

Treatment of Waste Copper Electrolytes Using Insoluble and Soluble Anodes

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The use of copper anodes with non standard content of impurities for the treatment of waste, sulphuric acid solutions that came as a result of the industrial process of electrolytic copper refining was investigated. Those solutions contain the high content of copper, nickel and arsenic, and because of that, the copper anodes with high content of Ni, Pb, Sn and Sb were prepared. Examination the effect of high impurities content as well as the influence of the solution temperature on the anodes behaviour during the electrolytic process under the conditions that are the same as the industrial was the aim of this work. Obtained results clearly indicate that tested anodes could be used for the refined during the electrorefining process. Dissolution of copper anodes was not stoppage after the first appearance of the passivation region for A1 and A2 anodes while appearance of passivation for A3 anode, for test duration of 72 h, was not registered. The start time of the first passivation appearance is shorter in the case of the anode with high content of all impurities, anode A1. The first passivation occurrence was detected on higher temperature after about 29 h from the test starts. The change of chemical composition of electrolyte was monitored during electrolysis. Concentration of nickel in the working electrolyte at the end of process is increased and it corresponds to the Ni content in anodes. The copper and arsenic concentrations are decreased during the process. Arsenic passes into the anode slime, while the copper is deposited on the cathode and also passed in the slime. After the process is finished, obtained solution could be used for the nickel recover using the electrochemically or chemically methods.

Keywords: soluble copper anodes, electrolytic refining, cathode copper, nickel

1. INTRODUCTION

The copper was the first metal that was mined and used for the manufacturing of tools, weapons and decorative items. The first use of copper is from 10000 years ago, due to its excellent electrical and thermal conductivity, resistance to the corrosion and simple procedures for working on it in the hot or cold state [1,2].

The exploitation of copper sulphide ore is carried out using the underground mining or open-pit mining method [3,4]. The copper bearing ore is enriched in order to obtain the copper concentrate from which, a copper anode (purity > 98.4 wt. %), is produced using the pyrometallurgical process [5,6]. The final stage in the production of cathode copper, with a purity of min. 99.95% Cu, is the process of the electrolytic refining of the anode copper. Copper ions dissolve at the anode, enter the electrolyte and deposit onto the cathode under the force of an applied direct current. Also, the impurities at the copper anode with a constant galvanostatic pulse could be dissolved at the anode and remain dissolved in the base electrolyte, remain at the anode and become part of the anode slime, form the “floating slime” and possibly deposit onto the cathode [7].

The composition of the electrolyte and the temperature are two very important parameters requested for the proper process of the electrorefining of copper anodes. The measurements have shown that increase in the concentration of copper and sulphuric acid as well as decrease of the temperature result in the increased speed of anode passivation in the industrial plants for copper electrolysis [8,9]. The speed of anodes passivation is also increased with the increased amounts of impurities like Ag, As, Au, Bi, Fe, Ni, O, Pt, Sb, Se, Te, Sn and Zn and their amount depends on the properties of the material of the anode. The increase of the amounts of impurities in the industrial anodes is a consequence of exploration of the raw material with very low amount of copper, the copper concentrate of the lower quality and the usage of the recycled materials [10].

Although the electrorefining procedures are known for the long time, problems that occur during the change depending on the general conditions for the electrolysis as well as electrolysis getting anode copper. The cathode deposit must not be contaminated and the anodes must not be passivated as a presumption for obtaining the copper of the desired physical and chemical characteristics. Therefore, strict procedures are requested in the processes of obtaining the cathode deposit. Usual procedure of controlling of the soluble impurities is continual bleeding of the parts of impure electrolyte that cannot be used for the further electrolysis, and therefore is waste solution. Electrolyte is bleeding from the circulation system and is electrolytically treated by using the insoluble anodes [11,12] for obtaining the copper that is present in the solution (decopperization). As, Sb and Bi are removed from the solution either in the form Cu-As-Sb-Bi or as a cathode sludge. Ni, Fe and Co are removed as a sulphides or the Ni is removed as a NiSO₄ [13]. The application of this method is very efficient for the removing of the impurities that are present in the electrolyte, but disadvantages are high costs, formation of the toxic arsine, and low quality of the NiSO₄ and the loss of the acid. [11,14]. Therefore, the research in this area should be continued by using the impure copper anodes [7,15,16].

The experiments in which the standard process of electrorefining were tested have shown that the presence of the Ni content of up to 0.3 wt.% has no effect on the solubility of copper anodes, anode

Ni dissolves in nearly 100 %, whereas the amount greater than that results in the formation of NiO. Nickel oxide is not soluble in a sulphuric acid electrolyte and may cause the anode passivation; it remains in the anode slime [17,18]. The amount of NiO formed in the anodes during the anode solidification is the function of oxygen content such as the quantity of NiO in the anode increases with the increase of the oxygen content. In the anodes in which the amount of Ni and Sb exceeds 3000 and 200 ppm respectively, secondary phase of the Cu-Ni-Sb ($3\text{Cu}_2\text{O}\cdot 4\text{NiO}\cdot \text{Sb}_2\text{O}_5$ or $\text{Cu}_3\text{Ni}_{2-x}\text{SbO}_{6-x}$ ($x = 0.1-0.2$)) could be formed during the last phase of the anode solidification. This phase is not soluble in sulphuric acid and can passivate the anode [10,15,19-21]. In this compound, as little as 17 ppm Sn can substitute Sb and/or join in the structure, forming the compound $\text{Cu}_3\text{Ni}_{2-x}(\text{Sb},\text{Sn})\text{O}_{6-x}$ ($x = 0.1-0.2$), that causes the anode passivation as well as the reduction of As ion from the working electrolyte [16,20-22].

The Sb content in anode below 0.01 wt. %, has no significant effect on the electrochemical behaviour of anodes but it could cause the spheroidization of Cu_2O in the eutectic region, whereas the Sb content greater than 0.05 wt. % in the presence of Ni of 0.25 wt. % leads to the formation of thin laminated inclusions on the copper grain boundaries [23-25]. As and Sb may form a complex of a $2\text{As}_2\text{O}_5\cdot 3\text{Sb}_2\text{O}_3$ type that easily precipitates from the soluble to the fine dispersive solid state, known as the “floating slime”, while the white precipitate of $\text{Sb}(\text{AsO}_4)$ is formed after the sub-cooling of the electrolyte [26-27]. Pb, if present in small amounts in the anode, could be found in the form of a compact solution, but it is the most often present in the form of oxide inclusions. It is considered that a high Pb content in the anode, used in the conventional processes of electrorefining, decreases the concentration of As, Sb and Bi ions in the electrolyte due to the formation of oxides [28]. It is assumed that Pb dissolves on the anode together with Cu and precipitates as PbSO_4 . The increase of the Pb content facilitates the anode passivation. However, it has been established that in the presence of oxygen, besides Pb, the anodes are not passive. It is well known that in copper anodes Sn is mostly present as SnO_2 , and only rarely in the composite forms of oxides, formed at the copper grain boundaries. Only 10 wt. % of the total Sn is present in the solid Cu solution. During the electrolysis process, Sn could be oxidized in the acidic sulphate solution to Sn^{4+} ions, which further precipitate as the stannic hydroxide and remain in the anode slime.

The goal of this work was to test the possibility of application of the copper anodes with high amount of Ni, Pb, Sn and Sb for the reduction of the copper ion concentration in the electrolyte by increasing the cathode deposit weight, the reduction of the concentration of arsenic ions, and the enrichment of the electrolyte with nickel ions. For experiments in this work, the waste electrolyte from the industrial process was used. Beside copper, the high concentration of the nickel is also present. Electrochemical testing were done on the equipment on the semi-industrial scale in the duration of 72 hours with the density of current which corresponds to the industrial values [29]. The aim of the increase of the working solution temperature comparing to the standard value was providing higher solubility of salts that are present in the electrolyte. The decrease of the copper ions concentration and increase the nickel ions concentration in the solution as well as the decrease of the anode mass has shown that those anodes have the characteristics of the both type of anodes, soluble and insoluble anode during the process of the electrorefining. Also, the investigation of such anodes is of great importance because they could be obtained by the processing of copper and nickel scrap materials.

2. EXPERIMENTAL

2.1. Electrochemical treatment of the waste sulphuric acid solution using soluble anodes

The copper anodes, used in the process of electrorefining, were prepared from the pure metal components: copper, nickel, lead, tin and antimony. The nickel content was approximately 5 wt. %, while the content of lead, tin and antimony was variable, where the total maximum content of these elements was up to 3 wt. %. The copper content in the anodes was the calculated difference to 100 wt. %. During the electrolysis process, the values of the following parameters were measured: the direct current (A), cell voltage (V), anode potential (V) and the electrolyte temperature (°C). The used current density was 250 mA cm⁻².

2.1.1 Device and Measuring Methods

The induction furnace (Balzers), power of 10 to 15 kW with a graphite crucible and a volume of 1.8 dm³, was used for the preparation the suitable mixture. Upon reaching the melting temperature of 1300 °C, the other metal components were added. Graphite rods were used for the oxygen reduction, and the amount of oxygen in the melt was checked using the device for the determination of the oxygen content (LECO Corp. RO-II6). The melt was cast into suitable steel moulds at a temperature of 1300 °C when the oxygen content was under 200 ppm.

Direct current was supplied by an external source of direct current (HEINZINGER TNB-10-500), with characteristics of 50 A and 10 V. The starting cathode sheet was made of stainless steel with a surface area of 0.0891 m² and the reference electrode was made of pure copper (99.95 wt. %). The cell voltage was measured and recorded every 10 seconds of the experiment's duration, i.e. during 72 hours. The data collecting system (DA100, Yokogawa), is equipped with two multi-purpose output modules and a communication module. The data processing was performed using the software MCPS 5.0.

The electrochemical cell is rectangular, made of PP and has an internal size of (L×W×H): 140 × 105 × 470 mm. The volume of the electrolyte without electrodes is 6.91 dm³, and Atomic absorption spectrophotometer (PERKIN ELMER 403) was used. Working volume of the electrolyte is maximum 6 dm³. The distribution system of N₂, used for mixing the electrolytes during the electrorefining process, consists of a cylinder with N₂, a washer, plastic pipes for connecting with the flow meter, as well as plastic pipes used for connecting the flow meter with the glass pipe, dipped into the electrolytic cell. A thermostat HAAKE B7 – PHOENIX 2 was used to keep the electrolyte temperature constant.

The chemical composition of the electrolyte and the cathode sludge was determined by the ICP method, using a simultaneous optical emission spectrometer with inductively coupled plasma (SPECTRO CIROS VISION). The cyclic voltammograms were recorded using potentiostat PAR 273A.

The experiments were carried out in a standard three electrode arrangement cell (200 cm³). The working electrode (the analyzed samples of pure Cu and Ni metals, as well as the copper anodes) had a surface area of 1 cm². The saturated calomel electrode is used as the reference electrode, while the

counter electrode was platinum foil with the same characteristics as those of the working electrode. Before the experiments were begun, the samples were held in a solution at open circuit potential during 10 min in order to establish the stable corrosion potential. The samples were analyzed starting from the cathode potential of -1 V towards the anode potential of 1 V, at the potential change rate of 2 mV s⁻¹.

3. RESULTS AND DISCUSSION

3.1. The use of anodes with high content of Ni, Sb, Pb and Sn for electrochemical treatment of an acidic waste solution

Based on the method of anodic linear sweep voltammetry (ALSV), the behaviour of different anodes in a sulphuric acid solution was investigated in the laboratory conditions.

During the 72-hour electrorefining process, at the constant current in semi-industrial condition, the changes of the chemical composition of the electrolyte were observed as a function of the temperature solution. Mass of anodes, mass of cathode deposit and mass of anode slime are measured at the end of each test aim to prepare the data for the mass balance.

All values of the standard potential of the impurities in copper anodes are more negative than the standard potential of pure copper. From a thermodynamic point of view, all elements present in the anode, at the duration of constant galvanostatic, pulse could be dissolved from the anode as so as the copper.

3.1.1. Characterization of anodes using the anodic linear sweep voltammetry analysis (ALSV)

The oxygen content in each anode was up to 200 ppm aim to decrease the part of oxide and "kupferglimmer" forms in the anode [19]. The average values of the content of particular elements in the anodes, obtained by analyzing the samples taken from the bottom, middle and top of the anode, are presented in Table 1.

Table 1. Chemical composition of copper anodes

Anode	Elements				
	Ni	Pb	Sn	Sb	Cu
	Content, wt. %				
A1	4.79	1.11	0.654	1.15	92.1
A2	4.63	0.767	0.100	1.027	93.21
A3	4.97	0.213	0.136	0.099	94.94

The samples of pure electrolytic copper and pure nickel metals form, as well as the samples of the copper anodes with the chemical composition presented in Table 1, were analyzed using the ALSV method, at room temperature in 2 mol dm⁻³ H₂SO₄. Based on the dissolution voltammograms,

presented in Figure 1, it is evident that all examined materials were passivated in the analyzed working electrolyte, but at various potential values and current densities. The same results are obtained during the polarisation measurements using the copper anodes where the maximal concentrations of some elements were (ppm): Ni -10200, Pb - 1484, Sn - 1500 and Sb – 1500 [19].

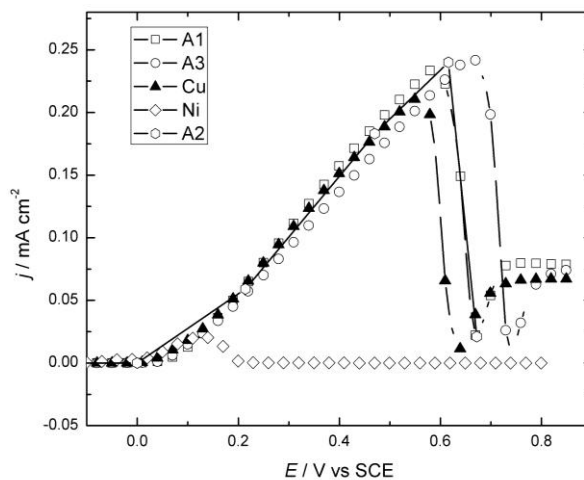


Figure 1. Voltammograms of the dissolution of pure metals of Ni and Cu and copper anodes with high impurities content in 2M H₂SO₄, at the rate of potential change of 2 mV/s

Ni first starts to dissolve through the two peaks and after the region of active metal dissolution get into the passivation stage. That is confirmed by the earlier investigations using the different electrolyte [31-32]. Also, at the lowest potential values Ni first enters into the passivation region. The amount of electrical charge which accompanies dissolution is the lowest. Thereupon, Cu starts to dissolve. Figure 1 also shows that the dissolution current density and the suitable electrical charge of the copper anodes with high content of impurities are higher than in the case of pure metals.

Figure 1 also shows that there is only one dissolution peak on the voltammograms of the dissolution of the copper anodes, which indicates that Cu and Ni form a solid solution, while at the rate of potential change of 2 mV/s, using 2M H₂SO₄ as the working electrolyte, the peaks corresponding to the dissolution of impurities Pb, Sn and Sb could not be observed.

Having in mind that the Ni content is approximately 5 wt. %, the observations could be made regarding the influence of other alloying elements (Pb, Sn and Sb). The anode with the maximum content of alloying elements starts to dissolve actively, and it first enters into the passivation area, whereas the anode with the minimum content of alloying elements is the last to enter it. The same influence of the impurities on copper anode behaviour has also been reported by some previous investigators [7,16,19]. The obtained values of the current density of the copper anodes dissolution are greater than those for the pure copper, which means that they could be used in the process of electrolytic refining at the same process parameters, as well as in the commercial production of cathode copper.

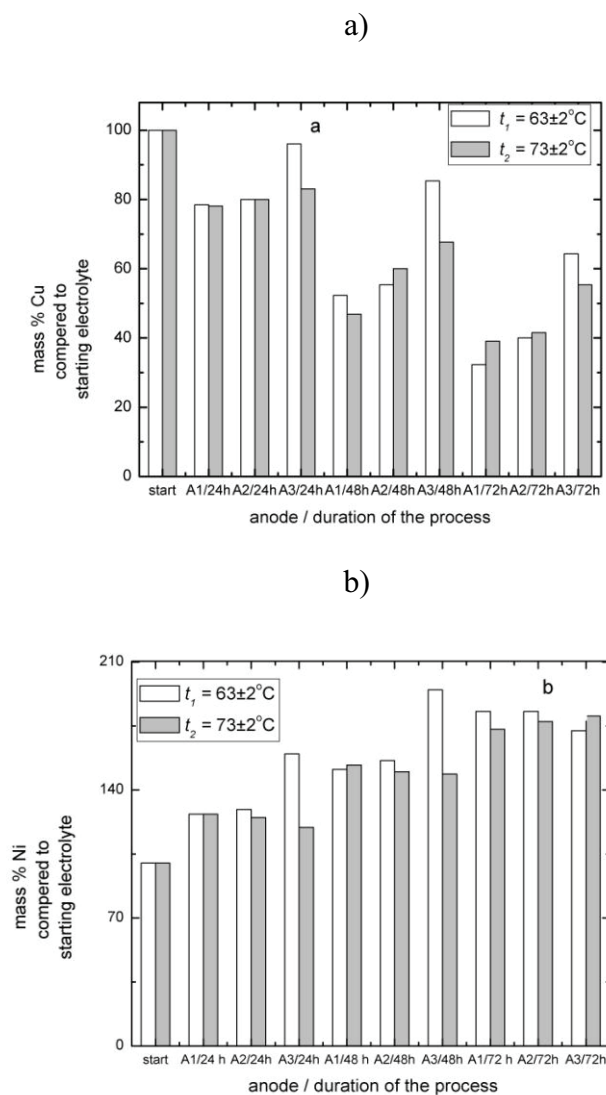
3.2. Change of electrolyte chemical composition

In all experiments, the industrial sulphur-acid waste solution (impure industrial electrolyte) was used as the starting electrolyte. The chemical composition of the solution is presented in Table 2.

Table 2. Chemical composition of the starting electrolyte

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

The changes in the chemical composition of the electrolyte were observed at different electrolyte temperatures ($T_1 = 63 \pm 2^\circ\text{C}$ and $T_2 = 73 \pm 2^\circ\text{C}$) during 72 h, and the obtained results are shown in Figure 2.



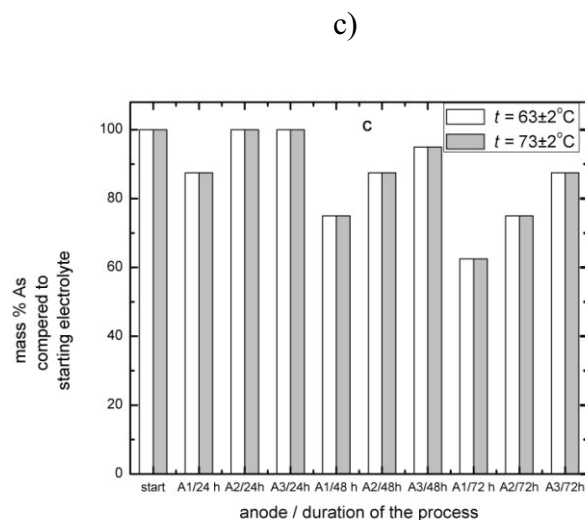


Figure 2. Chemical composition change of a) Cu, b) Ni, c) As in a solution, at temperatures $T_1 = 63 \pm 2^\circ\text{C}$ and $T_2 = 73 \pm 2^\circ\text{C}$, during a 72-hour electrolysis

During the standard industrial electrolysis process, the Cu and Ni ions concentration in the electrolyte increases with time [11]. As it can be seen in Figure 2, for all copper anodes with a non-standard chemical composition, concentration of Cu and As in the electrolyte was decreased during the process and Ni concentration was increased. The increase of the amount of the nickel in the electrolyte is the consequence of the dissolving of the nickel which is mostly present as the solid solution in the anode [19].

A comparison of the values of the Cu concentration at the end of process at two different temperatures shows that the Cu content in the working electrolyte is mainly higher at a lower temperature, in contrast to the nickel content in the working electrolyte, which is mainly lower at lower temperatures, while temperature has no significant influence on the As content.

The decrease of the concentration of the copper in the electrolyte indicates the passivation of the researched anodes and, consequently, they partly behave as the insoluble anodes [32-33]. The anode surface is during the process covered with the insoluble layer. As Sn and Pb are present in the layer (beside Ni and Sb), this layer is electrically conductive. When the amount of the sludge becomes the block for the diffusion of the copper ions from the anode, the following reaction occurs: $2\text{H}_2\text{O} = \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$. High amount of hydrogen ions that are generated on the anode induces the disintegration of the sludge from the anode surface, and this surface retains activity [8].

At the end of the process of the electrolytic refining of anode A1, at both temperatures, the lowest concentrations of Cu and As in the working electrolyte: 32 wt.% and 62 wt.%, respectively, compared to the starting value – and the highest nickel content – 183 wt.% in relation to the starting value – were reached.

The measured values of the Cu content in the working electrolyte could not be considered separately, but in relation to the observed changes in the content of other elements in the working electrolyte, as well as in relation to the electrolysis conditions. The continual decrease in the

concentration of SO_4^{2-} ions during the electrolysis process is due to the formation of poorly soluble sulphate salts with ions of dissolved metals and that was confirmed by the concentration decrease of certain elements in the working electrolyte.

The decrease of the As concentrations in the working electrolyte is the result of formatting of low solubility of antimony-arsenate complexes ($2\text{As}_2\text{O}_5 \cdot 3\text{Sb}_2\text{O}_3$) other complex types known as the flotation slime. The quantity and form of those complexes are the function of electrolyte working temperature. The occurrence of arsine was not recorded.

3.3. Chemical characterization of the anode slime

After the process of electrorefining of anodes had been completed, an amount of the anode slime was present at the surface of the anode, at the bottom of the electrolytic cell and in the form of the "floating slime".

The chemical analysis of the cumulative anode slime sample was carried out after the process ending. The percentage of anode slime in relation to the mass of dissolved anodes was calculated. Table 3 shows that the highest value of anode slime weight percent was obtained using anode A1, with the highest quantity of alloying elements, whereas the lowest weight percent of anode slime was obtained using A3 anode, with the lowest quantity of impurities, as well as larger quantity of slime is obtained at lower working temperature of the solution what is due to less solubility of metals at lower temperatures.

Table 3. Mass percentages of the anode slime in relation to the weight of the dissolved anode, obtained at the end of the electrorefining process ($T_1=63\pm 2^\circ\text{C}$ i $T_2=73\pm 2^\circ\text{C}$)

Anode	A1	A2	A3
Slime (anode), wt. %	1.02	0.12	0.38
Slime (cell bottom), wt. %	5.71	3.06	0.44
Total wt. % , $t_1=63\pm 2^\circ\text{C}$	6.73	3.18	0.82
Slime (anode), wt. %	0.74	0.52	0.18
Slime (cell bottom), wt. %	5.07	3.31	0.42
Total wt. % , $t_2=73\pm 2^\circ\text{C}$	5.80	3.85	0.61

During the process of electrolysis, the elemental copper may occur in the slime as the result of the processes developed at the cathode and anode. However, as the oxygen concentration in the anodes is less than 200 ppm, the entire amount of the copper in the slime is obtained by falling off from the cathode during the electrolysis process. The highest copper content (10 wt.% of the total mass of the slime at $T_1 = 63 \pm 2^\circ\text{C}$ and 7 wt.% at $T_2 = 73 \pm 2^\circ\text{C}$) in the anode slime was obtained by refining the A1 anode, which has the highest content of impurities.

The reduction of the copper content in the electrolyte during a 72-hour refining (Figure 3a), is the reason for the occurrence of the non-compact cathode deposit and transfer of the copper powder

deposition in the sludge [11]. With the Cu concentration decrease, the limiting diffusion current density of copper deposition also decreases. A significantly lower Cu content in the slime of max 0.78 wt. % of the total mass of anode slime was observed at the higher working electrolyte temperature and the anode with the lowest impurities content (anode A3). The limiting diffusion current density is temperature dependent and its value for copper is higher at higher temperatures. Therefore, a more compact cathode deposit and less copper powder were obtained at higher temperatures.

The Ni content in the anode slime is almost constant and it is the result of an incomplete washing of the anode slime in which Ni remains in the form of the soluble nickel sulphate salt (max 3 wt. % of the total mass of anode slime).

The values of the Pb content in the investigated anodes are identical to the values of the Pb content in the anode slime (max. 25 wt. % of to the total mass of the anode slime). During the electrorefining of the anodes with low Pb content, lead from various Cu-Pb-As-Sb-Bi oxide phases is transferred to the sludge in the form of the PbSO_4 together with Cu, As, Sb is dissolved. Part of the dissolved As and Sb is re-deposited. At the anodes with the high amounts of Pb, Cu-Pb-As-Sb-Bi oxide phases are dissolved slower or directly transfers to the low soluble Pb-Sb-As-Bi-S-O phase and at the same time is precipitated again in the form of the insoluble oxide forms Pb-Sb or Pb-Bi which induces the decrease Sb and Bi in the electrolyte [10]. Lead in the slime can be present in the metallic form and during the secondary reactions in the electrolyte, compound $6\text{PbOx As}_2\text{O}_5$ is formed which confirms the decrease of the concentration of the As in the electrolyte, as presented on the Figure 2 c).

The content of Sb and Sn is nearly constant at both temperatures, though their content in the slime at a higher temperature is twice higher (max. 23 wt. % of the total weight of slime). The Sn content is the lowest in the copper anode A3, and, at the same time, it is the lowest in the electrolyte and the highest in the anode slime (under both working temperatures).

During the electrolysis process, in the acidic sulphate solution, Sn can oxidize to the Sn^{4+} ion, which further precipitates as the stannic hydroxide and remains in the anode slime. When the copper anodes with the highest content of Sb and Sn (A1) were used, the lowest As content in the working electrolyte was recorded after 72 h of the electrolysis process. It has been known that As and Sb form a compound of $2 \text{As}_2\text{O}_5 \cdot 3\text{Sb}_2\text{O}_3$ type, with the solubility degree as a function of temperature. The compounds of this type pass through a characteristic transformation from the soluble to the finely dispersed solid state.

The analysis of the chemical composition of the anode slime has revealed that it depends on the composition of the anode and, electrorefining conditions, as well as that it is affected by the changes of the composition of the working electrolyte composition during the process.

3.4. Mass ratio of the copper dissolved at the anode and cathode deposit

A comparison of the experimentally obtained masses of the copper dissolved at the anode and those of the cathode deposit at two different temperatures is presented in Table 4 ($T_1=63 \pm 2^\circ\text{C}$ and $T_2=73 \pm 2^\circ\text{C}$).

Table 4. Mass of the copper dissolved at the anode and the mass of the cathode deposit

	$t_1=63 \pm 2^\circ\text{C}$		$t_2=73 \pm 2^\circ\text{C}$	
	Cu (an.), g	Cathode dep., g	Cu (an.), g	Cathode dep., g
A1	1648.6	1785.0	1586.0	1709.0
A2	1667.5	1771.0	1669.3	1770.0
A3	1663.3	1768.0	1664.3	1763.0

The mass of the cathode deposit is higher than the mass of the copper dissolved at the anode. This difference is greater when the copper that has become part of the anode slime by the from cathode surface during the electrolysis process is added to the cathode deposit. The increased weight percentage of copper in the cathode, compared to the starting Cu content in the anode, could be explained using Figure 3a, which shows that the Cu concentration in the working electrolyte decreases during the electrolysis process. This is characteristic of electrowining process and by this way is confirmed that those anode have the characteristics of soluble and insoluble anodes. It means that the complete amount of Cu dissolved at the anode, as well as a part the Cu amount from the starting working electrolyte, was involved in obtaining the cathode copper deposit.

3.5. Cell voltage

During the electrorefining process of copper anodes with a non-standard chemical composition, the cell voltage was measured at every 10 s and for each test there are about 25 000 data.

Several characteristic changes of the cell voltage were marked in Figure 3. Characteristic regions of a chronopotentiogram for a commercial copper anode are categorized as: 1. active dissolution region, 2. pre-passivation region, 3. passivation onset and 4. passivation [34]. Region when the cell voltage increases slowly as a function of time is called the stable phase, whereas the oscillation phase is the period when the amplitude of the oscillations increases gradually with time. If the cell voltage change occurs suddenly during the electrolysis process, the peaks that appear in the diagram could be interpreted as the anode passivation peaks.

The cell voltage and anode potential values that accompany these changes for all of the tested anodes are shown in Table 5.

The data from Table 5 and Figure 4 show that the usage of A1 and A2 anodes results in appearance of the total passivation. The total time needed to reach total passivation using the A1 anode is about 35.5 h; for anode A2, the time for the appearance of full passivation peak is longer (about 54.5 h), whereas there is no passivation on A3 anode at temperature of $63 \pm 2^\circ\text{C}$.

The occurrences of full passivation are significant at higher temperatures, whereas there is no passivation on A3 anode.

During the electrolysis process, the values of cell voltage and anode potential slightly increase at both electrolyte temperatures.

Table 5. Characteristic cell voltage changes during the electrolysis process at different electrolyte temperatures

t ₁ =63 ±2°C			
Anode	A1	A2	A3
End of the stable phase			
Time, h	32:07	41:57	/
Cell voltage, V	0.45	0.438	/
Anode potential, V	0.145	0.17	/
End of the oscill. phase			
Time, h	64:46	72:00	/
Cell voltage, V	0.751	0.525	/
Anode potential, V	0.433	0.177	/
Start of full passivation			
Time, h	35:37	54:39	/
Cell voltage, V	2.335	2.336	/
Anode potential, V	1.963	1.912	/
Average cell voltage, V	0.312	0.5	0.471
t ₂ =73 ±2°C.			
End of the stable phase			
Time, h	42:19	/	/
Cell voltage, V	0.442	/	/
Anode potential, V	0.169	/	/
End of the oscill. phase			
Time, h	58:55	/	/
Cell voltage, V	1.372	/	/
Anode potential, V	1.21	/	/
Start of full passivation			
Time, h	29:10	35:31	/
Cell voltage, V	2.24	2.16	/
Anode potential, V	1.598	2.031	/
Average cell voltage, V	0.536	0.465	0.380

Anode passivation is influenced by numerous factors: the chemical composition of the anode, the chemical composition of the working electrolyte, electrolyte temperature, current density, mixing of electrolytes, etc. Since all of the anode were prepared with the increased Ni content (5 wt. %) and alloying elements like Pb, Sn and Sb (maximum 3 wt. %), the anode passivation occurred due to the formation of poorly soluble compounds such as: Sb₂(SO₄)₃, SbAsO₄, NiO, mixing oxides, etc. These compounds adhere to the surface of anode, causing its passivation. It should be pointed out that passivation may be interrupted by breaking the adhesive layer from the surface of the anode while the electrorefining process of anodes continues [8].

4. CONCLUSION

The increase in the amounts of impurities in the industrial copper anodes is the consequence of the raw material refining in which the amount of copper is lower, concentrate of the copper with very low quality and using of the recycled material of various chemical compositions.

The amount of copper in the copper anodes of non-standard chemical composition that are used for the treatment of the waste electrolyte from the industrial process from the industrial copper electrolysis was between 92.1 and 94.94 wt.%, the amount of nickel 4.63 to 4.97 wt.%, while the overall amount of Pb, Sn and Sb was between 0.448 and 2.914 wt.%

The results for the chemical composition of the electrolyte during the process of the electrolytic process of those anodes have shown that amount of copper in the solution decreases, and that after 72 hours of the duration have the minimal value of roughly 32 wt. %, compared to the starting amount. The amount of As in the solution is decreased as well to the value of roughly 62 wt. % compared to the starting value. This decrease is obtained at the anode A1 in which the total amounts of impurities was the highest. The concentration of the nickel in the solution was increased up to the maximal value of 183 wt.% compared to the starting value.

The results for the values of the masses of the anodes and the cathode deposit show that mass of the cathode deposit is higher than the mass of the dissolved copper at the all anodes that confirms that tested anodes during the process have the characteristics of the insoluble and soluble materials. The change of the temperature has no significant influence neither to the solution of the copper from the anodes A2 and A3 or to the masses of the corresponding cathode deposit.

The lowest mass of dissolved copper at the anode as well as the lowest mass of corresponding cathode deposit are observed at the anode A1 (1586 g, 1705.9 g, respectively) which is confirmed by the shortest time (29 hours) before the presence of the pick of total passivation.

All of the results have shown that neither of tested anodes during the 72 h of process of electrolytical treatment in the conditions that corresponds to the industrial has entered the area of total passivation. Anodes have the characteristics of the soluble and the insoluble, so those anodes could be use for the electrolytic treatment the impure, waste electrolyte from the copper electrolysis industrial process which contains high amount of copper, nickel and arsine.

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References

1. F. Habasi, *Copper. History & Metallurgy*, Metallurgie Extractive Quebec, Quebec City (2009).
2. <http://www.copper.org/environment/uk>
3. C. Stuhlberger, *Mining and Environment in the Western Balkans*, ENVSEC, New York (2010).
4. Z. Stevanović, M. Antonijević, R. Jonović, Lj. Avramović, R. Marković, M. Bugarin and V. Trujić, *Journal of Mining and Metallurgy*, 45 B (2009) 45.
5. M.Schlesinger, M.King, K.Sole, W.Davenport, *Extractive Metallurgy of Copper*, Elsevier (2011).
6. G. Moldoveanu, Precipitation of nickel-sulphate from deccoperized acid solution by solvent displacement crystallization, Department of Mining and Metallurgical Engineering McGill University, Montreal, Canada, September, 1999
7. R. Marković, B. Friedrich, J. Stajić–Trošić, B. Jordović, B. Jugović, M. Gvozdenović, J. Stevanović, *Journal of Hazardous Materials*, 182 (2010) 55.

8. X.Ling, Z.H.Gu, T.Z.Fahidy, *Journal of Applied of Electrochemistry*, 24, (1994) 1109.
9. J.Sedzimir and W.Gumowska, *Hydrometallurgy*, 24, (1990) 203.
10. T.T.Chen and J.E.Dutrizac, *Proceedings of Copper 99 – COBRE 99, Vol.III – Electrorefining and Electrowining of Copper*, The Minerals, Metals & Materials Society (1999) 437.
11. J. E.Hoffman, *Journal of Metals/JOM*, 56 (2004) 30.
12. H. Cartes, C. H. Domingo, United States Patent Application 20070125659, (2007).
13. K. Popov, S. Đokić, B. Grgur, *Fundamental Aspects of Electrometallurgy, Chapter 7: Electrorefining*, Springer (2002).
14. G.J. Houlachi, P.L.Claessens, *US Patent: 4146447*, (1979).
15. G. Jarjoura and G. J. Kipouros, *Journal of Applied Electrochemistry*, 36 (2006) 283.
16. G. Jarjoura and G. J. Kipouros, *Canadian Metallurgy Quarterly*, 45 (2006) 283.
17. T. T. Chen, J.E. Dutrizac, *Journal of Metals/JOM*, 42 (1990) 39.
18. T. T. Chen, J. E. Dutrizac, *Metallurgical and Materials Transactions B*, 36B (2005) 229.
19. Z.Mubarok, H. Antrekowisch, G. Mori, *Proceedings of the 6th International Copper/Cobre Conference*, Toronto, Canada, 25 - 30 August 2007, 59.
20. O. Forsen, K.Lilius, *Proceedings of the Electrorefining and Winning of Copper*, Denver, Colorado, USA: 24.-26. Feb., (1987) 47.
21. J.B.Hiskey and S.C.Campin, *Proceedings of Copper 2003 – Cobre 2003 International Conference, Vol. V: Electrorefining and Electrowining of Copper*, (2003) 309.
22. C. Wenzl, A. Filzweiser, H. Antrekowitsch, *Erzmetall*, 60 (2007), 77.
23. W. Gumowska, J. Sedzimir, *Hydrometallurgy* 28 (1992) 237.
24. H. Gauthier, M.Manzini, E. Ghali, *Canadian Metallurgy Quarterly* 38 (1999) 22.
25. V.D.Jović, R.M. Zejnilović, A. R .Despić, J.S.Stevanović, *Journal of Applied Electrochemistry* 18 (1988) 511.
26. X. Wang, Q.Chen, Z.Yin, L.Xiao, *Hydrometallurgy* 84 (2006) 211.
27. X. Wang, Q.Chen, Z.Yin, M. Wang, B. Xiao, F. Zhang, *Hydrometallurgy* 105 (2011) 355.
28. J.E. Dutrizac and T.T. Chen, *Copper 2003-Cobre 2003, Vol. V, Copper Electrorefining and Electrowinning*, The Metallurgical Society of CIM, Montreal, Canada, (2003), 249.
29. S. Gurmen, G. Orhan, C. Arslan, and S. Timur, *ARI The Bulletin of the Istanbul Technical University*, 54, (2004) 40.
30. R.Stevanović, J.Stevanović, A.Despić, *Journal of Applied Electrochemistry*, 31 (2001) 855.
31. G. Nemțoi, H. Chiriac, O. Dragoș, M. Apostu, D. Lutic, *Acta Chemica Iasi*, 17 (2009) 151.
32. T.Marsden, and J.Jickling, *Hydrometallurgy Conference 2009, The Southern African Institute of Mining and Metallurgy*, 249.
33. I. Ivanov, Y. Stefanov, Z. Noncheva, M. Petrova, Ts. Dobrev, L. Mirkova, R. Vermeersch, J.-P. Demaerel, *Hydrometallurgy* 57 (2000) 109.
34. F.Safizadeh, E.Ghali, *Electrochimica Acta*, 56 (2010) 93.