International Journal of Mineral Processing 94 (2010) 52–57

Contents lists available at ScienceDirect

International Journal of Mineral Processing

journal homepage: www.elsevier.com/locate/ijminpro

Investigation of the sulfur speciation during chalcopyrite leaching by moderate thermophile *Sulfobacillus thermosulfidooxidans*

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ARTICLE INFO

Article history:
Received 15 July 2009
Received in revised form 16 October 2009
Accepted 29 November 2009
Available online 4 December 2009

Keywords:
Sulfur speciation
Bioleaching
Chalcopyrite
Sulfobacillus thermosulfidooxidans
XANES

ABSTRACT

The surface sulfur speciation of chalcopyrite leached by moderately thermophilic *Sulfobacillus thermosulfidooxidans* was investigated by employing scanning electron microscopy (SEM), X-ray diffraction (XRD) and sulfur K-edge X-ray absorption near edge structure spectroscopy (XANES), accompanying with the leaching behavior elucidation. Leaching experiment showed that there was an optimum range of the redox potential for chalcopyrite dissolution. Leaching products were found accumulating during the leaching process, which might be jarosite according to the XRD analysis. The sulfur K-edge spectra indicated that chalcocite might be the intermediate sulfur compound under a critical redox potential, which might explain the existence of optimum range of the redox potential and provide an evidence for the two-step leaching model of chalcopyrite at low Eh. In addition, the results of sulfur K-edge spectra showed jarosite would accumulate on mineral surface, which might be the main component of the passivation layer.

1. Introduction

Chalcopyrite ($CuFeS_2$) is the most abundant copper sulfide mineral in terms of availability. Bioleaching low-grade chalcopyrite ores with microbes has been increasingly considered in recent years, due to its lower energy cost as well as its environmental benefit compared with the conventional metallurgy methods (Al-harahsheh et al., 2006). In order to enhance the leaching rate and yield of copper, it is important to understand the process of chalcopyrite biooxidation.

To evaluate the passivation layer formed on the mineral surface during the leaching process is becoming a focus considered by researchers, however, up to date, the chemical compositions of the passivation layer are still in dispute. For example, elemental sulfur or/and a series of compounds of polysulfide (S_n^{2-}, $n \geq 2$) (Hackl et al., 1995; Harmer et al., 2006; Klauber et al., 2001), jarosite (Parker et al., 2003; Sandström et al., 2005) and the simultaneous existence of them (Kinnunen et al., 2006) are reported.

In addition, chalcopyrite leaching may involve the formation of iron-deficient secondary minerals and intermediates (Sasaki et al., 2009). And those compounds are the key to understand the decomposition mechanism of chalcopyrite. It is reported that chalcocite and/or covellite might be formed during the leaching process (Hiroyoshi et al., 2001; Sandström et al., 2005; Sasaki et al., 2009), and those more dissoluble copper sulfides may accelerate the leaching process. Therefore, investigating the sulfur speciation during chalcopyrite dissolution is contributive to understand the mechanisms of chalcopyrite oxidation, besides the composition of passivation layer.

It is reported that the nature of passivation layer and the intermediate compounds would vary at different conditions (pH, temperature, Eh, etc.) (Rodríguez et al., 2003; Todd et al., 2003; Sandström et al., 2005; Dutrizac, 2008). In order to find out the optimum conditions for chalcopyrite bioleaching, taking the minimization of passivation effect as well as maximization of the intrinsic decomposition rate of chalcopyrite into consideration, the surface speciation of chalcopyrite during the leaching process under different conditions along with different microorganisms which thrive in such conditions should be investigated.

In the previous study (He et al., 2009), we investigated the sulfur speciation on chalcopyrite surface in the presence of extreme thermophilic microorganism *Acidians manzaensis* by scanning electron microscopy (SEM), X-ray diffraction (XRD), sulfur K-edge X-ray absorption near edge structure spectroscopy (XANES), finding jarosite might mainly attribute to the passivation of chalcopyrite, and covellite formed during the leaching process. In this study, *Sulfobacillus thermosulfidooxidans*, a kind of moderate thermophile, which is widespread in sulfur-rich acid environment (Dopsonm and Indstrom, 2004), and possesses higher bioleaching activity at elevated temperature compared with the mesophilic bacteria, was introduced into chalcopyrite leaching system. Its leaching characteristics as well as

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doi:10.1016/j.minpro.2009.11.005

sulfur speciation on the surface of chalcopyrite were investigated by using the similar methods cited above. From this study, we hope to provide some information about the nature of the passivation layer and secondary minerals formed during chalcopyrite bioleaching process with moderate thermophiles.

2. Materials and methods

2.1. Strain and culture condition

The moderately thermophilic and acidophilic *S. thermosulfidooxidans* (Accession number of 16S rDNA in GenBank: DQ650351) was isolated from an acid hot spring sample in Tengchong, Yunnan Province, China. The medium used for cell cultivation consisted of the following components (per litre): $(NH_4)_2SO_4$ 1.5 g, KH_2PO_4 0.25 g, $MgSO_4 \cdot 7H_2O$ 0.25 g, and $CaCl_2 \cdot 2H_2O$ 0.01 g, supplemented with yeast extract 0.2 g.

2.2. The metal sulfide sample and jarosite

The source and size of chalcopyrite, covellite, chalcocite and jarosite samples used in this study were the same as the ones used by He et al. (2009), and provided by the School of Minerals Processing and Bioengineering, Central South University, China. The main elements of chalcopyrite sample and their contents were: Cu 32.6%, S 31.05%, Fe 27.11%, O 2.7% Zn 1.94% Ba 0.502% Ca 0.43% Si 0.37%, Al 0.17%, Mg 0.09%, Pb 0.08% and As 0.05% according to the X-ray fluorescence spectroscopic analysis.

2.3. Bioleaching experiment

For leaching experiments, *S. thermosulfidooxidans* cells were inoculated into 250-mL flasks containing 100 mL of sterilized culture medium and 1 g of chalcopyrite that was washed previously according to the description of Klauber et al. (2001). The initial pH and cells concentration were 1.5 and 1.0×10^6 cells mL^{-1}, respectively. The cells were incubated at 53 °C with 180 rpm of shaking. The parallel experiments without cells, but with the same culture medium and chalcopyrite, were prepared as sterile controls. The monitoring of cell growth, Eh (measured by a platinum electrode with Hg/Hg_2Cl_2 reference), concentrations of copper and iron (either total iron, or ferrous and ferric iron, respectively), and the preparation of the samples for XANES tests were performed as described in our previous study (He et al., 2009). Triplicate leach experiments were performed under identical conditions.

2.4. The mineral morphology and composition studies

All of the SEM, XRD, and X-ray fluorescence spectroscopic studies were performed as the description of He et al. (2009).

2.5. XANES

The sulfur K-edge XANES spectra were recorded at 4B7A beam-line (medium X-ray beamline 2100–6000 eV) using synchrotron radiation from Beijing Synchrotron Radiation Facility, the Institute of High Energy Physics, the Chinese Academy of Sciences.

Chalcopyrite, chalcocite, covellite, elemental sulfur and jarosite were chosen as the standard compounds. Before the experiment all the samples and standard compounds were grinded into fine powder and homogeneously placed on a conductive double sided carbon adhesive tape (SPI Supplies) in a N_2-filled and airtight glove box, then mounted onto the vertical sample holder.

The tests were performed in fluorescence mode and each sample was mounted approximately 45° to the X-ray beam to insure the emitted fluorescent signal could be detected vertically by the fluorescent ion chamber Si (Li) detector (PGT LS30135) mounted at 90° to the incident beam. To minimize the absorption of X-ray by air, all the tests were performed in a high vacuum. The spectra were scanned with step widths of 0.3 eV and with an integration time of 3000 ms per point in the region between 2450 and 2520 eV. Background determined by the pre-edge data was subtracted from the original data to eliminate the effect of absorption from higher shells and supporting materials. All other parameters of the equipments and procedures of measurement as well as the data calculation (energy calibration) were the same as our previous report (He et al., 2009). The normalization of the spectra was performed at 2.510 KeV where the variation of the absorption cross-section is already very small. All the data was calculated with WinXas (3.0) (Ressler, 1998), and the normalized spectra data with main features (2.46–2.49 KeV) were fitted with the LSFitXAFS (Paktunc, 2004).

3. Results

3.1. The leaching characteristics of S. thermosulfidooxidans

The leaching characteristics of chalcopyrite by cells, in terms of changes in cell concentration, pH, Eh, concentration of $Cu^{2\pm}$, and ratio of $[Fe^{3\pm}]/[Fe^{2\pm}]$, are shown in Fig. 1 (a, b) and these parameters in sterile controls are shown in Fig. 1 (c, d). It shows that in the bioleaching system the pH increased with time at the beginning and reached a maximum at day 8, and thereafter decreased continuously to 1.25 (Fig. 1a), and other parameters including cell concentration, $[Cu^{2\pm}]$ (Fig. 1a) Eh, and ratio of $[Fe^{3\pm}]/[Fe^{2\pm}]$ (Fig. 1b) increased with time. A maximum $Cu^{2\pm}$ leaching rate was detected between day 8 and day 16, and thereafter decreased. At day 20, the final concentrations of Cu^{2+} for the bioleaching and the sterile control experiment were 1.35 g L^{-1} (Fig. 1a) and 0.34 g L^{-1} (Fig. 1c), respectively. It is worthy to note that both pH and ratio of $[Fe^{3+}]/[Fe^{2+}]$ in the bioleaching system changed with time differently from the sterile control (Fig. 1c and d), which was due to the $H^{\pm}$ and $Fe^{3\pm}$ provided by the cells in chalcopyrite bio-oxidation.

3.2. The surface morphology and composition analysis of chalcopyrite

The SEM micrographs shown in Fig. 2(a–c) show obvious changes in morphology occurred in chalcopyrite surface during the leaching experiment. After 12 days of leaching, visible corrosion of chalcopyrite was observed, and numerous of leaching products were adsorbed on the mineral surface (Fig. 2b and c). In contrast, the chalcopyrite surface was a little changed after leached for 20 days by the sterile control (Fig. 2d). XRD analysis (Fig. 3) indicated that a significant amount of jarosite was formed on the chalcopyrite surface after bioleaching, while no visible change happened after chemical leaching. It suggested that the leaching products observed in SEM might contain jarosite.

3.3. The surface sulfur speciation analysis of chalcopyrite

The sulfur K-edge XANES spectra of standard compounds such as covellite (CuS), chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), jarosite ($KFe_3(SO_4)_2(OH)_6$ and elemental sulfur (S) are shown in Fig. 4. The sulfur K-edge XANES spectra of chalcopyrite during leaching process are shown in Fig. 5a. The results show that chalcopyrite bioleached for 8 days presented almost the same absorption features to the original chalcopyrite and thereafter in the post edge region a new peak at 2.4804 KeV appeared, which could be assigned to SO_4^{2-} absorption peak after compared with the XANES spectra of the model compounds. In contrast, the sulfur K-edge XANES spectra of chalcopyrite leached with the sterile controls did not show change in the absorption features after leaching for 20 days.

The fitted XANES spectra of the surface residues at day 16 of bioleaching with those of the standard compounds are shown in