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Characteristics of anode slime obtained from secondary copper anodes with high Ni content

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ABSTRACT

In this paper are presented the results of major element distribution from copper anode to anode slime as so as the percentage of anode slime that was obtained during the copper anode electrorefining process. The conventional copper anodes were changed with anodes with 87.70 wt. % Cu and 93.31 wt. % Cu. Nickel content in anodes was approximately 5 or 10 wt. %, respectively to the copper content. The summary content of lead, tin and antimony was up to 3 wt. %. The waste sulfuric acid solution, generated during the conventional copper electrorefining process, was used as working electrolyte. Despite the presence of copper ions in a concentration of 30 g/dm^3, other major components are nickel and arsenic. Ni ions concentration was 20.5 g/dm^{3}and As ions concentration was 4 g/dm^3. Experiments were carried out in galvanostatic mode at current density of 250 A/m^2. The electrolyte temperature was maintained in the value of 63 ± 2 ^{0}C. Anode slime percentage was calculated based on the values for mass of dissolved anodes, mass of anode slime and based on the data for chemical composition of anode slime. By mathematical calculation was obtained the next values of anode slime percentage: 5.06 % (anode with 87.7 wt. % Cu) and 3.18 % (anode with 93.31 wt.% Cu).

1. INTRODUCTION

Copper is one of the most famous metals that are known to have been worked by some of the oldest civilizations. Corrosion resistance, good workability, high thermal conductivity, attractive appearance, is some of the main useful characteristics of this metal [1]. Commercial method for production of copper cathodes with 99.99 wt. % Cu is based on pyrometallurgical methods. The purity of copper anodes is in range from 98.0 to 99.5 wt. %. Demand for copper are continue to encourage the discovery of new deposits and the further development of technology for processing the secondary raw materials based on copper. Besides treating primary material, copper smelters are also showing an increasing interest in treating secondary materials. Data collected from the literature (European Union, EU-27, 2008) show that 67 % Cu from copper smelters came from primary production, and 33 % from secondary production [2]. The lowering quality of copper concentrate and increasing the use of the second materials leads to the production the copper anodes with non-standard chemical composition. Specially, the contents of nickel, antimony, tin and lead in commercial copper anodes tend to be higher in the anode produced from secondary raw materials based on copper [3].

Most industrial plants use the electrolyte that containing 40-50 g/dm^3 of Cu and 170-200 g /dm^3 free H2SO4, the maximum permissible concentration of Ni is in the range of from 10 to 20 g/dm^3 of Ni, and the concentration of As of up to 20 g/dm^3 [4]. The content of other impurities is conditioned by the content of them in the anode. In order to maintain constant electrolyte composition, part of the electrolyte must be derived from the circulatory system.

In this article, the waste process electrolyte is used as the working solution in the electrolytic refining process of the anodes with an increased content of nickel, lead, antimony and tin. Current density and temperature values were the same as in a commercial electrolytic refining process. The aim was to determine distribution of nickel, lead, antimony, tin and arsenic in the anode slime, as well as the percentage of anode slime.

2. EXPERIMENTALS

The experiments are carried out on the enlarged laboratory equipment with copper anodes of different composition, at electrolyte temperature of 63±2^{o}C, with constant current density of 250 A/m^2. Time duration of each experiment was 72 h.

Copper anodes were prepared from fire-refined copper and the next pure metal components: nickel, lead, tin and antimony. In one type of anodes, nickel content was approximately 5 wt. % and in other, nickel content was approximately 10 wt. %. The summary content of lead, tin and antimony was up to 3 wt. %. Copper content in the anodes was a difference up to 100 wt. %. Stainless steel was used for starting cathode sheet preparation. The cathode active surface area was 0.0891 m^2. The reference electrode was made of pure copper (99.95 wt. %). Electrochemical cell is rectangular, with internal size (L×W×H): 140 × 105 × 470 mm, made of PP. Electrolyte working volume is maximum 6 dm^3. Distribution system of N_2 was used for electrolyte circulation. Thermostat "HAAKE B7–PHOENIX 2" was used for maintenance the electrolyte temperature. Direct current was supplied by an external source (HEINZINGER TNB-10-500), with characteristics of 50 A and 10 V.

RFA method (Axios, PANalytical) is used for chemical analysis of anodes and anode slime.

During the electrolysis process, values of the following parameters were measured: direct current (A), cell voltage (V) and electrolyte temperature (^{o}C). Cell voltage was measured and recorded every 10 seconds for experiment duration of 72 h by data collecting system (DA100, Yokogawa). MCPS 5.0 (CAD computer GmbH) software was used for data processing.

3. RESULTS AND DISCUSSION

3.1. Chemical composition of copper anodes

The average values of some elements content in anodes (from bottom, middle and top of the anode), obtained by RFA standard method on the 26 elements, are presented in the Table 1. Copper content is difference up to100 wt. %.

Table 1. Anode composition obtained by RFA standard method

No.	Element	Anode Cu-Ni 5	Anode Cu-Ni 10
		Average content/ planed content, wt. %	
1	Ni	4.63 / 5.0	10.36/ 10.0

2	Pb	0.767 / 1.0	1.02 / 1.0
3	Sn	0.100 / 0.1	0.119 / 0.1
4	Sb	1.027 / 1.0	0.910 / 1.0
5	Cu	93.31/ 92.9	87.7/ 87.9
No.	**Element**	**Average content, wt. %**	
6	Zn	<0.0015	0.0058
7	P	/	0.0065
8	Mn	<0.0005	<0.0005
9	Fe	0.0153	0.015
10	Si	0.0042	0.012
11	Mg	<0.0002	<0.0002
12	Cr	<0.0003	0.0006
13	Te	/	0.022
14	As	0.0287	0.020
15	Cd	0.0019	0.0011
16	Bi	0.0036	0.0028
17	Ag	0.0670	0.054
18	Co	<0.0015	<0.0015
19	Al	<0.0010	<0.001
20	S	0.0031	0.0049
21	Be	<0.0001	<0.0001
22	Zr	<0.0003	<0.0003
23	Au	<0.0005	0.0018
24	B	<0.0005	<0.0005
25	C	0.0300	0.029
26	Ti	0.0017	0.0025
27	Se	0.0060	0.0079

Based on the obtained values for content of the main components it could be say that the value for Ni content is lower in anode which planed content was 5 wt. % and higher for the planed value of 10 wt. %.

The maximum difference in the content (23.3 %) was registered for the Pb content in the anode with a planned value of 5 wt. % Ni. The best matching between real and planed values are achieved for Sn content, in anode with 5 wt. % Ni. Content of Zn, P, Fe, Si, As, Cd, Bi, Ag, S, Au, C, Ti was with minimal difference for both anodes and moved within the global values in industry practice [5].

3.2. Mass balance and chemical characterization of anode slime

Anode slime generated in the electrorefining process consists of the particles with different configuration, particles size and composition and it is results of the electrochemical and chemical processes on anodes. Anode slime can be classified as adherent, bottom and floating slime based on their location.

The particles in the anode slime originating from the anodes with high Ni content have a heterogeneous chemical composition that is presented in the Table 2.

Table 2. Some characteristics of anode slime

Explanation	**Anode Cu-Ni 5**	**Anode Cu-Ni 10**
Chemical composition of anode slime		

Cu, wt. %	13.1	59.0
Ni, wt. %	3	1.2
Pb, wt. %	31.9	17.5
Sn, wt. %	2.8	1.3
Sb, wt. %	19.7	6.3
As, wt. %	6.2	2.5
Mass of anode slime		
Adherent slime, g	2.2	14.25
Bottom slime and floating slime, g	54.7	74.32
Total, g	56.9	88.57
Anode slime percentage		
Adherent slime, %	0.12	0.81
Bottom slime and floating slime, %	3.06	4.25
Total, %	3.18	5.06

Mass of anode slime is the higher in the case when the total content of impurities was higher (Table 2, Anode Cu-Ni 10).

The high content of Cu in the slime could be explained as a consequence of dropping the copper from cathode surface and the presence of Ni as a result of the presence of some of the insoluble phase [6]. The presence of As in the slime could be explain as the result of the floating slime formation as a result of the low ratio of As/Sb (0.033) in the electrolyte, which should be greater than 2 in order to avoid the formation of floating slime [7].

Anode slime percentage is calculated based on the dissolved mass of anodes during the 72 h of continual experiment. Mass of dissolved anodes is measured after the anode washing. The measured values were: 1583 g and 1749 g, respectively to anodes: Anode Cu-Ni 5 and Anode Cu-Ni 10. Distribution of copper and major elements from anode in anode slime is calculated based on the dissolved mass of the each element from anode and mass of each element in obtained anode slime based on the Equation (1):

$$\mathrm{x} = \frac{m_{x\,an.slime}}{m_{x\,anode}} \cdot 100\ \%\ (\%) \qquad (1)$$

Where:
x – element distribution, (%)
$m_{x\ \mathrm{an.\ slime}}$ – mass of element in anode slime (g)
$m_{x\ \mathrm{anode}}$ - mass of element dissolved from anode (g)

Results are presented on Figure 1.

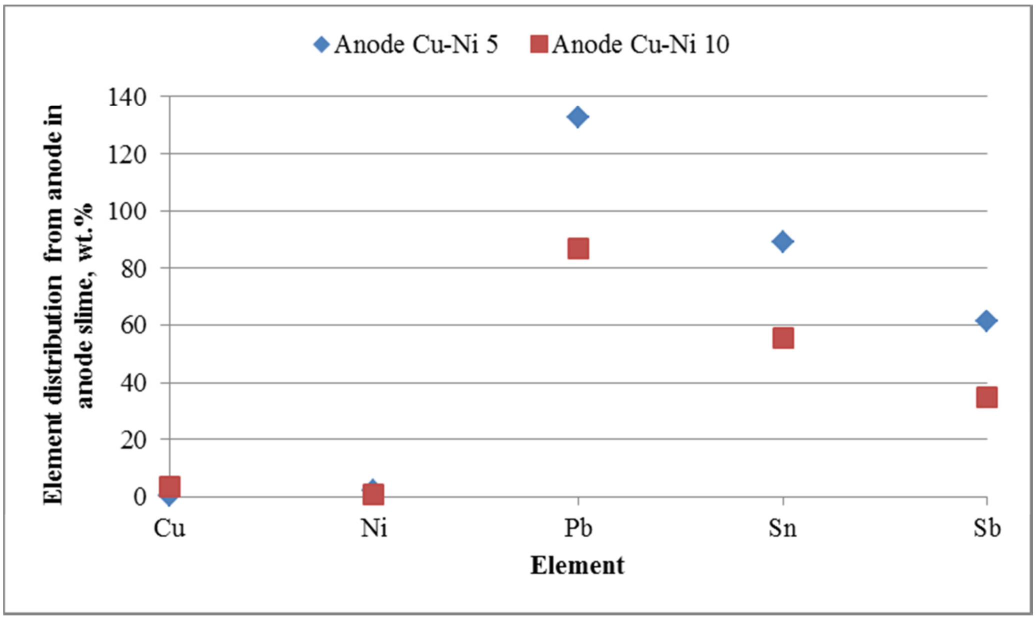

Figure 1. Major elements distribution from anode in anode slime

The higher value for distribution of the Pb, Sn and Sb from anode in anode slime is obtained for anode with approximately 10 wt. % Ni. Maximal percentage from anode in anode slime (132,429 %) is registered for anode with approximately 5 wt. % Ni. It could be explain by the value of cell voltage during the electrorefining process. Based on the data for the cell voltage changing during the 72 h, the start of passivation phase is registered after 35h 31 min for Anode Cu-Ni 5 and for Anode Cu-Ni 10 the start of full passivation is not registered [8] . Full passivation phase is not appeared. During the time of full passivation anode slime was adhered on anode surface. After that the passivation peak was break and the electrorefining process is continued. In this case it is possible that elements dissolution from anode were un-uniform. The same situation is registered for the Sn and Sb distribution percentage. The values are higher for the anode where is registered the appearance of full passivation peak.

4. CONCLUSION

The aim of this paper was to determine the major element distribution from anode into anode slime based on the measured parameters and chemical composition of anodes and anode slime. Copper content in copper anodes was lower than the copper content in commercial anodes. Nickel content in anodes was approximately 5 or 10 wt. %, respectively to the copper content. The summary content of lead, tin and antimony was up to 3 wt. %. As electrolyte is used the waste sulfuric acid solution, generated during the conventional copper electrorefining process (Cu ions: 30 g/dm^3, Ni ions: 20.5 g/dm^3 and As ions: 4 g/dm^3. Experiments were carried out at current density of 250 A/m^2 which is the same as the current density in commercial copper electrolyses. The electrolyte temperature was maintained in the value of 63 ± 2 ^{0}C. Anode slime percentage was 5.06 % for anode with 87.7 wt. % Cu and 3.18 % for anode with 93.31 wt.% Cu. Distribution percentage of Pb, Sn and Sb is higher is higher for the anode where is registered the appearance of full passivation peak.

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