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THE EFFECT OF Ni CONTENT ON PASSIVATION OF COPPER ANODES WITH NON-STANDARD CHEMICAL COMPOSITION

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ABSTRACT

In this paper are presented the results of the first appearance of full pasivation during the treatment of the waste sulphuric-acid solution generated in the conventional copper electrorefining process. The copper anodes with non-standard content of nickel, lead, tin and antimony were used as material for electrochemical refinement. Nickel content in anodes was approximately 5 or 7.5 wt. %, and the summary content of lead, tin and antimony was up to 3 wt. %. Copper content was a difference of up to 100 wt. %. Chemical analysis of the waste solution from copper refining process which was used as electrolyte has shown that the Ni and As ions are present in concentrations of Ni - 20.5 g dm⁻³ and As - 4 g dm⁻³. The experiments were carried out in galvanostatic mode at current density of 250 A m⁻², at electrolyte temperatures of T₁ = 63 ± 2 °C and T₂ = 73 ± 2 °C for a process duration of 72 h. The data obtained on the basis of the measured values of cell voltage for each anode where the nickel content was approximately 5 wt. % (anodes marked as A1-A4) and nickel content of approximately 7.5 wt.% (anodes marked as A5-A8) shown that using the anodes with lower nickel content (A2 and A3) leads to the appearance of full pasivation phenomenon at both electrolyte temperature. The apperance of full passivation for anodes with higher nickel content (A5-A7) is registered only at lower electrolyte temperature.

INTRODUCTION

Conventional copper electrolytic refining process using the commercial anodes with copper content from 98.0 to 99.5 mass %, and the working solution with Cu²⁺ ion concentrations ranging from 35 to 50 g dm⁻³ and sulphuric acid concentrations ranging from 150 to 250 g dm⁻³ [1]. The lowering quality of copper concentrate and increasing the use of the second materials leads to the preparing 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. However, during of electrolysis time, the copper concentration in the solution increases as well as all chemical elements that are more electronegative than copper. To maintain a constant composition, a part of electrolyte is derived from the system. Therefore, the possibility of processing the electrolyte derived from the system during electrolytic copper refining process by the soluble anodes with non-standard content of elements Ni, Sn, Sb and Pb was investigated [2]. Copper anodes with non-standard content of those elements are increasingly questioned, since they could be obtained using the recycled materials, sludge treatment with more than 90 wt. % Cu.

The process is developed under the force of an applied direct current, as the same density as so as in conventional copper refining process, such as Cu ion dissolves at the anode, enter the electrolyte and then selectively deposit onto the cathode. Other elements from anodes could be dissolved at the anode with possibility: to remain dissolved into the base electrolyte, remain at the anode and become part of anode slime, forming the “floating slime” and possible deposit onto a cathode sheet.

Presence of Ni content up to 3000 ppm, has no effect on solubility of copper anodes, whereas in excess of that amount, resulted into formation of NiO or with other elements and compound formation of type $3\text{Cu}_2\text{O}\cdot 4\text{NiO}\cdot \text{Sb}_2\text{O}_5$ known as "kupferglimmer" [3]. Nickel oxide is not soluble in the sulphur acidic electrolyte, remains in the anode slime and may cause the effect known as anode passivation [4]. As and Sb both of this compose are not soluble in the sulphur acidic electrolyte and may cause the effect known as anode passivation. Sb content less than 0.01 wt. %, has no significant effect on electrochemical behaviour of anodes, but it could cause Cu_2O spheroidization in the eutectic region, until Sb content higher than 0.05 wt. % at presence of Ni of 0.25 wt. %, leads to the formation of thin laminated inclusions at the copper grain boundaries. As and Sb may form a complex of $2\text{As}_2\text{O}_5\cdot 3\text{Sb}_2\text{O}_3$ type that easily precipitates from soluble into the fine dispersive solid state, known as the "floating slime". Pb, if is present in small amounts in anode, could be found in a form of compact solution, but it is the most often present in a form of oxide inclusions [5]. It is consider that high Pb content in anode, used in the conventional processes of electrorefining, decreases As, Sb and Bi ions concentration in electrolyte due to the formation of oxides [6]. It is assumed that Pb dissolves at the anode together with Cu and precipitates as PbSO_4 . Increase of Pb content facilitates the anode passivation, but it was established that if oxygen is present besides Pb, the anodes will not be passive [7]. It is well known that Sn in copper anodes is mostly present as SnO_2 , and rarely in the composite forms of oxides, formed at the copper grain boundaries. Only 10 wt. % of total Sn is present in the solid Cu solution [8]. During the electrolysis process, Sn could be oxidized in the acidic sulphate solution to Sn^{4+} ion, which then precipitates as the stannic hydroxide and remains in the anode slime.

The aim of this paper is to define the first appearance of full pasivation during the treatment of the waste sulphuric-acid solution generated in the conventional copper electrorefining process.

2 EXPERIMENTAL

Copper anodes, used in the process, were prepared from copper, nickel, lead, tin and antimony. Nickel content was approximately 5 wt. % or 7.5 wt. %, while lead, tin and antimony content was variable, where total maximum content of these elements was up to 3 wt. %. Copper content in the anodes was a difference up to 100 wt. %. Induction furnace and a graphite crucible were used for preparation the suitable mixture. Upon reaching the melt temperature of 1300 °C, the other metals were added. Graphite rods were used for oxygen reduction, and oxygen quantity in the melt was checked using device for determination the oxygen content (LECO Corp. RO-II6). Melt was casted into the suitable steel moulds at temperature of 1300 °C, only when the oxygen content was under 200 ppm. After self-cooling, the anodes were prepared for the electrolysis process by mechanical processing on the lathe removing approximately 2 mm of material from surface, polishing and degreasing the surface with ethanol.

Atomic absorption spectrophotometer (PERKIN ELMER 403) was used for determination the chemical composition of anodes.

During the electrolysis process values for direct current (A), cell voltage (V), anode potential (V) and electrolyte temperature (°C) were measured. For all experiments, the applied current density was 250 mA cm^{-2} . Starting cathode sheet was made of stainless steel with surface area of 0.0891 m^2 and reference electrode was made of cathode copper (99.95 wt. %). Cell voltage was measured and recorded every 10 seconds for experiment duration of 72 h.

Electrochemical cell is rectangular, made of PP, working volume of electrolyte is 6 dm^3 . Distribution system of N_2 was used for mixing of electrolytes during the process. Chemical composition of electrolyte and anode slime was determined by the ICP method, using simultaneous optical emission spectrometer with inductively coupled plasma (SPECTRO CIROS VISION).

In all experiments of refining the copper anodes, the real sulphur acidic waste solution was used as starting electrolyte. Chemical composition of this solution is presented in Table 1.

Table 1 Chemical composition of the starting electrolyte

Component	Cu	Ni	Pb	Sn	Sb	As	SO ₄ ²⁻
Concentration, g dm ⁻³	30	20.5	0.004	0.01	0.7	4	225

3 RESULTS AND DISCUSSION

3.1. Chemical composition of copper anodes

The average values of some elements content in anodes (obtained by analyzing the samples from bottom, middle and top of the anode), are presented in Table 2.

Table 2 Chemical composition of copper anodes

Anode	Elements				
	Ni	Pb	Sn	Sb	Cu
	Content, mass %				
A1	4.79	1.11	0.654	1.15	92.1
A2	4.75	0.816	0.439	0.442	93.41
A3	4.63	0.767	0.100	1.027	93.21
A4	4.97	0.213	0.136	0.099	94.94
A5	7.49	0.123	0.873	0.902	90.47
A6	7.52	0.367	0.815	0.889	90.30
A7	7.49	0.728	0.825	0.893	89.91
A8	7.35	0.129	0.432	0.429	91.51

Oxygen content which was registered in the tested anodes was below minimum value of 200 ppm so that the possibility of formation the insoluble phases in anode was reduced to minimum. Content of As was also analyzed and the mean value of 0.022 wt. % As was obtained, which is also slightly higher than in commercial anodes.

3.2 The first appearance of full passivation

During the electrolysis process of copper anodes with non-standard chemical composition, the value of cell voltage was measured (Figure 1).

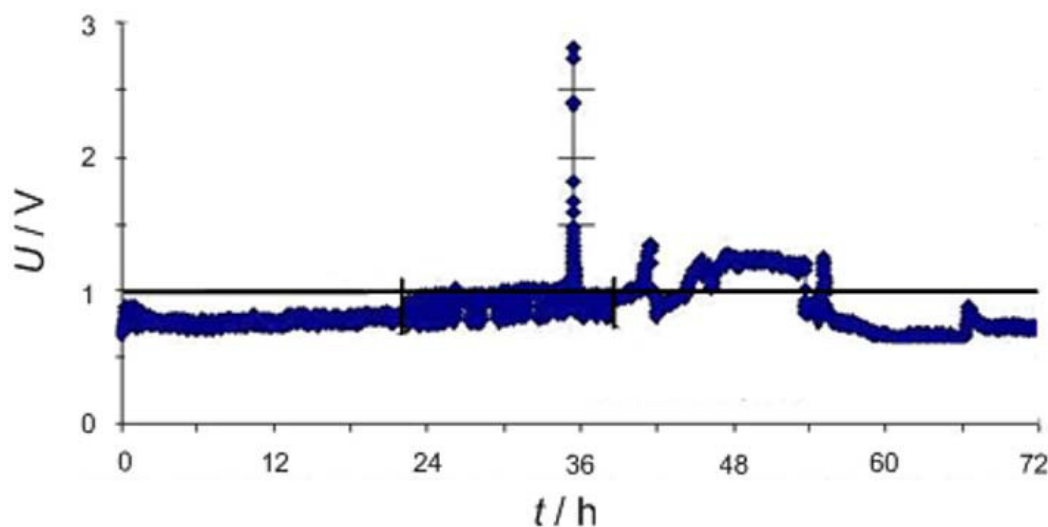


Figure 1 Cell voltage changing during the electrorefining process, registered using the A6 anode at $T_1=63 \pm 2 \text{ }^\circ\text{C}$

If the cell voltage change occurs suddenly during the electrolysis process, the peaks appeared in a diagram, (Figure 1), could be explained as the anode passivation peaks. Data from Table 3 present that the usage of A2 and A3 anodes results into occurrence of full passivation on a both temperature whereas there are passivation on A5, A6 and A7 anode only at a lower working temperature.

The occurrence of full passivation was not observed on anode with the lowest ingredient content (A4 and A8).

Table 3 The first occurrence of full passivation at different electrolyte temperatures

$T_1=63\pm 2\text{ }^\circ\text{C}$								
Anode	A1	A2	A3	A4	A5	A6	A7	A8
The first occurrence of full passivation								
Time, h	no	52:22	54:39	no	27:03	35:30	28:25	no
Cell voltage, V	no	2.444	2.336	no	2.457	2.809	2.189	no
Anode potential, V	no	0.928	1.912	no	0.768	2.592	1.887	no
$T_2=73\pm 2\text{ }^\circ\text{C}$								
The first occurrence of full passivation								
Time, h	29:10	45:45	35:31	no	no	no	no	no
Cell voltage, V	2.24	2.046	2.16	no	no	no	no	no
Anode potential, V	1.598	1.427	2.031	no	no	no	no	no

The process was not interrupted, but continued during refining of 72 hours. Anode with 5 wt. % Ni comes later into the passivation area. Anode A5 first enters into the passivation area after 27 hours on lower electrolyte temperature. Many factors have effect on anode passivation: anode chemical composition, working electrolyte chemical composition, electrolyte temperature, current density, electrolytes mixing etc. When the anode is passivated, Cu ions from electrolyte is deposited onto the cathode. Decreases of Cu concentration in electrolyte causes the increasing hydrogen evolution onto the cathode and the part of powder deposit become the higher [39-43].

Unlike the copper anodes with 7.5 wt. % Ni that are not passivated at high temperatures of electrode with 5 wt. %, they are subjected to the passivation without any rules. The interesting thing is that when it comes to the anode passivation then they start to behave as insoluble anodes, for example, lead-antimony. The process is not interrupted, but only copper from the solution is deposited on the cathode. The process is called decopperization. The longer passivation leads to the more powdered, darker, tends to self shaking deposit. When the passivation stops, the anode continues to dissolve, and therefore the appearance of cathode deposit is also changed.

4 CONCLUSION

The aim of this work was treatment of real waste sulphur acidic solution, obtained in the process of conventional copper refining process, with increased concentrations of Ni and As. Therefore, the copper anodes were prepared with increased Ni content of approximately 5 wt. %

and 7.5 wt. %, and the other elements, Pb, Sn and Sb which total content was up to 3 wt. %. Oxygen content was below 200 ppm as formation of undissolved phases in the anodes would be avoided. The data obtained on the basis of the measured values of cell voltage for each anode where the nickel content was approximately 5 wt. % (anodes marked as A1-A4) and nickel content of approximately 7.5 wt.% (anodes marked as A5-A8) shown that using the anodes with lower nickel content (A1, A2 and A3) leads to the appearance of full passivation phenomenon at both electrolyte temperature. The appearance of full passivation for anodes with higher nickel content (A5-A7) is registered only at lower electrolyte temperature. When the passivation stops, the anode continues to dissolve during the time of 72 h for each test.

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5 REFERENCES

- [1] A. K. Biswas and W. G. Davenport, Extractive Metallurgy of Copper, 2nd edition, Pergamon Press. London, (1980) 230-238.
- [2] R. Marković, B. Friedrich, J. Stajić–Trošić, B. Jordović, B. Jugović, M. Gvozdenović, J. Stevanović, Behaviour of non-standard composition copper bearing anodes from the copper refining process, Journal of Hazardous Materials, 182 (2010) 55–63.
- [3] J.B.Hiskey and S.C.Campin, Morphological and XRD Characterization of Kupferglimmer in Copper Anode Slimes, Proceedings of Copper 2003- Cobre 2003 International Conference, Vol. V, Electrowinning and Electrorefining of Copper, 309-324.
- [4] G.Jarjoura and G.J.Kipouros, Electrochemical studies on the effect of nickel on copper anode passivation in a copper sulphate solution, Canadian Metallurgical Quarterly, 45 (2006) 283-294.
- [5] C. Wenzl, A. Filzweiser, H. Antrekowitsch, Review of Anode Casting-Part I: Chemical Anode Quality, World of Metallurgy-Erzemetal, 60 (2007) 77-83.
- [6] T. T. Chen and J. E. Dutrizac, The Mineralogy of Copper Electrorefining-JOM, (1990), 39-44.
- [7] W. Gumowska and J. Sedzimir, Influence of the Lead and Oxygen content on the Passivation of Anodes in the Process of Copper Electro-Refining, Hydrometallurgy, 28 (1992) 237-253.
- [8] T. T. Chen and J. E. Dutrizac, Mineralogical Characterization of a Copper Anode and Anode Slimes from La Caridad Copper Refinery of Mexicana da Cobra, Met. and Met. Trans. B. 36B (2005) 229-240.