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The role of trivalent arsenic in removal of antimony and bismuth impurities from copper electrolytes

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ARTICLE INFO

Article history:

Received 26 September 2011

Received in revised form 12 May 2012

Accepted 16 May 2012

Available online 23 May 2012

Keywords:

Trivalent arsenic
Removal mechanism
Copper electrolyte
Antimony
Bismuth

ABSTRACT

The effect of trivalent arsenic on the removal mechanism of antimony and bismuth from copper electrolyte was investigated. The electrolyte was filtered and the precipitate structure, morphology and composition were analyzed by means of chemical analysis, scanning electron microscopy, transmission electron microscopy, energy dispersive spectra, X-ray diffraction, and infrared spectroscopy. The precipitate in the form of fine spherical particles mainly consists of As, Sb, Bi and O elements. The characteristic bands in the IR spectra of the precipitate are O–H, As–OH, As–OX (X = As, Sb), As–O–Sb, Sb–OY (Y = As, Sb, Bi) and O–As–O. The precipitate is a mixture of microcrystalline (Sb, As)₂O₃, BiSb₂O₇, and an amorphous phase. The impurities of Sb and Bi are effectively removed from copper electrolytes by trivalent arsenic owing to these precipitates.

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1. Introduction

Copper produced by pyrometallurgical technologies is impure, and does not satisfy the purity requirements for most applications, thus, it needs to be electro-refined (Navarro et al., 1999). However, during copper electro-refining, As, Sb and Bi impurities are dissolved along with copper from the anode in the electrolyte and gradually accumulate in the electrolyte, which results in a variety of intolerable problems, such as cathodes contamination and floating slime formation (Wang et al., 2011a, 2011b). Therefore, the removal of As, Sb and Bi impurities has become a key problem faced by copper smelting plants in the world. At present, most copper smelting plants still use electrowinning to remove As, Sb and Bi in the electrolyte, even if this method has many drawbacks, e.g. high-energy consumption and formation of toxic arsine gas (Deorkar and Tavlarides, 1997; Navarro and Alguacil, 2002). Recently, various technologies have been proposed for As, Sb and Bi removal from copper electrolyte, including extraction of arsenic from copper electrolyte with Cyanex 925, Cyanex 301 or their mixtures (Iberhan and Winiewski, 2002, 2003), antimony and bismuth removal using ion exchange resins (Riveros, 2010), bismuth and antimony co-precipitation by adding barium carbonate, strontium, or lead (Hyvarinen, 1979), antimony and arsenic adsorption by activated carbon (Navarro and Alguacil, 2002). However, it is difficult for these methods to be applied in production due to various reasons.

It was found that a part of the As, Sb and Bi impurities can spontaneously precipitate from the electrolyte to the anode slimes or residue during copper electro-refining (Wang et al., 2011a; Xiao, 2008). Meanwhile, electrolytes purification technologies based co-precipitation reactions among As, Sb and Bi impurities in the bath have been utilized in the copper smelting industry (Kamath et al., 2003; Zheng et al., 2008). However, until now the purification mechanism has not been fully understood. It was generally regarded that the arsenate formed from As (V), Sb (III) and Bi (III) was the main reason of Sb and Bi removal by arsenic (Braun et al., 1976; Hoffmann, 2004; Yannopoulos and Agarwal, 1977). Wang et al. (2006, 2011a) stated that, in copper electrolyte, the combination of As (V) and Sb (V) could form arsenato-antimonic acid (AAAc), which further reacted with As (III), Sb (III) and Bi (III) ions to produce arsenato antimonate precipitates. Obviously, As (V) ion is indispensable whether in arsenate or arsenato-antimonate form. In fact, Xiao et al. (2008) reported that Sb and Bi can be removed by As (III) ion from the copper electrolyte in the absence of As (V) ion. They proposed that the As (III) ion could react with Sb (III), Sb (V) ions to form antimony arsenantimonate, resulting in the decline of Sb and Bi concentration in the electrolyte, while the XRD pattern of antimony arsenantimonate has not been confirmed until now. Obviously, there is still a dispute about the purification mechanism of the copper electrolyte.

In this work, the influence of As (III) ion initial concentration on the removal rate of Sb and Bi was investigated by adding As (III) ion in various concentrations to the solution containing H₂SO₄, Cu²⁺, Sb (III, V) and Bi (III) ions. The removal mechanism of antimony and bismuth by As (III) ion in the co-precipitation reactions was investigated by characterizing the sediment structure.

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2. Material and methods

Analytically pure As₂O₃, Sb₂O₃, Bi₂O₃, H₂O₂, NaOH and H₂SO₄ reagents were used. A sample of As₂O₃ was mixed with solid NaOH according to 1:1.5 As to Na molar ratio, and 100 mL of water was added, stirred and heated to dissolve solids. Then concentrated sulfuric acid was added to obtain As (III) stock solutions. Sb (III) and Bi (III) stock solutions were prepared by dissolving Sb₂O₃ and Bi₂O₃ in concentrated sulfuric acid and diluted with water. The Sb (V) stock solution was prepared by adding hydrogen peroxide to the Sb (III) stock solution under stirring. Excess H₂O₂ was decomposed by boiling the solution for about half an hour. The total content of the elements was determined by Atomic Absorption Spectroscopy (AA700, Perkin Elmer Corp.). The valence of the elements was determined by standard chemical methods.

The electrolytes used in the experiments contained the following basic components: 44–46 g/L Cu²⁺, 180–185 g/L free H₂SO₄ and arsenic, antimony and bismuth as impurities. The initial concentration of the synthetic electrolytes is shown in Table 1. The purification experiments were carried out by heating the synthetic electrolytes to 65 °C under 300 rpm stirring for 2 h. The purified electrolyte was then filtered to remove the precipitate. The content of the filtrate elements was determined. The removal rate of impurities was calculated using the following formula:

$$R = \frac{\Delta c}{c} \times 100\% \quad (1)$$

where *R* is the removal rate of As (Sb, Bi); Δc is the concentration difference of As (Sb, Bi) before and after the experiment; and *c* is the initial concentration of As (Sb, Bi).

The precipitate composition was determined by chemical methods and Energy Dispersive Spectrometry (EDS) (Genesis 60S, EDAX Company). Microscopic observations were carried out using transmission electron microscope (JEM-2100, Japanese Electron Company) and scanning electron microscope (Sirion 200, Holland FEI Company). Additionally, the X-ray diffraction (XRD) patterns were recorded on a D8 ADVANCE diffractometer with Cu K α X-ray radiation at 35 kV and 20 mA. IR spectra were obtained using the KBr disk method with a VERTEX70 (Japan) spectrophotometer operating in the 4000–400 cm⁻¹ wavenumber range.

3. Results and discussion

3.1. Influences of the initial As (III) ion concentration on Sb and Bi removal rate

The purification experiments were carried out according to the above experimental procedure and the removal rates of As, Sb and Bi were calculated. The effects of the initial As (III) ion concentration on arsenic removal rate (*R*) and amount (Δc) are shown in Fig. 1. The effects of initial As (III) ion concentration on the removal rate of Sb and Bi are illustrated in Fig. 2.

It can be seen from Figs. 1 and 2 that the removal rates of As, Sb and Bi initially increased and then decreased with the increase of

Table 1
Initial concentrations of the synthetic copper electrolytes (g/L).

Electrolyte	1#	2#	3#	4#	5#	6#	7#	8#
As (III)	0.5	1.0	2.0	4.0	7.0	10.0	12.0	15.0
Sb (III)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sb (V)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Bi	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Cu ²⁺	45.5	45.6	45.5	45.3	44.6	44.2	45.7	45.2
H ₂ SO ₄	184.3	184.7	183.5	183.5	183.9	184.6	184.3	184.1

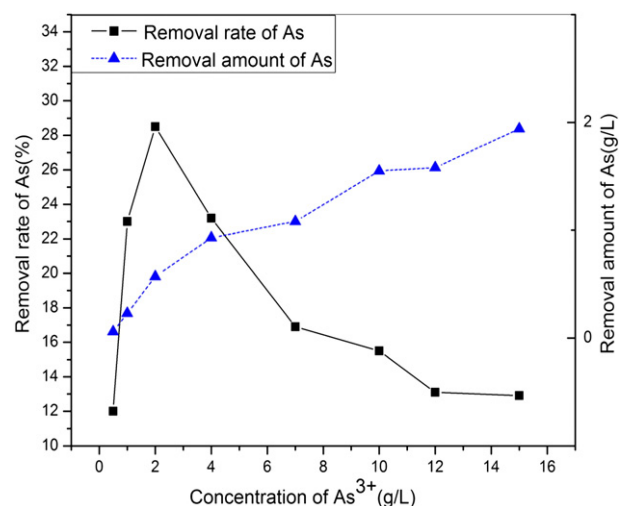


Fig. 1. Effects of As (III) ion concentration on the arsenic removal rate and amount.

initial As (III) ion concentration in the synthetic electrolyte, and the removal rates of Sb and Bi reached the maximum of 53% and 52%, respectively, when initial As (III) ion concentration was 1 g/L at 65 °C and 300 rpm stirring for 2 h. The As removal amount increased continuously with the increase of initial As (III) ion concentration in the synthetic electrolyte. The similar results were obtained by dissolving As₂O₃ solid or copper arsenite in the commercial copper electrolytes at 65 °C under stirring (Xiao et al., 2007, 2008; Zheng et al., 2008). In those reports, it was found the removal rates of Sb and Bi increased with purification time increase. These results show that As (III) ion concentration has prominent effects on Sb and Bi removal. It also indicates that some precipitate reactions occur among As, Sb and Bi impurities in the synthetic copper electrolyte. Precipitate structural characterization should be performed to identify the removal mechanism of antimony and bismuth impurities by As (III) ion. Industrial filter residue was collected from the Larox filter in the electrolyte circle of Hubei Daye copper smelter in China, and its structure was characterized in this paper.

3.2. Precipitate structure characterization

A 500 mL of synthetic electrolyte containing 1 g/L As (III), 0.5 g/L Sb (III), 0.5 g/L Sb (V), 0.5 g/L Bi (III), 185 g/L H₂SO₄ and 45 g/L Cu²⁺ was

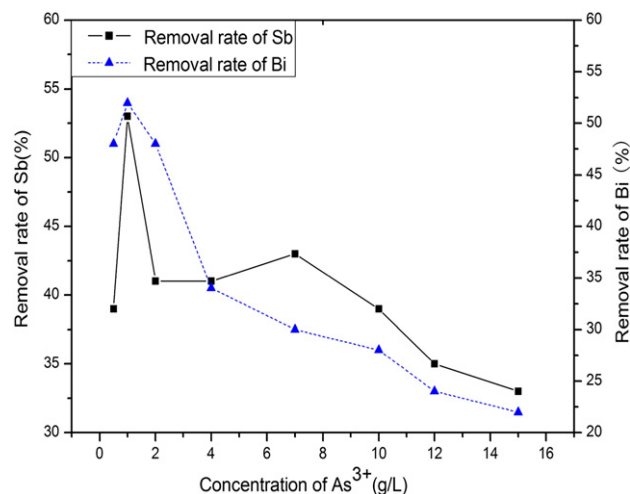


Fig. 2. Effects of As (III) ion concentration on Sb and Bi removal rate.

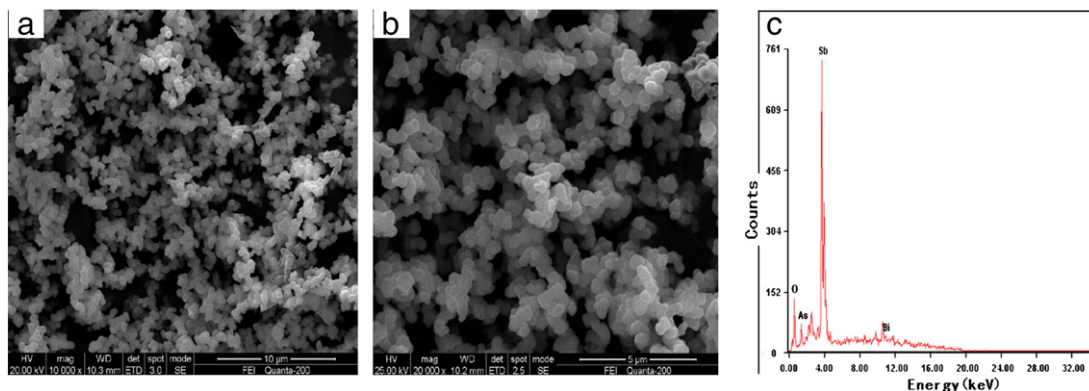


Fig. 3. SEM micrographs (a and b) and EDS spectrum (c) of the synthetic precipitate.

purified according to the experimental steps described above. The precipitate was collected for structural characterization. The SEM micrograph and precipitate components determined by EDS are shown in Fig. 3. Based on Fig. 3, the precipitate is composed of many fine spherical particles with 0.5–1 μm diameter and mainly consists of As, Sb, Bi and O elements. The exact contents of As, Sb and Bi of the precipitate from the synthetic electrolyte and the industrial filter residue were determined by chemical methods, and the results are listed in Table 2.

From Table 2, the total content of As, Sb and Bi in synthetic precipitate is 74.52%, which indicates that As, Sb and Bi are the key elements in the synthetic precipitate. The Sb content is larger than that of As and Bi, since the molar ratio $n_{As}:n_{Sb}:n_{Bi}$ is 1.61:7.51:1. Overall, the industrial filter residue composition is similar to the synthetic precipitate, although the Sb content in the industrial filter residue is lower than in the synthetic precipitate. The difference in the contents between the precipitate and filter residue may be caused by the fact that there were not only As (III), Sb, and Bi elements, but also As (V), Pb, Sn and other elements presented in the filter residue.

X-ray diffraction pattern in Fig. 4 shows that synthetic precipitate is a mixture consisting of crystalline and amorphous phases as there are some amorphous areas (Regions B, C and D) in the bottom background of pattern and some crystalline diffraction reflections appearing at the diffraction angle of 12.7°, 28.0°, 29.5°, 32.6°, 37.1°, 44.8°, 50.1°, 59.1° and 65.6°. In other word, the precipitate is in the transition state from amorphous phase to the crystalline structure. Even so, a mixture of $BiSb_2O_7$ and $(Sb, As)_2O_3$ were identified according to the PDF pattern numbers of 42-0591 and 01-0758, respectively. In contrast to the synthetic precipitate, the crystal performance of the industrial filter residue is nicer, although some amorphous phases (Region A) are included in this residue. And the $BiSb_2O_7$ and $(Sb, As)_2O_3$ diffraction reflections are also found in the residue. Some diffraction reflections that appear in the industrial filter residue XRD pattern do not appear in that of the synthetic precipitate, which points to the more complex components of copper electrolyte. In addition, the main phase of $(Sb, As)_2O_3$ and Sb–Bi oxides were found in the filtrate residue, obtained during electro-refining of Yunnan copper smelter after it was

heated to 654 °C (Hua and Zhang, 2011). Although the formation conditions were different, it can be concluded that $(Sb, As)_2O_3$ and Sb–Bi oxides can be generated in the copper electrolyte.

TEM analysis was carried out to obtain further information about the precipitate structure, and the results are shown in Fig. 5. TEM images in Fig. 5(a, b and c) show that the precipitate is composed of granular particles. Electron diffraction patterns in Fig. 5(d, e and f) were taken from corresponding regions in Fig. 5(a, b and c), respectively. Fig. 5(d and e) indicates that the precipitate contains crystalline phases. The inter-planar distances were calculated, and the corresponding R values are displayed in Tables 3 and 4.

The diffraction patterns shown in Fig. 5(d and e) were indexed based on the inter-planar distances. From Table 3, it can be seen that the inter-planar distances of the crystal in Fig. 5(d) are similar to those of $(Sb, As)_2O_3$. Similarly, the inter-planar distances of the crystal in Fig. 5(e) are consistent with those of $BiSb_2O_7$, according to Table 4. These results further confirm that the precipitate contains $(Sb, As)_2O_3$ and $BiSb_2O_7$, consistent with the XRD result. The diffraction pattern in Fig. 5(f) shows a diffuse halo structure, which indicates that the precipitate contains amorphous phase, thus the structure can not be obtained from the diffraction pattern. This result corresponds with the bottom background of XRD pattern (Regions B, C and D). The EDS spectrum of the region in Fig. 5(c) is shown in Fig. 6. The region in Fig. 5(c) mainly consists of As, Sb, Bi and O

Table 2
Chemical analysis results of the synthetic precipitate and industrial filter residue (wt.%).

Sample	As	Sb (III)	Sb (V)	Bi (III)
Synthetic precipitate	7.23	35.80	18.99	12.50
Industrial filter residue	9.28	20.75	10.77	12.33

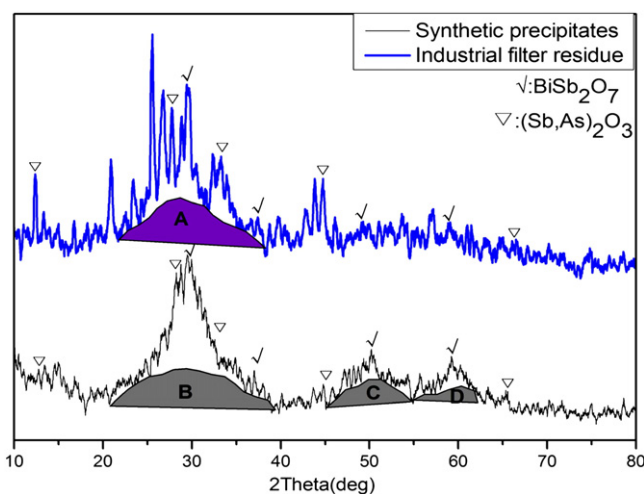


Fig. 4. XRD patterns of synthetic precipitate and industrial filter residue (Regions A, B, C and D exhibit the amorphous phase in the precipitate).

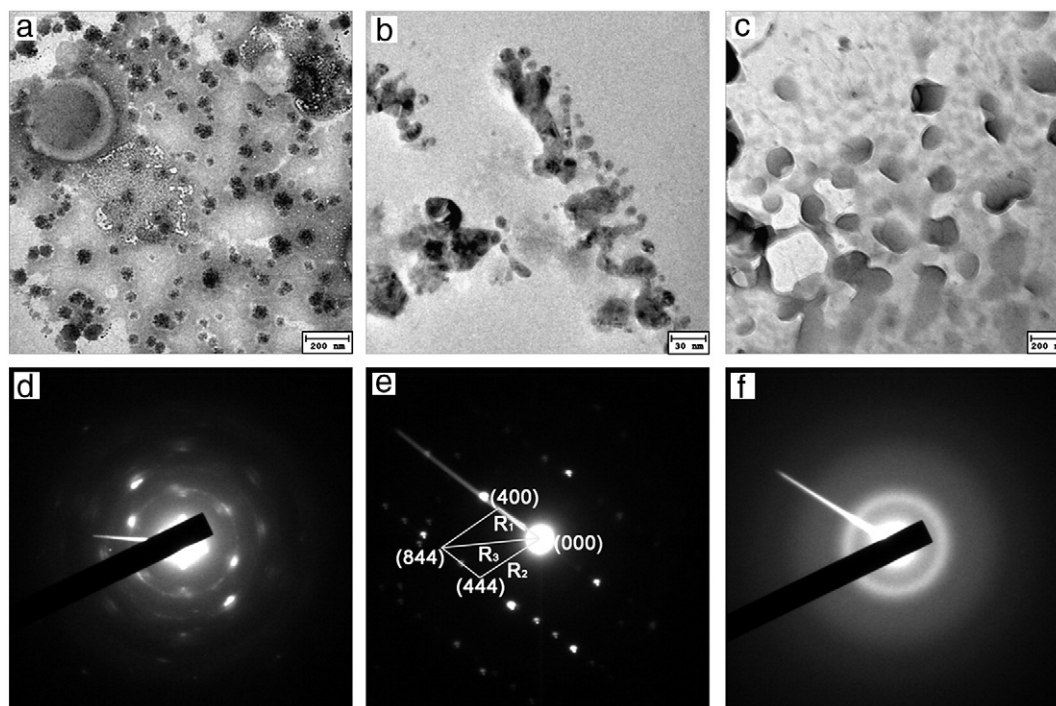


Fig. 5. TEM images showing the morphology (a, b and c) and electron diffraction patterns (d, e and f) of the synthetic precipitate.

elements, which indicates the amorphous phase in the precipitate is composed of As, Sb, Bi and O elements.

The IR spectra of the synthetic precipitate and the industrial filter residue recorded in the 4000–400 cm^{-1} wavenumber range are given in Fig. 7. The FTIR bands at 3377.85 cm^{-1} and 1625.53 cm^{-1} are symmetrical and anti-symmetrical stretching vibrations of O–H absorption spectra (Losilla et al., 1998). The band at 448.45 cm^{-1} is the twisting vibrations of O–As–O absorption spectrum (Nakamoto, 1986). The bands at 1046.28 cm^{-1} , 821.3 cm^{-1} , 726.10 cm^{-1} and 528.39 cm^{-1} are the anti-symmetrical stretching vibrations absorption spectra of As–OH, As–OX (X=As, Sb), As–O–Sb and Sb–OY (Y=As, Sb, Bi), respectively (Colomban et al., 1989; Qureshi and Kumar, 1971; Wang et al., 2006; Xiao, 2008). Therefore, the valence bands of O–As–O, As–OH, As–OX (X=As, Sb), As–O–Sb, Sb–OY (Y=As, Sb, Bi), and O–H are included in the structure of the precipitate.

The structural formulas of $\text{Sb}_2\text{O}_4^{2-}$ and As_2O_3 are shown in Fig. 8. It can be inferred that some of Sb atoms replace the position of the As atoms in the structural formula of As_2O_3 to form $(\text{Sb}, \text{As})_2\text{O}_3$. Thus the valence bands of Sb–O–As and O–As–O are included in $(\text{Sb}, \text{As})_2\text{O}_3$. Similarly, the valence bands of Sb–O–Bi and Sb–O–Sb are included in the crystal structure of BiSb_2O_7 . All these valence bands were present in the precipitate, which further verifies the XRD results. Similar conclusions can be drawn based on the IR spectrum of the industrial filter residue.

3.3. Mechanism analysis

Structural analysis shows that the precipitate is composed of a mixtures of microcrystalline BiSb_2O_7 and $(\text{Sb}, \text{As})_2\text{O}_3$, and an amorphous

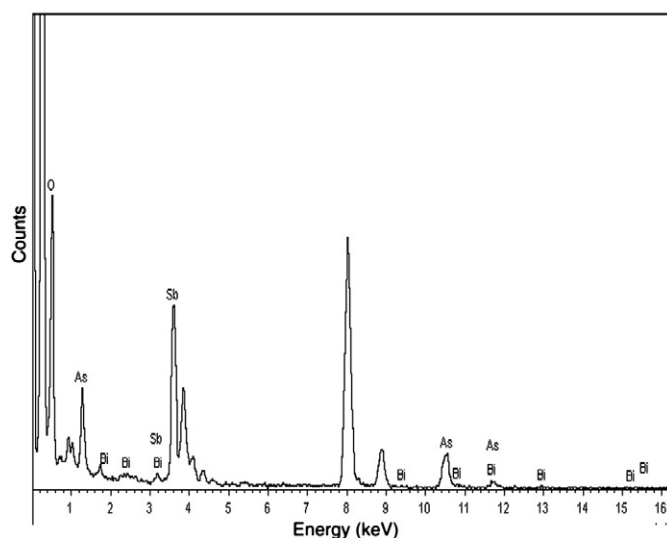


Fig. 6. EDS spectrum of Fig. 5(f) region.

phase containing As, Sb, Bi and O. It is found that As (III), Sb (V) and Sb (III) exist in the forms of AsO^+ , HASO_2 , HSb(OH)_6 and SbO^+ , respectively in the copper electrolyte, according to the thermodynamic calculations (Wang, 2003; Xiao, 2008). Also BiO^{2+} was found in the acid solution by S. Becker (Becker and Dietze, 1983). Therefore, the

Table 3
The inter-planar distances of the precipitate in Fig. 5(d) compared with $(\text{Sb}, \text{As})_2\text{O}_3$.

Number	R/mm	d/Å	d/Å (PDF01-0758 $(\text{Sb}, \text{As})_2\text{O}_3$)	hkl
1	15.3	2.1046	2.1100	–112
2	17.4	1.8506	1.8600	042
3	24.0	1.3417	1.3400	133
4	30.2	1.0662	1.0600	432

Table 4
The inter-planar distances of the precipitate in Fig. 5(e) compared with BiSb_2O_7 .

Number	R/mm	d/Å	d/Å (PDF42-0591 BiSb_2O_7)	hkl	The angle between R_1 and R_2
1	12.4	2.5968	2.6000	400	59°
2	21.6	1.4907	1.4980	444	
3	30.2	1.0662	1.0590	844	

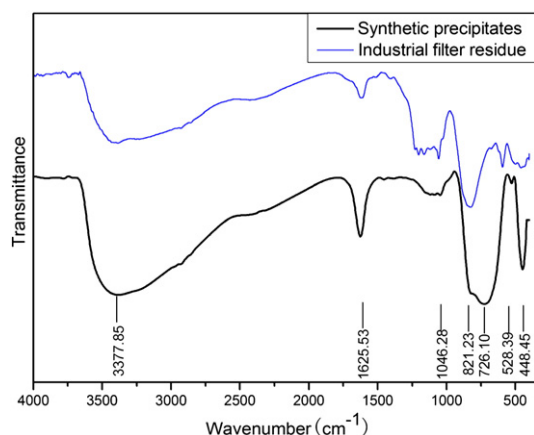


Fig. 7. IR spectrums of synthetic precipitate and industrial filter residue.

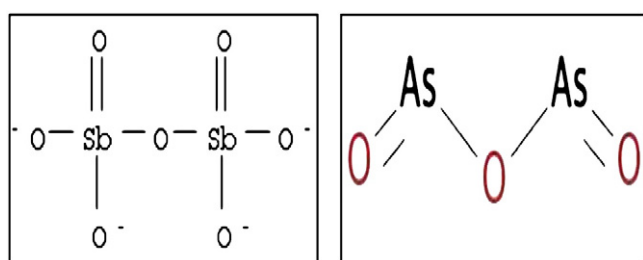
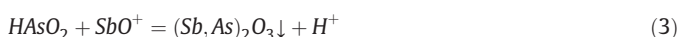


Fig. 8. Structural formulas of $\text{Sb}_2\text{O}_7^{4-}$ and As_2O_3 .

following reactions may happen in the process of electrolyte purification:



The mixture of $(\text{Sb, As})_2\text{O}_3$ and BiSb_2O_7 formed and deposited in the synthetic electrolyte according to reactions (2) and (3), besides, an amorphous compound mainly contained As, Sb, Bi and O elements deposited in the synthetic electrolyte based on XRD and TEM results. Therefore, Sb and Bi impurities are removed from the synthetic electrolytes by As (III) ion. The mixture of $(\text{Sb, As})_2\text{O}_3$, BiSb_2O_7 , and the amorphous phases form simultaneously when the initial As (III) ion concentration is less than 1 g/L, which results in the increase of Sb and Bi removal rate. The removal rate of Sb and Bi decreases with further increase of the initial As (III) concentration, which may be caused by the faster formation rate of the amorphous compound than that of BiSb_2O_7 and $(\text{Sb, As})_2\text{O}_3$. The contents of Sb and Bi in the amorphous phase decreases with further increase of initial As (III) concentration after it exceeds to 1 g/L.

4. Conclusions

- The removal rates of antimony and bismuth initially increase and then decrease with the increase of the initial As (III) ion concentration in the synthetic copper electrolyte, and reach the maximum of 53% and 52%, respectively, when the initial As (III) concentration is 1 g/L at 65 °C and 300 rpm stirring for 2 h.
- The precipitate is composed of fine spherical particles and mainly consists of As, Sb, Bi and O elements. The characteristic bands in the IR spectra of the precipitate are O–H, As–OH, As–OX (X = As, Sb), As–O–Sb, Sb–OY (Y = As, Sb, Bi) and O–As–O.

- The mixtures of $(\text{Sb, As})_2\text{O}_3$, BiSb_2O_7 and amorphous phases form and deposit in the synthetic and commercial copper electrolytes. The impurities of Sb and Bi are effectively removed from copper electrolytes by trivalent arsenic owing to these precipitates.

Acknowledgments

The authors acknowledge the financial support from the National Natural Scientific Foundation of China (50904023), the Natural Science Fund of Department of Education of Henan Province (2010B450001) and the Science Fund for Youth of HAUST (2009QN0022).

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