

Separation and recovery of Cu and As during purification of copper electrolyte

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Abstract: Cu, As, Sb and Bi in copper electrolyte could be efficiently removed by reducing with SO_2 followed by evaporative crystallization. As_2O_3 and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were obtained after crystallized product was treated by dissolution, oxidation, neutralization, sedimentation, filtration and evaporative crystallization. The removal rates of Cu, As, Sb and Bi are 87.1%, 83.9%, 21.0% and 84.7%, respectively, when As (V) in copper electrolyte is fully reduced to As (III) by SO_2 , and the H_2SO_4 in concentrated copper electrolyte is 645 g/L. The removal rate of As is 92.81% when 65 g crystallized product is dissolved in 200 mL water at 30 °C. The $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ content is 98.8% when the filtrate is purified under the conditions that $n(\text{Fe}):n(\text{As})$ is 1.2, the dosage of H_2O_2 is 19 times the stoichiometric needed, temperature is 45 °C, time is 40 min, pH is 3.7, and then is evaporation crystallized.

Key words: copper electrolyte; sulfur dioxide; purification; copper sulfate; arsenic trioxide

1 Introduction

Removal of As, Sb and Bi impurities from copper electrolytes is a primary target in copper electrorefineries. The conventional process to control these impurities involves multistage electrolytic deposition cells. This process has a number of disadvantages, such as low current efficiency, high power consumption, possibility of forming toxic arsine gas in the final stage of the process and loss of high value copper in a low value recycle product [1–3]. Many methods have been proposed for the purification of copper electrolyte, such as solvent extraction [4], absorption [1,3], chemical precipitation [5] and ion exchange [6]. However, they can only be used as the auxiliary process for the purification of copper electrolyte due to various reasons. The chemical reduction method has been proposed in order to overcome these disadvantages [7].

In this work, copper electrolyte was purified by SO_2 reduction method. Firstly, As(V) was reduced to As(III) in copper electrolyte by SO_2 . Then the reduced copper electrolyte was subjected to evaporative crystallization to remove Cu, As, Sb and Bi in copper electrolyte and to obtain crystallized product containing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and As_2O_3 . Copper sulfate has many applications, such as the

control of fungal diseases and copper electrolysis. The impure copper sulfate should be purified to meet the demand of industry. The As content in the crystallized product is up to 4.42%. The As_2O_3 was recovered by dissolving crystallized product in water, followed by filtration, whereas $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was almost completely soluble in the water. Since there is still much As in the resulting filtrate, which was purified by H_2O_2 oxidization, neutralization, sedimentation and filtration, then $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was recovered via evaporative crystallization.

2 Experimental

2.1 Purification of copper electrolyte

300 mL copper electrolyte whose composition is shown in Table 1 was put in a 500 mL flask. The copper electrolyte was reduced with SO_2 for 2 h at a stirring rate of 300 r/min at 65 °C. The reduced electrolyte was then subjected to evaporative crystallization. The copper electrolyte was purified and the crystallized product

Table 1 Compositions of copper electrolyte (g/L)

Cu	As(T)	As(V)	Sb	Bi	H_2SO_4
32	6.0	5.7	0.75	0.42	203

containing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and As_2O_3 was obtained after filtering.

2.2 Separation and recovery of As in crystallized product

65 g crystallized product was dissolved in 200 mL water for 20 min at an agitation rate of 200 r/min at different temperatures. The As_2O_3 residue and copper sulfate solution were obtained respectively after filtering.

2.3 Recovery of copper sulfate

200 mL copper sulfate solution was placed in a 500 mL beaker, then H_2O_2 (30%) and $\text{Fe}_2(\text{SO}_4)_3$ solution were added. After 40 min of stirring, the pH of the solution was adjusted to 3.7 with Na_2CO_3 solution (10%) and the solution was further stirred for 1 h. Thereafter, impurities were filtered and removed. Then the purified copper sulfate solution was subjected to evaporative concentration. After the solution was cooled to room temperature, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was separated by filtration. The crystals were dried at 60 °C and analyzed for impurities via a re-dissolution method.

2.4 Technique flow sheet

The flow sheet of the separation and recovery of Cu and As during purification of copper electrolyte according to the above experiment steps is shown in Fig. 1.

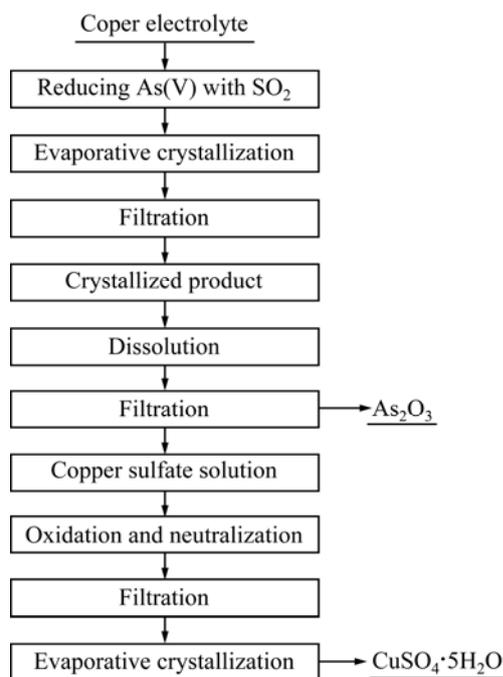


Fig. 1 Flow sheet of separation and recovery of Cu and As during purification of copper electrolyte

2.5 Analysis and detection

The mass concentrations of the impurities present in the solution were determined by an inductively coupled

plasma optical emission spectrometer (ICP-OES, Intrepid II XSP). The contents of products were determined by a X-ray fluorescence spectrometer (XRF, S4 pioneer). The phases of products were analyzed by a X-ray diffractometer (XRD, D/max-rA, Rigaku corporation, Japan).

3 Results and discussion

3.1 Purification of copper electrolyte

3.1.1 Effect of SO_2 flow rate on reduction rate of As(V)

The effect of SO_2 flow rate on reduction rate of As(V) is shown in Fig. 2 when the reaction time is 2 h and reaction temperature is 65 °C.

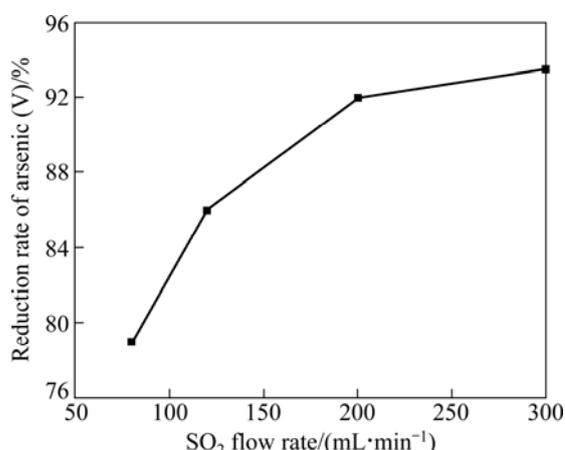


Fig. 2 Effect of SO_2 flow rate on reduction rate of As (V)

It can be seen from Fig. 2 that the increase in the reduction rate of As(V) was rapid up to a SO_2 flow rate of 200 mL/min, beyond which the rate of increase was comparatively slow.

Figures 3 and 4 show the predominance diagrams for the SO_2 , As(V) and As(III) species at 25 °C.

The H_2SO_4 concentration in the copper electrolyte is 203 g/L, which means that the pH is about -0.32. It can be seen from Fig. 3 and Fig. 4 that H_2SO_3 , H_3AsO_4 ,

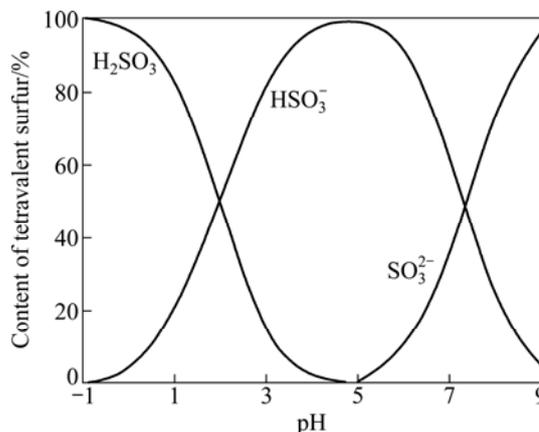


Fig. 3 Distribution of S(IV) as function of pH

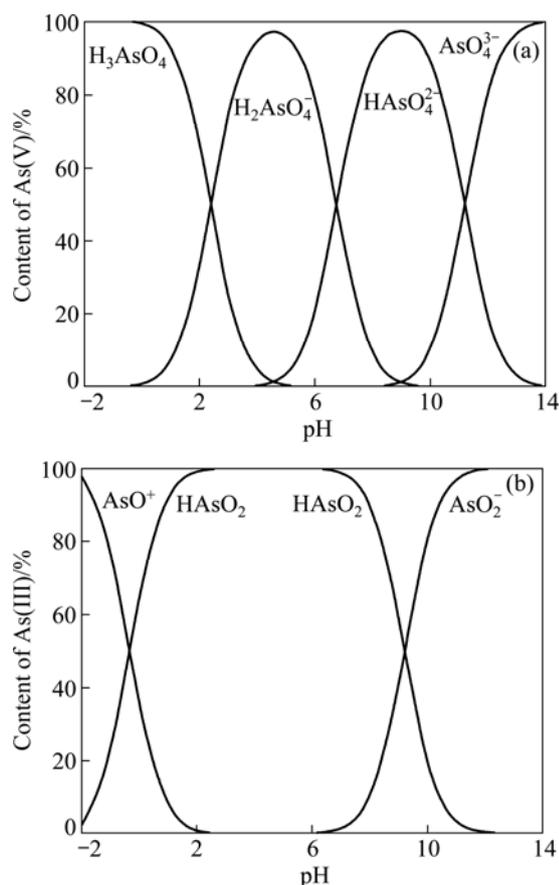
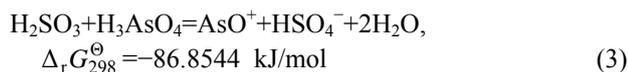
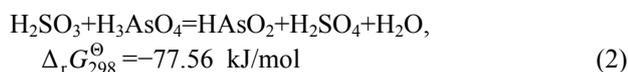


Fig. 4 Distribution of arsenic as function of pH: (a) Distribution of As(V) as function of pH; (b) Distribution of As(III) as function of pH

AsO^+ and HAsO_2 are the predominant species in the copper electrolyte. The species in the copper electrolyte at 65 °C are almost the same as those at 25 °C.

The reduction of H_3AsO_4 by SO_2 consists of two steps, the dissolution of SO_2 and the reduction reaction between H_3AsO_4 and SO_2 , the reactions are shown as follows [8–11]:



As the standard Gibbs free energies for reactions (2) and (3) are both large and negative, and the equilibrium constants are large, hence the reactions have tremendous thermodynamic impetus and can go completion. But the homogeneous reactions between H_3AsO_4 and H_2SO_3 are rate limited as the solution of SO_2 is sufficiently rapid to maintain a constant concentration of SO_2 in solution to provide the gas flow rate reasonably high [10], and surplus SO_2 will escape from the copper electrolyte.

Therefore, the appropriate SO_2 flow rate is 200 mL/min.

3.1.2 Purification of copper electrolyte

500 mL reduced copper electrolyte was concentrated till H_2SO_4 concentration reached 645 g/L, then the concentrated copper electrolyte was cooled to 10 °C and crystallized product was obtained after filtering. The compositions of copper electrolyte after reducing and crystallizing are listed in Table 2. The XRD patterns of the crystallized product are shown in Fig. 5. The components of crystallized product which was dried under 105 °C are listed in Table 3.

Table 2 Compositions of copper electrolyte after reducing and crystallizing (g/L)

Cu	As(T)	As(III)	Sb	Bi
4.122	0.966	0.773	0.592	0.064

Table 3 Components of crystallized product (mass fraction, %)

Cu	As	Sb	Bi	Ni	S	O
32.66	4.42	0.15	0.22	1.51	18.35	41.00
Fe	Zn	Pb	Co	Ca	Others	
0.22	0.17	0.004	0.007	0.283	1.036	

It can be calculated from Table 1 and Table 2 that the removal rates of Cu, As, Sb and Bi in copper electrolyte are as high as 87.1%, 83.9%, 21.0% and 84.7%, respectively.

Figure 5 shows that the crystallized product consists of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and As_2O_3 . It can be seen from Table 3 that the contents of Cu and As in the crystallized product are 32.66 % and 4.42 %, respectively. The content of Cu in the crystallized product is greater than 25.47%, which illuminates that $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was dehydrated during drying. The impurities in copper sulfate, especially As, compared with common copper sulfate product, are high, so the crystallized product must be purified to meet the demand of industry.

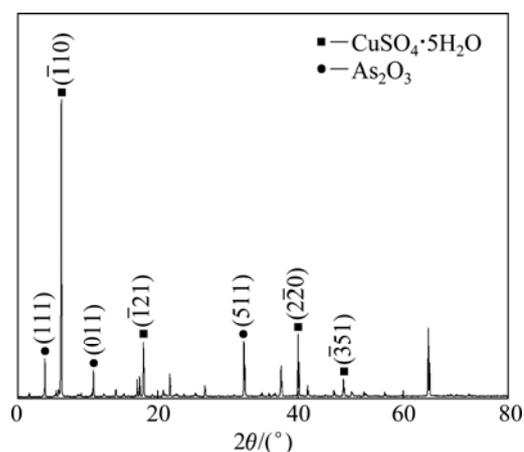


Fig. 5 XRD pattern of crystallized product

H₂SO₄ concentration in copper electrolyte increases in the process of concentration; however, the solubility of trivalent arsenic decreases to a rock bottom gradually when H₂SO₄ concentration increases from 0 to 850 g/L [12], and trivalent arsenic will deposit in the form of arsenic trioxide. Antimony and bismuth in copper electrolyte could also be removed due to the function of co-crystallization. The reactions are shown as follows:



3.2 Separation and recovery of As in crystallized product

The effect of temperature on the removal rates of As, Sb and Bi is shown in Fig. 6 when 65 g crystallized product whose composition is shown in Table 3 was dissolved in 200 mL water at an agitation rate of 200 r/min for 20 min.

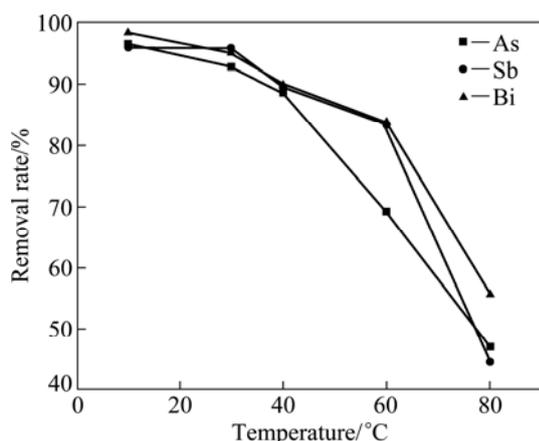


Fig. 6 Effects of temperature on removal rates of As, Sb and Bi

It can be seen from Fig. 6 that the removal rates of As, Sb and Bi decrease with increasing temperature. The removal rates of As, Sb and Bi are 92.81%, 95.75% and 95.05%, respectively, when the temperature is 30 °C. In order to separate As, Sb and Bi from copper sulfate, the reaction temperature should be 30 °C.

At 30 °C, the components of the filtrate are shown in Table 4, the compositions of the filter residue are listed in Table 5, and XRD pattern of the filter residue is shown in Fig. 7.

Table 4 shows that the concentrations of Cu and As in the filtrate are 65.70 and 0.61 g/L, respectively, and the pH of the solution is 1.54.

Table 4 Components of filtrate at pH 1.54 (g/L)

Cu	As	Sb	Bi	Fe
65.7	0.61	0.012	0.014	0.42

Table 5 Compositions of filter residue (mass fraction, %)

Cu	As	Sb	Bi	Fe	Zn
3.18	45.75	1.13	1.04	0.08	0.01
Pb	Ni	O	S	Ca	Others
0.05	0.16	31.10	10.45	3.42	3.63

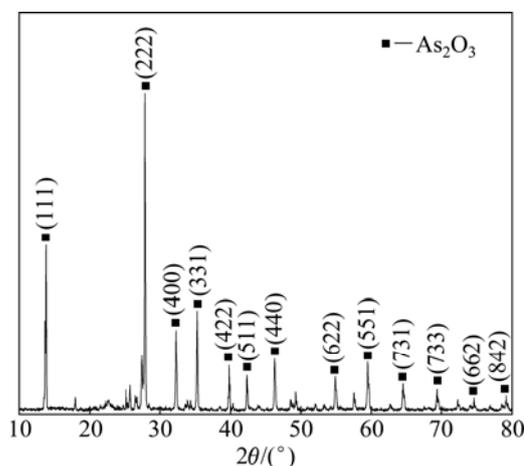


Fig. 7 XRD pattern of filter residue

Table 5 shows that the contents of Cu and As in filter residue are 3.18 % and 45.8 %, respectively. Figure 7 shows that filter residue is As₂O₃.

The solubilities of CuSO₄·5H₂O and As₂O₃ increase with the increase of temperature, and they are 37.8 g and 2.31 g in 100 g water, respectively, at 30 °C [11]. Because of the low solubility and the slow dissolution process of As₂O₃, most As₂O₃ exists in the residue after filtering, and CuSO₄·5H₂O is almost completely soluble in the water. The As was separated and recovered from copper sulfate.

3.3 Recovery of copper sulfate

Table 4 shows that there is still much As in the copper sulfate solution. The method of recovery of copper sulfate outlined in this paper can be used. In the following section, various experimental parameters were examined.

3.3.1 Effect of dosage of H₂O₂ on content of As in copper sulfate

The effect of the dosage of H₂O₂ on the content of As in copper sulfate is shown in Fig. 8 when the n(Fe):n(As) is 1.2, the reaction temperature is 60 °C, oxidation time is 40 min and the final pH is 3.7.

It can be seen from Fig. 8 that the As content in copper sulfate decreases with the increase of dosage of H₂O₂. The As content in copper sulfate is 0.00083% when the dosage of H₂O₂ is 2.4 mL. The As content in copper sulfate is lower than the quality of second class of copper sulfate (YS/T94—2007).

Arsenic and iron in the copper sulfate solution exist in the form of HAsO₂ and Fe²⁺, respectively [13].

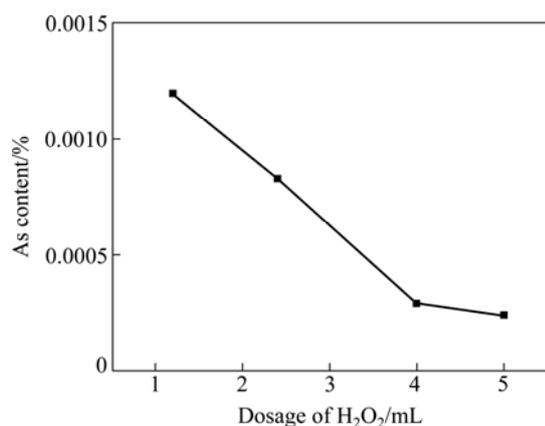
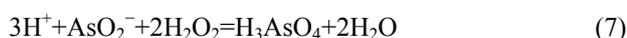


Fig. 8 Effect of dosage of H₂O₂ on content of As in copper sulfate

Trivalent arsenic is difficult to be removed from water using the normally available treatment process. It is usually necessary to change the arsenic to the pentavalent form by adding an oxidant [14], and H₂O₂ is the most widely applied oxidant with its advantages of powerful oxidation capacity and no pollution. HAsO₂ and Fe²⁺ are oxidized to H₃AsO₄ and Fe³⁺ with H₂O₂, respectively. Then H₃AsO₄ reacts with Fe³⁺ to form a FeAsO₄ precipitate. The reactions are listed as follows [15,16]:



$$\text{pH} = 1.027 - 0.33 \lg[\text{Fe}^{3+}][\text{H}_3\text{AsO}_4]$$

The total reaction is as follows:



The solubility product constant of FeAsO₄ is 5.7×10^{-21} , according to reaction (8), arsenic can be removed more completely after the arsenic is fully oxidized into H₃AsO₄ when the pH of the solution and the Fe content are appropriate [15,16]. Therefore, the appropriate dosage of H₂O₂ is 2.4 mL which is 19 times the stoichiometric ones according to reaction (9).

3.3.2 Effect of oxidation temperature on content of As in copper sulfate

The effect of oxidation temperature on the content of As in copper sulfate is shown in Fig. 9 when the dosage of H₂O₂ is 2.4 mL and other conditions above are fixed.

Figure 9 shows that the As content in copper sulfate decreases with the increase of temperature. The As content in copper sulfate is 0.00034% when the oxidation temperature is 45 °C. Then As content decreases slowly with further increasing the oxidation temperature.

The oxidation of Fe²⁺ and As (III) by H₂O₂ is slow in acidic conditions [17]. Increasing the temperature can

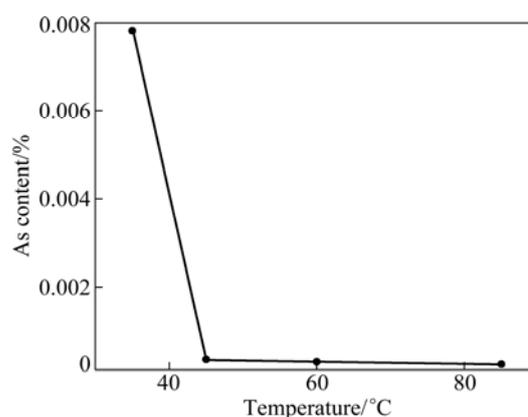


Fig. 9 Effect of temperature on content of As in copper sulfate

increase the rate of chemical reactions, so the rise in temperature is favorable for the removal of As. However, it is difficult to adjust solution pH at a high temperature, and the higher the temperature, the higher the energy consumption. Therefore, the appropriate oxidation temperature is 45 °C.

In order to remove arsenic in the copper sulfate solution, the appropriate conditions are that the $n(\text{Fe}):n(\text{As})$ is 1.2, dosage of H₂O₂ is 19 times the stoichiometric ones, oxidation temperature is 45 °C, oxidation time is 40 min, final pH is 3.7.

2000 mL copper sulfate solution after being treated under the appropriate conditions above was heated to evaporate water and the volume of the solution was concentrated to 500 mL, then copper sulfate crystals were obtained after cooling crystallization and filtering. The quality of the copper sulfate crystals is shown in Table 6.

Table 6 Quality of copper sulfate (mass fraction, %)

Component	CuSO ₄ ·5H ₂ O	As	Pb	Cd	Water insoluble substance
Sample	98.8	0.00029	0.0031	0	0.003
Second-grade of copper sulfate	≥96.0	≤0.001	≤0.008	≤0.001	≤0.1

Table 6 shows that the contents of CuSO₄·5H₂O, As, Pb, Cd and water insoluble substance in copper sulfate crystals are 98.8%, 0.00029%, 0.0031%, 0 and 0.003%, respectively. The quality of copper sulfate is up to the standard of second grade of copper sulfate (YS/T94—2007).

4 Conclusions

1) The removal rates of Cu, As, Sb and Bi can reach 87.1%, 83.9%, 21.0% and 84.7%, respectively, when Cu,

As, Sb and Bi in the copper electrolyte are 32 g/L, 6 g/L, 0.75 g/L and 0.42 g/L, after the As (V) is reduced to As (III) with SO_2 , and H_2SO_4 in the reduced copper electrolyte is concentrated to 645 g/L, then cooled to 10 °C to crystallize and filter. The mass fractions of Cu and As in the crystallized product are 32.66% and 4.42%, respectively.

2) The removal rate of As is 92.81% when 65 g crystallized product is dissolved in 200 mL water at 30 °C. The XRD result shows that the filter residue is As_2O_3 . The As content in the filter residue is 45.8 %.

3) The content of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is 98.8% when the copper sulfate solution is purified under the conditions that the $n(\text{Fe}):n(\text{As})$ is 1.2, dosage of H_2O_2 is 19 times the stoichiometric ones, oxidation temperature is 45 °C, oxidation time is 40 min, final pH is 3.7, and the purified copper sulfate solution is concentrated from 2000 mL to 500 mL, then cooling crystallized and filtered.

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铜电解液净化中铜砷的分离与回收

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摘要: 经二氧化硫还原、蒸发结晶, 使铜电解液中铜、砷、锑和铋得到有效去除。结晶产物经过溶解、氧化、中和、沉淀、过滤和蒸发结晶, 得到三氧化二砷和硫酸铜。当采用 SO_2 将铜电解液中 As (V) 充分还原为 As (III), 并加热蒸发浓缩铜电解液中硫酸浓度至 645 g/L 时, 铜电解液中铜、砷、锑和铋的去除率分别为 87.1%, 83.9%, 21.0% 和 84.7%。在温度 30 °C, 将 65 g 结晶产物溶于 200 mL 自来水时, 砷的去除率为 92.81%。将所得滤液在如下条件下净化: $n(\text{Fe}):n(\text{As})$ 为 1.2, 双氧水为理论用量的 19 倍, 氧化温度为 45 °C, 氧化时间为 40 min, 终点 pH 为 3.7, 净化后蒸发浓缩结晶, 所得硫酸铜溶液中硫酸铜含量达到 98.8%。

关键词: 铜电解液; SO_2 ; 净化; 硫酸铜; As_2O_3

(Edited by YANG Hua)