Minerals Engineering 106 (2017) 22–32

Contents lists available at ScienceDirect

Minerals Engineering

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

Comparative study of S, Fe and Cu speciation transformation during chalcopyrite bioleaching by mixed mesophiles and mixed thermophiles

Hong-chang Liu [a,d], Jin-lan Xia [a,b,*], Zhen-yuan Nie [a,b], Li-zhu Liu [a], Lei Wang [a], Chen-yan Ma [c], Lei Zheng [c], Yi-dong Zhao [c], Wen Wen [e]

[a] School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China
[b] Key Lab of Biometallurgy of Ministry of Education of China, Central South University, Changsha 410083, China
[c] Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 10049, China
[d] CAS Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
[e] Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201204, China

ARTICLE INFO

Article history:
Received 19 July 2016
Revised 20 December 2016
Accepted 28 January 2017
Available online 13 February 2017

Keywords:
Bioleaching
Mixed culture
Chalcopyrite
Chemical speciation
Intermediates

ABSTRACT

The bioleaching experiments of chalcopyrite were conducted with mixed mesophilic culture (30 °C), moderately thermophilic culture (45 °C) and extremely thermophilic culture (65 °C), respectively. During bioleaching, the S/Fe/Cu speciation was analyzed by synchrotron radiation (SR) based X-ray diffraction (XRD) and S, Fe and Cu K-edge X-ray absorption near edge structure (XANES) spectroscopy. The results showed that the chalcopyrite dissolution could be significantly promoted by these mixed cultures, and the promotion effects were enhanced with the increase of bioleaching temperature. For all bioleaching tests, the formation of intermediates S^0, jarosite and secondary minerals (chalcocite, bornite and covellite) was detected, in which the formation of bornite, chalcocite and covellite was just related with redox potential. The formation of bornite could accelerate chalcopyrite dissolution, while the decrease of bioleaching microorganisms could reduce chalcopyrite dissolution.

1. Introduction

Chalcopyrite is very refractory and recalcitrant because of the forming the surface layer and iron deficient secondary minerals (Klauber, 2008; Harmer et al., 2006). Biohydrometallurgy is an emerging technology and takes an important role in copper recovery from chalcopyrite with attractively economic, environmental and social benefits (Pradhan et al., 2008).

The dissolution of chalcopyrite by bioleaching microorganisms has been widely studied (Brierley, 2010; Crundwell, 2003; Klauber, 2008; Li et al., 2013), which is mainly by the "indirect action" mechanism (Crundwell, 2003). During dissolution of chalcopyrite, the release of copper and iron into solution was usually earlier than sulfur, resulting in the formation of metal-deficient layers ($Cu_{1-x}S$ or $Cu_{1-x}Fe_{1-y}S_2$) (Ghahremaninezhad et al., 2010; Mikhlin et al., 2004) and surface S^{2-} (Klauber, 2008). Then elemental sulfur (S^0) could be formed by the polymerization of S^{2-} via S_n^{2-} (Harmer et al., 2006). The CuS_n-like species also had been detected, which was proposed as a passivation layer during bioleaching of chalcopyrite by mesophiles and moderate thermophiles (Yang et al., 2013). The precipitation of jarosite-like species during bioleaching was also widely studied (Klauber, 2008; Liang et al., 2010; Rodríguez et al., 2003) and was thought to be one of the main factors hindering dissolution of chalcopyrite in either laboratory experiment or industry (Leahy and Schwarz, 2009; He et al., 2012). However, the hindering effect of jarosite was still controversial (Khoshkhoo et al., 2014).

On the other hand, the bioleaching microorganisms are mainly sulfur-oxidizing microorganisms (SOMs) and iron-oxidizing microorganisms (IOMs) (Rawlings and Johnson, 2007). According to their optimal growth temperature, these bioleaching microorganisms could be divided into mesophiles (e.g. *Acidithiobacillus* and *Leptospirillum*), moderate thermophiles (e.g. *Sulfobacillus*) and extreme thermophiles (e.g. *Acidianus*) (Ding et al., 2007; Emerson et al., 2010; Li et al., 2013). The mixed cultures, especially thermophilic cultures have been widely used in the bioleaching industry (Olson et al., 2003), because they can grow at broader and higher temperature, leading to higher reaction rate in bioleaching of the highly refractory ores than mesophiles (Pradhan et al.,

* Corresponding author at: School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China.
E-mail address: jlxia@csu.edu.cn (J.-l. Xia).

http://dx.doi.org/10.1016/j.mineng.2017.01.013
0892-6875/

2008; Plessis et al., 2007). Meanwhile, the mechanism and the formation of intermediates during bioleaching with mixed cultures have also been research hotspots (Peng et al., 2012; Rawlings and Johnson, 2007; Yang et al., 2013; Zhu et al., 2011). Because the cell structures and physiological properties, as well as the leaching efficiency are quite different among these microorganisms, it could be of value to comparatively study the formation of surface layers during bioleaching of chalcopyrite by them.

However, since the metal-deficient secondary minerals are always of low abundance and could be in unstable transition states, it is difficult to detect directly some species formed during bioleaching due to the low resolution of most traditional techniques (such as Raman spectroscopy and traditional XRD) (Sasaki et al., 2009; He et al., 2012). The problem could be resolved by synchrotron radiation (SR)-based technologies (Ferrer and Petroff, 2002). Because SR is an ideal X-ray source with high spatial resolution and high sensitivity for probing trace metallic elements (Lobinski et al., 2006).

Recently, by combining SR-XRD and S, Fe, Cu K-edge X-ray absorption near edge structure (XANES) spectroscopy, we had studied the evolutions of leaching intermediates of chalcopyrite by *Acidithiobacillus ferrooxidans* and *Sulfobacillus thermosulfidooxidans* (Liu et al., 2015a, 2015b). Interestingly, we found that bornite and/or chalcocite were formed when the redox potential (ORP) was <500 mV and then transformed to covellite when the ORP was ~550 mV, indicating the formation of intermediates was related with leaching process. Therefore, the surface chemical species could provide more convincing results by combining SR-XRD and XANES, and the study of intermediates formation during chalcopyrite bioleaching could give us new insights into the dissolution mechanism of chalcopyrite by bioleaching microorganisms.

In the present study, the bioleaching process and the evolution of intermediates during bioleaching of chalcopyrite by mixed mesophilic, moderately thermophilic and extremely thermophilic cultures were comparatively studied based on SR-XRD and S, Fe and Cu K-edge XANES spectroscopy. It will be helpful to comprehend the dissolution mechanism of chalcopyrite during bioleaching.

2. Material and methods

2.1. Strains and culture media

The bioleaching microorganisms used in the present study were provided by the School of Minerals Processing and Bioengineering, Central South University, Changsha, China. The mixed mesophilic culture was comprised by *Acidithiobacillus ferrooxidans* ATCC 23270, *Leptospirillum ferrooxidans* ZTS and *Acidithiobacillus thiooxidans* A01, and it was cultivated at 30 °C. The mixed moderately thermophilic culture was comprised by *Sulfobacillus thermosulfidooxidans* St, *Acidithiobacillus caldus* S1 and *Leptospirillum ferriphilum* YSK, and it was cultivated at 45 °C. The mixed extremely thermophilic culture was comprised by *Acidianus manzaensis* YN-25, *Acidianus brierleyi* DSM-1651, *Metallosphaera sedula* DSM-5348, *Sulfolobus metallicus* DSM-6482, and it was cultivated at 65 °C. All of these mixed cultures were adapted to the substrate and shown to be efficient during chalcopyrite bioleaching prior to bioleaching experiment according to the previous description (Zhu et al., 2011). The basal medium for cultivation of these cultures consisted of the following components: 3.0 g/L $(NH_4)_2SO_4$, 0.5 g/L $MgSO_4{\cdot}7H_2O$, 0.5 g/L K_2HPO_4, 0.1 g/L KCl, 0.01 g/L $Ca(NO_3)_2$. In addition, 0.2 g/L of yeast extracts should be added to the moderately thermophilic culture and extremely thermophilic culture.

2.2. Mineral samples

The chalcopyrite and the reference minerals used in the present study were provided by the School of Minerals Processing and Bioengineering, Central South University, Changsha, China (Liu et al., 2015). The mineralogical composition analysis (by XRD) indicated that chalcopyrite was the main mineral phase. X-ray fluorescence spectroscopic analysis showed that the main content of the original chalcopyrite contained (mass fraction, %): Cu, 32.6; S, 31.05; Fe, 27.11; O, 2.7; Zn, 1.94; Ba, 0.50; Ca, 0.43; Si, 0.37; Al, 0.17 and Mg, 0.09. The particle size of chalcopyrite was 37–75 μm.

2.3. Bioleaching experiment

The mixed cultures were conducted in the 250 mL Erlenmeyer flask containing 100 mL of culture medium and 1 g of chalcopyrite, with initial pH 1.8 adjusting by dilute sulfuric acid (A.R.). Bioleaching experiments of the mesophilic culture, moderately thermophilic culture and extremely thermophilic culture were conducted at 30 °C, 45 °C and 65 °C, respectively, in bath rotary shakers (SHZ-GW) at 170 r/min. The sterile control experiments were carried out with the same conditions. The bioleaching and sterile control experiments were performed in triplicate. During cultivation, the evaporated water was compensated with sterilized ultra-pure water based on weight loss at 12-h intervals.

2.4. Analysis methods

During leaching experiments, leaching solution was taken at 2-day intervals for mesophilic culture and moderately thermophilic culture, and at 1-day intervals for extremely thermophilic culture, until the cells of these cultures reached death period. The leaching parameters (such as cell density, pH and ORP values, total [Fe], percentage of $[Fe^{3+}]$ in total [Fe] and copper extraction rate) of solution samples were determined according to our previous description (Liu et al., 2016). Briefly, the cell density was monitored by directly counting with a blood corpuscle counter (XB-K-25). The pH value was measured with a pH meter. The ORP value was measured with a platinum (Pt) electrode, using a calomel electrode (Hg/Hg_2Cl_2) as reference. $[Fe^{3+}]$ and total [Fe] were determined by 5-sulfosalicylic acid spectrophotometry. Copper extraction rate was calculated by $[Cu^{2+}]$, which was determined by bis-(cyclohexanone)oxalyldihydrazone spectrophotometry.

The solid samples during bioleaching were taken at intervals according to changes of the leaching parameters in the leaching solution. The solid samples during leaching experiments were first washed three times with diluted sulfuric acid and diluted hydrochloric acid, respectively, in nitrogen, and then stored at −20 °C until analysis. The SR-XRD patterns of the solid samples were recorded at beamline BL14B1 of Shanghai Synchrotron Radiation Facility (SSRF), Shanghai, China, at a step of 0.01° and a dwell time of 0.5 s at each point. The energy and the spot size for SR-XRD analysis were 10 keV and 0.5 × 0.5 mm^2, respectively. The Fe and Cu K-edge XANES data were separately recorded in transmission mode at beamline BL15U1 of SSRF, Shanghai, China, from 7100 eV to 7200 eV and from 8960 to 9040 eV, respectively, with a step of 1 eV and a dwell time of 2 s at each energy. The S K-edge XANES data were collected at beamline 4B7A of Beijing Synchrotron Radiation Facility, Beijing, China, in fluorescence mode at ambient temperature and scanned at step width of 0.2 eV between 2450 eV and 2520 eV. The XANES spectra were normalized to the maximum of the absorption jump (Ide-Ektessabi et al., 2004), and fitted for their linear combinations using the reference spectra with IFEFFIT program (Ravel and Newville, 2005).