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Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 25(2015) 4110−4118
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Sulfur composition on surface of chalcopyrite during its bioleaching at 50 °C

Shi-fa WU, Cong-ren YANG, Wen-qing QIN, Fen JIAO, Jun WANG, Yan-sheng ZHANG

School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China

Received 2 February 2015; accepted 25 August 2015

Abstract: The composition of passive layer of chalcopyrite was investigated by X-ray photoelectron spectroscopy (XPS), accompanied with cyclic voltammetry (CV). The leaching experiment shows that the extraction rates of Cu with leaching for 30 d by sterile control and microorganisms are 4.0% and 21.5%, respectively. In comparison, 3.8% and 10.5% Fe are leached by sterile control and microorganisms, respectively. The results of XPS studies suggest that Fe atoms dissolve preferentially from the chalcopyrite lattice, and disulfide (S_2^{2-}), polysulfide (S_n^{2-}) and elemental sulfur (S^0) are identified on the chalcopyrite surfaces leached by sterile control and microorganisms. Additionally, sulfate (SO_4^{2-}) is detected on the chalcopyrite surfaces leached by microorganisms, and most of it probably originates from jarosite. The analysis of CV results reveals that metal-deficient sulfide ($Cu_{1-x}Fe_{1-y}S_{2-z}$, $y>x$) and elemental sulfur (S^0) passivate the surface of chalcopyrite electrode. The elemental sulfur and/or jarosite coating on the chalcopyrite surface may have impact on the leaching process; however, the disulfide, polysulfide or metal-deficient sulfide plays a more key role in the chalcopyrite leaching.

Key words: bioleaching; chalcopyrite; passive layer; electrochemistry

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1 Introduction

Chalcopyrite is the main source of copper in the world [1−3]. More than 80% copper is available as chalcopyrite, and around 20% copper in the world is obtained through hydrometallurgical process [3]. Much attention has also been paid to the bioleaching of chalcopyrite [4−8]. The mesophiles (30−40 °C), moderate thermophiles (about 50 °C) and extreme thermophiles (>65 °C) microbes are usually used to oxidize or assist in the oxidation of chalcopyrite, and such microbes are able to oxidize Fe^{2+} and/or S [1]. Moreover, it has generally been found that the use of moderate thermophiles and thermophiles are beneficial for chalcopyrite leaching [9−11]. Many researchers further suggested that there was clear benefit in leaching chalcopyrite within low solution potential, compared with high potential leaching [11−13].

The chalcopyrite is recalcitrant to both chemical and biological leaching due to the passivation of the mineral surface [6,14], and the passivation layer of chalcopyrite may be affected by leaching conditions such as the pH value and redox potential. Elemental sulfur [15−17], disulfide [15,16,18,19] polysulfide [16,18,20] and jarosite [16,17,21−23] identified on chalcopyrite surfaces leached by chemicals or microorganisms, have all been proposed as passivation candidates. KLAUBER et al [15,16] reported that the main species formed on the chalcopyrite surface are S^0 and S_2^{2-}. ACRES et al [18] identified that there was 16% S_2^{2-} and 43% S_n^{2-} on the surface of chalcopyrite leached in HCl solution for 2 h with the pH value of 1. ZHU et al [21] and HE et al [22] suggested that the jarosite might be the major component of the passivation layer of the chalcopyrite leached by thermophilic archaea.

Hence, it needs to further understand the component of a passivation layer of chalcopyrite bioleaching for successful industrial bioleaching implementation. The objective of the research was to investigate the sulfur speciation during chalcopyrite leaching at 50 °C.

Foundation item: Project (51274255) supported by the National Natural Science Foundation of China; Project (20130162110007) supported by the Doctoral Fund of Ministry of Education of China; Project supported by the Co-Innovation Center for Clean and Efficient Utilization of Strategic Metal Mineral Resources, China

Corresponding author: Cong-ren YANG; Tel: +86-13874962836; E-mail: yangcongren@csu.edu.cn

DOI: 10.1016/S1003-6326(15)64062-6

2 Experimental

2.1 Chalcopyrite

The high grade chalcopyrite was obtained from Daye, Hubei Province, China. The samples were splintered into small fragments with a geological hammer and dry ground in a porcelain ball mill. The product size was screened to less than 0.074 mm for bioleaching experiments. The chemical analysis of the sample shows 33.91% Cu, 30.62% Fe, 32.90% S, 0.039% Pb and 0.018% Zn (mass fraction). The X-ray diffraction analysis of the sample shows that the mineral is chalcopyrite.

2.2 Enrichment culture

A mixed moderately thermophilic culture was enrichment cultured from a leaching solution sample, which was obtained from Inner Mongolia, China, in 250 mL shake flasks using an orbital incubator with a stirring speed of 160 r/min at 50 °C. The medium used for cell cultivation consisted of the following components [24]: 3.0 g/L $(NH_4)_2SO_4$, 0.1 g/L KCl, 0.5 g/L $MgSO_4·7H_2O$, 0.5 g/L K_2HPO_4, 0.01 g/L $Ca(NO_3)_2$ and 0.02% yeast extract. All the cultures were sub-cultured into basal salts medium supplemented with 2% ore powder as the energy source. The resulting mixed culture was used as inoculums for all experiments. Three species (*Sulfobacillus thermosulfidooxidans*, *Acidithiobacillus caldus*, *Ferroplasma sp.*) were detected by community structure analysis as described by QIN et al [25].

2.3 (Bio)leaching experiments

For leaching experiments, the cells were inoculated into 250 mL flasks containing 100 mL sterilized culture medium and 2 g chalcopyrite. The initial cells concentration was 1.0×10^7 cell/mL. The flasks were placed in an orbital shaker at 50 °C with a stirring speed of 160 r/min. The parallel experiments without cells, but with the same culture medium and chalcopyrite, were run as the sterile experiments. All leaching experiments were supplemented with 0.02% yeast extract. The solution pH value was controlled at 1.6−2.0 with diluted sulfuric acid. Water lost by evaporation was supplemented periodically by adding sterile water until the mass of the flask equaled its initial mass.

2.4 Electrochemical measurements

Massive electrodes were prepared by cutting a high quality natural chalcopyrite sample into approximately cylinder shapes with areas of 1 cm^2 exposed to the solution. Before every electrochemical experiment, the working electrode surface was polished with carbide papers from 800 to 3000 grit, and then rinsed with deionized water.

Electrochemical experiments were carried out using a conventional three-electrode electrolytic cell with a graphite rod as the counter electrode and the prepared chalcopyrite electrode as the working electrode. A saturated Ag/AgCl electrode was used as the reference electrode for all the electrochemical tests. Electrochemical response was measured on a Princeton Model 283 potentiostat (EG&G of Princeton Applied Research) coupled to a personal computer with the M270 software. The electrolyte solution was prepared as follows: 3.0 g/L $(NH_4)_2SO_4$, 0.1 g/L KCl, 0.5 g/L $MgSO_4·7H_2O$, 0.5 g/L K_2HPO_4, 0.01 g/L $Ca(NO_3)_2$ with the pH value of 1.6. All the electrochemical experiments were performed at 50 °C in the electrolyte solution.

2.5 Analytical techniques

The mineralogical compositions of solid samples were examined by X-ray diffraction (XRD) (Rigaku D/max−2000). Solubles Cu and Fe were determined by atomic absorption spectroscopy (AAS). The pH value of the supernatant was measured with a pH meter (BPP−922, BELL) and the redox potentials in the leaching solution were measured with a Pt electrode with reference to a saturated Ag/AgCl electrode.

XPS was conducted with an ESCALAB 250Xi spectrometer with a monochromatic Al excitation (1486.6 eV) operating at 200 W. High resolution core level spectra were collected using a pass energy of 20 eV and an energy step of 0.1 eV. The chamber pressure was set to the limit of 1×10^{-7} Pa. The binding energy calibration was based on C 1s at 284.6 eV.

3 Results and discussion

3.1 (Bio)leaching characteristics of chalcopyrite

Figure 1(a) shows that the extraction rates of Cu for the leaching by sterile control and microorganisms for 30 d are 4.0% and 21.5%, respectively. In comparison, the Fe extraction rates are lower than those of Cu, only 3.8% and 10.5% Fe are leached by sterile control and microorganisms (Fig. 1(b)), respectively. The Fe extraction rate decreases due to the precipitation of the soluble ferric iron as the jarosite during bioleaching (Eq. (1)) [11,26]. Figure 1(c) shows that the acid is consumed in the whole leaching process. The redox potential of leaching with the microorganisms reaches and stabilizes at about 630 mV due to ferrous ions being oxidized to ferric ions by the microorganisms, while the redox potential of leaching by sterile control stabilizes at about 370 mV (Fig. 1(d)).

$$M^+ + 3Fe^{3+} + 2SO_4^{2-} + 6H_2O \rightarrow MFe_3(SO_4)_2(OH)_6 + 6H^+ \tag{1}$$

where M is a monovalent cation, e.g., H_3O^+, Na^+, K^+ and NH_4^+.