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Trans. Nonferrous Met. Soc. China 17(2007) 1069−1074
Transactions of Nonferrous Metals Society of China
www.csu.edu.cn/ysxb/

Novel technology of purification of copper electrolyte

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Received 29 December 2006; accepted 21 March 2007

Abstract: The effects of arsenic with different valence states on the purification of copper electrolyte were studied and a novel technology of purification of copper electrolyte by copper arsenite was proposed. The results show that the purification performance of As(Ⅲ) compounds is better than that of As(Ⅴ) compounds. The purification technology by copper arsenite has the advantages of simple operation, high purification performance and low cost in comparison with other technologies and its appropriate purification conditions are that copper arsenite concentration is 18 g/L, reaction temperature is 65 ℃ and reaction time is 8 h. The removal rates of Sb and Bi are 53.22% and 58.67% respectively under these conditions. The purification principle show that a kind of yellow precipitate mainly composed of arsenic, antimony (Ⅴ), bismuth and oxygen forms in electrolyte after copper arsenite is added, and consequently antimony and bismuth are removed from electrolyte.

Key words: purification; copper electrolyte; arsenic compound; Sb; Bi

1 Introduction

Recently, copper smelting plants expand rapidly due to the skyrocket of price of cathode copper, and the copper electrolysis enters a fast developing era[1−2]. At the same time, the problem of removing impurities restricts this expanding step in great part[3−5]. The cathode copper deteriorates with antimony and bismuth contamination in copper electrorefining[6−8]. Therefore, how to remove Sb and Bi becomes a key problem facing to copper smelting plants in the world.

At present, most smelting plants still adopt electrowinning method to remove Sb and Bi in electrolyte. In this method, current efficiency is low and energy consumption is high. To the worst, the toxic arsine gas is produced at the end of electrowinning[9−11]. Recently, many methods have been proposed for the removal of antimony and bismuth from copper electrolyte, e.g., ion exchange and solvent extraction. However, it is difficult for these methods to be applied in production due to various reasons[12−14].

The effects of arsenic with different valence states on the purification of copper electrolyte were studied and a novel technology of electrolyte purification was proposed in this study. This technology has the advantages of simple operation, high purification performance and low costs in comparison with other technologies, and it can be expected to be broadly applied in copper electrorefining.

2 Experimental

2.1 Purification of copper electrolyte

All the purification experiments were carried out by dissolving arsenic compounds in 200 mL copper electrolyte, which was stirred mechanically (200−400 r/min) under 65 ℃. The purified electrolyte was then leached to remove the precipitate. The content of antimony and bismuth in the electrolyte was determined by ICP emission spectroscopy (IRIS Intrepid II XSP, Thermo Elemental Corporation, America) and arsenic by chemical analysis. The solubility of arsenic compound was used to figure their dissolution performance in electrolyte. It was the ratio of arsenic quantity actually increased in electrolyte to added arsenic quantity. The copper electrolyte used in the experiments, which was provided by Daye Nonferrous Metal Ltd. contained the basic components: 4.16 g/L As, 0.65 g/L Sb, 0.15 g/L Bi, 45.16 g/L Cu and 185.48 g/L free H_2SO_4.

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2.2 Principle analysis of purification

The precipitate of purification experiments was washed and dried. The elements of precipitate and their relative contents were determined by Energy Dispersive X-ray detector (Genesis 60 s, American EDAX Company). The valence and quantitative contents of As, Sb and Bi of precipitate were exactly analyzed by chemical analysis. The appearance and size of precipitate were observed by Scan Electron Microscope (JSM-6360LV(JEOL), Japanese Electron Company). The phase of precipitate was detected by X-ray diffraction instrument (D/max-rA, Rigaku Corporation of Japan).

3 Results and discussion

3.1 Impacts of As_2O_5 concentration on purification of copper electrolyte

The impacts of As_2O_5 concentration on its solubility and the concentration of arsenic ion in electrolyte are shown in Fig.1. The impacts of As_2O_5 concentration on the removal rate of Sb and Bi are shown in Fig.2.

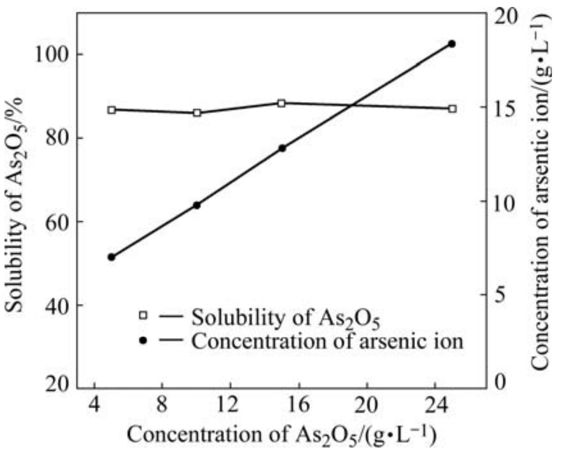

Fig.1 Impacts of As_2O_5 concentration on its solubility and concentration of arsenic ion

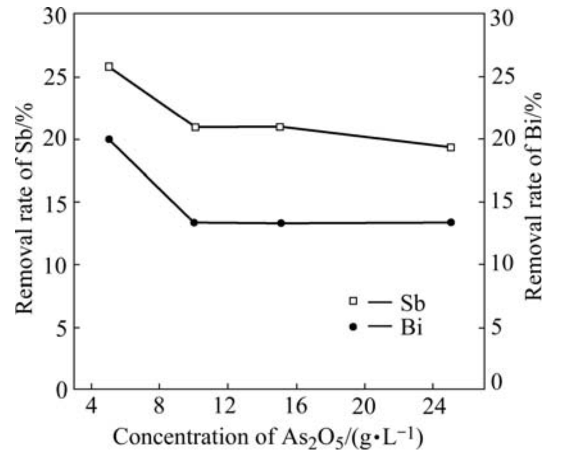

Fig.2 Impacts of As_2O_5 concentration on removal rate of Sb and Bi

It can be seen from Fig.1 that the solubility of As_2O_5 in electrolyte is as high as 86.06%−88.38% approximately, and the concentration of arsenic ion increases with the increase of As_2O_5 concentration. It is obvious from Fig.2 that the removal rate of Sb and Bi decreases with the increase of As_2O_5 concentration up to 10 g/L and remains constant with further increase.

The results above show that As_2O_5 has some effects on purification of copper electrolyte. The concentration of arsenic ion is 6.99 g/L and the removal rate of Sb and Bi gets up to the maximum of 25.81% and 20.0% respectively when As_2O_5 concentration is 5 g/L. Therefore, the appropriate concentration is 5 g/L in electrolyte purification by As_2O_5.

3.2 Impacts of copper arsenate on purification of copper electrolyte

The impacts of copper arsenate ($Cu_5As_4H_2O_{16}\cdot 9H_2O$) concentration on its solubility and the concentration of arsenic ion in electrolyte are shown in Fig.3. The impacts of copper arsenate concentration on removal rate of Sb and Bi are shown in Fig.4.

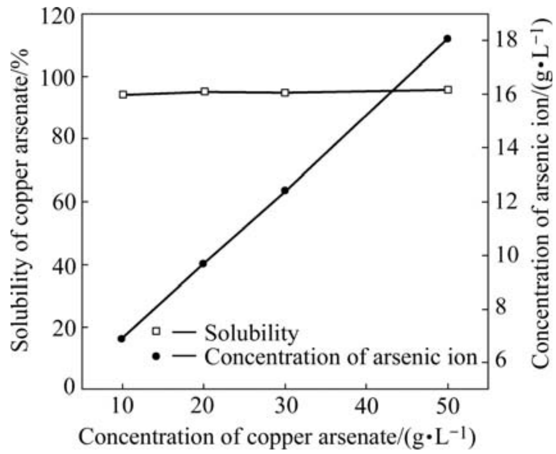

Fig.3 Impacts of copper arsenate concentration on its solubility and concentration of arsenic ion

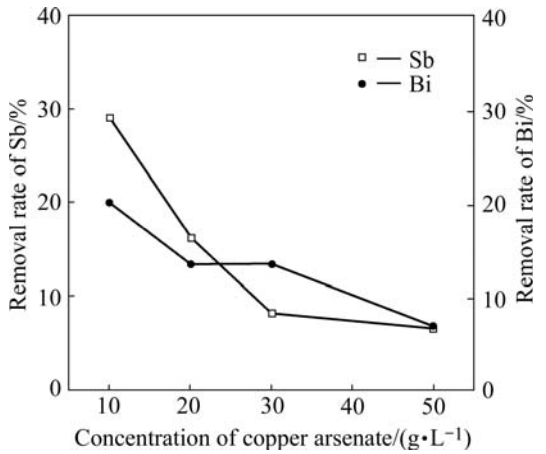

Fig.4 Impacts of copper arsenate concentration on removal rate of Sb and Bi

It can be seen from Fig.3 that the solubility of copper arsenate in electrolyte is 94.14%−95.79% approximately and the arsenic concentration increases with the increase of copper arsenate concentration. It is obvious from Fig.4 that the removal rate of Sb and Bi decreases with the increase of copper arsenate concentration. The concentration of arsenic ion is 6.89 g/L and the removal rate of Sb and Bi gets to the maximum of 29.03% and 20.0% respectively when copper arsenate concentration is 10 g/L. Therefore, the appropriate concentration is 10 g/L in electrolyte purification by copper arsenate.

3.3 Impacts of As_2O_3 on purification of copper electrolyte

The impacts of As_2O_3 concentration on its solubility and the concentration of arsenic ion in electrolyte are shown in Fig.5. The impacts of As_2O_3 concentration on removal rate of Sb and Bi are shown in Fig.6.

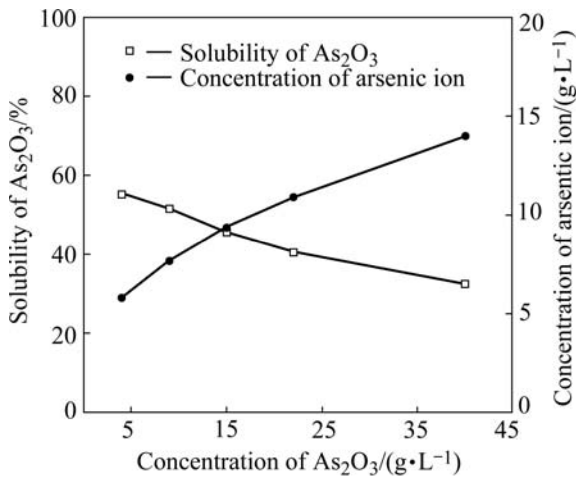

Fig.5 Impacts of As_2O_3 concentration on its solubility and concentration of arsenic ion

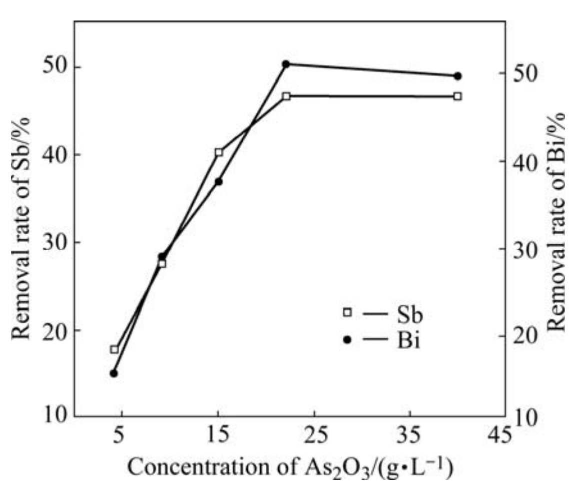

Fig.6 Impacts of As_2O_3 concentration on removal rate of Sb and Bi

It can be seen from Fig.5 that the solubility of As_2O_3 in electrolyte is as low as 32.48%−55.12% and the concentration of arsenic ion increases with the increase of As_2O_3 concentration. It is obvious from Fig.4 that the removal rate of Sb and Bi increases with the increase of As_2O_3 concentration up to 22 g/L and remains constant with further increase.

The results above show that As_2O_3 has obvious effects on purification of copper electrolyte. The removal rate of Sb and Bi gets to the maximum of 41.94% and 45.0% respectively when As_2O_3 concentration is 22 g/L. Therefore, the appropriate concentration is 22 g/L in electrolyte purification by As_2O_3.

3.4 Impacts of copper arsenite on purification of copper electrolyte

The impacts of copper arsenite ($Cu_5As_4H_2O_{12}$) concentration on its solubility and the concentration of arsenic ion are shown in Fig.7. The impacts of copper arsenite concentration on removal rate of Sb and Bi are shown in Fig.8.

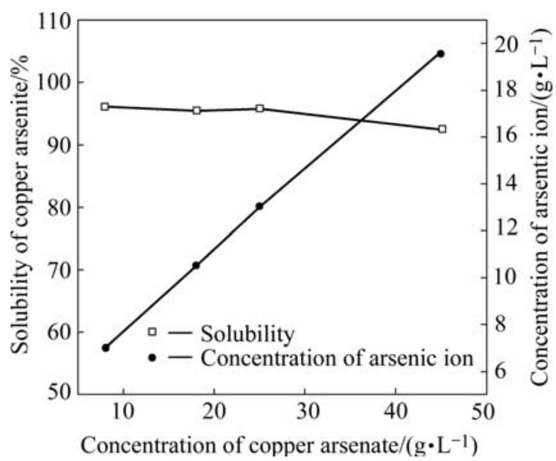

Fig.7 Impacts of copper arsenite concentration on its solubility and concentration of arsenic ion

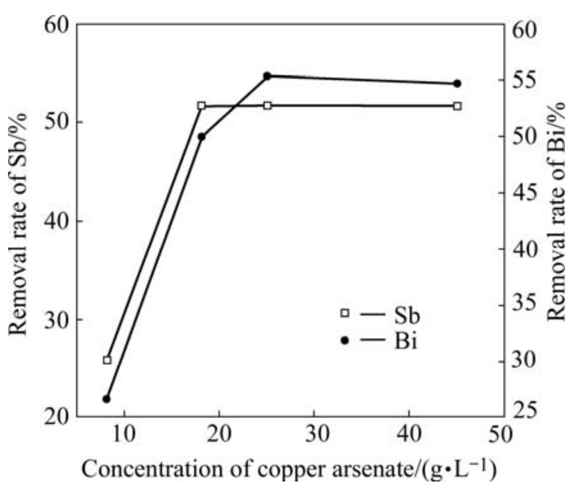

Fig.8 Impacts of copper arsenite concentration on removal rate of Sb and Bi

It can be seen from Fig.7 that the solubility of copper arsenite in electrolyte is as high as 92.55%−96.13% approximately and the concentration of arsenic ion increases with the increase of copper arsenite concentration. It is obvious from Fig.8 that the removal rate of Sb and Bi increases with the increase of copper arsenite concentration up to 18 g/L and remains constant with further increase.

The results above show that copper arsenite has obvious effects on purification of copper electrolyte. The arsenic concentration is 10.51 g/L and the removal rate of Sb and Bi gets up to the maximum of 51.61% and 50.0% respectively when copper arsenite concentration is 18 g/L. Therefore, the appropriate concentration is 18 g/L in electrolyte purification by copper arsenite.

3.5 Difference of purification performance by different arsenic compounds

The purification performance by different arsenic compounds are different according to results above, the results are listed in Table 1.

Table 1 Comparison of purification performance by different arsenic compounds

Arsenic compound	Appropriate concentration/(g·L^{-1})	Solubility/%
As_2O_5	5	86.62
Copper arsenate	10	94.14
As_2O_3	22	40.51
Copper arsenite	18	95.53

Arsenic compound	Concentration of arsenic ion after purification/(g·L^{-1})	Removal rate of Sb/%	Removal rate of Bi/%
As_2O_5	6.99	25.81	20.00
Copper arsenate	6.89	29.03	20.00
As_2O_3	10.91	46.77	55.33
Copper arsenite	10.51	51.61	50.00

It can be seen from Table 1 that the solubility of As_2O_3 in copper electrolyte is far lower than that of other arsenic compounds, and the purification performance of As(Ⅲ) compounds is far better than that of As(Ⅴ) compound. In comparison with other arsenic compounds, the electrolyte purification by copper arsenite has the advantages of high removal rate of impurities and high dissolution performance. Its appropriate purification conditions are that the copper arsenite concentration is 18 g/L, the reaction temperature is 65 ℃ and the reaction time is 8 h.

1 L copper electrolyte was taken and the purification experiment was conducted under above conditions. The results show that concentration of antimony ion in electrolyte decreases from 0.65 g/L to 0.29 g/L and the concentration of bismuth ion from 0.15 g/L to 0.065 g/L. The removal rate of Sb and Bi is as high as 53.22% and 58.67% respectively.

Obviously, the purification technology by copper arsenite has the advantages of simple operation, high purification performance and low cost. It can be expected to be applied in copper electrorefining broadly.

3.6 Principle analysis of purification of copper electrolyte by copper arsenite

A kind of yellow precipitate was found in the electrolyte of purification experiment by copper arsenite. The results of SEM and EDX analysis are shown in Fig.9 and Fig.10, respectively.

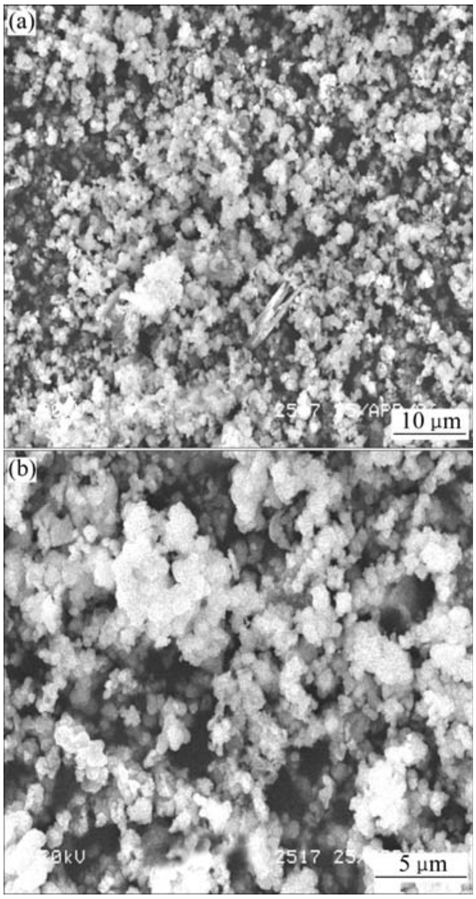

Fig.9 SEM images of yellow precipitate

It can be seen from Fig.9 that this precipitate is floccules, and its size is 1−5 μm. It can be seen from Fig.10 that the precipitate is composed of O, As, Sb, Bi, Cu, Zn and Fe, and the main components are O, As, Sb and Bi. The exact content of As, Sb and Bi of the precipitate is listed in Table 2.

It can be seen from Table 2 that the total content of As, Sb and Bi is 56.94%, the As content is 11.72%, the molar ratio of As(Ⅲ) to As(Ⅴ) is 1.82, the Sb content is 34.95% and the molar ratio of Sb(Ⅲ) to Sb(Ⅴ) is 0.16.

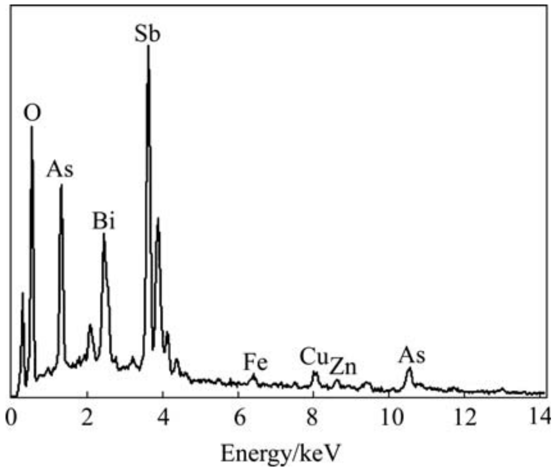

Fig.10 EDX pattern of yellow precipitate

Table 2 Component analysis result of yellow precipitate (mass fraction, %)

As_T	As(III)	As(Ⅴ)	Sb_T	Sb(III)	Sb(Ⅴ)	Bi
11.72	7.56	4.16	34.95	4.83	30.12	10.27

Therefore the precipitate is mainly composed of As, Sb(Ⅴ) and Bi. The XRD pattern (Fig.11) of the precipitate indicates that the structure of the precipitate is amorphous, thus the structure can not be directly gained from XRD information.

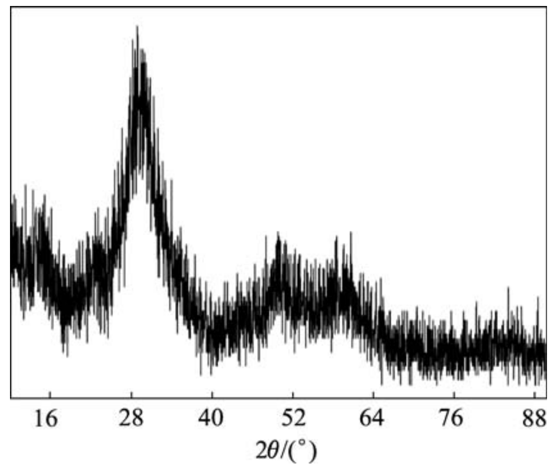

Fig.11 XRD pattern of yellow precipitate

It can be concluded that a kind of yellow floccules mainly composed of As, Sb(V), Bi and O forms in copper electrolyte after arsenic is added, and its granularity is 1−5 μm and its structure is amorphous. It is insoluble in electrolyte, therefore Sb and Bi are removed from electrolyte.

The As exists in the form of As(Ⅴ) mostly in the electrolyte before purification and the following reactions occur after arsenic is added:

$$SbO_4^{3-} + AsO_3^{3-} = SbO_3^{3-} + AsO_4^{3-}$$

$$SbO_3^{3-} + AsO_4^{3-} + 6H^+ = SbAsO_4\downarrow + 3H_2O$$

$$AsO_4^{3-} + Bi^{3+} = BiAsO_4\downarrow$$

$$SbO_4^{3-} + AsO_3^{3-} + 6H^+ = AsSbO_4\downarrow + 3H_2O$$

The arsenate and antimonite that are indissoluble in electrolyte form according to reactions above and therefore the concentration of Sb and Bi in electrolyte greatly is decreased[15]. WANG et al[3,16] reported that As(Ⅴ) and Sb(Ⅴ) can form a series of arsenato antimonic acids. Arsenato antimonic acid (AAAc) can further react with As(III), Sb(III) and Bi(III) to form arsenato antimonates that are indissoluble even in strongly acidic solution.

4 Conclusions

1) As(Ⅴ) compounds have some effects on purification of copper electrolyte. The removal rate of Sb and Bi decreases with the increase of arsenic concentration and gets to the maximum of 25.81%−29.03% and 20% respectively when the arsenic concentration is 5.82−6.99 g/L.

2) As(Ⅲ) compounds have obvious effects on purification of copper electrolyte. The removal rate of Sb and Bi increases with the increase of arsenic concentration up to10.51−11.2 g/L and remains constant with further increase.

3) The purification technology by copper arsenite has the advantages of simple operation, high purification performance and low costs in comparison with other technologies. Its appropriate purification conditions are that the copper arsenite concentration is 18 g/L, the reaction temperature is 65 ℃ and the reaction time is 8 h. The removal rate of Sb and Bi is as high as 53.22% and 58.67% respectively under these conditions.

4) A kind of yellow floccules mainly composed of As, Sb(Ⅴ), Bi and O forms in copper electrolyte after arsenic is added, its granularity is 1−5 μm and its structure is amorphous. It is insoluble in electrolyte and therefore Sb and Bi are removed from electrolyte.

Acknowledgement

The authors are grateful for the support of Daye Nonferrous Metal Ltd.

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(Edited by LI Xiang-qun)