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Solubilities of As, Sb and Bi in Copper Electrolyte and Their Existing Forms in Copper Anode Slime

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Abstract: Since copper electrorefining has been used in industrial production, the purification of copper electrolyte has received much attention, but the solubilities of As, Sb and Bi in copper electrolyte have not been systematically studied. In this paper, the solubilities of As, Sb and Bi in copper electrolyte and their existing forms in copper anode slime were studied. It was found that the solubilities of Sb(III), Bi(III) and Sb(V) all increase first and then decrease sharply with the increase in H_2SO_4 concentration. As(V) can increase the solubilities of Sb(III), Bi(III) and Sb(V) in H_2SO_4 solution as it can combine with them to form complexes, while As(III) can only make the solubility of Sb(III) increase. Though As(V) can make the solubilities of Sb(III), Bi(III) and Sb(V) increase, their solubilities in copper electrolyte don't increase but decrease with the increase in arsenic concentration because they can combine with each other to form the precipitate of arsenato antimonates under normal conditions. The solubility of Sb(III) in copper electrolyte decreases noticeably with the decrease in temperature from 55°C to 33°C, which leads to the obvious increase in copper electrolyte turbidity. Moreover, it was confirmed that the As, Sb and Bi containing in copper anode slime and floating slime are all in the form of amorphous, and they cannot be turned into crystal until the treatment temperature rise to over 500°C.

Keywords: Copper Electrolyte, Arsenic, Antimony, Bismuth, Solubility

1. Introduction

As long as copper electrorefining has been commercially applied, the solubilities of As, Sb and Bi in copper electrolyte and their existing forms in copper anode slime have received much attention [1-4] as they are the most harmful impurities to the quality of cathode copper due to the similarity of their standard reduction potentials to that of Cu [5].

It has been found that in copper electrolyte, the valence of Bi is only +3, while that of As and Sb is +3 and +5 [6]. As(III), As(V), Sb(III), Bi(III) and Sb(V) in copper electrolyte can combine with each other to form complicated compounds [7, 8]. Therefore, there are many compounds in copper anode slime, such as arsenates, antimontates [6] and arsenato antimonates [8]. These compounds are mainly in the form of amorphous [9, 10], especially in the floating slime containing Sb(V) [11-13]. However, recently some authors claim that

they found that impurities As, Sb, and Bi existing in copper anode slime are in the form of crystals, such as $BiSbO_4$, $AsSbO_4$, and Bi_3SbO_7 [14-16]. Moreover, the concentration of Sb(V) is more than 0.4 g/L in the copper electrolytes synthesized by the authors [14-16], which is much higher than that in industrial copper electrolyte. To clear up the differences, it is necessary to study the solubilities of As, Sb and Bi in copper electrolyte and to identify their existing forms in copper anode slime once again.

The motivation of this study is the need to get insight into the varied regularity of the solubilities of As, Sb and Bi in copper electrolyte and their existing forms in copper anode slime. The solubilities of As, Sb and Bi in H_2SO_4 solution, the effect of As(III) and As(V) on the solubilities of Sb(III), Sb(V) and Bi(III) in copper electrolyte, and the thermochemical behavior of impurities As, Sb and Bi in copper anode slime were all investigated in the present work.

2. Experimental

To study the solubilities of As, Sb and Bi in copper electrolyte, synthetic and industrial copper electrolytes were used, and their compositions are listed in Table 1. The industrial electrolyte was taken from Guixi Smelter. H_2SO_4, $CuSO_4 \cdot 5H_2O$, As_2O_3, $Sb_2O_3 \cdot xH_2O$, $Sb_2O_5 \cdot xH_2O$, $Bi_2O_3 \cdot xH_2O$, H_2O_2 and CuO were used in the experiments, which are all analytical grade. In order to determine the thermochemical behavior of impurities As, Sb, Bi in copper anode slime, industrial copper anode slime and floating slime were used. They were supplied by Daye Smelter. Their compositions are listed in Table 1 as well.

Table 1. Compositions of copper electrolytes, copper anode slime and floating slime.

Sample	Pb	Ag	Se	Sb	Sb(III)	As	As(III)	Bi	Cu	H_2SO_4
Industrial electrolyte, g/L	---	---	---	0.48	0.46	13.99	1.15	0.48	45.26	178.90
Synthetic electrolyte, g/L	---	---	---	0.69	0.66	13.95	3.53	0.46	30.64	182.61
Copper anode slime, %	6.66	15.88	9.19	5.55	4.68	3.58	0.23	3.28	26.41	---
Floating slime, %	3.21	0.63	0.33	34.83	4.91	14.16	3.45	5.50	0.90	---

The solutions of Sb(III), Sb(V) and Bi(III) were prepared by dissolving $Sb_2O_3 \cdot xH_2O$, $Sb_2O_5 \cdot xH_2O$ and $Bi_2O_3 \cdot xH_2O$ in sulfuric acid solution respectively under stirring. The solution of As(III) was prepared by dissolving As_2O_3 in water by heating and stirring. The solution of As(V) was obtained by oxidizing As_2O_3 in water with H_2O_2. Then the excess H_2O_2 in the oxidized solution was decomposed by adding trace CuO powder.

The electrolytes used in the study contained the basic components: 34-36 g/L Cu, 180-185 g/L free H_2SO_4, and the impurities As, Sb and Bi. They were synthesized respectively at about 80°C, and then placed in a beaker with cover for ageing in a water bath at 65°C and 20°C.

The composition of experimental samples was determined by chemical methods and inductively coupled plasma emission spectroscopy (ICP) with a PS-6 PLASMA SPECTROVAC, BAIRD (USA). The valence of the elements was determined by standard chemical methods [17] and X-ray photoelectron spectrum (XPS) technique. The XPS measurement was carried out with a K-Alpha 1063 Electron Spectrometer where non-monochromatic Al Kα X-ray radiation (1486.6 eV) was used. The X-ray diffraction (XRD) patterns were recorded on a Rigaku Miniflex diffractometer with Cu Kα X–ray radiation at 35 kV and 20 mA. The turbidity was determined by a DRT-15CE turbidimeter (HF scientific, inc.).

3. Results and Discussion

3.1. Solubilities of As, Sb and Bi in H_2SO_4 Solution

During electrorefining, the basic component of copper electrolyte is 40-45 g/L Cu and 160-220 g/L free H_2SO_4. It seems that the solubilities of As, Sb and Bi in copper electrolyte is only related to the acidity of 160-220 g/L H_2SO_4, but that's not exactly the case. Water is added into copper electrolyte cycling system to make up its volume every day, local acidity decrease is inevitable [18]. By contrast, local acidity will be increased when concentrated H_2SO_4 is added into the cycling system to maintain the balance of Cu^{2+} and H^+ in the electrolyte. Therefore, it is necessary to have a complete understanding of their solubilities in H_2SO_4 solution.
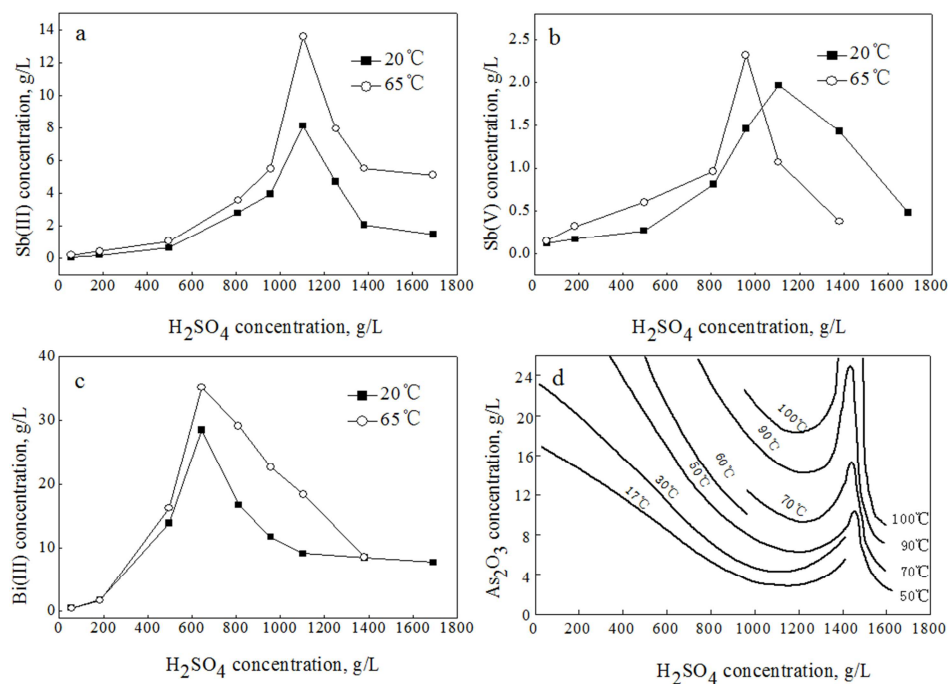

Figure 1. Solubilities of As(III), Sb(III), Sb(V) and Bi(III) in sulfuric acid solution at different temperature.

The solubilities of As(III), Sb(III), Bi(III) and Sb(V) in H_2SO_4 solution are shown in Figure 1. In addition to As(III) solution, the others were synthesized by adding $Sb_2O_3 \cdot xH_2O$, $Sb_2O_5 \cdot xH_2O$ and $Bi_2O_3 \cdot xH_2O$ respectively into different concentration H_2SO_4 solution and dissolving to saturation under stirring at about 80°C, and then ageing in a water bath for 48 h at 65°C and 20°C respectively. Filtration was performed before their solubilities were determined. As can be seen, the solubilities shown in Figure 1a, Figure 1b and Figure 1c all increase first and then decrease sharply with the increase in H_2SO_4 concentration. The decrease in the solubilities of Sb(III) and Bi(III) is due to their anhydrous sulfates formed in concentrated H_2SO_4 solution, while the decrease in that of Sb(V) is caused by the formation of $Sb_2O_5 \cdot xH_2O$ [19]:

$$2HSb(OH)_6 = Sb_2O_5 \cdot xH_2O\downarrow + (7\text{-}x)H_2O \qquad (1)$$
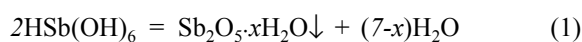
The solubility of As(III) shown in Figure 1d, was obtained by other authors [20, 21]. The existing form of As(III) turns from $HAsO_2$ into AsO^+ and As^{3+} with the increase in H_2SO_4 concentration [21]. The solubility of $HAsO_2$ decreases with the increase in H_2SO_4 concentration [22], and the anhydrous sulfate of As(III) can be formed in concentrated H_2SO_4 solution [21]. Therefore, with the increase in H_2SO_4 concentration, the solubility of As(III) is decrease first, then increase, at last decrease sharply.

Figure 1a shows that the solubility of Sb(III) is 0.40-0.43 g/L in 160-220 g/L H_2SO_4 at 65°C. In copper electrolyte, more than 90% antimony exists in the form of Sb(III), and the concentration of Sb can be ≥ 0.5 g/L sometimes [7]. This indicates that the solubility of antimony in copper electrolyte is more complex than expected.

Figure 1b shows that the maximum of Sb(V) solubility in H_2SO_4 solution are 2.3 g/L and 1.97 g/L respectively at 65°C and 20°C, and they appears respectively in 955 g/L H_2SO_4 and 1105 g/L H_2SO_4. The solubility of Sb(V) is < 0.34 g/L in 160-220 g/L H_2SO_4 solution. In theory, the copper electrolytes containing Sb(V) ≥ 0.4 g/L cannot be synthesized with the H_2SO_4 solution containing Sb(V) [14-16]. Though the solubility of Sb(V) in H_2SO_4 solution can be sharply increased by adding Cl^- as it can combine with Sb(V) to form complex ions [23, 24], the concentration of Cl^- in industrial copper electrolyte is strictly controlled in the range of 0.05-0.06 g/L. Arbitrary increase in the concentration of Cl^-, will lead to the loss of silver in the cathode, and the increase in power consumption caused by concentration polarization.

Figure 1c shows that the solubility of Bi(III) is > 1.5 g/L in 160-220 g/L H_2SO_4 at 65°C, while the concentration of bismuth is < 1.0 g/L (usually < 0.5 g/L) in industrial copper electrolyte [7]. This indicates that during copper electrorefining, bismuth is difficult to reach saturation in the electrolyte.

Usually the concentration of As is < 20 g/L in copper electrolyte, and the As(III) accounts for about 5% of the total arsenic under normal conditions [2]. Figure 1d shows that the solubility of As_2O_3 is > 50 g/L in 160-220 g/L H_2SO_4 at 65°C. This indicates that arsenic cannot reach saturation in copper electrolyte because the solubility of As(V) is much higher than that of As(III) [25]. The concentration of As is much higher than that of Sb and Bi in copper electrolyte because not only the content of As in the anode is higher than that of Sb and Bi, but also the solubility of As(III) and As(V) in copper electrolyte is much higher than that of Sb(III), Sb(V) and Bi(III).
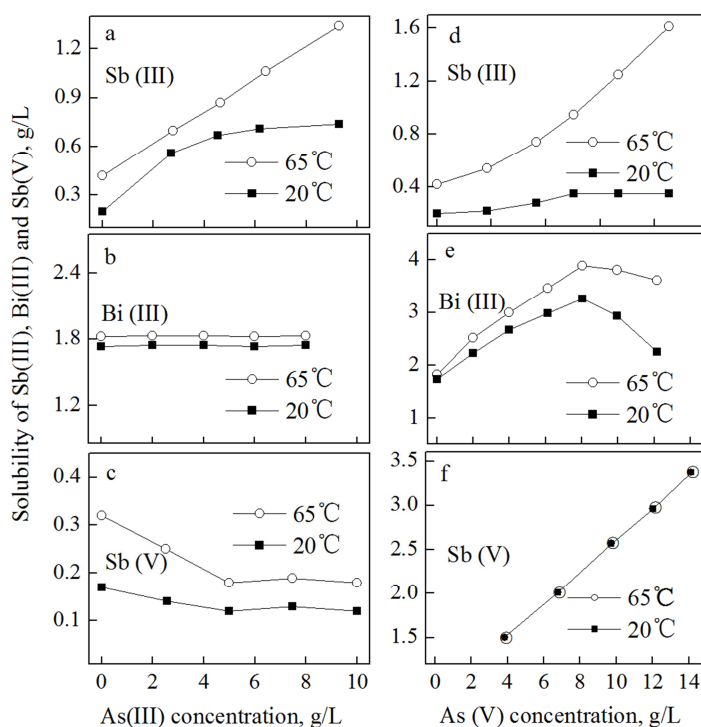

Figure 2. Effect of As(III) and As(V) on the solubility of Sb(III), Bi(III) and Sb(V) in copper electrolyte.

3.2. Solubilities of Sb and Bi in Copper Electrolyte

3.2.1. Effect of As(III) and As(V)

Figure 2 is the experimental results of the effect of As(III) and As(V) on the solubilities of Sb(III), Bi(III) and Sb(V) in copper electrolyte, which were obtained by adding $Sb_2O_3 \cdot xH_2O$, $Sb_2O_5 \cdot xH_2O$ and $Bi_2O_3 \cdot xH_2O$ respectively into the copper electrolyte containing As(III) or/and As(V) and dissolving to saturation under stirring at about 80°C, and then ageing in a water bath for 48 h at 65°C and 20°C respectively. Filtration was performed before their solubilities were determined. As seen from Figure 2a, the solubility of Sb(III) increases with the increase in As(III) concentration in the copper electrolyte without As(V), Bi(III) and Sb(V). Comparing Figure 2a with Figure 1a, it can be found that As(III) can make the solubility of Sb(III) increase. This indicates that As(III), like As(V), may also be combined with Sb(III) to form complexes [7].

Figure 2b shows that As(III) has no effect on the solubility of Bi(III) in the copper electrolyte without As(V), Sb(III) and Sb(V). Moreover, Sb(III) also has no effect on the solubility of Bi(III) in the copper electrolyte containing As(III) without As(V) and Sb(V). Moreover, the precipitate of $BiSbO_4$ has
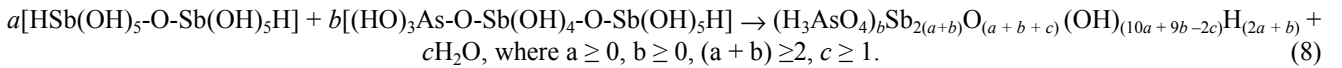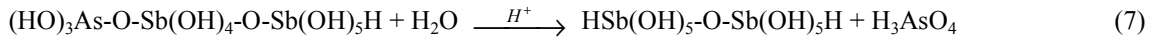
not be obtained in the copper electrolyte containing 1.53 g/L Bi(III) and 0.31 g/L Sb(V) at 65°C.

Figure 2c shows that when As(III) is added into the copper electrolyte containing Sb(V) without As(V), Sb(III) and Bi(III), the solubility of Sb(V) decreases with the increase in As(III) concentration. It was found that if $Sb_2O_5 \cdot xH_2O$ is added into the copper electrolyte containing As(III) without As(V), Sb(III) and Bi(III), not only the concentration of Sb increases with the increase in As(III) concentration, but also the electrolyte clarification becomes very difficult. They are all caused by the oxidation of As(III) by Sb(V), but the results are different. Once As(III) was oxidized, As(V) and Sb(III) were formed, which leads to the formation of arsenato antimonates in the former. However, in addition to arsenato antimonates, floating slime was formed in the latter. Adding $Sb_2O_5 \cdot xH_2O$ into the electrolyte, it is inevitable to increase the local concentration of Sb(V), and the Sb(V) will combine with As(V) to form the arsenato antimonic acid of AAAc(1:1), which has the structure of $(HO)_3As-O-Sb(OH)_4-O-Sb(OH)_4-O-As(OH)_3$. When AAAc(1:1) hydrolyzed in the electrolyte, floating slime formed. The formation of arsenato antimonates and floating slime can be expressed by the following equations [8, 26]:

$$HSb(OH)_6 + HAsO_2 + H^+ \rightleftarrows SbO^+ + H_3AsO_4 + 3H_2O \qquad (2)$$

$$a H_3AsO_4 + b H[Sb(OH)_6] + c MeO^+ \rightarrow Me_c As_a Sb_b O_{(3a+5b+c/2+1)} H_{(a+5b-2c+2)} \bullet x H_2O\downarrow + c H^+ + (a+b+c/2-1-x) H_2O, \text{ where Me}$$
$$= \text{As(III), Bi(III) and Sb(III); } a \geq 1, b \geq 1, c \leq (3a+b). \quad (3)$$

$$H_3AsO_4 + HSb(OH)_5 = H[H_2AsO_3\text{-}O\text{-}Sb(OH)_5] + H_2O \qquad (4)$$

$$2H[H_2AsO_3\text{-}O\text{-}Sb(OH)_5] = (HO)_3As\text{-}O\text{-}Sb(OH)_4\text{-}O\text{-}Sb(OH)_4\text{-}O\text{-}As(OH)_3 + H_2O \qquad (5)$$

$$AAAc(1:1) + H_2O \xrightarrow{H^+} (HO)_3As\text{-}O\text{-}Sb(OH)_4\text{-}O\text{-}Sb(OH)_5H + H_3AsO_4 \qquad (6)$$

$$(HO)_3As\text{-}O\text{-}Sb(OH)_4\text{-}O\text{-}Sb(OH)_5H + H_2O \xrightarrow{H^+} HSb(OH)_5\text{-}O\text{-}Sb(OH)_5H + H_3AsO_4 \qquad (7)$$

$$a[HSb(OH)_5\text{-}O\text{-}Sb(OH)_5H] + b[(HO)_3As\text{-}O\text{-}Sb(OH)_4\text{-}O\text{-}Sb(OH)_5H] \rightarrow (H_3AsO_4)_b Sb_{2(a+b)} O_{(a+b+c)} (OH)_{(10a+9b-2c)} H_{(2a+b)} +$$
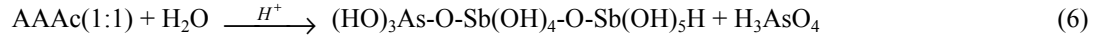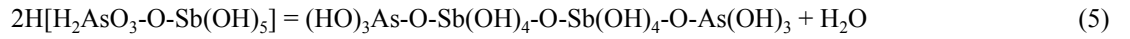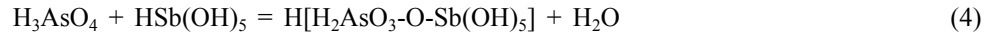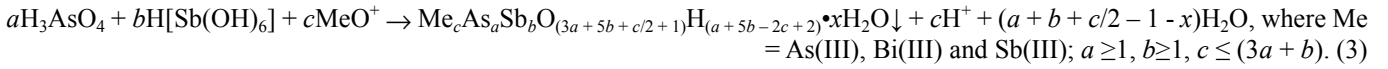$$c H_2O, \text{ where } a \geq 0, b \geq 0, (a+b) \geq 2, c \geq 1. \qquad (8)$$

Figure 2d is the solubility of Sb(III) in the copper electrolytes containing As(V) without Sb(V) and Bi(III). To avoid the oxidization of Sb(III) by As(V) [13], As(III) was added into the electrolyte to adjust the mole ratio of As(III)/As(V) to 0.3 before $Sb_2O_3 \cdot xH_2O$ dissolved. As seen, the solubility of Sb(III) increases with the increase in As(V) concentration at 65°C, while the effect of As(V) on the solubility of Sb(III) is not obvious at 20°C. This is due to that As(V) can combine with Sb(III) to form complexes in the copper electrolyte at 65°C [7].

Figure 2e shows that the solubility of Bi(III) increases from 1.82 g/L to 3.89 g/L with the increase in As(V) concentration from 0.00 g/L to 8.05 g/L in the copper electrolytes without Sb(III) and Sb(V) at 65°C, and then it decreases slightly with the increase in As(V) concentration from 8.05 g/L to 12.14 g/L. The solubility of Bi(III) in the electrolyte containing As(V) 12 g/L is over 2 g/L even at

room temperature. This is due to that As(V) can combine with Bi(III) to form complexes [27]. Recently, it was found that under normal conditions, the precipitate of $BiAsO_4$ cannot be formed in copper electrolyte unless the local acidity is decreased [27].

Figure 2f shows that the solubility of Sb(V) increases with the increase in As(V) concentration in the copper electrolyte without As(III), Sb(III) and Bi(III). This is due to that Sb(V) can combine with As(V) to form AAAc(1:1) [26]. However, it was found that once the copper electrolyte containing AAAc(1:1) is mixed with the copper electrolyte containing As(III) and Sb(III) or As(III) and Bi(III), the precipitate of arsenato antimonates will be formed immediately, and the concentrations of As, Sb and Bi will be decreased sharply. Therefore, though Sb(V) can combine with As(V) to form AAAc(1:1), only when the copper electrolyte is over oxidized, and there are no As(III) and Sb(III) in it, can Sb(V)

exist in the form of AAAc(1:1) [13]. In the opposite case, when the copper electrolyte is over reduced, the concentrations of Sb and Bi will increase gradually [28]. Therefore, under normal conditions, the concentrations of Sb and Bi in copper electrolyte are not increase but decrease with the increase in the concentration of As because of the formation of arsenato antimonates [8].

Figure 2f and Figure 2c indicate that the concentration of Sb(V) cannot be > 0.34 g/L in the copper electrolyte without As(V) because there is no As(V) in the copper electrolyte, AAAc(1:1) cannot be formed. However, recently some authors claim that they synthesized the copper electrolytes containing Sb(V) ≥ 0.4 g/L without As(V) [14, 15]. How to make the concentration of Sb(V) ≥ 0.4 g/L in the copper electrolytes without As(V), only the authors know.
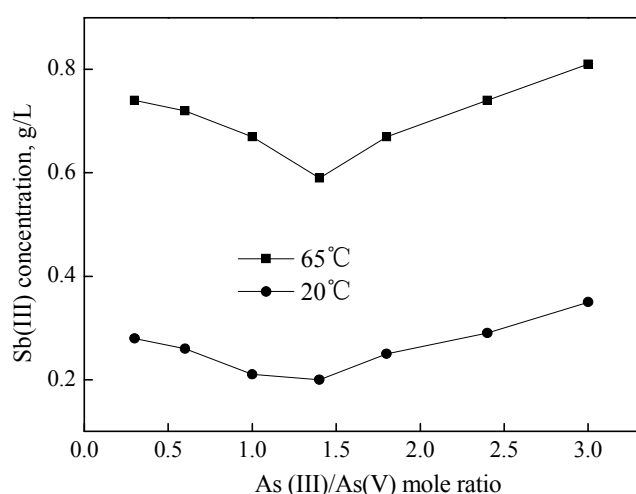

Figure 3. *Effect of As(III)/As(V) mole ratio on the solubility of Sb(III) in copper electrolyte.*

During copper electrorefining, there are As(III) and As(V) in the electrolyte. From Figure 2a and Figure 2d it can be found that As(III) and As(V) can both affect the solubility of Sb(III) in copper electrolyte. Therefore, it is necessary to study the synergistic effect of As(III) and As(V) on the solubility of Sb(III) in copper electrolyte. Figure 3 is the experiment results of the effect of As(III)/As(V) mole ratio on the solubility of Sb(III) in the copper electrolyte without Bi(III) and Sb(V), which was obtaining by dissolving $Sb_2O_3 \cdot xH_2O$ in the copper electrolytes containing 5.50 g/L As(V) with different As(III)/As(V) mole ratio to saturation under stirring at about 80°C, and then ageing in a water bath for 48 h at 65°C and 20°C respectively. Filtration was performed before the concentration of Sb(III) was determined. As can be seen, the solubility of Sb(III) decreases with the increase in As(III)/As(V) mole ratio from 0.3 to 1.4, and then it increases with the increase in As(III)/As(V) mole ratio from 1.4 to 3.0. This indicates that not only As(III) and As(V) can combine with Sb(III) to form complexes, but also As(III) and As(V) can combine with each other, and the binding ability of As(III) with As(V) is stronger than that of As(III) with Sb(III) or As(V) with Sb(III). When As(III)/As(V) mole ratio is 0.3, Sb(III) mainly combines with As(V) to form the complexes as

shown in Figure 2d. The Sb(III) in the complexes is replaced continually by As(III) with the increase in As(III)/As(V) mole ratio from 0.3 to 1.4, which results in the decrease in Sb(III) solubility. Then with the increase in As(III)/As(V) mole ratio from 1.4 to 3.0, Sb(III) combines with As(III) to form the complexes as shown in Figure 2a, so the solubility of Sb(III) increases again.

3.2.2. Effect of Temperature

Figure 4 is the experiment results of the effect of temperature on the turbidity in the industrial copper electrolyte listed in Table 1. As can be seen, the turbidity increases with the decrease in the temperature from 55°C to 33°C. Figure 4 shows that the formation of the precipitate starts at 55°C and ends at 33°C. For copper electrorefining workers, it is well known that once temperature is decreased to below 55°C, white precipitate will appear in the copper electrolyte, and the precipitate can be disappeared when the electrolyte is heated to about 60°C under stirring. It was found that not only synthetic and industrial copper electrolytes but also the sulfuric acid solution containing Sb(III) have the same turbidity change regularity. This indicates that the change of turbidity in copper electrolyte is caused by the variation of Sb(III) solubility with temperature.
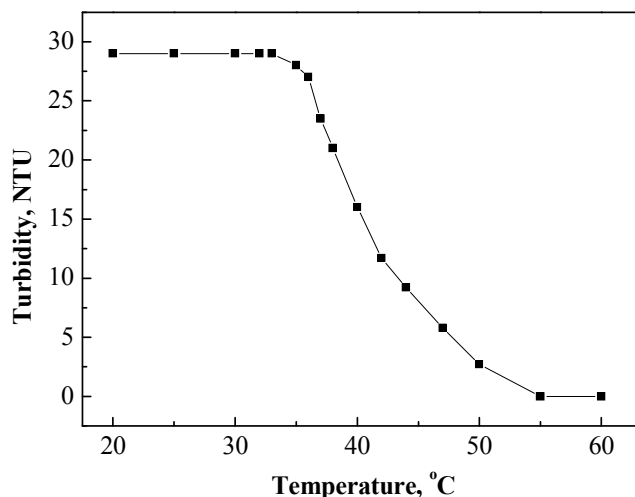

Figure 4. *Variation of turbidity in copper electrolyte during cooling.*

3.3. Existing form of As, Sb and Bi in Copper Anode Slime

Figure 5 is the XRD patterns of copper anode slime and floating slime at different temperature. As can be seen, the As, Sb and Bi containing in the anode slime and floating slime are all in the form of amorphous. The crystals of $BiSbO_4$, $AsSbO_4$, and Bi_3SbO_7 cannot be formed until the anode slime and floating slime were heated to over 500°C. This indicates that the samples used by the authors are heat treated samples because there are crystals $BiSbO_4$, $AsSbO_4$, and Bi_3SbO_7 in them [14-16]. These crystals formed in the heat treated samples have nothing to do with the purification of copper electrolyte. Another evidence of heat treated is that there is $BiSb_2O_7$ in the samples [14, 15], because the compounds of

Bi(V) can only form under alkaline conditions or at high temperature, and Bi(V) is a super strong oxidant in acid solution [19]. $BiSb_2O_7$ cannot be formed in copper electrolyte. Table 2 is the measurement results of XPS for bismuth in the copper anode slime and floating slime, which shows that the bismuth existing in the anode slime and floating slime is not Bi(V) but Bi(III) [29, 30].
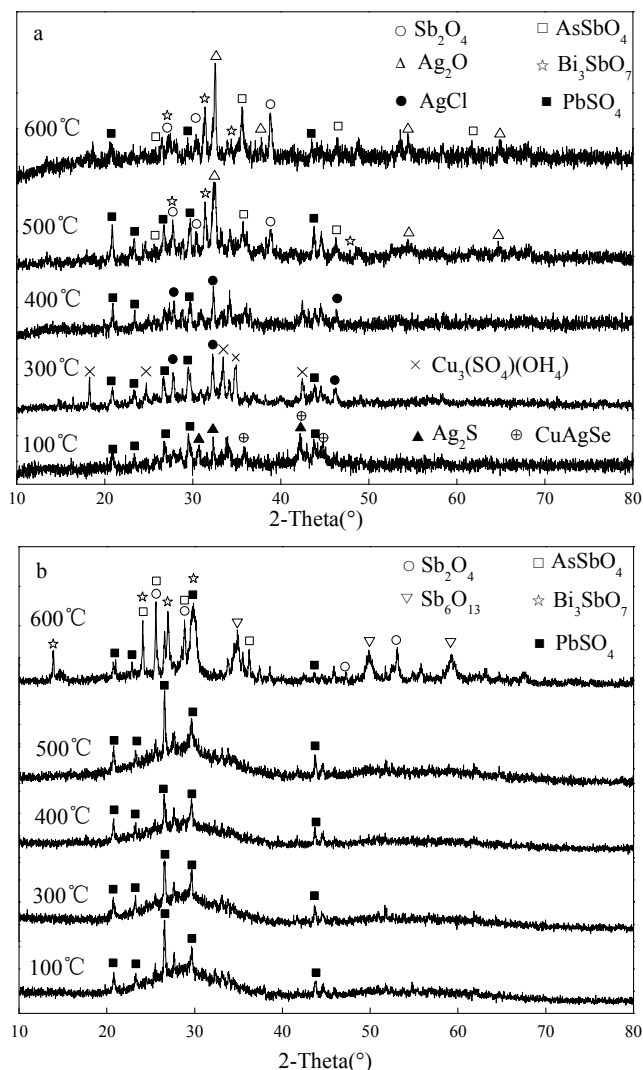

Figure 5. XRD patterns of copper anode slime and floating slime treated at different temperature: (a) copper anode slime; (b) floating slime.

Table 2. Binding energies of Bi4f7 and Bi4f5 peaks in XPS spectra, eV.

	Bi4f7	Bi4f5
Copper anode slime	159.7	164.8
Floating slime	160.1	165.0

4. Conclusions

The solubilities of Sb(III), Bi(III) and Sb(V) in H_2SO_4 solution all increase first and then decrease sharply with the increase in H_2SO_4 concentration. This is due to that in concentrated H_2SO_4 solution, anhydrous sulfates of Sb(III) and Bi(III) can be formed, and Sb(V) can condensed to form $Sb_2O_5 \cdot xH_2O$. It was found that As(V) can combine with

As(III), Sb(III), Bi(III) and Sb(V) respectively to form complexes. In H_2SO_4 solution, their solubilities all increase with the increase in As(V) concentration. But their solubilities in copper electrolyte doesn't increase but decrease with the increase in As(V) concentration because of the formation of arsenato antimonates under normal conditions. Arsenato antimonates are in the form of amorphous. The impurities As, Sb and Bi existing in copper anode slime and floating slime are all in the form of amorphous, and they cannot be turned into crystal until the treatment temperature rise to over 500°C. Moreover, the solubility of Sb(III) decreases significantly with the decrease in temperature from 55°C to 33°C, which results in the obvious increase in copper electrolyte turbidity.

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