



Short communication

## Homogeneous precipitation of As, Sb and Bi impurities in copper electrolyte during electrorefining<sup>☆</sup>

Xuwen Wang<sup>a,\*</sup>, Qiyuan Chen<sup>b</sup>, Zhoulan Yin<sup>b</sup>, Mingyu Wang<sup>a</sup>, Bingrui Xiao<sup>c</sup>, Fan Zhang<sup>c</sup>

<sup>a</sup> School of Metallurgical Science and Engineering, Central South University, Changsha 410083, China

<sup>b</sup> College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China

<sup>c</sup> Guixi Smelter, Jiangxi Copper Co., Jiangxi 335424, China

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### ABSTRACT

Experiments confirmed that the homogeneous co-precipitation of impurities As, Sb and Bi in a copper electrolyte can be obviously improved under certain conditions. In commercial copper electrorefining operation, by improving the homogeneous co-precipitation, the percentages of the impurities As, Sb and Bi dissolved from the copper anode and then deposited into the anode slimes were increased from 17.6%, 49.4% and 36.5% to 69.3%, 93.0% and 68.1% respectively. It was found that there are two control-steps in the homogeneous co-precipitation, namely oxidation of antimony from Sb(III) to Sb(V) and the formation of arsenato antimonates. When the arsenic concentration is over 7 g/L in the copper electrolyte, the rate of oxidation of antimony from Sb(III) to Sb(V) can be increased markedly, which results in the faster formation of arsenato antimonates provided that the mole ratio of Sb/As/Bi in the anode is suitable for arsenato antimonates formation. Moreover, to properly understand the homogeneous co-precipitation, the compounds contained in copper anode slimes were classified according to their formations.

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### 1. Introduction

In copper electrorefining, the impurities of arsenic, antimony and bismuth are dissolved with copper from the anode to the electrolyte. If no electrolyte were eliminated from the electrorefining circuit, the impurities would gradually accumulate in the electrolyte, which would result in a variety of intolerable problems such as contamination of the cathodes and passivation of the anodes. In order to assure the cathode quality, the electrolyte must be bled and treated – typically using the conventional purification scheme shown in Fig. 1. This bleed treatment presents many drawbacks, e.g. high-energy consumption and evolution of toxic arsine gas. Moreover, the disequilibrium between copper and sulfuric acid will be raised in the electrolyte if the volume of the electrolyte withdrawn to be purified is over a certain limit.

Therefore, a number of methods have been proposed for the purification of the copper electrolyte, such as with stannic acid (Schulze, 1972) or activated carbon (Toyabe et al., 1987; Navarro and Alguacil, 2002), co-precipitation of bismuth and antimony from the electrolyte by adding a carbonate of barium, strontium, or lead (Hyvarinen, 1979), extraction of antimony and bismuth from the copper electrolyte with LIX1104SM (Navarro et al., 1999), adsorption of bismuth and antimony with adsorbent containing antimony (Wang

et al., 2003), or removal of antimony and bismuth from the electrolyte using ion exchange resins (Cunningham et al., 1997), and separation and concentration of arsenic from the copper electrolyte using electro dialysis (Cifuentes et al., 2002).

It is well known that a part of the impurities arsenic, antimony and bismuth dissolved from the anode can spontaneously precipitate from the electrolyte to the anode slimes during copper electrorefining and the volume of the copper electrolyte withdrawn to be purified per ton cathode (VPTC) is diverse in different copper refineries. Even in the same refinery with the same anode, the VPTC is not the same under different electrorefining conditions (Wang, 2003), which indicates that the efficiencies of the homogeneous co-precipitation of arsenic, antimony and bismuth are different, i.e., the fraction of As, Sb and Bi dissolved from the anode and then deposited into the anode slimes varies under different electrorefining conditions. The forms of the arsenic, antimony and bismuth impurities contained in copper anode slimes have been well studied (Braun et al., 1976; Chen and Dutrizac, 1987; Petkova, 1994; Chen and Dutrizac, 2005). However, the causes of the different VPTC values remain to be investigated.

Recently, it was found that the combination of As(V) and Sb(V) can form arsenato antimonate acid (AAAc) (Wang, 2003; Wang et al., 2004a, 2005) and the reactions of As(V) and Sb(V) with As(III), Sb(III), and Bi(III) can produce the precipitates of arsenato antimonates in the copper electrolyte (Wang et al., 2004b, 2006a; Chen et al., 2004). If the mole ratio of As/Sb/Bi in the anode copper is suitable for the formation of arsenato antimonates, and arsenic concentration is maintained in the ranges of 7–15 g/L, most of the arsenic, antimony and bismuth

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\* Corresponding author.

E-mail address: [wxwcsu@163.com](mailto:wxwcsu@163.com) (X. Wang).

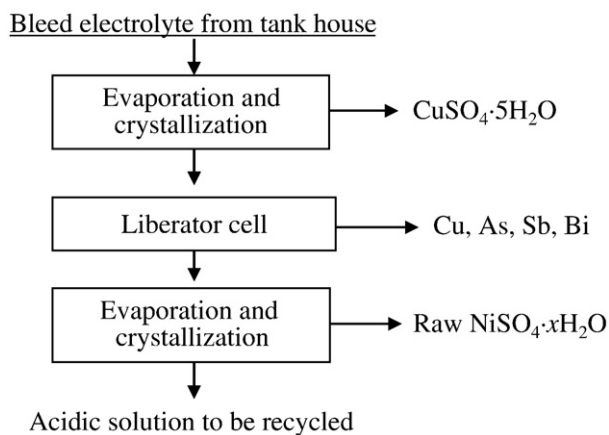


Fig. 1. Schematic flow-sheet of the conventional purification process.

impurities dissolved in the copper electrolyte can be deposited into anode slimes in the form of arsenato antimonates (Wang, 2003). The aim of this paper is to present improvements in the homogeneous co-precipitation of arsenic, antimony and bismuth in a copper electrorefining commercial operation.

## 2. Experimental

### 2.1. Materials, apparatus and analysis

To confirm the homogeneous co-precipitation of arsenic, antimony and bismuth impurities in the copper electrolyte, the test were first performed in the copper electrorefining system containing 50 cells with about 500 m<sup>3</sup> electrolyte re-circulating under the VPTC = 0.4 and the current density 275 A/m<sup>2</sup>. Then the method was applied in the commercial operation system of 150,000 t cathode per annum.

The high-arsenic solution was gradually added to increase the arsenic concentration in the electrolyte, which contained the basic components: 47.5 g/L Cu, 183.2 g/L H<sub>2</sub>SO<sub>4</sub>, 3020 mg/L As, 510 mg/L Sb and 650 mg/L Bi. The high-arsenic solution contained about 40 g/L As (including 12 g/L As(III)), 30 g/L H<sub>2</sub>SO<sub>4</sub> and 5 g/L Cu). The replacement cycle of the anode copper refined in the electrolyte was 12 days and the composition of the anode is listed in Table 1.

During the test, the composition of the electrolyte was analyzed every day to observe the change of impurities As, Sb and Bi. The total content of the elements was determined by inductively coupled plasma emission spectroscopy (ICP) (PS-6 PLASMA SPECTROVAC, BAIRD, USA). The valence of the elements was determined by standard chemical methods.

## 3. Results and discussion

### 3.1. Impurity homogeneous precipitation

Fig. 2 presents the test results of arsenic, antimony and bismuth impurities in the homogeneous co-precipitation performed in the circulating system of the 500 m<sup>3</sup> copper electrolyte. From Fig. 2 it can be seen that in the first anode replacement cycle, the impurities were dissolved from the anode to the electrolyte and then removed from the electrolyte and were balanced under normal copper electrorefining conditions. After the high-arsenic solution was added in, the

Table 1  
Composition of experimental anode copper, wt.%.

Cu	As	Sb	Bi	Fe	Ni	Pb	S	O	Au(g/t)	Ag(g/t)
99.4	0.19	0.065	0.046	0.003	0.038	0.023	0.003	0.14	31.5	450

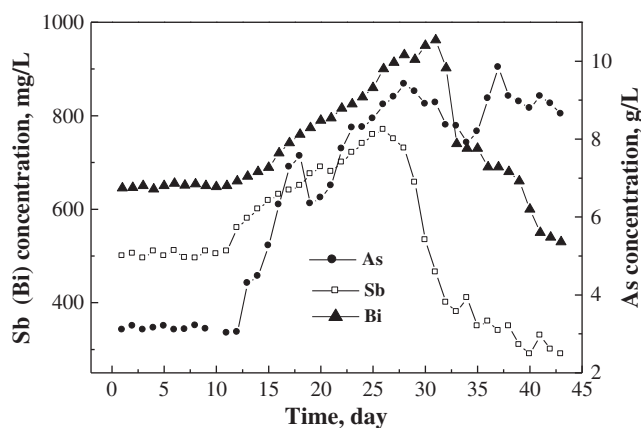
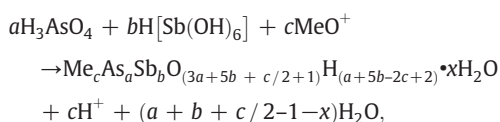


Fig. 2. Results of impurities As, Sb and Bi homogeneous precipitation in copper electrolyte during electrorefining.

concentrations of antimony and bismuth in the electrolyte increased gradually in the beginning, and then decreased sharply.

It is well known that antimony and arsenic dissolve electrochemically from copper anodes as trivalent ions and then oxidize to pentavalent ions by the air (O<sub>2</sub>) dissolved in copper refining electrolytes. Furthermore, As(III) oxidizes before Sb(III). Fig. 2 indicates that when As(III) carried by the added solution was oxidized, the oxidation of Sb(III) was halted in the electrolyte, which results in the pause of arsenato antimonates formation because they cannot be formed without Sb(V) (Wang et al., 2006a). Thus antimony and bismuth in the electrolyte were accumulated gradually at the beginning of the high-arsenic solution addition.

When As(III) was oxidized to a certain extent, the oxidation of Sb(III) took place and the rate of formation of arsenato antimonates was increased above their rate of dissolution from the anode. Thus the concentrations of antimony and bismuth decreased until a new balance between the dissolution and the precipitation was established in the electrolyte. This indicates that there are two control-steps; namely antimony oxidation from Sb(III) to Sb(V) and the subsequent formation of arsenato antimonates which can be expressed as follows (Wang et al., 2006a):



where Me = As(III), Sb(III) and Bi(III);  $a \geq 1$ ,  $b \geq 1$ , and  $c \leq (3a+b)$ .

Table 2 shows the percentage of arsenic, antimony and bismuth dissolved from the anode and then deposited into the anode slimes under normal copper electrorefining conditions and test conditions, in which, the percentages were obtained at the second anode replacement cycle after the high-arsenic solution addition, see Fig. 2. From Table 2 it can be clearly seen that homogeneous co-precipitation of arsenic, antimony and bismuth in the copper electrolyte was significantly improved by adding the high-arsenic solution. The addition of the high-arsenic solution results in an increase of the

Table 2  
Distribution ratio of impurities deposited into anode slimes before and after high-arsenic solution addition, %.

Impurities	As	Sb	Bi
Before	17.6	49.4	36.5
After	69.3	93.0	68.1

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