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# CELL VOLTAGE CHANGES DURING THE ELECTROREFINING OF COPPER ANODES WITH NON-STANDARD COMPOSITION

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*Abstract*

*This paper presents the results of cell voltage changing during the electrorefining process of copper anodes with non-standard chemical composition. The anodes with non-standard content of nickel, lead, tin and antimony were used as material for refining. Nickel content of all anodes was approximately 7.5 wt %, and the content of lead, tin and antimony was up to 1wt % for the each element. The sulphur acidic waste solution obtained in the conventional copper electrolysis was used as electrolyte with the copper concentration of 30 g dm*$^{-3}$*, nickel concentration of 20.5 g dm*$^{-3}$ *and arsenic concentration of 4 g dm*$^{-3}$*. The experiments were carried out in galvanostatic mode at current density of 250 A m*$^{-2}$*, on electrolyte temperature of* $T_1 = 63 \pm 2$ $^{0}$*C and process duration of 72 h. Diagrams constructed on the basis of the measured values of cell voltage for each anode (A1-A4) shown that the peak of total passivation is appeared by using the A1, A2 and A3 anodes, while for the A4 anode peak of total passivation is not registered.*

**Key words:** *non-standard copper anodes, Ni, As, sulphur acidic waste solution*

## 1. INTRODUCTION

The most amount of secondary waste materials that appear during the copper smelting process, are used for recycling. Suitable method depends on a material type for recycling. The most often usable process for copper, nickel, tin and lead production from various secondary materials, is the electro refining process. Refining of nickel and tin could be more efficient if metal flow would be done through the previous copper and nickel refining from lead and tin by the use of smelting where the copper anodes, ready for further electrolysis, are obtained.

High purity copper is produced by electrorefining of copper anodes containing at least 99.5 % copper, that is casts from fire refined blister copper [1]. Copper ions dissolve at the anode, enter the electrolyte and then selectively deposit onto the cathode under the force of applied direct current. The anode impurities have different mutual effects between themselves as well as with the electrolyte components in the electrolysis process. During the process, a part of impurities is dissolved into electrolyte or becomes a part of the anode slime. Negative effect of impurities on copper anodes range is existent over anode polarisation, copper losses in precipitation products to cathode inclusions during copper refining electrolysis [2].

The subject of this paper is to define the cell voltage changing during the electrorefining of copper anodes with high content of Ni, Sb, Sn and Pb by using the sulphur acidic waste solution obtained in the conventional copper electrolysis. The changing of cell voltage is measured each ten second during the duration period of 72 h and the all changes are registered and shown by the appropriate diagrams.

## 2. EXPERIMENTAL

The experiments are carried out on the enlarged laboratory equipment with copper bearing anodes of different composition, at electrolyte temperature of 63±2°C, in galvanostatic mode at constant current density. Time duration of each test was 72 h.

Copper bearing anodes, used in the process of electrorefining, were prepared from the next pure metal components: copper, nickel, lead, tin and antimony. In all anodes, nickel content was approximately 7.5 wt %, while lead, tin and antimony content was variable, where total maximum content of each element was up to 1 wt %. Copper content in the anodes was a difference up to 100 wt %.

After the casting and 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. For all experiments, the applied current density was 250 A $m^{-2}$ and during the electrolysis process, values of the following parameters were measured: the direct current (A), cell voltage (V), anode potential (V) and electrolyte temperature (°C).

Direct current was supplied by an external source (HEINZINGER TNB-10-500), with characteristics of 50 A and 10 V. Starting cathode sheet was made of stainless steel with surface area of 0.0891 $m^2$ and reference electrode was made of pure copper (99.95 wt %).

Cell voltage was measured and recorded every 10 seconds for experiment duration of 72 h. Data collecting by system DA100, Yokogawa.

Electrochemical cell was rectangular, made of PP, with internal size (L×W×H): 140 × 105 × 470 mm. Electrolyte volume without electrodes was 6.91 $dm^3$ and working volume of electrolyte was maximum 6 $dm^3$. Distribution system of $N_2$, used for mixing of electrolytes during electrorefining process, consists of cylinder with $N_2$, washer, plastic pipes for connecting with flow meter as well as the plastic pipes, used for connecting the flow meter with glass pipe, dipped into the electrolytic cell. Thermostat "HAAKE B7 – PHOENIX 2" was used for maintenance the electrolyte temperature.

## 3. RESULTS AND DISCUSSION

Chemical analyses of copper bearing anodes used for the tests are confirmed that oxygen content was up to 200 ppm. The anode samples for chemical analyses were prepared as a composite of the material from the bottom, middle and top of the each anode. The obtained values for Ni, Pb, Sn and Sb content are presented in Table 1. Copper content values were obtained as different up to 100 wt %.

Table 1 - Chemical composition of anodes

| Anode | Elements | | | | |
|---|---|---|---|---|---|
| | Ni | Pb | Sn | Sb | Cu |
| | Chemical composition, wt % | | | | |
| A1 | 7.49 | 0.123 | 0.873 | 0.902 | 90.47 |
| A2 | 7.52 | 0.367 | 0.815 | 0.889 | 90.30 |
| A3 | 7.49 | 0.728 | 0.825 | 0.893 | 89.91 |
| A4 | 7.35 | 0.129 | 0.432 | 0.429 | 91.51 |

During the electrolysis process, the cell voltage was measured every 10 s. The characteristic diagrams showing change of the cell voltage during the electrolysis process for each anode, are presented in Figures 1 – 4.

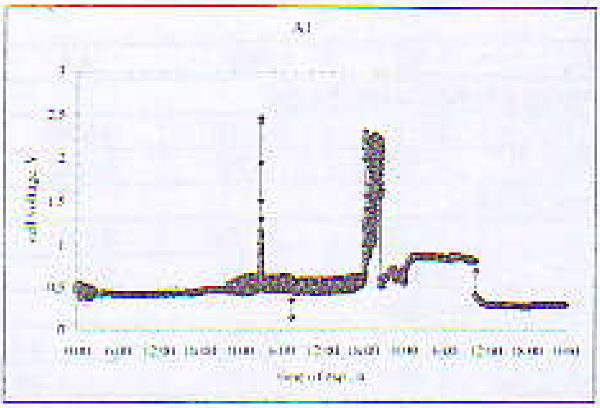

Figure 1 -Cell voltage changes during the electrolysis process of A1 anode

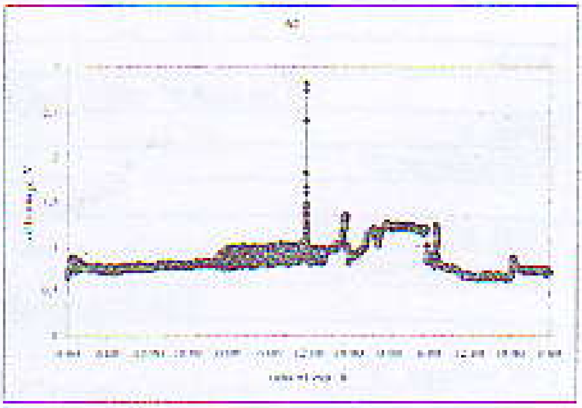

Figure 2 - Cell voltage changes during the electrolysis process of A2 anode

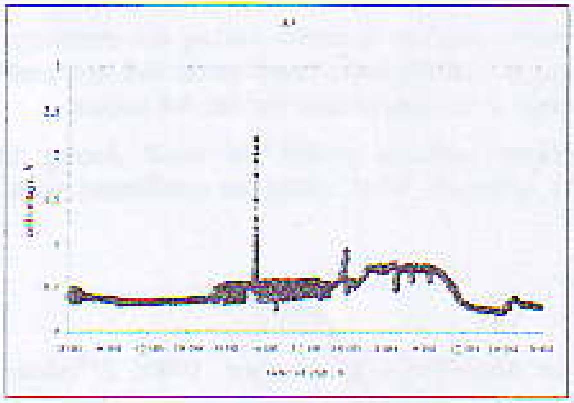

Figure 3 - Change of the cell voltage during the electrolysis process of A3 anode

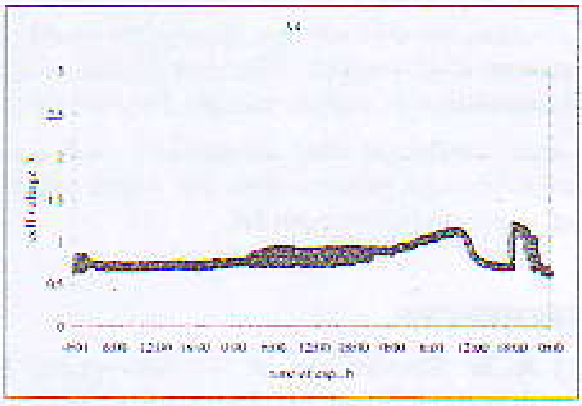

Figure 4 - Change of the cell voltage during the electrolysis process of A4 anode

On the diagrams shown in the Figures 1-4, based on the assumption that approximately 6 hours were needed to establish a regular flow of electrolysis, time period in which the cell voltage was not oscillate more than 0.2 V has been called - a stable phase and oscillatory phase - the period during which the change was greater than 0.2 V. In case of sudden change of cell voltage, during the electrolysis process, peaks would appear on the diagram. Those peaks indicate the occurrence of anode passivation phenomenon.

The characteristic values of cell voltage for the end of stable and the beginning of oscillation phase, the end of oscillation phase and the first appearance of total passivation are presented in Table 2.

Data from Table 2 show that the duration of stable phase for A1, A2 and A3 anode is almost identical and that it is the longest for the anode A4. The oscillatory phase duration is in range from 15.88 h for anode A2 to 19.9 h for the A1 anode. The data for the time of the first appearance of total passivation show that this time is shortest for A1 anode, whereas there is no passivation peak on A4 anode.

The average cell voltage values were similar for A2 and A4 anode, 0.863 V and 0.847 V, respectively, while values for the A1 and A3 anode were lower, 0.538 V and 0.463 V, respectively.

Table 2 – Change of the characteristic cell voltage during the electrolysis process

| Anode | A1 | A2 | A3 | A4 |
|---|---|---|---|---|
| The end of stable and the beginning of oscillation phase | | | | |
| Time, h | 22:18 | 22:15 | 22:18 | 26:40 |
| Cell Voltage, V | 0.458 | 0.784 | 0.36 | 0.742 |
| The end of oscillation phase | | | | |
| Time, h | 42:12 | 38:26 | 39:24 | 45:01 |
| Cell voltage (max), V | 0.689 | 0.969 | 0.54 | 0.911 |
| The first appearance of total passivation | | | | |
| Time, h | 27:03 | 35:30 | 28:25 | no |
| Cell voltage, V | 2.457 | 2.809 | 2.189 | no |

## 4. CONCLUSION

This paper presents the results of cell voltage changing during the electrolytic refining of chemical non-standard copper anodes.

The values for cell voltage, during the electrolysis process, slightly increase during the electrolytic treatment of all anodes. The time period of A1, A2 and A3 anode total passivation did not enable full dissolution of copper anodes. Passivation phenomenon is not registered for the A4 anode.

It was confirmed that chemically non-standard copper anodes could be used during the electrochemical process with the waste sulphuric-acid solution, what could be confirmed with a long active dissolution period.

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