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Surface species of chalcopyrite during bioleaching by moderately thermophilic bacteria

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Abstract: X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analyses were carried out to investigate the surface species and interfacial reactions during bioleaching of chalcopyrite by different strains of moderately thermophilic bacteria (45 °C). Results show that monosulfide (CuS), disulfide (S_2^{2-}), polysulfide (S_n^{2-}), elemental sulfur (S^0) and sulfate (SO_4^{2-}) are the main intermediate species on the surface of chalcopyrite during bioleaching by *A. caldus*, *S. thermosulfidooxidans* and *L. ferriphilum*. The low kinetics of dissolution of chalcopyrite in *A. caldus* can be mainly attributed to the incomplete dissolution of chalcopyrite and the passivation layer of polysulfide. Polysulfide and jarosite should be mainly responsible for the passivation of chalcopyrite in bioleaching by *L. ferriphilum* or *S. thermosulfidooxidans*. However, elemental sulfur should not be the main composition of passivation layer of chalcopyrite during bioleaching.

Key words: chalcopyrite; surface species; bioleaching; passivation; moderately thermophilic bacteria

1 Introduction

As a promising technology in processing low grade ores, bio-hydrometallurgy has been successfully applied for the recovery of metals such as copper, nickel, zinc, and refractory gold [1,2]. Chalcopyrite ($CuFeS_2$) is the most abundant and widespread copper-bearing mineral, accounting for approximately 70% of the copper resources [3,4]. However, it is still difficult to be effectively extracted by bioleaching mainly due to the low kinetics [5].

It has been generally accepted that the main cause of low leaching efficiency of chalcopyrite in bioleaching is the formation of passivation layer, which can inhibit the further dissolution of chalcopyrite [6−9]. Many researchers have focused on interpreting the dissolution process and the compositions of passivation layer, and different conclusions were proposed. Among the proposed conclusions, elemental sulfur, metal-deficient polysulfide and iron-hydroxyl compounds mainly consisting of jarosite were considered as the main compositions of passivation layer, but the specific compositions of passivation layer and the dissolution pathway are still being debated [8,10]. This can be mainly attributed to the differences of bioleaching systems, especially the bacteria used in bioleaching.

Three main types of microorganisms were classified according to their optimum growth temperature, including mesophiles, moderately thermophilic bacteria and extreme thermophilic bacteria [6,7]. Chalcopyrite can be easily passivated under the temperature less than 35 °C, and the extreme thermophilic bacteria are sensitive to high shear force caused by high pulp density as the absence of cytoderm, which restrict the further industrial application [2,11]. Moderately thermophilic bacteria are suitable to grow in heap and tank bioleaching as the relatively high temperature in heap and bioreactor, and they have a more extensive application prospect compared with the other two types

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of microorganisms [2,12].

Additionally, the intermediate species are usually with trace amount, and the passivation layer is usually too thin to be directly detected by the normal X-ray diffraction method [13]. X-ray photoelectron spectroscopy (XPS) has been widely used to characterize the surface layers, and it can provide reliable data on the chemical states of the surface species [13−15].

Therefore, in the present work, the compositions of formed product layers on chalcopyrite surface in bioleaching by moderately thermophilic bacteria were investigated mainly by X-ray photoelectron spectroscopy (XPS) to interpret the electrochemical dissolution process and the mechanisms of passivation.

2 Experimental

2.1 Materials

Chalcopyrite sample was obtained from geological museum of Guangxi Province of China. X-ray diffraction analysis (XRD) (Fig. 1) showed that it was of high purity. The chemical analysis showed that the chalcopyrite sample contained 34.46% Cu, 31.53% Fe, and 33.12% S (mass fraction), respectively. Ore samples were ground and sieved to less than 0.074 mm before being used for leaching experiments. All chemicals used were of analytical purity in this work.

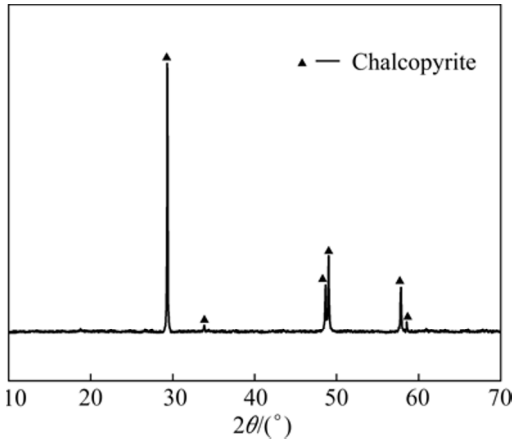

Fig. 1 XRD pattern of untreated chalcopyrite

2.2 Microorganisms and culture media

Moderately thermophilic bacteria, including *Acidithiobacillus caldus* (*A. caldus*), *Sulfobacillus thermosulfidooxidans* (*S. thermosulfidooxidans*) and *Leptospirillum ferriphilum* (*L. ferriphilum*), were obtained from the Key Laboratory of Bio-hydrometallurgy of Ministry of Education, Central South University, China. Bacteria were cultured in 250 mL shake flasks in an orbital incubator with a stirring speed of 170 r/min at a temperature of 45 °C. The basic culture medium was composed of the following compositions: $(NH_4)_2SO_4$ (3.0 g/L), $MgSO_4·7H_2O$ (0.5 g/L), K_2HPO_4 (0.5 g/L), KCl (0.1 g/L), $Ca(NO_3)_2$ (0.01 g/L). *L. ferriphilum* and *A. caldus* were sub-cultured into basal salts medium supplemented with 44.7 g/L ferrous sulphate ($FeSO_4·7H_2O$) and 10 g/L sulfur as energy sources, respectively. *S. thermosulfidooxidans* were sub-cultured into basal salts medium supplemented with 44.7 g/L ferrous sulphate ($FeSO_4·7H_2O$) and 10 g/L sulfur as energy sources. The resulting culture was used as inoculums for the bioleaching experiments.

2.3 Bioleaching experiments

10 mL of cell solution was inoculated into a 250 mL shake flask containing 90 mL of sterilized culture medium and 2 g of minerals. The initial cell concentration of bacteria was higher than 1.0×10^7 cells/mL. The shake flasks were placed into an orbital shaker at 170 r/min and 45 °C, pH value was adjusted to 1.7 by sulfuric acid regularly, and water lost by evaporation was supplemented periodically by adding deionized water. Copper 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 mol/L KCl) (BPP−922). The mineralogical compositions of solid samples were examined by X-ray diffraction (XRD) (DX−2700).

2.4 X-ray photoelectron spectroscopy (XPS)

The samples in different stages of bioleaching (7, 15, 22 d) were filtered and rinsed with deionized water three times, then transferred to vacuum drying oven (DZF−6050) to dry before X-ray photoelectron experiment (XPS) measurements.

X-ray photoelectron experiment (XPS) measurements were carried out on the model of ESCALAB 250Xi. Spectra were recorded at constant pass energy of 20 eV and energy step size of 0.1 eV, with Al K_α X-ray as the source. Binding energy calibration was based on C 1s at 284.6 eV. Thermo Avantage 5.52 software was used for fitting the XPS peaks. The Shirley method was chosen for obtaining the background of spectra, and the S 2p spectra were fitted by Gaussian−Lorentzian line (SGL) function.

3 Results and discussion

3.1 Bioleaching behaviors

Figure 2 shows that redox potential of bioleaching by *A. caldus* maintained at a low and steady value throughout the bioleaching process, during which the copper extraction continued to increase slowly and