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 SO_2 and

O_2 at elevated temperatures, which results in the sublimation of Mo in the form of $MoCl_4$ and MoO_2Cl_2 (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, R = C_8–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 × 100 mm) and iron cathodes (low-carbon steel mesh electrode, 100 mm × 100 mm) were fixed to the bath is
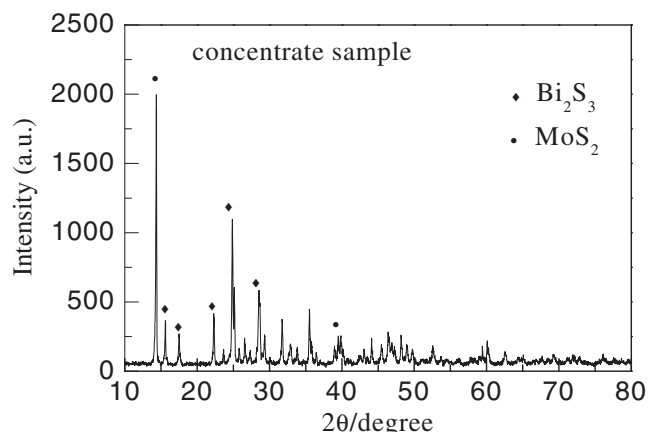

Fig. 1. X-ray diffraction pattern of the concentrate sample.

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 × 100 mm mesh electrode, effective area 2688 mm^2, the anode involved in electro-oxidation leaching tests), iron cathode (100 mm × 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, H_2O + concentrate sample, H_2O + NaCl, H_2O + NaCl + concentrate sample and
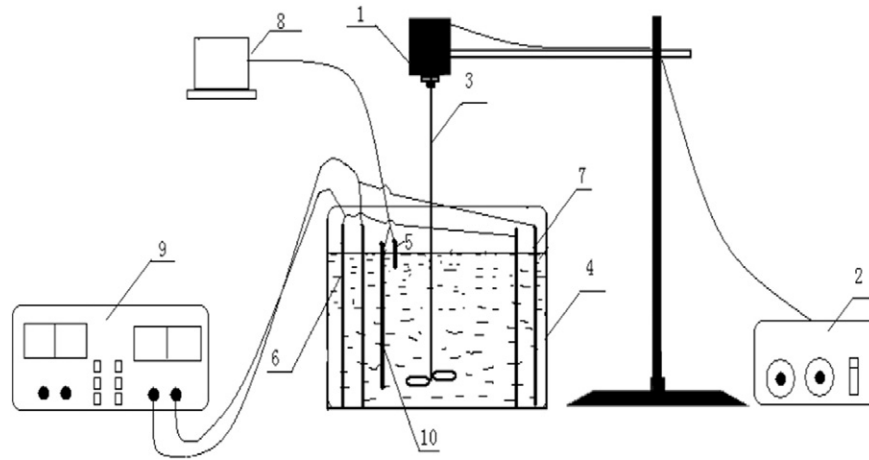
Fig. 2. Electro-oxidation process test set-up. 1—Stirring motor (73-1D electric blender produced by Specimen and Model factory, Shanghai, China), 2—stirring speeder, 3—stirring rod, 4—electrolytic bath, 5—feed inlet, 6—cathode, 7—anode, 8—buffer system controller, 9—DC regulated power supply, 10—pH meter electrode (pHS-3C pH meter produced by INESA Scientific Instrument Co., Ltd., Shanghai, China).

H_2O + NaCl + concentrate sample + Na_2CO_3. In these combinations, the amounts of H_2O, concentrate sample and NaCl were 150 mL, 5 g and 0.6 mol respectively, and Na_2CO_3 was responsible for keeping the pH of the solution at around 9.

2.2.3. Solvent extraction of Mo from leachate to organic phase

To recycle electrolyte, it is necessary to recover Mo from leachate. The common methods of Mo recovery from leachate are acid precipitation and solvent extraction (Xiang, 2002). Study of Mo transfer from leachate to organic phase consisting of 30% (mass fraction) N235, 20% sec-caprylic alcohol and 50% kerosene was performed with the leachate at pH 9 and containing 1.73 g/L of Mo. Concentration of HCl varied when the A/O ratio (aqueous phase volume/organic phase volume ratio) was kept constant at 1, and the A/O ratio changed when the concentration of HCl was 48 g/L. The extraction tests were carried out at room temperature with extraction time of 5 min and aqueous phase of 20 mL. The concentrations of Mo in leachate before and after solvent extraction were analyzed by atomic absorption spectrophotometer.

3. Results and discussion

3.1. Study of the mechanism of the electro-oxidation leaching of Mo from concentrate sample

3.1.1. Effect of scan rate

The voltammograms of the anode were drawn at different scanning speeds. The results shown in Fig. 3 indicate that the differences among the relevant curves were slight when the scanning speed was between 40 mV/s and 70 mV/s. Therefore, the scanning speed was set at 50 mV/s in the following tests.

3.1.2. Cyclic voltammograms of anode

Every curve shown in Figs. 4 and 5 stands for one of the five certain combinations mentioned in Section 2.2.2. It can be seen from Fig. 4 that the current of curve 1 increased sharply when voltage reached 1.1 V, it was probably because there was oxygen evolution reaction at the anode. Compared with curve 1, curve 3 possessed the higher limiting current, and the possible reason was that chlorine evolution reaction happened at the anode. The limiting current of curve 2 was the same as that of curve 1, suggesting that the reaction at the anode was perhaps
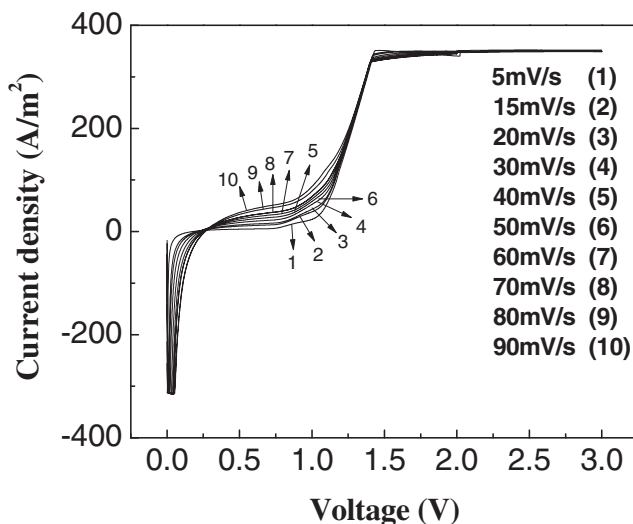

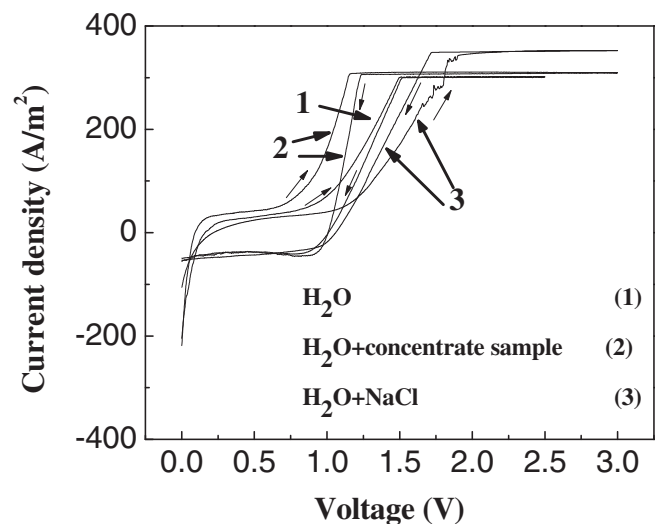**Fig. 3.** Voltammograms of anode at different scanning speeds.

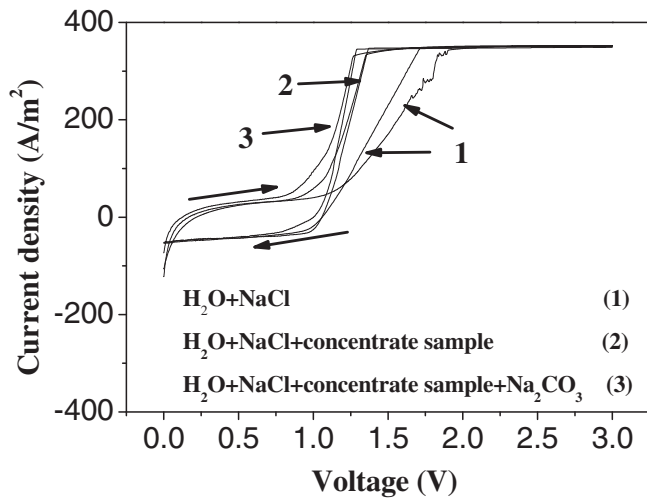**Fig. 4.** Cyclic voltammograms of anode (the former three combinations).

Fig. 5. Cyclic voltammograms of anode (the latter three combinations).

also oxygen evolution reaction. When voltage was between 0.75 V and 1.0 V, the current of curve 2 increased more rapidly in comparison with that of curve 1 and the reason was that the concentrate sample was directly oxidized by the current at the anode (Wang et al., 1995a). However, the analysis of leachate of curve 2 showed that little Mo existed in solution, which suggested that the electrically assisted leaching of Mo from bismuthinite concentrate did not result from current or oxygen evolution reaction at the anode and the difference between curve 1 and curve 2 might be the result of the electro-oxidation leaching of other minerals.

As presented in Fig. 5, curves 1, 2 and 3 had a similar trend and the same limiting current, which proved that the reactions of these three curves at the anode were probably chlorine evolution reactions. However, the currents of curves 2 and 3 reached the maximum earlier compared with that of curve 1, and similarly it should be considered as the oxidation of concentrates by the current at the anode which had been proved to be irrelevant to the leaching of Mo. The analyses of the leachate of curves 2 and 3 suggested that the contents of Mo in leachate were considerable, indicating that the existence of NaCl which would be converted into such chlorine oxidants as ClO^- and ClO_3^- during the slurry electrolysis process resulted in the leaching of Mo from concentrate sample.
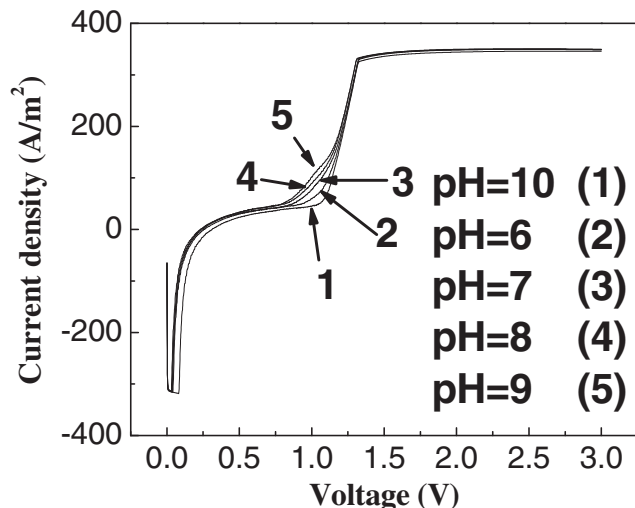
Based on the above analyses, it is confirmed that the leaching of Mo was attributed to the oxidation of the concentrate sample by chlorine oxidants. Additionally, no solid matters including Mo and sulfur were found to appear at the electrodes according to observation during electro-oxidation leaching and no elemental sulfur was found in the slag, suggesting that Mo could not be reduced at the cathode and sulfur coming from molybdenite should not exist in the form of elemental sulfur after the electro-oxidation.

3.2. Effects of process parameters on the electro-oxidation of concentrate sample

3.2.1. pH

3.2.1.1. Effect of pH on anodic polarization branch. It is indicated in Fig. 6 that pH had an effect on the chlorine-evolution reaction at the anode to some extent. Based on Eqs. (1), (2) and (3), the higher pH should facilitate chlorine generation reaction at the anode but suppress hydrogen evolution at the cathode. When pH was within the range between 6 and 9, the leaching efficiency of Mo increased (Fig. 7) and the voltage at which chlorine oxidant generation reaction appeared declined along with the rise of pH, suggesting that it was probably Eq. (1) enhanced by higher pH that dominated the whole electrode reaction. However, when pH reached 10, curve 1 lagged behind the other curves in terms of current increase indicating that it was Eq. (2) suppressed by higher pH that played the leading role in the whole electrode reaction and consequently chlorine oxidant generation reaction at the anode was restrained.

$$Cl^- + 2OH^- - 2e = ClO^- + H_2O \tag{1}$$

$$2H_2O + 2e = H_2 + 2OH^- \tag{2}$$

$$MoS_2 + 9NaClO + 6NaOH = Na_2MoO_4 + 2Na_2SO_4 + 9NaCl + 3H_2O. \tag{3}$$

(Xiang, 2002)

3.2.1.2. Effect of pH on selective electro-oxidation leaching of Mo. According to the results displayed in Fig. 7, it can be concluded that the leaching efficiencies of Bi and Mo were evidently impacted by pH. When pH ≤ 9, the leaching efficiency of Mo was enhanced while that of Bi decreased to almost zero along with the increase of pH, and when pH ranged from 9 to 12, a prominent selective separation of Mo from the concentrate sample could be obtained. The possible explanation for the trends

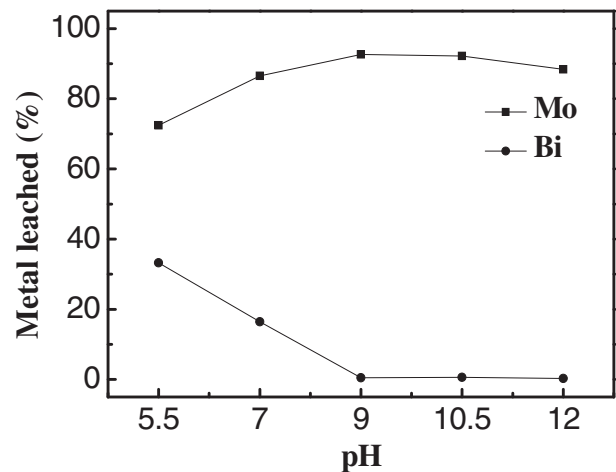Fig. 6. Effect of pH on anodic polarization branch.

Fig. 7. Effect of pH on electro-oxidation leaching of Mo and Bi from concentrate sample. Experimental conditions: applied potential = 4.0 V, NaCl concentration = 4 mol/L, stirring speed = 300 rpm, L/S ratio = 50.
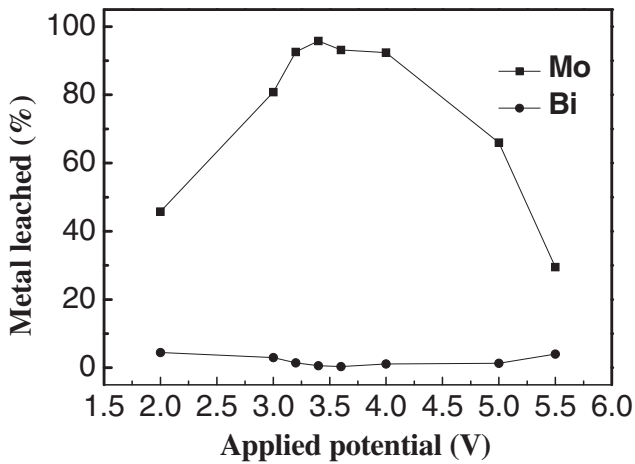
Fig. 8. Effect of applied potential on electro-oxidation leaching of Mo and Bi from concentrate sample. Experimental conditions: pH = 9–10, NaCl concentration = 4 mol/L, stirring speed = 300 rpm, L/S ratio = 50.

of the two curves is that Cl_2 and HClO played the leading roles in oxidizing molybdenite and bismuthinite when pH ≤ 7, so both Mo and Bi could enter leachate. Along with the rise of pH, ClO^- would serve as the key oxidant which has been proved to be able to selectively oxidize molybdenite (Xiang, 2002), therefore it became easier for molybdenite but more difficult for bismuthinite to be leached. However, when pH ≥ 10.5, as pointed out in Section 3.2.1.1, the chlorine oxidant generation reaction at the anode was suppressed. Consequently, it led to the decrease of the leaching efficiency of Mo.

Given that a preferable selective leaching of Mo could be achieved when pH = 9–10.5, the CO_3^{2-}–HCO_3^- buffer system regulated by amount of Na_2CO_3 would therefore be introduced in the following tests.

3.2.2. Effect of applied potential on selective electro-oxidation leaching of Mo

The leaching results presented in Fig. 8 show that accompanied by the increase of applied potential, the leaching efficiency of Mo increased while that of Bi declined when applied potential was ≤3.4 V. When applied potential was >3.4 V, in contrast, the leaching efficiency of Mo decreased while that of Bi was enhanced slightly.

The leaching efficiency–applied potential curve of Mo may be explained as follows: when applied potential was ≤3.4 V, the chlorine oxidants which came from the electrolysis of NaCl solution were

not sufficient for the leaching of concentrate sample; when voltage was >4.0 V, part of ClO^- was further oxidized into ClO_3^- of which the amount would gradually grow with the increase of applied potential and in the alkaline leachate, the relatively weak oxidation strength of ClO_3^- made it difficult for itself to be converted into Cl^-, which acted as the circulation medium during oxidation of concentrate sample, by oxidizing concentrate sample, thus contributing to the decline of concentration of Cl^- and the shortage of chlorine oxidants involved in the oxidation of concentrate sample. Hence, the growth of applied potential caused the decrease of the leaching efficiency of Mo when applied potential >4.0 V. When potential ranged from 2.0 to 3.5 V, the decline of the leaching efficiency of Bi could be considered as a result of the selective leaching of Mo by ClO^- which gradually became the major chlorine oxidant with the rise of applied potential.

When applied potential was = 3.4 V, the leaching efficiency of Mo could reach 95.8%, meanwhile the percentage of Bi remaining in the residue was 99.3%. Hence, in the following studies, applied potential was set at 3.4 V.

3.2.3. Effect of NaCl concentration on selective electro-oxidation leaching of Mo

As shown in Fig. 9, NaCl concentration had an evident effect on the leaching of Mo but no obvious influence on the leaching of Bi. When NaCl concentration was ≤4 mol/L, more Mo entered the leachate with the growth of NaCl concentration while Bi remained in the residue. The possible reason is that a low NaCl concentration resulted in inadequate Cl^- in the electrolyte, so the chlorine oxidants which made contribution to oxidizing the concentrate sample were not sufficient either. Based on curve Bi, NaCl concentration appeared to be irrelevant to the leaching of Bi, suggesting that the appropriate pH and applied potential determined after the implementation of previous electro-oxidation leaching experiments were able to convert the majority of Cl^- into ClO^- in the slurry electrolysis process, so it achieved a remarkable selective separation of Mo from concentrate sample.

According to the fact that when NaCl concentration was >4 mol/L, the growth of NaCl concentration hardly affected the leaching of Mo, therefore it would be set at 4 mol/L in the following studies.

3.2.4. Effect of stirring speed on selective electro-oxidation leaching of Mo

The results displayed in Fig. 10 show that the rise of stirring speed resulted in the increase of the leaching efficiency of Mo and seemed irrelevant to the leaching of Bi, and when stirring speed was ≥400 rpm, the increase of stirring speed just impacted the leaching efficiency of
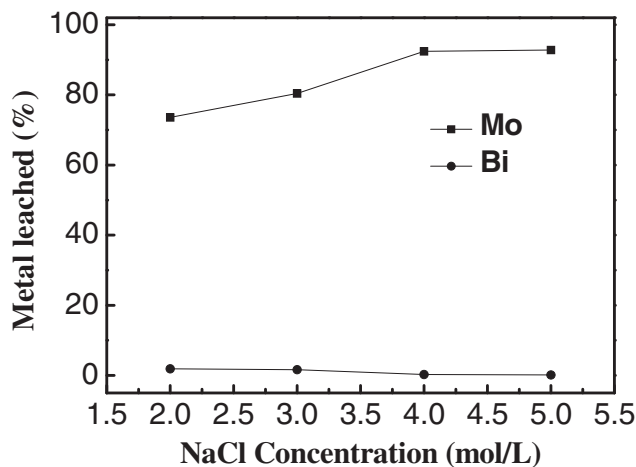

Fig. 9. Effect of NaCl concentration on electro-oxidation leaching of Mo and Bi from concentrate sample. Experimental conditions: pH = 9–10, applied potential = 3.4 V, stirring speed = 300 rpm, L/S ratio = 50.
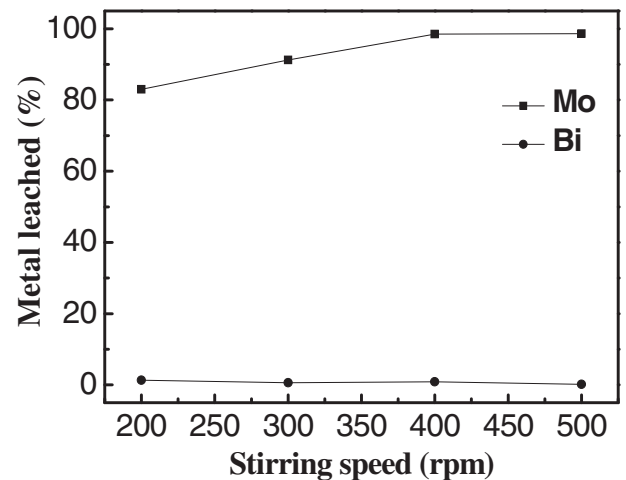

Fig. 10. Effect of stirring speed on electro-oxidation leaching of Mo and Bi from concentrate sample. Experimental conditions: pH = 9–10, applied potential = 3.4 V, NaCl concentration = 4 mol/L, L/S ratio = 50.

Mo slightly, so in the following tests the stirring speed was set at 400 rpm.

That higher stirring speed brought about higher leaching efficiency of Mo is understandable, because increasing the stirring speed led to the increase of diffusion rate of ions such as ClO⁻, so more Mo would have access to the leachate. But when stirring speed was ≥400 rpm, the possible reason for why its growth had little influence on the leaching of Mo is that 400 rpm was enough for concentrate particles to adequately contact with chlorine oxidants. The curve Bi illustrates that the generation of ClO⁻ depended on pH and applied potential rather than stirring speed, hence the selective leaching of Mo from concentrate sample, which meant Bi kept staying in the concentrate, was achieved by adopting appropriate pH and applied potential.

3.2.5. Effect of L/S ratio on selective electro-oxidation leaching of Mo

It is indicated in Fig. 11 that the higher L/S ratio led to the higher leaching efficiency of Mo within the range from 10 to 50, however just like stirring speed and NaCl concentration, L/S ratio seemed to have little effect on electro-oxidation leaching of Bi. On the basis of the fact that when L/S ratio ranged from 30 to 70, its change exerted no distinct effect on the leaching efficiency of Mo, consequently L/S ratio would be set at 30.

The following reason could be adopted to explain the trend of leaching efficiency curve of Mo. As L/S ratio rose, per gram of concentrate sample had access to much more chlorine oxidants, which finally improved the leaching efficiency of Mo, and L/S ratio 30 was adequate for the concentrate particles to contact with chlorine oxidants. The curve Bi in Fig. 11 suggests that whether bismuthinite was able to be leached in the electro-oxidation process did not depend on L/S ratio, proving that among the five process parameters, pH and applied potential were the key parameters for selective separation of Mo.

The usually used L/S ratio in treatment of bismuthinite by electro-oxidation is 3 (Wang et al., 1995a; Liu, 1998). By contrast, to obtain the optimal leaching results, the L/S ratio in this paper was as high as 30, which implies that if the technology for purifying bismuthinite is put to use in industry with such a high L/S ratio, the cost will be excessive. However, it is probably enough to remove 80–90% rather than 98% of Mo from concentrate to obtain a higher grade bismuthinite in industry, thus the L/S ratio will be within the acceptable range from 10 to 20.

X-ray diffraction pattern of the residue obtained under the optimized electro-oxidation conditions is presented in Fig. 12.

Fig. 12. X-ray diffraction pattern of the residue.

3.3. Results of solvent extraction of Mo from leachate to organic phase

The extraction results are displayed in Figs. 13 and 14. The extraction mechanism of Mo by N235 is widely considered as Eqs. (4) and (5) (the two equations are properly revised according to the specific experimental conditions in this paper) (Zeng and Hu, 1994; Xiang, 2002; Zhong et al., 2006). When concentration of HCl was low, the main extraction process was in line with Eq. (4). So the increase of concentration of HCl made more Mo interact with N235, which finally transferred more Mo from leachate to organic phase. However, when concentration of HCl exceeded 60 g/L, it was Eq. (5) not Eq. (4) that coincided with the extraction process. Therefore the increasing concentration of HCl would inevitably restrain Eq. (5), which ultimately undermined the extraction efficiency of Mo. The lower A/O ratio meant that Mo in leachate had access to more N235 in organic phase, which was helpful in improving the extraction efficiency of Mo. Given that the decrease of A/O ratio would just slightly enhance the extraction efficiency of Mo when A/O ratio is ≤1, concentration of HCl = 48 g/L and A/O ratio = 1 are regarded as the optimum conditions.

$$[MoO_2Cl_4]^{2-} + 2H^+ + 2R_3N = (R_3NH)_2MoO_2Cl_4 \qquad (4)$$

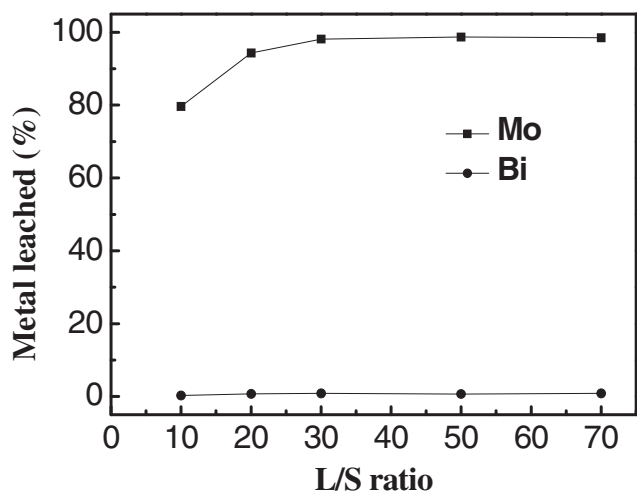$$2R_3NH \cdot Cl + [MoO_2Cl_4]^{2-} = (R_3NH)_2MoO_2Cl_4 + 2Cl^-. \qquad (5)$$

Fig. 11. Effect of L/S ratio on electro-oxidation leaching of Mo and Bi from concentrate sample. Experimental conditions: pH = 9–10, applied potential = 3.4 V, NaCl concentration = 4 mol/L, stirring speed = 400 rpm.
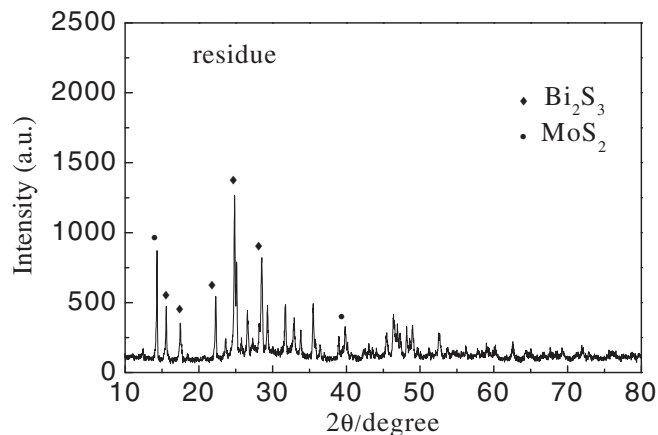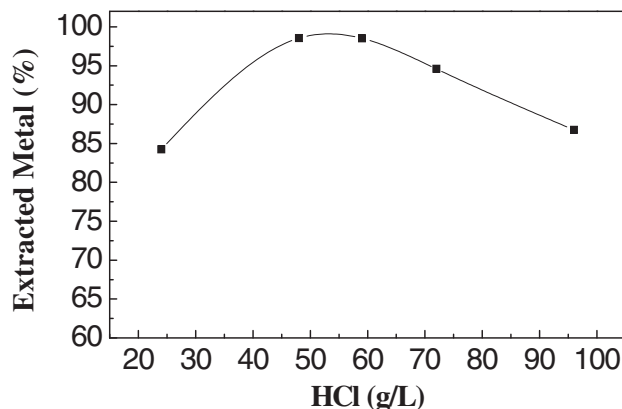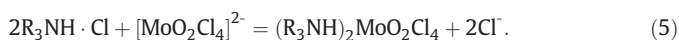

Fig. 13. Effect of concentration of HCl on extraction of Mo from leachate to organic phase.
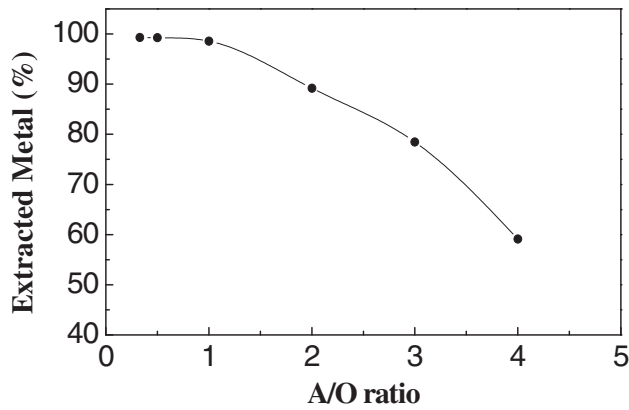
Fig. 14. Effect of A/O ratio on extraction of Mo from leachate to organic phase.

4. Conclusions

Electro-oxidation of Mo has been found to be selective relative to Bi in certain conditions, which can be used to reject Mo from a concentrate consisting of bismuthinite and molybdenite. Compared with the conventional flotation separation of Mo/Bi and/or the traditional electro-oxidation of metal sulfides, electro-oxidation of Mo is an efficient process as it is characterized by its fine application to a concentrate in which bismuthinite and molybdenite are intergrown closely and it is an environmentally friendly hydrometallurgy technology as little Cl_2 generates during the process with electro-oxidation conducted in alkaline solutions (pH = 9–10).

(1) The electro-oxidation leaching of Mo is mainly a result of the oxidation of concentrate sample by chlorine oxidants generated in the electrolysis of NaCl solution rather than by current at the anode.

(2) pH and applied potential are the parameters relevant to the leaching of Bi. When an appropriate pH value and applied potential were set, Bi could be selectively retained in the residue. Other parameters such as NaCl concentration, stirring speed and liquid/solid ratio are irrelevant for Bi leaching. These parameters, however, have distinct effects on the leaching efficiency of Mo, like pH and applied potential.

(3) The optimum leaching conditions were found as follows: room temperature, leaching time = 2.5 h, pH = 9–10, applied potential = 3.4 V, NaCl concentration = 4 mol/L, stirring speed = 400 rpm, liquid/solid ratio = 30 mL/g. Under above conditions, the leaching yield of Mo and the percentage of Bi remaining in the residue both could be more than 98%, thus the grade of Bi in the concentration could go up from 38.12% to 48%.

(4) pH and A/O ratio could evidently impact the extraction of Mo by N235 from leachate to organic phase. Under the optimum conditions of room temperature, extraction time = 5 min, concentration of HCl = 48 g/L and A/O ratio = 1, the extraction efficiency of Mo can reach 99.6%.

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