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Stepwise bioleaching of Cu-Zn mixed ores with comprehensive utilization of silver-bearing solid waste through a new technique process

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ABSTRACT

In this work, a new technique process for processing Cu-Zn mixed ores containing chalcopyrite and marmatite was proposed to avoid the complex Cu-Zn flotation and extraction separation processes, as well as for the comprehensive utilization of abandoned silver-containing zinc leaching residue (ZLR). In the first step, stepwise bioleaching of Cu-Zn mixed ores in the presence of mixed moderately thermophilic microorganisms and Fe^{3+} was conducted for recovering Zn from marmatite. Copper was then efficiently extracted from the copper-containing bioleaching residues through catalytic bioleaching by using ZLR as catalyst. The final bioleaching residues were subsequently leached by thiourea for recovering Ag efficiently. The provided technique process accomplished the stepwise dissolution of Cu-Zn mixed ores and the comprehensive utilization of silver-bearing ZLR. The intermediate species, the electrochemical dissolution process and the electrochemical interactions between chalcopyrite and marmatite were also discussed to interpret the detailed mechanisms of stepwise bioleaching.

1. Introduction

Currently, there is an imbalance between copper supply and world demand. The copper grade has declined with the depletion of high grade copper ores. Hence, clean, economical and efficient mineral processing techniques in processing low-grade copper ores are required to be developed in copper industry. Chalcopyrite ($CuFeS_2$) accounting for appropriately 70% of the total copper reserves is the most abundant copper-bearing resource in the earth (Li et al., 2013). As one of the promising hydrometallurgical technologies, bio-hydrometallurgical technology (bioleaching) has been successfully used in processing secondary copper sulfide minerals (like chalcocite) in copper industry. Many attempts have been made to process chalcopyrite by bioleaching, but it is still restricted in industrial application because chalcopyrite is extremely refractory to bioleaching (Li et al., 2013; Pradhan et al., 2008; Watling, 2013). Silver ion (Ag^+) was widely reported as an effective catalyst in chalcopyrite bioleaching but its commercial application is still limited due to the high price of silver and challenges in recovering silver catalyst from leaching residues (Blázquez et al., 1999; Feng et al., 2013; Gomez et al., 1999; Sato et al., 2000; Wang et al., 2004).

Currently, more than 80% of the total zinc is obtained from zinc sulfide mineral through roast-leach-electrowinning (RLE) or pressure leaching processes (Çoruh and Ergun, 2010; Li et al., 2012). Marmatite [(Zn, Fe) S] is an important zinc-bearing resource, which is difficult to be processed effectively by traditional technologies as its high content of iron and low content of zinc. However, marmatite is considered relatively suitable for bioleaching (Ban et al., 2013; Shi and Fang, 2004).

Chalcopyrite and marmatite are commonly coexisted in the Cu-Zn raw ores. In the traditional technology, chalcopyrite and marmatite are commonly recovered simultaneously through bulk flotation process, and the obtained mixed Cu-Zn concentrates are then separated by flotation to obtain copper concentrate and zinc concentrate, respectively. The copper concentrate and zinc concentrate are separately treated mainly by smelting and hydrometallurgy to obtain copper and zinc product. However, marmatite is always existed in chalcopyrite concentrate because marmatite can be activated by Cu^{2+}, and this caused the floatability of marmatite similar with chalcopyrite, thus resulting in poor quality of products, poor efficiency and high cost of smelting (Qin et al., 2012; Qin et al., 2013). Zinc leaching residue (ZLR) mainly consisting of zinc ferrite ($ZnFe_2O_4$) and silver-bearing species can be easily produced in large amounts during conventional hydrometallurgical process of zinc calcine (Yan et al., 2014). The produced ZLR is refractory to traditional acid leaching process and is abandoned as unvalued solid waste after valuable metals were totally recovered, which also cause serious environmental problems.

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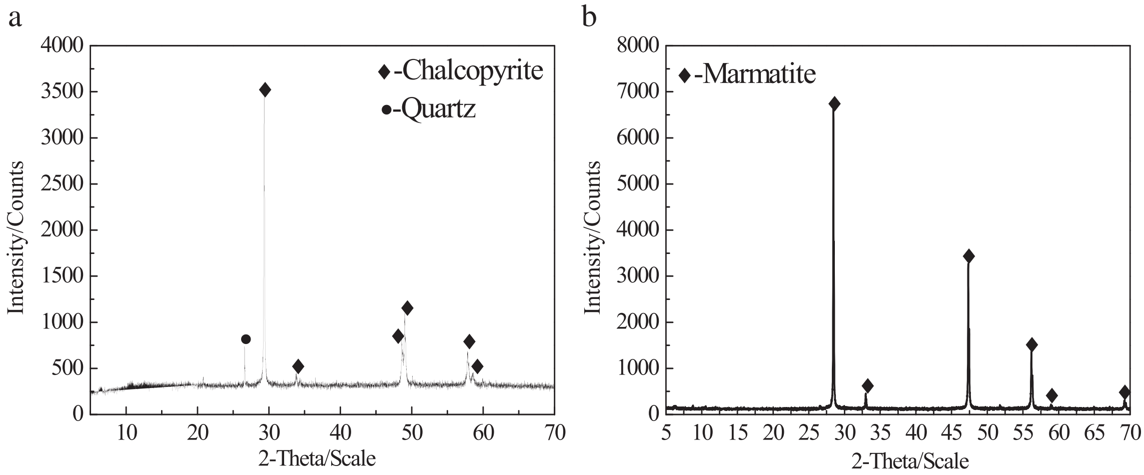

Fig. 1. XRD pattern of mineral samples: (a) chalcopyrite; (b) marmatite.

To avoid the complex hydrometallurgical process in separating Cu^{2+} and Zn^{2+}, and to avoid the complex flotation process in separating chalcopyrite and marmatite, the feasibility of stepwise bioleaching of Cu-Zn mixed ores containing chalcopyrite and marmatite was discussed in this work. The abandoned ZLR was used as silver catalyst to accelerate chalcopyrite bioleaching and silver was subsequently recovered from the bioleaching residue. It is an opportunity for using a waste material (ZLR) to extract metal value from chalcopyrite and chalcopyrite-marmatite ores. This work is potentially useful to provide a promising technique for effectively processing Cu-Zn mixed ores containing chalcopyrite and marmatite and for comprehensive utilization of silver-bearing solid wastes.

2. Materials and methods

2.1. Samples

The pure chalcopyrite and marmatite samples were obtained from geological museum of Hunan Province of China and Dachang Mine of Guangxi Province of China, respectively. X-ray diffraction (XRD) (Fig. 1) indicated that they were both of high purity. The chemical analysis showed that chalcopyrite sample contained 34.14% Cu, 31.52% Fe and 33.12% S (wt%), and marmatite contained 49.73% Zn, 12.43% Fe, and 27.90% S (wt%), respectively. The chosen silver-bearing zinc leaching residue (ZLR) was achieved from smelting plant in Chenzhou, Hunan Province, China. The main mineralogical compositions of ZLR were silicate and zinc ferrite, chemical elements analysis (Table 1) presented that the grade of silver in ZLR was about 0.0294%. Table 2 shows that metallic silver and silver sulfide were the main silver-bearing species, accounting for 61.78% and 23.85% of the total silver-bearing species in ZLR. Ore samples were all ground and sieved to less than 0.074 mm before used for leaching experiments and analysis. The Carbon Paste Electroactive Electrode (CPEE) consisting of 0.7 g of minerals (− 0.038 mm), 0.2 g of graphite and 0.1 g of solid paraffin was used in electrochemistry analysis. The electrodes were all polished by silicon carbide paper to obtain smooth surface before every electrochemical measurement. All chemicals used in this work were of analytical grade.

Table 1
The chemical elements analysis of zinc leaching residue (ZLR).

Element	O	Na	Al	Si	P	S	Cl	Ca
Content/%	33.089	0.748	0.764	2.082	0.018	6.007	0.113	1.924
Element	Ti	Cr	Mn	Fe	Cu	Zn	As	Sr
Content/%	0.054	0.016	1.627	23.449	0.203	22.940	1.650	0.510
Element	Ag	Cd	In	Sn	Sb	I	Pb	Bi
Content/%	0.0294	0.347	0.099	0.346	0.182	0.025	2.895	0.283

Table 2
The distribution of silver-bearing species in zinc leaching residue (ZLR).

Phase	Silver oxide	Metallic silver	Silver chloride	Silver sulfide	Iron minerals	Silicate minerals	In total
Content/%	0.39	61.78	0.67	23.85	12.49	0.81	100.0

2.2. Leaching experiments

Moderately thermophilic microorganisms of *Acidithiobacilluscaldus* (*A. caldus*) (CCTC AB 206240) and *Leptospirillumferriphilum* (*L. ferriphilum*) (CCTC AB 206239) were initially obtained from the Key Lab of Bio-hydrometallurgy of Ministry of Education, Central South University, Changsha, China. Microbial culture processes were conducted according to the previous publication (Zhao et al., 2015). Bioleaching experiments of mixed ores with different mass ratios of chalcopyrite and marmatite were carried out at 170 rpm, 45 °C and pH of 1.70. After solid-liquid separation, the further recovery of Cu from residues was conducted by catalytic bioleaching in the presence of silver-bearing ZLR. The final bioleaching residues were subsequently leached by thiourea. Thiourea leaching experiments were carried out in 50 mL shake flasks at liquid-solid ration of 10:1, pH value of 1.0 and temperature of 45 °C for 5.0 h.

2.3. Analytic techniques

Metal ions concentrations were analyzed through inductively coupled plasma-atomic emission spectrometer (ICP-AES) (America Baird Co. PS-6), the pH value was monitored with a pH meter (PHSJ-4A) and the redox potential was detected by an ORP (Oxidation-Reduction Potential) meter (BPH-221). X-ray diffraction (XRD) (DX-2700) and X-ray photoelectron spectroscopy (XPS) (ESCALAB 250Xi) were utilized to analyze solid samples. XPS peaks were fitted by Thermo Avantage 5.52 software according to our previous publications (Wang et al., 2016). Electrochemistry tests were conducted by conventional three-electrode system (Princeton Model 283 Potentiostat, EG & G of Princeton Applied Research). All potential values mentioned were referred to the Ag/AgCl electrode (vs. Ag/AgCl) in this work.

3. Results and discussion

3.1. Leaching experiments

Fig. 2 shows the leaching results of Cu-Zn mixed ores consisting of