



Purification of bismuthinite concentrate by selective electro-oxidation of molybdenite



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ABSTRACT

The flotation separation is the general method to recover molybdenite from a concentration containing molybdenite and bismuthinite, although the whole circuit could be long and complicated. In this paper, a novel selective electro-oxidation of molybdenite process has been introduced and systematically investigated for bismuthinite purification. It was found that Mo could be selectively separated by the electro-oxidation method under the conditions of pH not less than 9.0 and the applied potential at between 3.0 V and 4.0 V, by this circumstance Bi was hard to extract. The effects of NaCl concentration, liquid/solid ratio and stirring speed on electro-oxidation leaching were investigated. Optimum leaching conditions were found as follows: operated at room temperature, leaching time = 2.5 h, NaCl concentration = 4 mol/L, pH = 9–10, applied potential = 3.4 V, liquid/solid ratio = 30 mL/g, stirring speed = 400 rpm. Under these conditions, Mo extraction yield was obtained at 98.4% and 99.3% of Bi remained in the residue. The chlorine evolution reaction at the anode which was effected by leaching pH was studied by linear scan voltammetry. Mechanism of electro-oxidation leaching of Mo was studied by cyclic voltammetry. Furthermore, the mass transfer of Mo from leachate to organic phase was introduced, and the two phase transfer could obtain as high as 99.6%.

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1. Introduction

In China, bismuthinite associated with low grade molybdenite is quite abundant. At present, a flotation process is the main method of Mo separation from Bi concentrate (Shang et al., 2010; Liu, 2011). In the conventional froth flotation process, most of the molybdenite floats along with the Bi sulfides, forming Bi–Mo concentrates. This stream would ultimately be turned into a higher grade bismuthinite concentrate after going through differential flotation. To acquire the high grade bismuthinite, Mo removal is necessary, therefore the whole flotation process would be inevitably long and complicated (Guo and Zhou, 2009). In cases where bismuthinite and molybdenite are intergrown closely, it is especially difficult to remove Mo from the concentrate only processed by froth flotation.

Other methods used to separate Mo from polymetallic ores have been reported (Lee et al., 1980; Feng et al., 2010; Tang et al., 2011; Warren and Mounsey, 1983). Selective separation of Mo as volatile halides from deep-sea ferromanganese modules can be achieved by the sulfation of the ground nodule material with a gas mixture of SO₂ and

O₂ at elevated temperatures, which results in the sublimation of Mo in the form of MoCl₄ and MoO₂Cl₂ (Lee et al., 1980). Some authors have proposed the separation of Mo from the Cu–Mo collective concentrate, and the process flow includes three steps: heating pretreatment, separating Cu and Mo after grinding and finally regrinding concentration (Feng et al., 2010). The adoption of two-stage leaching at different temperatures to selectively recover Mo from alkaline Bi smelting slag has been reported, and the leaching efficiency of Mo could reach 94.51% under optimum conditions (Tang et al., 2011). Sodium hypochlorite was employed to selectively leach Mo from Cu/Mo sulfide minerals (Warren and Mounsey, 1983). The separation of Mo from sulfide concentrate by electro-oxidation has been reported in a few articles (Darjaa et al., 2000; Cao et al., 2010).

As a relatively novel technology in hydrometallurgy, electro-oxidation combines the leaching of polymetallic concentrates which can be oxidized by a current at the anode or oxidants generated at the anode with the electrowinning of metals at the cathode in acid solutions. The oxidants generated at the anode usually refer to chlorine oxidants which come from electrolysis of such acid chloride solutions as NaCl solution and KCl solution at the anode and electro-oxidation is mainly used to leach metal sulfides (Brace, 1969; Kruesi, 1972; Everett, 1978; Qiu, 1999; Yang and Zhang, 2000). Application of electro-oxidation to treat bismuthinite has been reported in some

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articles, and the leaching of bismuthinite is basically considered as a result of the oxidation of concentrates by chlorine oxidants and Fe^{3+} generated at the anode (Wang et al., 1995a,b; Liu, 1998). Furthermore, formation and oxidation mechanisms of sulfur in the process of slurry electrolysis on bismuthinite have been investigated to make better sense of the electro-oxidation process of bismuthinite (Wang et al., 2002). However, all the articles related to the electro-oxidation of bismuthinite focused on the leaching of Bi but not the impurity removal.

The oxidation sequence of metal sulfides at the anode (Qiu, 1999) makes it possible to selectively separate Mo from bismuthinite. NaClO has been especially recognized as the oxidant which can selectively oxidize molybdenite from polymetallic sulfides under appropriate conditions (Xiang, 2002), which means selective leaching of Mo from bismuthinite concentrate may be achieved by converting as much Cl^- as possible into ClO^- at the anode in the electrically assisted leaching through altering relevant process parameters. This paper investigated the effects of five process parameters, namely pH, applied potential, NaCl concentration, stirring speed and liquid/solid ratio, on the leaching of Mo from bismuthinite. Cyclic voltammetry was adopted to study the mechanism of the electro-oxidation of Mo from bismuthinite concentrates. With solvent extraction adopted to recover Mo from leachate, the study on how to transfer Mo from leachate to organic phase efficiently was carried out.

2. Experimental

2.1. Concentrate sample, reagents and electro-oxidation leaching process setup

The concentrate sample, of which the XRF result is listed, is as follows: Mo 5.26%, S 18.88%, Bi 38.12%, Cu 3.35%, Fe 8.70%, Ca 2.91%, Si 3.89%, Al 1.24%, O 10.44%, were provided by Shizhuyuan Mine, Hunan Province (EDX1800B X-ray Fluorescence meter produced by Skyray Instrument Co., Ltd., Kunshan, China). The particle size ranged from 10 μm to 100 μm and 83% less than 40 μm . X-ray diffraction of the concentrate sample (Fig. 1) shows that bismuthinite and molybdenite were the major phases (Rigaku 2500 X-ray Diffract meter produced by Rigaku Corporation, Japan). Except for N235 (tertiary amine R_3N , $\text{R} = \text{C}_8\text{--C}_{10}$), sec-caprylic alcohol and kerosene, which were industrial grade and water was tap-water, all other reagents used in the experiments were of chemical grade purity. A self-made septum-free electrolytic bath fitted with pH and temperature detectors was chosen, and how DSA anodes (dimensionally stable anode, RuO_2 , IrO_2 , SnO_2 coated mesh electrode, 100 mm \times 100 mm) and iron cathodes (low-carbon steel mesh electrode, 100 mm \times 100 mm) were fixed to the bath is

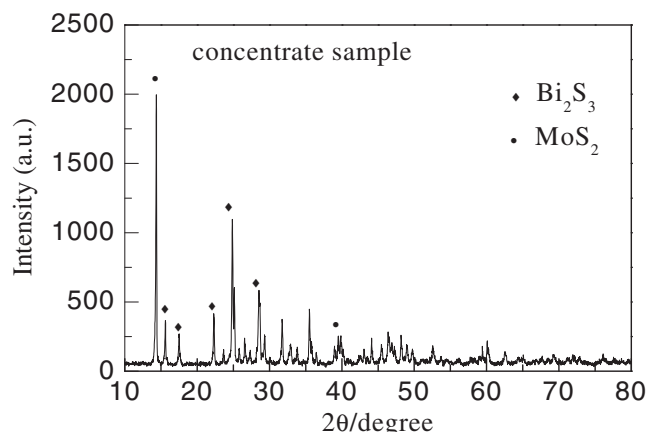


Fig. 1. X-ray diffraction pattern of the concentrate sample.

displayed in Fig. 2. Each anode was 10 mm away from the corresponding cathode.

2.2. Procedure

2.2.1. Electro-oxidation leaching experiments

The concentrate pulp was prepared by mixing the concentrate sample and reagents (H_2O , NaCl and Na_2CO_3); the amount of each component depended on the corresponding test. Then the pulp was put into the self-made electrolytic bath (Fig. 2) where the electro-oxidation leaching tests were carried out and the applied potential between DSA anode and iron cathode was supplied by S22 Regulated Power Supply System (Chenhua Instruments Co., Ltd., Shanghai, China). The effects of five process parameters, namely pH, applied potential, NaCl concentration, stirring speed and L/S ratio (liquid/solid ratio, mL/g), on selective leaching of Mo from bismuthinite were investigated, and the selective leaching of Mo herein refers to the leaching of molybdenite with Bi remaining in the residue. All these leaching tests were conducted at room temperature with the leaching time of 2.5 h and concentrate sample of 5.0 g. It is noted that for the tests in Section 3.2.2, they were carried out with the same electric quantity of 1.6 A h rather than the same leaching time, and electric quantity in each leaching test in Section 3.2 was much larger than the theoretical electric quantity based on Eqs. (1) and (3). In leaching tests designed to investigate the effect of pH on electro-oxidation leaching, HCl , Na_2CO_3 and NaOH were used to sustain the specific pH value of the corresponding leaching test. The other specific experimental conditions of each leaching test are listed in Section 3.2. The concentrations of Bi and Mo in leachate were analyzed by atomic absorption spectrophotometer (S4AA atomic absorption spectrophotometer produced by Thermo Electron Corporation, America).

Linear scan voltammetry was employed to examine how pH affected the chlorine evolution reaction at the anode. In linear voltammetry tests, DSA electrode (100 mm \times 100 mm mesh electrode, effective area 2688 mm^2 , the anode involved in electro-oxidation leaching tests), iron cathode (100 mm \times 100 mm mesh electrode, effective area 2688 mm^2 , the cathode involved in electro-oxidation leaching tests) and SCE (Saturated calomel electrode) were anode (the working electrode), cathode (the counter electrode) and reference electrode respectively. CHI660B Electrochemical Integrated Test System (Chenhua Instruments Co., Ltd., Shanghai, China) was responsible for providing the potential between DSA anode and iron cathode and drawing anodic polarization branches.

All linear voltammetry tests were implemented in the self-made electrolytic bath and exposed to the air. Except for the pH and applied potential, the other experimental conditions (including stirring speed) of each linear voltammetry test were the same as those of leaching tests designed to investigate the effect of pH on electro-oxidation leaching.

2.2.2. Study of the mechanism of the electro-oxidation of molybdenite

The anode (the working electrode), cathode (the counter electrode) and reference electrode in cyclic voltammetry were the same as those in linear voltammetry. Similarly CHI660B Electrochemical Integrated Test System was responsible for providing the potential between DSA anode and iron cathode and drawing I-E curves. All cyclic voltammetry tests were conducted in the self-made electrolytic bath with agitation and were exposed to the air.

To obtain a fine scanning speed, different scanning speeds ranging from 5 to 90 mV/s were adopted to draw voltammetry curves of anode when there was only NaCl solution in electrolytic bath. Afterwards, the corresponding cyclic voltammogram of the anode was drawn when there was only a certain combination of reagents and concentrate sample involved in the leaching tests in the electrolytic bath. These combinations are listed as follows: H_2O , $\text{H}_2\text{O} + \text{concentrate sample}$, $\text{H}_2\text{O} + \text{NaCl}$, $\text{H}_2\text{O} + \text{NaCl} + \text{concentrate sample}$ and

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