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# Analysis of sulfur speciation on chalcopyrite surface bioleached with *Acidithiobacillus ferrooxidans*

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ABSTRACT

The typical mesophile *Acidithiobacillus ferrooxidans* was used to leach chalcopyrite. The characteristics of mineral surface, main components of mineral and the sulfur speciation on the mineral surface were investigated combining with SEM, XRD and sulfur K-edge XANES spectroscopy. SEM micrographs showed that the mineral surface was obviously corrupted and covered by some visible crystalline floccules after 24 days bioleaching. XRD analysis indicated that jarosite and chalcopyrite were the main components in the leaching residue. The sulfur K-edge XANES spectra indicated that the jarosite was the main component of the passivation layer and the chalcocite was the transient intermediate sulfur compound during the bioleaching of chalcopyrite.



## 1. Introduction

Bioleaching low-grade chalcopyrite with acidophilic microbes offers alternative methods to conventional leaching which has developed rapidly in many countries. Among all the reported acidophilic microbes, *Acidithiobacillus ferrooxidans* is the most widely studied acidophilic bioleaching bacterium, which obtains energy by oxidizing ferrous ions, elemental sulfur and reduced sulfur compounds (Bevilaqa et al., 2002; Devasia and Natarajan, 2010). It has been reported that the efficiency of bioleaching chalcopyrite decreased with time and the leaching process eventually ceased at ambient temperature and pressure due to the formation of passivation layer on the mineral surface (Rodwerder et al., 2003). However, the detailed components of the passivation layer are still in dispute. Several sulfur species including elemental sulfur, chalcocite, covellite, jarosite and other polysulfides had been found on the mineral surface when chalcopyrite was oxidized to sulfate by *Acidithiobacillus* via the polysulfide pathway (Klauber et al., 2001; Daoud and Karamanev, 2006; Ahmadi et al., 2011). It was reported that the elemental sulfur was the initial leaching inhibitor during the bioleaching chalcopyrite (Klauber et al., 2001). In contrast, another reports mentioned that the main components of passivation layer might be copper polysulfide (i.e. $CuS_n$, $n > 2$) (Hackl et al., 1995; Harmer et al., 2006). Nevertheless, except elemental sulfur, sulfate and disulfide surface species, the polysulfide phase was not detected in the chemically leached chalcopyrite (Parker et al., 2003). Thus, they proposed that the passivation was caused by the jarosite, rather than the polysulfide, which was corroborated by a subsequent report (Sandsröm et al., 2005). In our previous reports, covellite and chalcocite were presented as the intermediate sulfur compounds, while jarosite might be the main component of the passivation layer during chalcopyrite bioleached with *Acidianus manzaensis* and *Sulfobacillus thermosulfidooxidans*, respectively (He et al., 2009b; Xia et al., 2010). It has been proposed that reduction of refractory chalcopyrite to more soluble minerals such as chalcocite and covellite could accelerate the bioleaching efficiency of copper, whereas the formation of jarosite was the main reason of decrease of solution rate of chalcopyrite (Ahmadi et al., 2011). Based on the above description, it can be concluded that analysis the sulfur speciation of the mineral surface is very necessary for understanding the bioleaching process of chalcopyrite. The aim of this study is to quantify the sulfur speciation occurring in the course of bioleaching chalcopyrite by typical mesophile *A. ferrooxidans* with XRD, SEM and sulfur K-edge XANES.

## 2. Materials and method

### 2.1. Strain, metal sulfide and jarosite sample

*A. ferrooxidans* was cultured in the 9 K basal salts media (He et al., 2009a) supplemented with chalcopyrite, and the initial pH was adjusted to 2.0 with 1 M $H_2SO_4$. The pure and natural covellite

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(CuS), chalcopyrite ($CuFeS_2$), chalcocite ($Cu_2S$) samples were provided by Institute of Mineral Processing Engineering, School of Resources Processing and Bioengineering, Central South University, China. The main components of chalcopyrite were as follows: Cu 32.6%, S 31.05% and Fe 27.11% and the size of which was no larger than 75 μm. The jarosite ($KFe_3(SO_4)_2(OH)_6$) was synthesized according to our previous reported method (He et al., 2009b).

### 2.2. Bioleaching experiment

For leaching experiments, *A. ferrooxidans* cells were inoculated into 250-mL flasks containing 100 mL sterilized culture medium and 3 g chalcopyrite (the initial cells concentration was $1.0 \times 10^6$ cells $mL^{-1}$), and were incubated at 30 °C with 180 rpm shaking. Parallel experiments (without cells, but the same mixed culture medium and chalcopyrite) were prepared as sterile control. Cell's concentration was monitored by using a counting chamber, the Eh was measured by using a platinum electrode with Hg/$Hg_2Cl_2$ reference, the total copper and iron ions were measured by atomic absorption spectroscopy. Triplicate leach experiments were performed under identical conditions. In order to analyze the intermediate sulfur compounds, the mineral samples were prepared at different interval times according our previous report (He et al., 2009b)and stored in an anaerobic jar (Mart HP025) until XANES test.

### 2.3. SEM

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

### 2.4. 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 analyzed with X-ray Diffractometer (Japan, D/ruax2550PC), 0.02 two-theta steps from 10° to 85°, and a count time of 2 s per step.

### 2.5. XANES

X-ray absorption spectra were recorded at 4B-7A beamline (medium X-ray beamline, 2100–6000 eV) using synchrotron radiation at the Beijing National Synchrotron Radiation Facility, Institute of High Energy Physics of China. The possible intermediate compounds such as covellite, chalcopyrite, chalcocite, jarosite and elemental sulfur were chosen as reference compounds. In our present work, the samples spectra were fitted with the reference compounds based on least squares linear-combination fitting method as our previous reports (He et al., 2009a,b).

## 3. Results and discussion

### 3.1. Bioleaching characteristics of A. ferrooxidans

The growth characteristics of cells and the leaching curves of chalcopyrite by cells and sterile control are shown in Figs. 1–3, respectively. It shows that the leaching process of cells can be divided into three stages. As shown in Fig. 1, at the initial 4 days, the cells concentration remains invariable, then increases slowly during the next 12 days and enter the logarithmic period after 16 days. It shows that the *A. ferrooxidans* significantly promotes the leaching process of chalcopyrite, with a final copper and total iron concentration of 1.87 g $L^{-1}$ (leaching rate 47.8%) and 412 mg $L^{-1}$ (leaching rate 12.7%), respectively (Fig. 2). In contrast, the concentration of both metal ions were 0.21 g $L^{-1}$ (leaching rate 5.36%) and 58 mg $L^{-1}$ (leaching rate 1.78%) in the sterile control after 24 days leaching (Fig. 2).As expected, an increase pH was observed at the initial 8 days of bioleaching and began to decrease after 16 days (Fig. 3), however, it was not lower than the initial pH as our previous report (He et al., 2009b). It has been known for a long time that the leaching efficiency of chalcopyrite is dependent on the redox potential (Eh) in solution and it is enhanced when leaching is performed at appropriate range of redox potential (Ahmadi et al., 2011; Sandsröm et al., 2005; Vilcáez et al., 2008). As shown in Fig. 3, the Eh of the bioleaching slurry has almost synchronous variation with the iron and copper concentration (Fig. 2). During the range of 233–391 mV (Ref. $Hg/Hg_2Cl_2$), the concentration of copper ions increased along with the Eh, thereafter, the leaching rate of copper gradually decreased after 16 days. Actually, the Eh of leaching slurry during bioleaching of chalcopyrite depended on the ferric to ferrous ion ratio ($Fe^{3+}/Fe^{2+}$) as described by Nernst equation (Ahmadi et al., 2010). On the other hand, keeping high Eh of leaching slurry needs to consider both the activity of leaching microbes and the pH of leaching system. According to the following equations (Eqs. (1)–(4)) (Xia et al., 2010; Ahmadi et al., 2010), the ferric ions formed from bio-oxidation of ferrous ions (Eq. (1)) and consumed during the chalcopyrite oxidation (Eq. (2)) and precipitation of jarosite (Eq. (4)). Nevertheless, the protons of leaching system are consumed in the redox of ferrous ions (Eqs. 1 and 2) and formed from the precipitation of jarosite (Eq. (4)). In our present work, the highest microbes' concentration and Eh took place between the 16–24 days, and the results were consistent with the concentration of copper and iron. By contrast, the bioleaching efficiency of copper entered stationary stage and the pH began to decline. Apparently, the precipitation of large amounts jarosite could inhibit the leaching reaction (Eq. (4)).

$$Fe^{e+} + 1/4O_2 + H^+ \xrightarrow{A.ferrooxidans} Fe^{3+} + 1/2H_2O \quad (1)$$

$$4Fe^{3+} + CuFeS_2 + O_2 + 4H^+ \rightarrow 5Fe^{2+} + 2S^o + Cu^{2+} + H_2O \quad (2)$$

$$S^o + H_2O + 3/2O_2 \xrightarrow{A.ferrooxidans} H_2SO_4 \quad (3)$$

$$3Fe^{3+} + X^+ + 2HSO_4^- + 6H_2O \rightarrow XFe_3(SO_4)_2(OH)_6 + 8H^+ \quad (4)$$

where $X = K^+$, $Na^+$, $NH_4^+$ or $H_3O^+$.

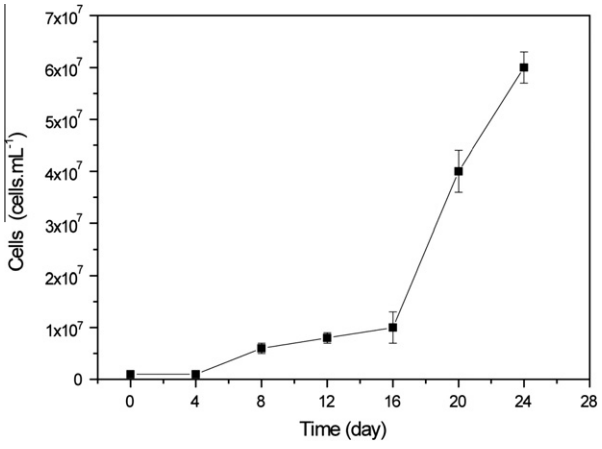


**Fig. 1.** Growth characteristics of chalcopyrite-grown *A. ferrooxidans* cells.