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Electrochemical dissolution process of chalcopyrite in the presence of mesophilic microorganisms

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ABSTRACT

The dissolution process of chalcopyrite in the presence of mesophilic microorganisms was investigated by electrochemical measurements. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analysis, accompanied by leaching experiments. Results proved that the presence of *Acidithiobacillus ferrooxidans* enhanced the initial reduction of chalcopyrite to intermediate species (Cu_2S), thus promoting the dissolution of chalcopyrite in the initial stage of bioleaching. However, chalcopyrite tended to be directly oxidized to polysulfide (S_n^{2-}) and CuS in the later stage of bioleaching when redox potential was higher than 0.5 V (vs. Ag/AgCl), the formed polysulfide and jarosite can be responsible for the passivation of chalcopyrite in the later stage of bioleaching by *A. ferrooxidans*. On the contrary, Chalcopyrite was mainly directly oxidized to polysulfide and CuS in the presence of sterile 9K medium or *Acidithiobacillus thiooxidans*, and the initial reduction reaction was still the rate-limiting step, thus resulting in low copper extraction rate.

1. Introduction

The hydrometallurgical technology, especially the bio-hydrometallurgical technology, has been successfully applied to the processing of secondary copper sulfide minerals. This technology has a brighter prospect as it is considered simple, low cost, efficient and eco-friendly (Brierley and Brierley, 2001; Songrong et al., 2002). Chalcopyrite ($CuFeS_2$), which accounts for approximately 70% of the worldwide copper resources, is the most abundant and widespread copper-bearing mineral. However, chalcopyrite is recalcitrant to both chemical and biological leaching mainly due to the slow dissolution kinetics (Olson et al., 2003). Many researchers have studied the mechanisms and rate determining factors of chalcopyrite dissolution, but different conclusions were drawn. Most of the researchers proposed that the slow dissolution of chalcopyrite was attributed to a passivation layer, which can hinder the further dissolution (Pradhan et al., 2008; Watling, 2006). Jarosite, elemental sulfur and metal deficient polysulfide were considered as the possible compositions of the passivation layer according to most of the reports, but the specific compositions of passivation layer and the dissolution pathway are still being debated (Klauber, 2008; Rodrıguez et al., 2003; Stott et al., 2000).

Furthermore, as reported by many researchers, the passivation layer and the intermediate compounds would vary with the variation of physicochemical conditions, and so would the dissolution process (Dutrizac, 1983; Vilcáez et al., 2008). This may be one of the main reasons why different conclusions were obtained. Among all the conditions during bioleaching, the types of microorganisms can be important factors affecting the compositions of passivation layer and the dissolution process.

Acidithiobacillus ferrooxidans (*A. ferrooxidans*) and *Acidithiobacillus thiooxidans* (*A. thiooxidans*) are the most common mesophilic leaching microorganisms (Johnson, 2014; Johnson and Hallberg, 2003; Olson et al., 2003; Pradhan et al., 2008; Rohwerder et al., 2003; Vera et al., 2013). *A. ferrooxidans* was widely applied to the bioleaching of copper sulfide ores and was considered as the dominate species in many acid mine drainages (AMD) of sulfide mineral mines. *A. thiooxidans* is a sulfur-oxidizing bacterium, which is also an important strain of mesophilic microorganisms in bioleaching (Johnson, 2014; Johnson and Hallberg, 2003).

Therefore, the electrochemical dissolution processes of chalcopyrite in the presence of the above mesophilic microorganisms were investigated to contribute to a deeper understanding of the mechanisms of bioleaching of chalcopyrite.

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2. Materials and methods

2.1. Minerals and reagents

The chalcopyrite mineral was obtained from Meizhou, Guangdong Province of China. X-ray diffraction analysis (XRD) showed that it was of high purity. The chemical analysis indicated that chalcopyrite contained 34.46% Cu, 31.53% Fe, and 33.12% S (wt%), respectively. High-purity chalcopyrite was cut into a cylinder with a diameter of about 1.5 cm, a thickness of about 5 mm, and area of 1 cm^2. Ore samples were ground and sieved to −0.038 mm before being used for leaching experiments. All chemicals used were of analytical grade in this work.

2.2. Microorganisms and growth conditions

Acidithiobacillus ferrooxidans (*A. ferrooxidans*) (CBCBSU CSU 206059) and *Acidithiobacillus thiooxidans* (*A. thiooxidans*) (CBCBSU CSU 206051) were obtained from the Key Lab of Bio-hydrometallurgy of Ministry of Education, Central South University, Changsha, China. Bacteria were cultured in 250 mL shake flasks in an orbital incubator, with a stirring speed of 200 rpm and temperature of 30 °C. The 9K medium used for cell cultivation consisted of the following components: $(NH_4)_2SO_4$ (3.0 g/L) (CAS Number 7783-20-2), $MgSO_4{\cdot}7H_2O$ (0.5 g/L) (CAS Number 10034-99-8), K_2HPO_4 (0.5 g/L) (CAS Number 7758-11-4), KCl (0.1 g/L) (CAS Number 7447-40-7), $Ca(NO_3)_2$ (0.01 g/L) (CAS Number 10124-37-5) (Silverman and Lundgren, 1959). *A. ferrooxidans* and *A. thiooxidans* were sub-cultured into basal salts medium supplemented with 44.7 g/L ferrous sulfate ($FeSO_4{\cdot}7H_2O$) and 10 g/L sulfur as energy source, respectively. The resulting culture was used as inoculums for the bioleaching experiments.

2.3. Bioleaching experiments

The culture medium was previously sterilized by autoclave under the pressure of 0.1 MPa and temperature of 121 °C for 30 min, and then was sterilized by ultraviolet light. During all the leaching process, pH meter and potentiometer were sterilized by ethyl alcohol. 10 mL of cells were inoculated into a 250-mL shake flask containing 90 mL of sterilized 9K medium and 4 g of mineral. The initial cell concentration was higher than 1.0×10^7 cells/mL. The sterile leaching experiments were carried out under the same conditions except for bacteria inoculums. The shake flasks were placed into an orbital shaker at 200 rpm and 30 °C, pH was adjusted to 1.8 by sulfuric acid regularly, and water lost by evaporation was supplemented periodically by adding sterile 9K medium. Redox potential, copper concentration and total iron concentration were monitored regularly during bioleaching.

2.4. Electrochemical experiments

For all the electrochemical experiments, a conventional three-electrode system consisting of a working electrode, a graphite rod as counter electrode and Ag/AgCl (3.0 M KCl) electrode as reference electrode was used. The basic electrolyte was sterile 9K medium, and pH of the solution was adjusted to 1.8 by sulfuric acid. For the medium with bacteria, the cell concentration was higher than 1.0×10^7 cells/mL. Prior to a scan, the electrode was put into electrolyte for 15 min to ensure the adsorption of bacteria and the stabilization. The electrochemical experiments were conducted on a Princeton Model 283 potentiostat (EG&G of Princeton Applied Research) coupled with a personal computer. Cyclic voltammetry measurements were all carried out at the sweep rate of 20 mV/s, and the potentiostatic tests were all performed for the duration of 120 s. All the potential values were expressed with respect to the Ag/AgCl system.

2.5. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was used to investigate the phase transformation of mineral surfaces in the initial stage of dissolution. The samples leached for 7 days were analyzed. The mineral samples were filtered and rinsed with deionized water three times, then transferred to a vacuum drying oven (DZF-6050) to prevent any further oxidation. Afterwards, dry samples were transferred to the spectrometer in an argon atmosphere before tests.

X-ray photoelectron spectroscopy (XPS) measurements were carried out with the model ESCALAB 250Xi. Spectra were recorded at constant pass energy of 20 eV and energy step size of 0.1 eV with Al Kα X-ray as the source. Binding energy calibration was based on C 1s at 284.6 eV. XPS PEAK 4.1 software was used for fitting the XPS peaks. The Shirley method was chosen to obtain the background of spectrum, and the S 2p spectra were fitted by the Gaussian–Lorentzian line (SGL) function (Shirley, 1972).

2.6. Analytical techniques

The mineralogical compositions of solid samples were examined by X-ray diffraction (XRD) (DX-2700). Copper and iron concentrations were determined by inductively coupled plasma-atomic emission spectrometer (ICP-AES) (America Baird Co. PS-6). The pH values were measured with a pH meter (PHSJ-4A) and the redox potentials of leaching solution were measured by a Pt electrode with reference to a Ag/AgCl electrode (3.0 M KCl) (BPP-922).

3. Results and discussion

3.1. Leaching of chalcopyrite

Fig. 1 shows the variations of redox potential, total iron concentration, acid consumption and copper concentration, respectively. Redox potential of bioleaching with *A. ferrooxidans* increased sharply from the 7th day, and reached at about 670 mV after 30 days. In contrast, for bioleaching with sterile 9K medium and with *A. thiooxidans*, redox potential kept increasing slowly to about 410 mV and 430 mV, respectively. Since the redox potential is known to be mainly determined by the concentration ratio of Fe^{3+} to Fe^{2+}, a significantly higher redox potential in the presence of *A. ferrooxidans* can be attributed to the oxidation of ferrous ions (Reaction (1)). The total iron concentration shown in Fig. 1(b) increased sharply to a value around 2.5 g/L for the bioleaching with *A. ferrooxidans* in the first 10 days, and declined after leaching for 20 days, indicating that ferric ions were removed from the solution by the formation of jarosite (Reaction (2)). The total iron concentrations during leaching with *A. thiooxidans* and with sterile 9K medium both increased steadily in the initial 20 days. Afterwards, the concentrations maintained at about 1.2 g/L and 0.9 g/L, respectively. It can be concluded that *A. ferrooxidans* significantly accelerated the dissolution of iron elements from chalcopyrite in the initial stage of bioleaching. Fig. 1(c) shows that the acid consumption for leaching with sterile 9K medium, *A. ferrooxidans* and *A. thiooxidans* were 4.24 mmol, 2.94 mmol and 2.29 mmol, respectively. Fig. 1(d) indicates that the copper concentrations of leaching with *A. ferrooxidans* increased sharply in the initial 20 days, and then reached at a value around 6.0 g/L. In contrast, the copper concentrations of leaching with *A. thiooxidans* and with sterile 9K medium increased slowly in the initial 20 days, and reached at the levels of 3 g/L and 2 g/L, respectively. Therefore, *A. ferrooxidans* can promote the dissolution of chalcopyrite in the initial stage of bioleaching, but *A.*