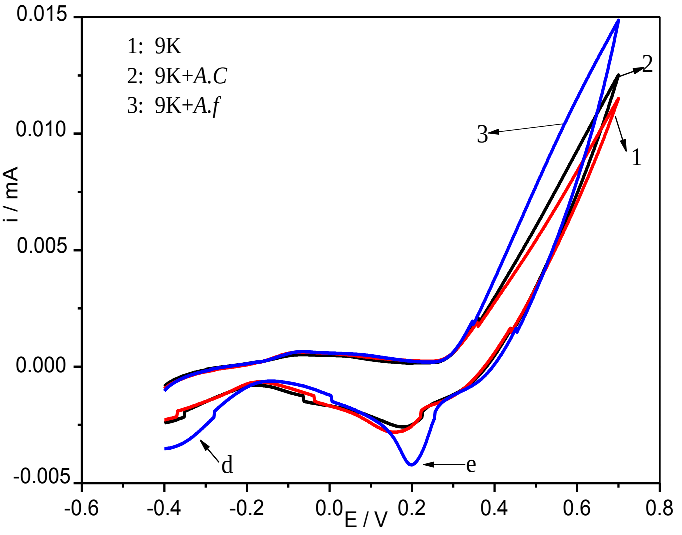

Figure 2. Cyclic voltammograms of massive chalcopyrite electrode in the 9K medium (pH = 2.0) in the presence or the absence of *A.c/A.f*. Sweep rate = 20 mv/s; Reference electrode: Ag/AgCl electrode (3 mol/L KCl).

The results of Fig.2 showed that the electrochemical behaviors of chalcopyrite dissolution in the presence or absence of *Acidithiobacillus ferrooxidans* and *Acidithiobacillus caldus* were similar, indicating that the chosen bacteria do not change the interface reactions of chalcopyrite dissolution.

It can be found that higher anodic currents in the presence of *Acidithiobacillus ferrooxidan or Acidithiobacillus caldus* were measured between the potential of 0.3 V to 0.6 V, where the main decomposition reactions of chalcopyrite occurred. It indicated that the rate of chalcopyrite decomposition reactions increased with the addition of the two strains of bacteria, this might be mainly attributed to the catalytical oxidation of ferrous iron to ferric iron ions by *Acidithiobacillus ferrooxidans*, and the catalytical oxidation of sulfur by *Acidithiobacillus caldus*, respectively, accelerating the dissolution of elements from chalcopyrite crystal lattice. Additionally, the cathodic current density of peak d significantly increased as the addition of *Acidithiobacillus ferrooxidans*, revealing that chalcopyrite was prone to be reduced to bornite or talnakhite, which was considered as the rate-limiting step during chalcopyrite bioleaching, thus accelerating the dissolution rate of chalcopyrite.

3.3 SEM and EDX study

The results of SEM and EDX analysis of massive chalcopyrite electrodes were shown as follows (Fig.3-Fig.6, Table 1 and Table 2). Corrosive regions were observed on the chalcopyrite electrode surface by SEM. Results showed that the atomic ratio of chalcopyrite surface in 9 K medium was approximately 1:1.06:2.41, and that of the chalcopyrite surface in the presence of *Acidithiobacillus ferrooxidans* was approximately 1:1.007:2.28.

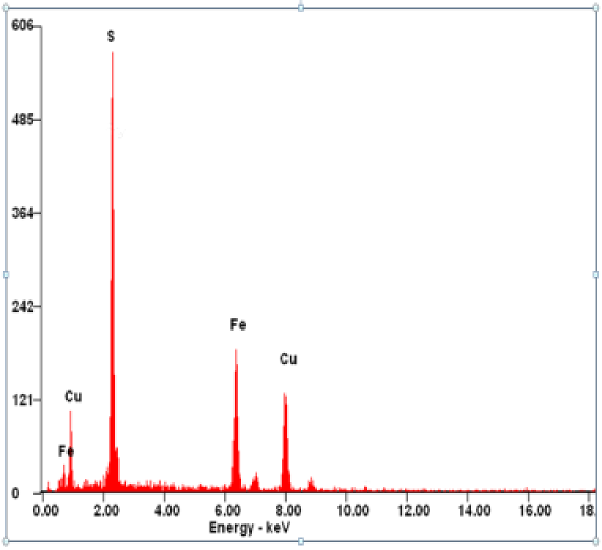

Figure 3. EDX of electrode surface (surface a) in 9K medium (pH=2.0) in the absence of bacteria.

It can be found that metal-deficient or sulfur-rich compounds were formed on the chalcopyrite surface. Additionally, the ratio of iron element and sulfur element of chalcopyrite surface in the presence of *Acidithiobacillus ferrooxidans* was less than that of chalcopyrite surface in sole 9 K medium, indicating that the dissolution rate of iron and sulfur elements from chalcopyrite crystal lattice was higher in the presence of *Acidithiobacillus ferrooxidans* when compared with that of chalcopyrite electrode in sole 9 K medium, this could be attributed to the catalytic effect of *Acidithiobacillus ferrooxidans* on accelerating the oxidative reactions of ferrous iron and sulfur, it was in accordance with the analytical results of cyclic voltammetry test [22, 32, 33].

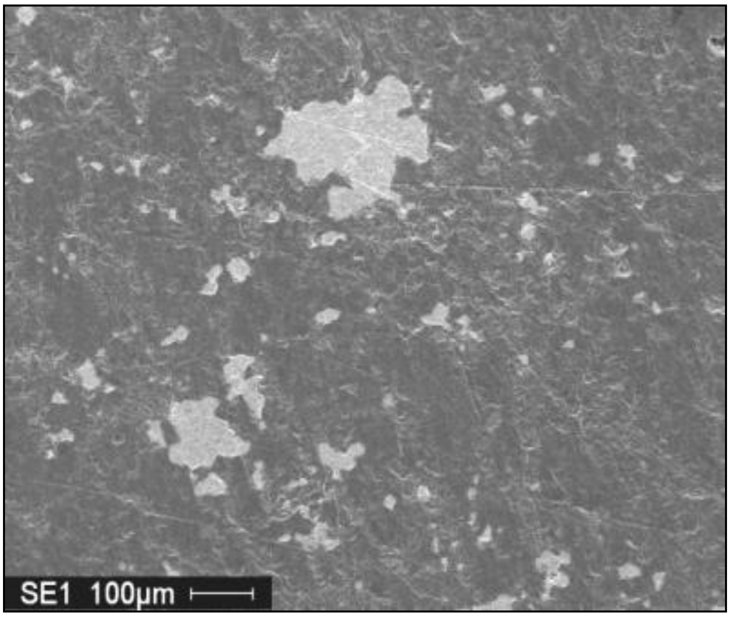

Figure 4. SEM of electrode surface (surface a) in 9K medium (pH=2.0) in the absence of bacteria.

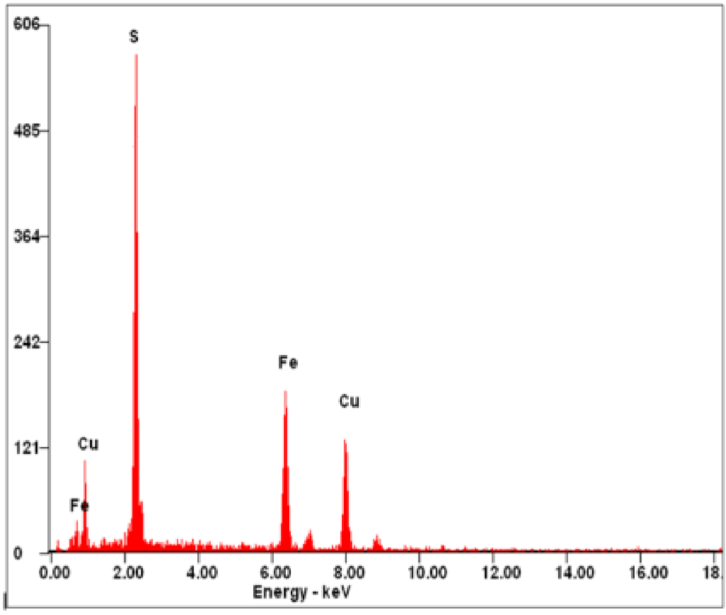

Figure 5. EDX of electrode surface (surface b) in the presence *A.f* (pH = 2.0).

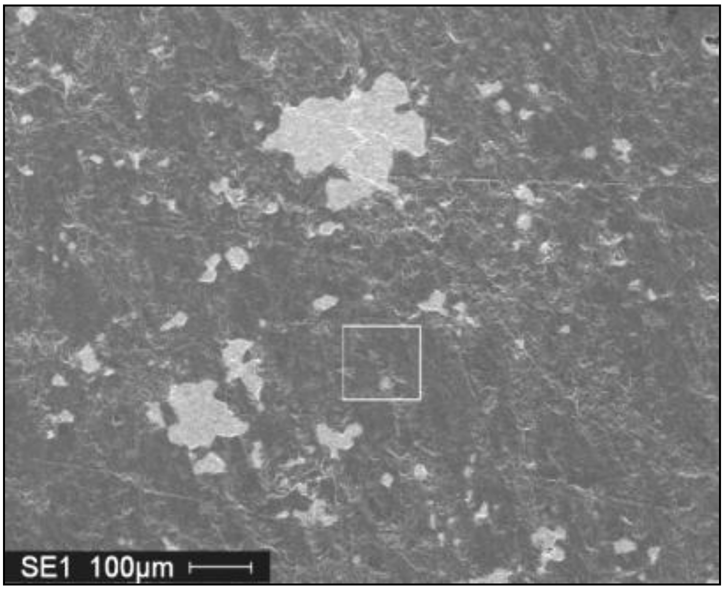

Figure 6. SEM of electrode surface in the presence of *A.f* (pH = 2.0).

Table 1. Chemical elements analysis of chalcopyrite surface a

Element	Wt/%	At/%
S	35.72	52.92
Fe	27.52	23.41
Cu	29.41	21.99

Table 2. Chemical elements analysis of chalcopyrite surface b

Element	Wt/%	At/%
S	36.43	52.74
Fe	28.00	23.27
Cu	31.63	23.10

4. CONCLUSIONS

(1) The dissolution of chalcopyrite involves series of complex interface reactions, several intermediate species could be formed during the oxidation-reduction of chalcopyrite in the presence or absence of bioleaching bacteria.

(2)The pH values and chosen bacteria of *Acidithiobacillus ferrooxidans* and *Acidithiobacillus caldus* do not change the interface reactions of chalcopyrite dissolution.

(3)A lower pH value or the presence of *Acidithiobacillus ferrooxidans* could accelerate the oxidation rate of chalcopyrite, and made chalcopyrite prone to be reduced to bornite or talnakhite, thus accelerating the dissolution rate of chalcopyrite, while the presence of *Acidithiobacillus caldus* only accelerated the oxidation rate of chalcopyrite.

ACKNOWLEDGMENTS
This work was supported by National High-tech Research and Development Program of China (project No. 2012AA061501), Research Fund for the Doctoral Program of Higher Education of China (project No. 20120162120010), Fundamental Research Funds for the Central Universities of China (project No. 721500275) , National Key Basic Research Program of China (project No. 2010CB630905) and Natural Science Foundation of China (project No. 51374248).

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