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Sulfur speciation on the surface of chalcopyrite leached by *Acidianus manzaensis*

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ABSTRACT

Sulfur speciation on the surface of chalcopyrite leached by extremely thermophilic *Acidianus manzaensis* was investigated by employing scanning electron microscopy (SEM), X-ray diffraction (XRD) and sulfur K-edge X-ray absorption near edge structure spectroscopy (XANES). SEM micrographs showed that the cells were attached to the surface of chalcopyrite and the mineral surface was covered with many floccules after 20-day bioleaching. XRD spectra indicated that the leach residue was mainly composed of chalcopyrite and jarosite, whilst the sulfur K-edge spectra indicated that the jarosite might be the main component of the passivation layer of the chalcopyrite leached by *A. manzaensis*. The results of spectral graphic analysis suggested that covellite was the intermediate sulfur compound during bioleaching of chalcopyrite.

1. Introduction

Chalcopyrite ($CuFeS_2$) is the most widespread copper sulfide mineral and is also the most refractory (Parker et al., 2003, Harmer et al., 2006). Bioleaching low-grade chalcopyrite with microbes offers attractive alternative methods to conventional leaching methods which has been successfully applied in many countries.

In the last decade, extremely thermophilic microbes have been widely employed in the bioleaching metal sulfides, such as chalcopyrite and pyrite. For example, extreme thermophiles are employed to leach chalcopyrite- and pyrite-containing copper concentrate and the extent of leaching of copper ions could reach up to 98% (Gericke and Pinches, 1999; Gericke et al., 2001; Konishi et al., 2001). However, the rate of chemical and biological leaching of chalcopyrite has been shown to decrease with time and the leaching process eventually ceased at ambient temperature and pressure due to the formation of a passivation layer on the mineral surface (Hackl et al., 1995; Parker et al., 2003; Harmer et al., 2006) whose main components are still in dispute.

Hackl et al. (1995) investigated the passivation layer using Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) and found that its main components might be copper polysulfide (i.e. CuS_n, $n>2$). In contrast, Klauber et al. (2001) reported that leached chalcopyrite produced elemental sulfur and polysulfide; and the former was the initial leaching inhibitor. In addition, Parker et al. (2003) did not detect polysulfide phase in the chemically leached chalcopyrite, but found elemental sulfur, sulfate and disulfide surface species. Thus they proposed that the passivation was caused by the jarosite, rather than polysulfide, which was subsequently corroborated by Sandström et al. (2005).

Although the main components of the passivation layer on the surface of leached chalcopyrite are distinct, we can see that the reported passivation products are all related to various sulfur speciations. So understanding the sulfur speciation of the surface products is very necessary for performing bioleaching of chalcopyrite. The aim of this study is to quantify the sulfur speciation occurring in the course of bioleaching chalcopyrite by *Acidianus manzaensis* with the use of an integrated approach including X-ray diffraction (XRD), scanning electron microscopy (SEM), and sulfur K-edge X-ray absorption near edge spectroscopy (XANES).

2. Materials and methods

2.1. Strain and culture condition

The extremely thermophilic and acidophilic *Archaea A. manzaensis* (accession number 16S rDNA in GeneBank: EF522787) 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 liter): $(NH_4)_2SO_4$, 1.5 g; KH_2PO_4, 0.25 g; $MgSO_4 \cdot 7H_2O$, 0.25 g; $CaCl_2 \cdot 2H_2O$, 0.01 g; yeast extracts 0.2 g and 1 mL trace elements solution containing (g L^{-1}) ($FeCl_3 \cdot 6H_2O$, 20 g; $MnCl_2 \cdot 4H_2O$,

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Table 1
The main components of chalcopyrite.

	Cu	S	Fe	O	Zn	Ba	Ca	Si	Al	Mg	Pb	As
t %	32.6	31.05	27.11	2.7	1.941	0.502	0.43	0.37	0.17	0.09	0.08	0.05
moles/100 g	0.51	0.97	0.49	0.17	0.03	0.003	0.01	0.01	0.006	0.003	0.0004	0.001

1.8 g; $Na_2B_4O_7 \cdot 2H_2O$, 4.5 g; $ZnSO_4 \cdot 7H_2O$, 0.22 g; $NaMoO_4 \cdot 2H_2O$, 0.03 g; $CoSO_4 \cdot 7H_2O$, 0.01 g; $CuCl_2 \cdot 2H_2O$, 0.05 g and $VSO_4 \cdot xH_2O$ 0.03 g). The initial pH of the medium was adjusted to pH 1.5 with 1 M sulfuric acid.

2.2. The metal sulfide sample and jarosite

The pure and natural chalcopyrite, covellite and chalcocite samples were provided by the School of Mineral Processing and Bioengineering, Central South University, China. The mineral powders used in the experiments had a particle size of <75 μm. Jarosite was synthesized by adding 44.5 g L^{-1} ferrous sulfate into the *A. manzaensis* growth medium according to the reported methods (Sasaki and Konno, 2000; Ding et al., 2007).

2.3. Bioleaching experiment

For leaching experiments, *A. manzaensis* cells were inoculated into 250-mL flasks containing 100 mL sterilized culture medium and 3 g chalcopyrite. The initial cells concentration was 1.0×10^6 cells mL^{-1}, and the cells were then incubated at 65 °C with 180 rpm shaking. Parallel experiments without cells, but with the same mixing culture medium and chalcopyrite, were prepared as sterile controls. Cell growth was monitored by using a counting chamber; Eh was measured by a platinum electrode with Hg/Hg_2Cl_2 reference; total copper and iron were measured using atomic absorption spectroscopy, and the ferrous concentration was determined by standard potassium dichromate titration. Triplicate leach experiments were performed under identical conditions.

In order to analyze intermediate sulfur compounds, several experiments were stopped at different times and aliquots of 1 mL leach slurry were transferred into a 1.5 mL tube and centrifuged at 10,000 rpm for 10 min. The supernatants were removed and the chalcopyrite powder was frozen in liquid N_2 and stored in an anaerobic jar (Mart HP025) until the XANES test. All these operations were performed in an N_2-filled and airtight glove box.

2.4. Scanning electron microscopy

The mineral samples collected at different time intervals for SEM analysis were placed into a 1.5 mL tube containing 1 mL formaldehyde (25%v/v). The samples were dehydrated, then coated with gold and introduced into the SEM (JEOL JSM-6360 LV) chamber for observation.

2.5. X-ray fluorescence spectroscopy and XRD

X-ray fluorescence spectroscopy and XRD were employed to examine the main components of chalcopyrite, covellite, chalcocite and jarosite. The original and residual leached chalcopyrite samples were analysed with a Diffractometer (Japan, D/ruax2550PC), operating at 0.02 two-theta steps from 10 to 85° and a count time of 2 s per step.

2.6. XANES

X-ray absorption spectra were recorded at 4B7A beam-line (medium X-ray beamline 2100 eV–6000 eV) using synchrotron radiation from Beijing Synchrotron Radiation Facility, Institute of High Energy Physics of China. The storage ring was operated at an energy of 2.5 GeV with an electron current of 100 mA. The synchrotron radiation was filtered by a monochromator equipped with Si (111) double crystals. The measurements were performed in fluorescence mode and the spectra were recorded using a fluorescent ion chamber and Si (Li) detector (PGT LS30135). The spectra were scanned with step widths of 0.3 eV in the region between 2450 and 2520 eV. The X-ray energy was calibrated with reference to the spectrum of the highest resonance energy peak of $ZnSO_4$ at 2480.4 eV. According to the step width, the reproducibility of this value was found to be ±0.1 eV. In all cases, the spectra were normalized to the maximum of the absorption spectrum with WinXas (3.0) (Ressler, 1998). The spectra of the sulfur containing model compounds were obtained as performed before (He et al, 2009). All the data was calculated with WinXas (3.0) and the spectra were fitted with the LSFitXAFS program (Paktunc, 2004).

3. Results and discussion

3.1. Bioleaching performance of A. manzaensis

X-ray fluorescence spectroscopy analysis confirmed that the employed samples were mainly composed of chalcopyrite mineral (Cu, S and Fe accounts for up to 91%, as shown in Table 1). The cell number in the bioleaching system increased with time and reached a maximum of 4.2×10^8 cell mL^{-1} on the 12th day, and thereafter decreased (Fig. 1). The pH in the bioleaching system increased with time and reached a maximum on the fourth day and thereafter decreased to less than pH 1.28 (Fig. 1). The Eh, Fe^{3+}/Fe^{2+} and Cu^{2+} concentration in the bioleaching system increased with time synchronously (Fig. 1).

After 20 days of leaching, the concentrations of copper ions released from chalcopyrite in the bioleached and control reactions were 7.25 g L^{-1} and 0.55 g L^{-1}, corresponding to 78.3% and 5.9% copper extraction, respectively. The leaching rate of copper significantly decreased after 16 days, which is in agreement with previous studies (Parker et al., 2003; Harmer et al., 2006). It has been reported that the copper is an essential trace element for all cells. However, the accumulation of copper ions beyond a certain concentration in a bioleaching system will become toxic to bacteria, thereby affecting the bioleaching rate (Li and Ke, 2001). Thus, the cell numbers significantly decrease because of the accumulation of copper ions after 12 days of

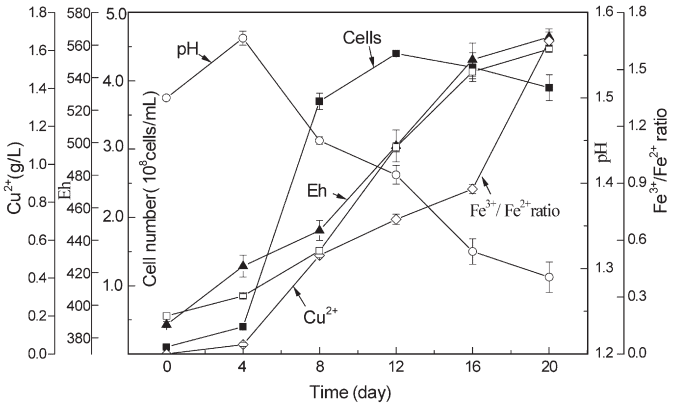

Fig. 1. Growth characteristics of chalcopyrite-grown *A. manzaensis* cells. (■: cell numbers, ▲: Eh (ref. Hg/Hg_2Cl_2), ○: pH value and ●: ratio of Fe^{3+}/Fe^{2+}).