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THE BEHAVIOUR OF LOW ARSENIC COPPER ANODES AT HIGH CURRENT DENSITY IN ELECTROREFINING

Arsenic is the only beneficial impurity for copper electrorefining through inhibiting anode passivation and the formation of floating slimes. The behaviour of copper anodes with different content of arsenic were studied at high current density (>280 A/m^2). It showed that low arsenic anodes (As < 300 ppm) easily generated anode passivation, floating slimes and cathode nodules during the electrorefining proccess. The floating slimes, electrolyte, cathode and anode were observed and analyzed. As result, low arsenic anodes were more likely to be passivated due to their microstructure defects and irregular microstructure. Increasing electrolyte temperature and addition of glycerol were propitious to reduce low arsenic anodes' passivation. The floating slimes occured when the concentration of As(III) in electrolyte decreased to 1 g/L, and they would be precipitated by polyacrylamide. All measures greatly improved the cathode quality at current density of 300 A/m^2.

Keywords: low arsenic anodes; high current density; anode passivation; floating slimes; cathode nodules

1. Introduction

Copper electrorefining is the essential processes to produce high purity copper and precious metals. The copper anodes used in the processes always contain impurities, most frequently including As, Sb, Bi, Au, Ag, Fe, Ni, Zn, Se, Te and O. The composition of copper anodes depends on the raw ores or scraps and the impurity removal technology of anode copper by fire refining in the anode furnace. To achieve high quality cathode and decrease energy consumption, the anode should have a certain physical and chemical quality to meet the requirements of electrorefining.

Arsenic is the only beneficial impurity in anode during electrorefining process [1]. Krusmark et al. indicated that 300 ppm As was necessary at the San Manuel refinery [2]. It has been identified in practice so that the content of arsenic is always controlled from 500 ppm to 3000 ppm in commercial anodes. Many attentions have been paid to the roles of arsenic in electrorefining. As known, arsenic partly dissolves as As(III) into the electrolyte and partly forms insoluble slimes during the electrochemical dissolution of the anodes. The distribution of arsenic between the electrolyte and the slimes depends on a lot of factors which include the current density, the concentration and composition of the impurity ions in the electrolyte [3-6]. Besides, arsenic could provide H$^+$ and facilitate the dissolution of metal oxide on anodes which are always considered as one of the main components of the passivation layers [7-8].

Anode passivation, floating slimes and cathode nodules are the major problems of low arsenic anodes in electrorefining [9-11]. Anode passivation may be related to copper sulfate and H$^+$ concentration near anode surface. Because of copper anodes dissolving too fast at high current density, the rapid concentration increasing of copper ions causes H$^+$ to move towards the cathode in the region. Then the non-conductive surface layer, which mainly contains copper sulfate precipitation and metal oxide, appears on the surface of the anode. Consequently, the cell voltage will increase sharply, and the electrorefining process is difficult to proceed. The floating slimes, formed with the decreasing of As(III) and increasing of Sb(V) in electrolyte, has amorphous structure and irregular shape [12-17]. Most of them are smaller than 20 μm, and especially partly form colloid and suspend in electrolyte [18]. These floating slimes will contaminate the cathodes and worsen their quality. Cathode nodules are the most common surface quality problem in the electrorefining of low arsenic copper anodes. Nodules are formed as small particles adhere on the cathode surface, which are encased by the copper depositing and growing around them [19-22]. Based on mentioned above, most of the copper smelters refuse to use the anodes or acutely decrease the current density in electrorefining.

In this paper, the copper anodes with different content of arsenic were studied, and the results partly revealed the new role of arsenic in anodes and the behaviour of low arsenic anodes at high current density in electrorefining. Furthermore, a series

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of measures were adopted to depress the harmful impacts and obtained qualified products.

2. Experimental

Two types of anodes with different level of impurities, especially for arsenic, were used to perform a series of electrorefining tests. The low arsenic anodes from Zambia have the regular physical specifications, including weight (398 ±5 kg), geometry (cuboid, 990*952*50 mm^3), smooth surface and structure (low porosity). The normal anodes were produced by Guixi Smelter. Their compositions are listed in TABLE 1. The 316L stainless steels were used as cathodes.

TABLE 1

Chemical Compositions of the Anodes

Type of anodes	Cu	As	Sb	Te	Ni	Pb	Se	Bi	Fe	O
	%	ppm								
low arsenic anodes	99.40	45	45	81	2400	350	660	45	83	1500
normal anodes	99.34	1900	530	110	1500	470	240	120	55	1600

The electrolyte in the experiment was from Guixi Smelter and the basic components were as follows: 42 ±2 g/L Cu, 170 ±5 g/L free H_2SO_4, 10 ±1.5 g/L As, 14 ±2 g/L Ni, 0.3 ±0.03 g/L Sb.

The entire experiments were carried out in Guixi Smelter (Jiangxi, China). The Electrolytic System was consist of 1 m^3 cell with 5 anodes and 4 cathodes, electrolyte circulation unit with a dosing pump (GM0300, Qunyuan Co., LTD), current rectifier (KDF3000A/3V, Chengtian Electrical Appliance Co., Ltd), temperature controlling unit (tubular heat exchanger, Hunan Xinhan Electromechanical Equipment Co., Ltd) and additive automatic addition unit with 3 peristaltic pumps (BT100-2J/YZ1515X, Longer Precision Pump Co., Ltd). The electrolyte was pumped into the cell to a certain liquid level. Then electrolyte circulation unit, temperature controlling unit and additive automatic addition unit started up. When the electrolyte heated up to 65°C and maintained the temperature, the process started with the required currents through opening the current rectifier. The gap of anode and cathode was 50 mm in the electrolytic cell. The cathodic cycles were 10 days and each anode had two cathodic cycles. The flow input to cell was controlled at 3 L/min.

Glycerol (type G810575, Macklin reagent) and poly-acrylamide (MW = 7,000,000, Macklin reagent) were used as the electrolytic additive. The required concentration of additives in the electrolyte were obtained by adding the appropriate amount of their aqueous solution continuously during electrorefining.

The content of the elements was determined by the atomic emission spectrometry with inductively-coupled plasma technique (ICP-AES) (model Spectro Ciros Vision, SPECTRO Analytical Instruments GmbH, Kleve, Germany). The trivalent and quinquivalent compounds of arsenic in the industrial copper refining electrolytes were separated by potassium borohydride reduction method.

Raman spectra were acquired by a LabRAM HR800 Raman spectroscope (Horiba Jobin Yvon S.A.S), using Ar laser (532 nm) as excitation source. The microstructure of anodes were investigated by utilizing optical microscope (ZEISS Axio Vario). The samples were polished automatically and then etched with ferric chloride. Etching time was 15 seconds. The morphologies of the filtrated precipitate and floating slimes were examined by field-emission scanning electron microscopy (APREO S HiVac, ThermoFisher) with element energy dispersive spectrometer. (Octane Elect Super, AMETEK). The pretreatment samples were coated on the special conductive carbon tape to enhance the electric conductivity.The accelerating voltage was fixed at 30 kV.

3. Results and discussion

3.1. Microstructure

3.1.1. SEM analysis

Microstructure defects were found on the surface of low arsenic anodes while the regular anodes had not those as seen in Fig. 1. These defects with high atomic activity became the origin of dissolution. This might lead to the concentration of copper sulfate and pH increasing too rapidly in the region. The copper sulfate precipitates and metal oxide generated when copper ion increased to the saturated concentration and H^+ decreased to certain concentration. Then the non-conductive surface layer appeared on the surface of the anode. It should be one of the fundamental reasons of the anode passivation.
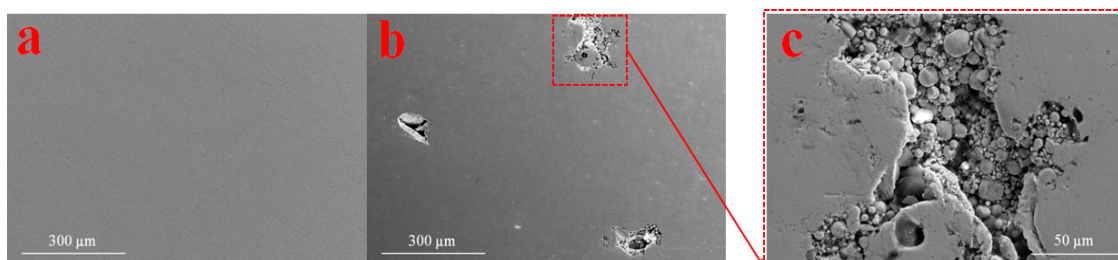

Fig. 1. SEM images of normal anode (a), low arsenic anode (b) and microstructure defects (c), respectively

3.1.2. Metallographic analysis

Metallographic analysis is one of the main methods to study the internal organization of metal and its alloys. The comparison of normal anode and low arsenic anode as shown in Fig. 2, the grain sizes and shapes of the low arsenic anodes were extremely irregular while those of normal anodes were uniform. The arsenic might play an important role in the copper anodes. Due to rapid cooling, the complex insoluble arsenic compounds were formed in Cu-As system during pyrorefining processes, and Cu_3As might be existed [7]. Cu_3As in the anodes was also confirmed by Noguchi Fumio [23]. These substances were enriched in the grain boundaries, which inhibited the rate of grain growth to regular and eliminated the possibility of selective dissolution along the grain boundaries. Besides, areas with larger grain sizes required higher voltage for passivation because they presented fewer surfaces where impurities were located [24]. Almost all of the normal anodes' grains were between 100-200 μm contrast to only 30 μm grains in partial region of low arsenic anodes. Therefore, the region with smaller grain sizes of the low arsenic

anodes were more likely to be passivated and easily generate copper powder particles than the normal anodes.

3.2. SEM-EDS and Raman spectra analysis

The floating slimes were washed with deionized water several times, then filtered using low qualitative filter paper, and finally dried at ambient temperature for maintaining their structure. The slimes obtained were characterized by SEM-EDS. The results are presented as following.

TABLE 2

Chemical Compositions of the Floating Slimes (wt. %)

Element	O	As	Sb	Bi	Ni	Pb	Se	Sn
Content	31.20	15.43	35.50	12.94	0.04	4.37	0.02	0.50

Fig. 3 shows the SEM image and EDS elemental distribution map of the floating slimes. Several observations can be con-
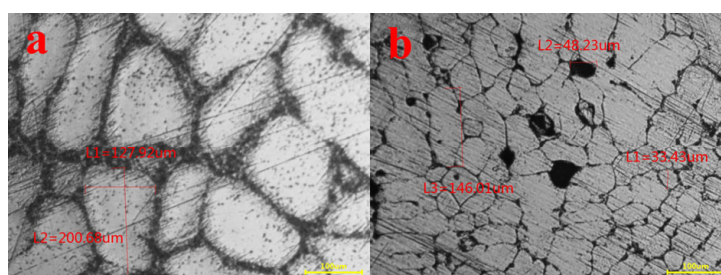

Fig. 2. Micrographs of the normal anode (a) and low arsenic anode (b), respectively
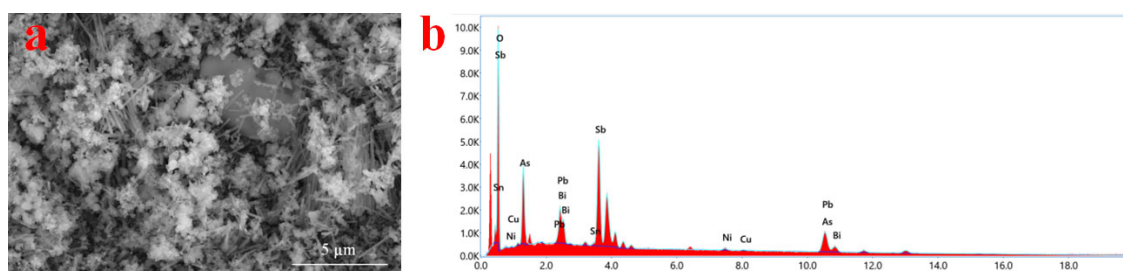

Fig. 3. The SEM image (a) and EDS elemental distribution map (b) of the floating slimes.
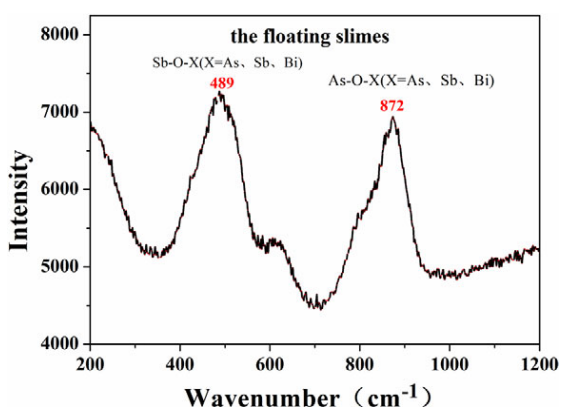

Fig. 4. Raman spectra of the floating slimes

cluded from the SEM-EDS of the floating slimes. Firstly, Fig. 3a illustrates the overall morphology of sample. There were long strips, granular objects and flocculations in the floating slimes. They mainly had quite fine particle size and especially part of them were smaller than 5 μm. Plus, the phenomenon of particle assembly was obvious. Secondly, Fig. 3b shows the elements existed in floating slimes and the contents of major chemical compositions were presented in TABLE 2. The oxygen, arsenic, antimony and bismuth were the absolutely dominant elements in floating slimes and the chemical structure of floating slimes was investigated by Raman spectra in Fig. 4. There were two main peaks of 489 cm^{-1} and 872 cm^{-1} in Raman spectra, which were assigned to Sb-O-X(X = As, Sb, Bi) and As-O-X(X = As, Sb,

Bi), respectively. These features would make floating slimes be settled with difficulties in the electrolyte. Floating slimes might contaminate the cathodes and worsen the cathode quality when they adhered on the surface of cathodes.

3.3. Electrorefining studies

Electrorefining experiments revealed: the low arsenic anodes appeared passivation with the current density increasing to 250 A/m² while the current density of normal anodes kept electrochemical dissolution with the current density exceeding 300 A/m² in Fig. 5.

Electrolyte temperature is one of the critical factors for anode passivation. The anode passivation appeared and the cell voltage rose to 0.6-0.8 V immediately when the electrolyte temperature droped to 57°C. This should be associated to lower solubility of copper sulfate and over-saturated crystallization occurred with the electrolyte temperature decreasing [7]. Raising electrolyte temperature appropriately was propitious to inhibiting anode passivation. Anode passivation always occurred during the second half of the anode period when the electrolyte temperature was 63°C. The temperature further raised to 65°C, and anode passivation rarely occurred.

Arsenic and antimony electrochemically dissolved from the copper anodes as trivalent ions and were oxidized to pentavalent by the oxygen dissolved in the electrolytes (Eqs. (1) and (2)) [25]. At the same time, the contents of trivalent arsenic (As(III)) and total arsenic (As(T)) in the electrolyte could not be supplemented in time when the low arsenic anodes dissolved. Hence, as shown in TABLE 3 and Fig. 6, the concentrations of As(T) and As(III) in the electrolyte were decreasing during the electrorefining process.

TABLE 3

Chemical Compositions of the Electrolytes (g/L)

Time	As (T)	Sb	Bi	Cu	Pb	Fe	Ni	As (III)
1st day	11.10	0.30	0.24	42.9	0.03	0.34	12.50	1.73
4th day	10.70	0.28	0.22	41.8	0.02	0.33	12.40	1.36
7th day	10.30	0.26	0.20	41.2	0.02	0.32	12.30	1.02
10th day	10.10	0.24	0.19	40.8	0.02	0.31	11.80	0.70

The floating slimes appeared in the electrolyte when the concentration of As(III) decreased to 1 g/L. The reducibility of As(III) was stronger than Sb(III) in the electrolyte. Sb(III) was oxidized to Sb(V), which was widely recognized as the key factor for the formation of floating slimes, when the As(III) decreased to a certain concentration.

$$2HAsO_2 + O_2 + 2H_2O = 2H_3AsO_4 \qquad (1)$$

$$2Sb^{3+} + O_2 + 4H^+ = 2Sb^{5+} + 2H_2O \qquad (2)$$
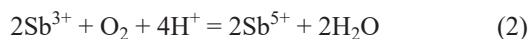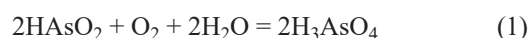
Under the industrial conditions, small copper particles occurred during the low arsenic anodes dissolution. The chemical compositions of the small copper particles were presented in TABLE 4.

TABLE 4

Chemical Compositions of the Small Copper Particles

Element	Cu	As	Sb	Te	Ni	Pb	Se	Bi	Fe	S
	%	ppm								
Content	99.86	100	66	2	53	45	660	4	160	270

There were two reasons for copper particles formation: one was the microstructure defects of low arsenic anode, which made copper particles be prone to mechanically shedding during

Fig. 5. Images of low arsenic anode passivation, 65°C, at current density of 250 A/m² (a) and normal anode dissolution, 65°C, at current density of 300 A/m² (b) respectively
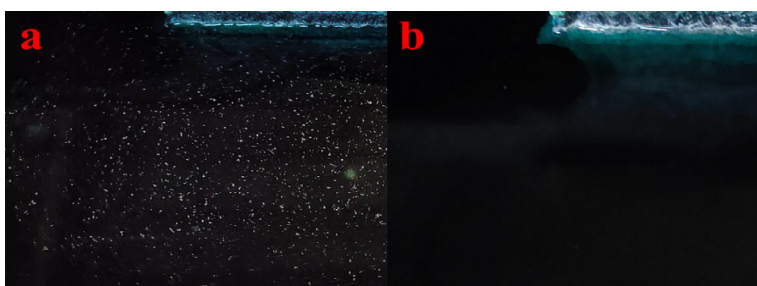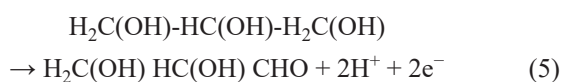

Fig. 6. Images of floating slimes(a) and normal electrolyte surface(b) respectively

electrorefining; the other one was from the disproportionation reaction of cuprous ions (Eqs. (3) and (4)). Cuprous ions were more likely to generated with cell voltage increasing. They were unstable and prone to disproportionate under electrorefining conditions. Some copper particles adhered to the anode surface to form a layer of spongious copper. Others dropped into the electrolyte which could adhere to the cathode and form nodules with its gradually growth (Fig. 7). The nodules would decrease the purity of cathodes and might cause short circuit of cathode-anode.

$$Cu - e \rightarrow Cu^+ \qquad (3)$$

$$2Cu^+ \rightarrow Cu^{2+} + Cu \qquad (4)$$
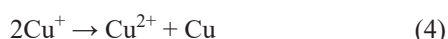
The above mentioned problems were solved by adjusting the electrorefining conditions, including increasing the circulating flow and the electrolyte temperature, reducing the content of Cu^{2+} and sulphuric acid in the electrolyte, and adding new additives. Glycerol and polyacrylamide were found that they were beneficial to inhibit anode passivation and floating slimes respectively. Glycerol might supply the H^+ near the anode when it was oxidized (Eqs. (5)) [26], which was similar to the effect of arsenic. The hydrolysis of arsenic oxide could also produce acid, which dissolved copper oxides adhered on the anodes and it was favor for reducing the tendency of passivation and the generation of copper powders (Eqs. (6)).

$$H_2C(OH)\text{-}HC(OH)\text{-}H_2C(OH)$$
$$\rightarrow H_2C(OH)\, HC(OH)\, CHO + 2H^+ + 2e^- \qquad (5)$$

$$As_2O_3 + 5H_2O \rightarrow 2H_3AsO_4 + 4H^+ + 4e \qquad (6)$$

With the addition of polyacrylamide into the electrolyte, the floating slimes were significantly suppressed. This was because polyacrylamide could flocculate the floating slimes. The decreasing concentration of copper sulfate and the increasing temperature further reduced the electrolyte density and viscosity which were critical to the precipitation of floating slimes.

After a series of measures were adopted, cathode quality got great improvements at current density of 300 A/m² in the eletrorefining as well (Fig. 8).

4. Conclusions

In this paper, we studied the copper anodes with different contents of arsenic and partly revealed the new roles of arsenic in anodes and the behaviour of low arsenic anodes in electrorefining. A series of measures were adopted to depress the harmful impacts of low arsenic copper anode in electrorefining at high current density. The results can be summarized as follows;

(1) The observations with SEM indicated that there were microstructure defects on the surface of low arsenic anodes. Meanwhile, metallographic analysis showed that the grain sizes and shapes of the low arsenic anodes were extremely irregular, and almost all of the normal anodes' grains were between 100-200 μm contrast to only 30 μm grains in partial region of low arsenic anodes. These should be the fundamental reasons of the anode passivation.

(2) Anode passivation, floating slimes and cathode nodules were the most harmful problems of the low arsenic anode at high current density. The lower limit of electrolyte temperature was 57°C for the low arsenic anode at 300 A/m²
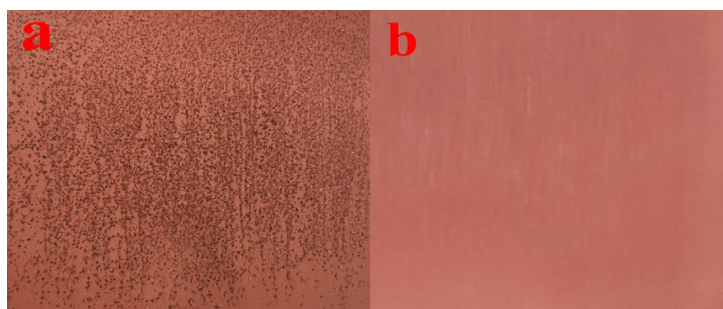

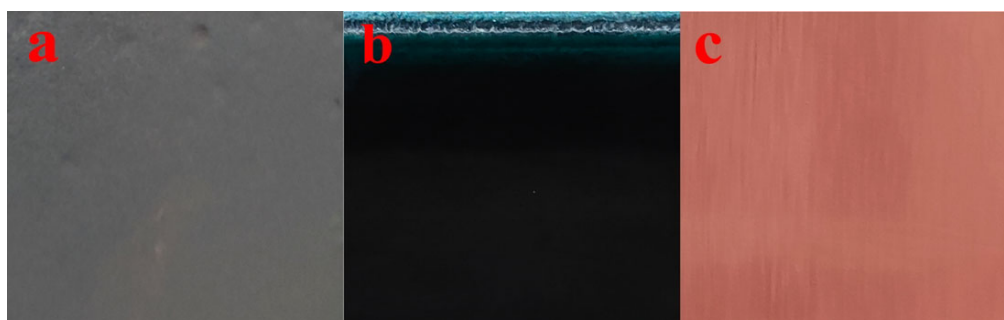Fig. 7. Images of cathode nodules (a) and normal cathode (b) respectively

Fig. 8. Images of after improvements of anode dissolution (a), electrolyte (b) and cathode (c) of low arsenic anode respectively, 65°C, at high current density of 300 A/m²

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in electrorefining. Raising the temperature of electrolyte appropriately was propitious to inhibiting anode passivation. The floating slimes occurred when the concentration of As(III) decreased to about 1 g/L in the electrolyte. The emergence of adhered copper powder particles was depending on the anode passivation, leading to cathode nodules.

(3) Based on the results of electrorefining experiments, the effective measures obtained and discussion could be summarized as follows: raising electrolyte temperature to 65℃ and addition of glycerol were propitious to reduce passivation tendency; polyacrylamide promoted the flocculation precipitation of the floating slimes. The cathode quality got great improvements at current density of 300 A/m^2 in the eletrorefining while these measures were adopted.

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