



Promotion of copper electrolyte self-purification with antimonite oxides



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ABSTRACT

The promotion of copper electrolyte self-purification with antimonite oxides was studied. It was found that the mixed oxides of Sb(III) and Sb(V) can be used to promote copper electrolyte self-purification. The mixture of $Sb_2O_3 \cdot xH_2O$ and $Sb_2O_5 \cdot xH_2O$ with Sb(V)/Sb(III) molar ratio 0.05 was used to promote the self-purification of copper electrolyte containing 353.21 g/L H_2SO_4 , 19.38 g/L Cu, 20.88 g/L As, 2.29 g/L Sb and 1.51 g/L Bi. Experimental results show that the removal of impurities As, Sb and Bi from copper electrolyte mainly depends on the ratio of the molar number of arsenic in the electrolyte to the molar number of antimony in the promoter, namely the As/Sb mole ratio. When the promoter was added into the electrolyte with the As/Sb mole ratio 1:0.7 at 60 °C stirring for 0.5 h, the removal efficiencies of As, Sb and Bi are 62.0%, 93.0% and 95.0% respectively. Then the As and Bi were separated from the used promoter by adding it into 2 mol/L Na_2CO_3 stirring for 0.5 h at above 60 °C in pH 8–9. After filtration, the regenerated promoter was obtained by washing the filter cake with diluted sulfuric acid, and the As and Bi were separated from the regenerated solution by crystallizing $Na_3AsO_4 \cdot 12H_2O$ at room temperature, and by precipitating $Bi_2O_3 \cdot xH_2O$ under the pH above 12, respectively.

1. Introduction

As long as copper electrorefining has been commercially applied, the purification of copper electrolyte has received much attention since the impurities As, Sb and Bi are dissolved with Cu from the anode into the electrolyte during electrorefining due to the similarity of their standard reduction potentials to that of Cu (Zhao, 1981). The traditional method used to remove As, Sb and Bi from copper electrolyte is to electrodeposit them with copper (Navarro et al., 1999; Wan, 2010; Peng et al., 2012b). But the method has a number of drawbacks, e.g., high energy consumption and evolution of toxic arsine gas. Therefore, many other methods have been proposed to remove the impurities from copper electrolyte, such as adsorption of Sb and As using ion exchange (Cunningham et al., 1997; Mckevitt and Dreisinger, 2009; Riveros, 2010; Salari et al., 2017), removal of Sb and Bi by solvent extraction (Navarro et al., 1999), co-precipitation of Bi and Sb by adding a carbonate of barium, strontium, or lead (Hyvarinen, 1979), and reduction and crystallization of As with SO_2 (Zheng et al., 2012). However, these methods can only be used as auxiliary measures for the purification of copper electrolyte, and they cannot completely replace the electro-deposition method (Wang, 2003).

It is well known that during copper electrorefining, a portion of As, Sb and Bi dissolved from the anode can spontaneously precipitate from

the electrolyte into the anode slime (Wang et al., 2011a; Wang et al., 2011b). What is more, the amounts of them deposited into the anode slime depend on their content in the anode, their concentrations in the electrolyte and the electrorefining conditions (Eichrodt and Schloen, 1954; Braun et al., 1976). This indicates that As, Sb and Bi in copper electrolyte have a certain self-purification ability. It has been found that copper electrolyte self-purification can be significantly improved by adjusting the relative content of Sb in the anode and increasing the concentration of As in the electrolyte (Wang, 2003; Wang et al., 2008).

It has been found that the increase in copper electrolyte self-purification is limited, since during commercial operation, it is difficult to change the relative content of Sb in the anode at will, and the concentration of As in the electrolyte cannot be increased without restraint. But the self-purification of As, Sb and Bi in copper electrolyte can be promoted with some compounds containing antimony or arsenic and bismuth (Wang et al., 2003; Zheng et al., 2008; Xiao et al., 2011). This indicates that the self-purification of copper electrolyte can be divided into direct self-purification and indirect self-purification. Direct self-purification is the spontaneous precipitation of As, Sb and Bi in the electrolyte during copper electrorefining, (Wang et al., 2008), while indirect self-purification is to promote their precipitation with compounds containing antimony or arsenic and bismuth (Wang et al., 2014).

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Table 1
Composition of the copper electrolyte used in the experiments, g/L.

As	Sb	Bi	Na	Cu	H ₂ SO ₄
20.88	2.29	1.51	0.40	19.38	353.21

The motivation of this study was the need to promote the self-purification of As, Sb and Bi in copper electrolyte. The effects of the promoter addition, reaction temperature and contact time on the removal of As, Sb and Bi from copper electrolyte, as well as the reuse of the promoter were investigated in the present work.

2. Experimental

2.1. Materials and analysis

The solution used in the experiments was the copper electrolyte from which a portion of water had been evaporated and CuSO₄·5H₂O had been crystallized, and was supplied by Guixi Smelter, Jiangxi Copper Industry Co. The composition of the electrolyte is listed in Table 1. To study the promotion of copper electrolyte self-purification, Sb₂O₃·xH₂O, Bi₂O₃·xH₂O, Sb₂O₅·xH₂O, H₂SO₄, NaOH and Na₂CO₃ were used and they were of analytical grade.

The compositions of experimental samples were determined by chemical methods and inductively coupled plasma emission spectroscopy (ICP-AES) with a PS-6 PLASMA SPECTROVAC, BAIRD (USA). The valencies of the elements were determined by standard chemical methods (Peng et al., 2012a). The X-ray diffraction (XRD) patterns were recorded on a Rigaku Miniflex diffractometer with Cu K α X-ray radiation at 35 kV and 20 mA.

2.2. Experimental procedure

The experiment was performed according to the flow sheet as shown in Fig. 1. The mixture of Sb₂O₃·xH₂O and Sb₂O₅·xH₂O with Sb(V)/Sb(III) molar ratio 0.05 was used as the promoter of copper electrolyte

self-purification. For each experimental run, 250 mL of the electrolyte was mixed with the promoter under stirring in a 500 mL beaker. The beaker was placed in a water bath at about 60 °C to promote electrolyte self-purification. At the end of the self-purification process, the suspension was separated by filtration, and the filtrate and the used promoter were sampled for analysis.

The used promoter (15 g) was mixed with water under stirring in a 250 mL beaker with the desired liquid-solid (L/S) ratio (from 2:1 mL/g to 6:1 mL/g). The beaker was placed in a water bath at the desired temperature (≥ 60 °C) to regenerate the promoter. During the regeneration, the solution pH was adjusted with NaOH and/or Na₂CO₃. After the pH was adjusted to the desired value (8–9), the solution was stirred for scheduled time (0.5–1.5 h), the regeneration was ended. By filtration and washing with 0.5 mol/L H₂SO₄, the regenerated promoter was obtained.

The As was removed from the regenerated solution by cooling to crystallize Na₃AsO₄·12H₂O at room temperature. After the crystal was separated, NaOH and/or Na₂CO₃ were added into the solution to adjust the pH to precipitate the Bi. After filtration, the solution after Bi removal can be returned to the regeneration process.

3. Results and discussion

3.1. Selection of the promoter

It has been found that the As, Sb and Bi in copper electrolyte can combine with each other to form the precipitate of arsenato antimonates (Wang, 2003; Wang et al., 2006), and the compounds containing antimony or bismuth can be used to remove the impurities As, Sb and Bi from copper electrolyte (He and He, 1996; Xiao et al., 2008). This indicates that the oxides of antimony or bismuth may be used to promote copper electrolyte self-purification. But in copper electrolyte, the dissolution of Sb₂O₃, Bi₂O₃ and Sb₂O₅ are all very difficult. Hence, their hydrous oxides were used as the optional promoter. The promoter was added into the copper electrolyte with As/(Sb + Bi) mole ratio 1:1, in which the As is the mole number of arsenic in the electrolyte, and the (Sb + Bi) is the total mole number of antimony and bismuth in the

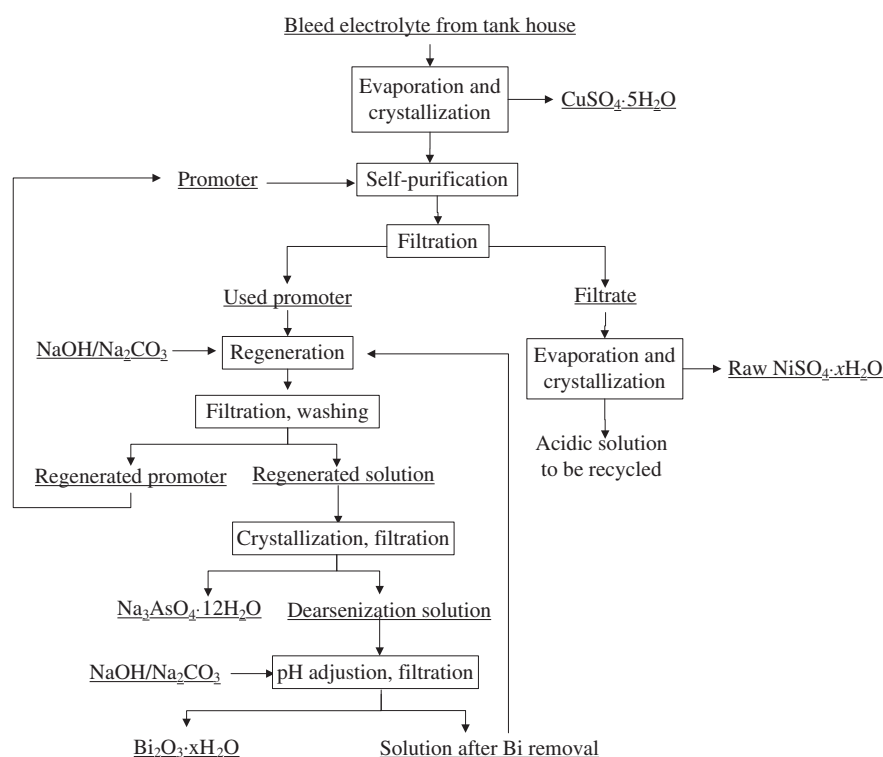


Fig. 1. Flowsheet of copper electrolyte indirect self-purification process.

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