



Study on catalytic mechanism of silver ions in bioleaching of chalcopyrite by SR-XRD and XANES



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ABSTRACT

Ag⁺ is one of the efficient and recoverable catalysts to improve chalcopyrite bioleaching. Because of the complexity of the surface reaction during chalcopyrite bioleaching, there is still controversy on catalytic mechanism of Ag⁺ in improving dissolution of chalcopyrite. In the present study, we studied the catalytic effect of Ag⁺ on bioleaching of chalcopyrite by extreme thermophile *Acidianus manzaensis*. Based on synchrotron radiation X-ray diffraction (SR-XRD) and X-ray absorption near edge structure (XANES) spectroscopy, the relevant iron and sulfur speciation of leaching residues was analyzed. Bioleaching experiments showed that copper extraction was significantly promoted by adding Ag⁺, and the optimum concentration of Ag⁺ was 0.05% (mass fraction of Ag⁺ to chalcopyrite). SR-XRD and XANES analyses showed that, during bioleaching in the presence of 0.05% of Ag⁺ and in the absence of Ag⁺, the intermediates S⁰, jarosite and secondary minerals (chalcocite, bornite and covellite) were formed. The linear combination fitting of XANES spectra further revealed that the addition of silver ions remarkably promoted the formation of bornite and covellite, while had no effect on formation of chalcocite, indicating that bioleaching of chalcopyrite should be catalyzed by Ag⁺ with promoting the generation of bornite and its conversion to covellite. This model suggested that the rapid formation of bornite like species contributed to positive effect of Ag⁺ on chalcopyrite bioleaching, while the accumulation of covellite slowed leaching rate at the end period of chalcopyrite bioleaching.

1. Introduction

Chalcopyrite (CuFeS₂) is the most abundant copper mineral among all kinds of copper sulfide ores (Li et al., 2013; Pradhan et al., 2008). However, it is also the most refractory and recalcitrant in contrast to other copper minerals (Marsden and Wilmot, 2007). Bio-hydrometallurgy is considered as one of the most promising techniques to solve this problem with attractively environmental and economic effects, and it has been widely studied at laboratory and industrial levels since last decades (Brierley and Brierley, 2013; Johnson, 2014; Panda et al., 2015). Though it is of great value to treat low-grade copper ores, the biggest problem restraining this technology in chalcopyrite bioleaching is that the leaching rate is still low by comparing with other copper minerals. The reason for low dissolution rate of chalcopyrite has been mostly studied, and some researches indicate that it is caused by the formation of a passive film on chalcopyrite surface (Harmer et al.,

2006; Klauber, 2008). The passive layer could be S⁰, jarosite and iron deficient secondary minerals (Franz et al., 2009; Klauber, 2008). However, some other researchers suggest that these intermediates cannot hinder chalcopyrite dissolution (Jiang et al., 2009; Khoshkhoo et al., 2014; Liu et al., 2017). Nevertheless, it is crucial to improve bioleaching process to meet the commercial requirement.

So far, many efforts have been made to enhance the bioleaching process of chalcopyrite, including using thermophiles (Johnson et al., 2008; Marhuala et al., 2008), adding catalysts (Ag⁺, cysteine, Cl⁻ and activated carbon) (Hu et al., 2002; Liang et al., 2010; Liang et al., 2012), and optimizing the redox potential (ORP) and the acidity (Liu et al., 2016a; Vilcáez et al., 2008). Among these methods, Ag⁺ is known to catalyze chalcopyrite leaching with efficient leaching rate and has been used in industrial copper-zinc concentrate, and the recovery of Ag⁺ by acidic brine leaching of residue has also been developed, making this method economic to industrial application (Carranza et al.,

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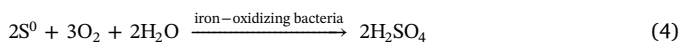
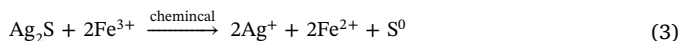
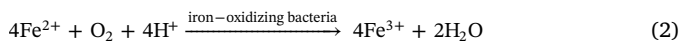
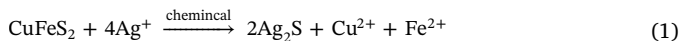
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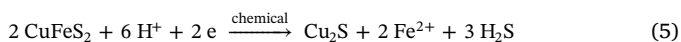
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1997; Palencia et al., 1998; Romero et al., 1998). The mostly accepted catalytic reactions by Ag^+ during bioleaching of chalcopyrite are shown as followings (Eq. (1)–(4)) (Gómez et al., 1999a,b; Hu et al., 2002; Miller and Portillo, 1981; Muñoz et al., 1998; Sato et al., 2000):



Unlike to the above model, Hiro Yoshi et al. (2002) propose that Ag^+ catalyzes chalcopyrite dissolution by reacting with hydrogen sulfide released in acidic solutions (Eq. (5)–(6)), which is so-called indirect catalysis model. On the other hand, by considering how to eliminate the passive layer ($\text{Cu}_{1-x}\text{Fe}_{1-y}\text{S}_2$) on chalcopyrite surface, Ghahremaninezhad et al. (2015) suggests that surface sulfur is combined with Ag^+ and released into solution by taking copper and iron vacancy positions, and then the porous sulfur-based product forms on chalcopyrite surface, so silver ion can continue to catalyze chalcopyrite dissolution by entering the sulfur vacancy.



It is no doubt that Ag^+ can rapidly interact with sulfur, but the proposed models are still defective, because of the complexity of the surface reaction in bioleaching of chalcopyrite, especially when the formation of surface secondary minerals and other intermediates is involved. The formation and evolution of leaching intermediates have been research hotspots recently, which benefit from the development of new technologies with high spatial and high resolution, such as synchrotron radiation techniques (He et al., 2009; Majuste et al., 2012; Liu et al., 2015a; Liu et al., 2017). Recently, we used synchrotron radiation (SR)-based techniques studied leaching intermediates during bioleaching, and the evolution of leaching intermediates was illustrated (Liu et al., 2015a, 2017, 2015b). Based on these studies, SR-based S K-edge XANES spectroscopy accompanying with linear combination (LC) fitting was confirmed for the detection of leaching intermediates, such as bornite, chalcocite, covellite, jarosite and S^0 . As the evolution of surface intermediates is useful to illustrate the mechanism during bioleaching, it can also be of value to explain catalytic mechanism of Ag^+ in bioleaching of chalcopyrite.

Therefore, in the present study, we use a widely studied thermophilic Archaea strain *Acidianus manzaensis* with high leaching efficiency and synchrotron radiation based techniques to study bioleaching of chalcopyrite in the presence of Ag^+ . Through investigating what intermediates form during bioleaching of chalcopyrite with catalysis Ag^+ and how they form, we are trying to explain the catalytic mechanism models of silver ion to chalcopyrite bioleaching by *A. manzaensis*.

2. Material and methods

2.1. Strain and culture medium

The extremely thermoacidophilic Archaea strain *A. manzaensis* YN-25 (Accession number of 16S rDNA in GeneBank: EF522787) was provided by the School of Minerals Processing and Bioengineering, Central South University, Changsha, China. The strain was cultivated at 65 °C and pH 1.5–2.5, and it was widely used in bioleaching test at laboratory and pilot scale (Liang et al., 2010; Liu et al., 2015a; Zhu et al., 2011). Prior to bioleaching experiment, the strain was adapted to the substrate, i.e. chalcopyrite, by several generations of cultivation according to Liang et al. (2012). The basal medium for cultivation of

this strain consisted of the following components: $(\text{NH}_4)_2\text{SO}_4$, 3.0 g/L; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.5 g/L; K_2HPO_4 , 0.5 g/L; KCl, 0.1 g/L; $\text{Ca}(\text{NO}_3)_2$, 0.01 g/L; and yeast extracts 0.2 g/L.

2.2. Mineral samples

The chalcopyrite and the reference minerals (i.e. bornite, chalcocite, covellite, jarosite) were provided by the School of Minerals Processing and Bioengineering, Central South University, Changsha, China, and they have been widely used in our previous studies (He et al., 2009; Liu et al., 2015a). The mineralogical compositions tests (by XRD) indicate that the original chalcopyrite is basically pure mineral (not shown). X-ray fluorescence spectroscopic analysis shows that the original chalcopyrite comprised of (mass fraction, %): Cu, 33.48; S, 33.05; Fe, 28.99; O, 1.75; Zn, 0.84; Ba, 0.52; Ca, 0.44; Si, 0.38; Al, 0.18; and Mg, 0.09. The original chalcopyrite was ground and passed through the sieves of –200 and –400 meshes, obtaining fine particles with the size of 37–75 μm .

2.3. Bioleaching experiment

For bioleaching experiments, *A. manzaensis* cells were incubated in 500 mL Erlenmeyer flasks containing 200 mL sterilized basal medium and 2 g chalcopyrite in a high-temperature bath rotary shaker (SHZ-GW) at 170 r/min and 65 °C. In order to examine the effect of Ag^+ on the bioleaching of chalcopyrite, Ag_2SO_4 was added to the culture media. The concentrations of Ag^+ in solution was 2, 5, 10 and 20 mg/L, respectively, i.e. 0.02%, 0.05%, 0.1%, 0.2% of the weight of silver to the weight of chalcopyrite. The initial pH of the culture medium was adjusted to 1.7 with dilute sulfuric acid. The initial inoculated cell density was 2×10^7 cells/mL. The bioleaching assay without Ag^+ , as well as the sterile assay adding 0.02%, 0.05%, 0.1% or 0.2% of Ag^+ served as control. The leaching experiments were triplicate at the same conditions for 8 d. During bioleaching, evaporated water was compensated with sterilized ultra-pure water based on weight loss at 12 h intervals.

2.4. Analysis methods

2.4.1. Leaching parameters

During bioleaching experiment, leaching solutions were taken out at 1 d intervals to determine cell densities, pH and ORP values, and the concentrations of Fe^{3+} , total iron (TFe) and Cu^{2+} . The pH value was determined with a pH meter (PHS-3C). The ORP value was measured with a platinum (Pt) electrode, using a calomel electrode ($\text{Hg}/\text{Hg}_2\text{Cl}_2$) as reference. $[\text{Cu}^{2+}]$ was determined by bis-(cyclohexanone)oxalyldihydrazone spectrophotometry. $[\text{Fe}^{3+}]$ and total iron concentrations ([TFe]) were determined by 5-sulfosalicylic acid spectrophotometry.

2.4.2. Surface morphology

The surface morphology of chalcopyrite particles in bioleaching and in abiotic experiment was observed by scanning electron microscopy (SEM) (Nova™ NanoSEM 230, FEI, USA). The solid samples for SEM were first treated according to previous description (Liu et al., 2015b), and then coated with gold by sputter (JEOL, JFC-1600, Japan) and introduced into the SEM chamber for observation.

2.4.3. Chalcopyrite compositions

The compositions of chalcopyrite during bioleaching were analyzed by SR-XRD and XANES spectroscopy, respectively. Before these analyses, the solid samples were first washed gently (Liu et al., 2015b) and dried in vacuum with a vacuum drying oven (DZF-6020), and stored in nitrogen atmosphere at –70 °C.

The SR-XRD patterns was recorded at beamline BL14B1 of Shanghai Synchrotron Radiation Facility, Shanghai, China, at a step of 0.01° and

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