Behaviour of non-standard composition copper bearing anodes from the copper refining process

R. Marković [a], B. Friedrich [b], J. Stajić–Trošić [c], B. Jordović [d], B. Jugović [e], M. Gvozdenović [f], J. Stevanović [g,*]

[a] IRM, Mining and Metallurgy Institute Bor, 19210 Bor, Serbia
[b] IME Process Metallurgy and Metal Recycling, 52068 Aachen, Germany
[c] ICTM, Institute of Chemistry Beograd, 11000 Belgrade, Serbia
[d] Technical Faculty Čačak, 32000 Čačak, Serbia
[e] ITS-Serbian Academy of Science and Arts, 11000 Belgrade, Serbia
[f] Faculty of Technology and Metallurgy, University of Belgrade, 11000 Belgrade, Serbia
[g] ICTM, Institute of Electrochemistry, 11000 Belgrade, Serbia

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ABSTRACT

This paper addresses on investigation the possibility of electrolytic treatment the sulphur acidic waste solution, obtained in the conventional electrolytic copper refining process. Beside the high copper concentration, the high concentration of other metals, in this case nickel, is the main characteristic of these waste solutions. Due to this fact, the copper bearing anodes with non-standard nickel, lead, tin and antimony content were specially prepared for the refining process. Nickel content of all anodes was approximately 7.5 mass%, and the content of lead, tin and antimony was varied. The preliminary results, obtained using the standard electrochemical techniques, have indicated that the copper bearing anodes could be used under the same conditions as well as in the conventional copper refining process. The measurements in constant galvanostatic pulse have pointed out that the all chemical elements from copper bearing anodes were dissolved and only copper was deposited onto the cathode. It was also pointed out that Ni concentration in the base working electrolyte (sulphur acidic waste solution), after 72 h of process, increased to 102 mass% at $T_1 = 63 \pm 2 \,^\circ C$ and up to 122 mass% at $T_1 = 73 \pm 2 \,^\circ C$, while arsenic concentration decreased to a minimum value.

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1. Introduction

The commercial anodes with copper content from 98.0 to 99.5 mass%, obtained in the flame refining process and the base working solution with Cu^{2+} ion concentrations ranging from 35 to 50 g dm^{-3} and sulphuric acid concentrations ranging from 150 to 250 g dm^{-3}, are used in the conventional copper electrolytic refining process [1]. The process is developed under the force of an applied direct current such as Cu ion dissolves at the anode, enter the electrolyte and then selectively deposit onto the cathode.

Except the base metal (Cu), the anodes also contain the other ingredients that with positive effect on anode solubility as well as the quality of cathode slime, are called the alloying elements, and without those properties, are called the anode impurities.

The ingredients have impact on the structure of anode material. Thus, by changing its properties, they could be dissolved at the anode, remain dissolved into the base elec-

trolyte, remain at the anode and become part of anode slime, forming the "floating slime" and possible deposit onto a cathode.

The aim of the present investigations was to examine the possibility of using waste sulphur acidic solutions from conventional electrolytic refining process. Waste solution, besides the high concentration of copper ion, also contains the high concentration of other metal ions, in this case Ni and As.

Therefore, the copper bearing anodes with non-standard content of alloying elements were prepared to the aim of enabling: decrease of concentration the copper ion in electrolyte by an increases the cathode deposit mass, decrease of concentration the arsenic ions, and to enable the enrichment of electrolyte with nickel ions. Chemical and electrochemical characteristics of other alloying elements were not such that significantly reduce the solubility of anode material, and all with the aim of reduction or prevention the formation of unsoluble Ni oxide, that causes the anode passivation as well as the reduction of As ion from working electrolyte [2].

Presence of Ni content up to 0.3 mass%, has no effect on solubility of copper bearing anodes, whereas in excess of that amount,

* Corresponding author. Tel.: +381 113303702.
E-mail address: jaca@tmf.bg.ac.rs (J. Stevanović).

resulted into formation of NiO. Nickel oxide is not soluble in the sulphur acidic electrolyte, remains in the anode slime and may cause the effect known as anode passivation [2–4]. The quantity of NiO in anodes and anode slime is also the function of oxygen content such as the quantity of NiO in anode and anode slime increases with the oxygen content increase.

Sb content less than 0.01 mass%, has no significant effect on electrochemical behaviour of anodes, but it could cause Cu_2O spheroidization in the eutectic region [5,6], until Sb content higher than 0.05 mass% at presence of Ni of 0.25 mass%, leads to the formation of thin laminated inclusions at the copper grain boundaries [7]. As and Sb may form a complex of $2As_2O_5 \cdot 3Sb_2O_3$ type that easily precipitates from soluble into the fine dispersive solid state, known as the "floating slime" [6]. Pb, if is present in small amounts in anode, could be found in a form of compact solution [6], but it is the most cases in a form of oxide inclusions [7]. It was 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 [7]. It is assumed that Pb dissolved 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 [8,9]. It is well known that Sn in copper bearing anodes is almost always present as SnO_2, and rarely in the composite forms of oxides, formed at the copper grain boundaries. Only 10 mass% of total Sn is present in the solid Cu solution [10]. 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 Ni ion concentration in some synthetic electrolyte used in electrorefining process of unrefined anodes, was ranging between 0 and 40 g dm^{-3} [11] but no enough data can be found for behaviour of real waste sulphur acidic solutions with high concentration of the other ions, in this case As.

A degree of anode material solubility, change of real working solution composition with duration time of electrorefining process, quantity and composition of obtained anode slime and quality of cathode deposit are investigated in this paper. The subject of this work was investigation of possible use of copper bearing anodes in electrolytic treatment of the real waste sulphur acidic solutions with higher concentration of Ni and As ions, obtained in conventional copper refining process, not previously treated with some conventional technology. Respectively, the aim was to obtain the pure cathode copper from real waste electrolyte, decrease the concentration of As in the working solution by forming the unsoluble salts and increase Ni concentration in the treated waste solution.

According to the all facts, this way of treatment the real waste sulphur acidic solutions could be environmentally justified and economically payable.

2. Experimental

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 mass%, while lead, tin and antimony content was variable, where total maximum content of these elements was up to 3 mass%. Copper content in the anodes is a difference up to 100 mass%.

Induction furnace (Balzers), power of 15 kW and a graphite crucible, volume of 1.8 dm^3, were used for preparation the suitable mixture. Upon reaching the melt temperature of 1300 °C, the alloying elements 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 (PerkinElmer 403) was used for determination of chemical composition of anodes.

During the electrolysis, values of the following parameters were measured: the direct current (A), cell voltage (V), anode potential (V) and electrolyte temperature (°C). For all experiments, the applied current density was 250 mA cm^{-2}. Direct current was supplied by an external source of direct current (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 mass%).

Cell voltage was measured and recorded every 10 s for experiment duration of 72 h. Data collecting system (DA100, Yokogawa) is equipped with two multi-purpose output modules and a communication module. There were 20 channels for direct current measuring and voltage within ±20 and ±50 mV limits, with temperature-dependent resistance (up to 600 °C) and digital indicators. All inputs were independent. Scanning rate could be set to the values from 0.5 up to 60 s. MCPS 5.0 (CAD computer GmbH) software was used for data processing.

Electrochemical cell was rectangular, made of PP, with internal size ($L \times W \times H$): 140 mm × 105 mm × 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.

Chemical composition of electrolyte was determined by the ICP method, using simultaneous optical emission spectrometer with inductively coupled plasma (SPECTRO CIROS VISION). A part of electrolyte samples were analyzed without any previous preparation, but the occurrence of slime during solution cooling, as the result of saturated solution with metal salts, presents a significant problem for sample analyzing. Therefore, the electrolyte samples were prepared as follows: 10 ml of electrolyte from cell medium + 10 ml 37% HCl + deionised water up to 50 ml. By this way of sample preparation, the problem of precipitation was avoided.

Chemical composition of the anode slime was determined by the ICP method, and particle-size analysis was carried out using MALVERN – particle-size analyzer.

Polarization curves and cyclic voltammograms were recorded using potentiostat PAR 273A at ambient temperature of 25 ± 1 °C in aqueous sulphuric acid solution. The experiments were carried out in a standard three electrode arrangement cell (200 cm^3). The working electrode (analyzed samples of pure metals Cu and Ni as well as copper bearing anodes) had surface area of 1 cm^2. The saturated calomel electrode was used as the reference electrode, while the counter electrode was platinum foil with the same characteristics as working electrode. Prior to each experiment, the samples of working electrodes were subjected to double-stage wet polishing using 1 and 0.05 μm alumina, washed with 18 MΩ cm deionised water first and than with ethanol.

All potential values are given regarding to the saturated calomel electrode. Before the start of experiments, the samples were held in the solution at open circuit potential during 10 min in order to establish the stable corrosion potential. The samples were ana-

Table 1
Chemical composition of copper bearing anodes.

Anode	Elements				
	Ni	Pb	Sn	Sb	Cu
	Chemical composition, mass%				
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

lyzed 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. Chemical composition of copper bearing anodes

Chemical analysis of all anodes showed that oxygen content was up to 200 ppm. The average values of Ni, Pb, Sn, Sb and Cu content, obtained by analyzing the composite samples preparing from the material from bottom, middle and top of the anode, are presented in Table 1.

3.2. The use of anodic linear sweep voltammetery analysis (ALSV) for characterization the copper bearing anodes

The samples of pure Cu and Ni metals as well as the samples of copper bearing anodes, with chemical composition, presented in Table 1, were analyzed using the ALSV method, at room temperature in 2 mol dm^{-3} H$_2$SO4. Based on dissolution voltammograms, it is evident from Fig. 1, that the all examined materials were passivated in the analyzed working electrolyte, but at various potential values and current density.

Fig. 1 shows that Ni first starts to dissolve through two peaks, after the region of active metal dissolution occurred. Also, Ni at the lowest potential values first entered into the passivation region. The amount of electrical charge witch accompanied the dissolution, was the lowest. Thereupon, Cu started to dissolve with the peak
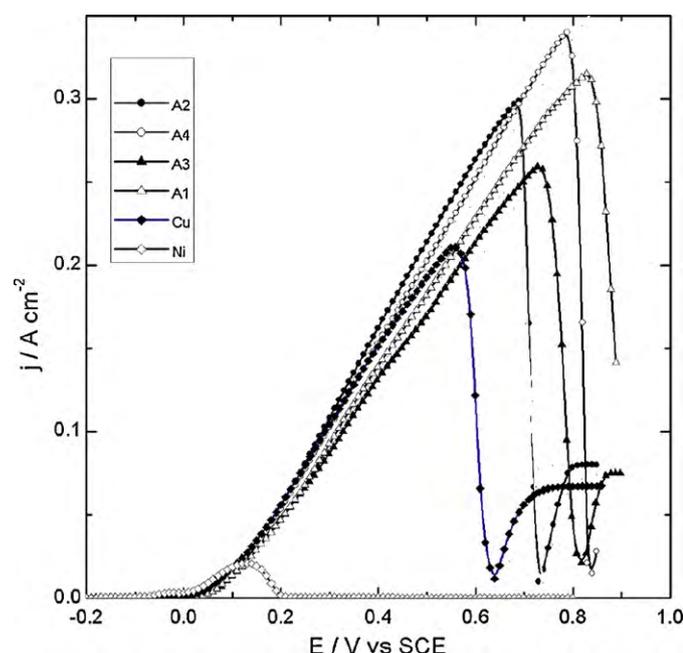
maximum, of about 220 mA cm^{-2}, what is suitable to the current density range of 200–270 mA cm^{-2}, at which the most conventional copper refining plants operate.

Fig. 1, also shows that dissolution currents density of copper bearing anodes, as well as suitable electrical charge, were higher than in the case of pure Cu and Ni metals and that the recorded current density values, at the dissolution peak maximum, were higher than 250 mA cm^{-2} even at room temperature. Fig. 1 also shows that there was only one dissolution peak on the voltammograms of copper anodes dissolution that pointed out that Cu and Ni formed a solid solution. At scan rate of 2 mV s^{-1}, there were no peaks that could correspond to dissolution of Pb, Sn and Sb impurities.

Considering that Ni content is approximately 7.5 mass%, the observations could be made regarding the influence of other alloying elements (Pb, Sn and Sb) on electrochemical characteristics of copper bearing anodes. Anode (A3) with the highest Pb content, last one started to dissolve and the voltammogram shows that this dissolution was associated with the lowest amount of electrical charge, as well as the value of current density that corresponds to a dissolution peak maximum had the lowest value, slightly higher than 250 mA cm^{-2}. Comparing the dissolution voltammograms of A1 and A4 anodes with the same Pb content, and A4 has double less content of Sn and Sb, and total the least content of ingredients, it was observed that the dissolution value of current density, corresponding to maximal dissolution peak of A4 anode, had higher value than 350 mA cm^{-2}.

With decrease of Pb content, active dissolution of copper bearing anodes started earlier. The lowering of Pb content in anode lead to larger amount of dissolved anode material. All voltammograms show that active dissolution of copper bearing anodes was developed continuously at current density of 250 mA cm^{-2}, and that they are able to be used even at significantly higher values of current density. Based on measured values of copper bearing anodes current density dissolution and comparing to values of current density dissolution in the sulphur acidic electrolyte in conventional production, it was found that the obtained values for the copper bearing anodes were higher. Also, it was found that the copper bearing anodes were in the region of active dissolution all the time at the current density used in conventional production.

Based on the obtained results shown in Fig. 1, it could be concluded that copper bearing anodes with non-standard content of ingredients could be used in the electrolytic refining process, with the same technological parameters used in conventional production of cathode copper.

3.3. Analyzing the corrosion characteristics of pure nickel, copper and copper bearing anodes

For the purpose of analyzing the corrosion stability of Ni, Cu and copper bearing anodes, the corrosion current density as well as anode and cathode Tafel slopes was determined in sulphuric acid solution.

Fig. 2 shows the values of corrosion potentials as well as corrosion current density of Ni, Cu and copper bearing anodes. Corrosion
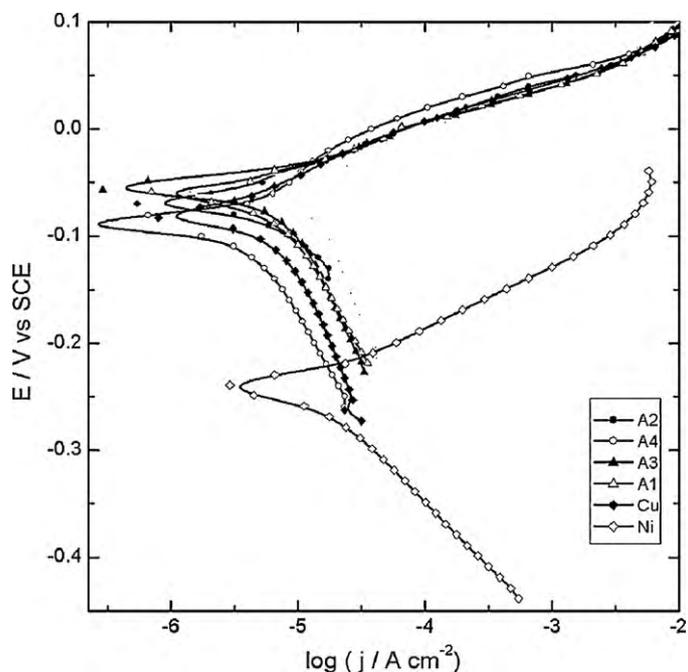

Fig. 1. Voltammograms of pure metals Ni, Cu and copper bearing anodes dissolution in 2 mol dm^{-3} H$_2$SO$_4$, at scan rate of 2 mV s^{-1}.

Fig. 2. Corrosion characteristics of pure metals Ni, Cu and copper bearing anodes in 2 mol dm^{-3} H$_2$SO$_4$, at scan rate of 2 mV s^{-1}.

potentials of Cu and copper bearing anodes were not stable in contrast to Ni, because the section of anode and cathode Tafel lines was not at corrosion potential. Value of Ni corrosion current density was higher than the appropriate values for Cu and copper bearing anodes and corrosion potential of Ni was more than 150 mV negative than corrosion potential of Cu and copper bearing anodes.

Fig. 2 shows that corrosion current density of Cu as well as the appropriate values for copper bearing anodes had very low values of about 6 mA cm^{-2}, while Ni corrosion current density value was about 12.5 mA cm^{-2}.

Values of the anode Tafel slopes of all analyzed materials were quite stable. For pure copper and copper bearing anodes, the obtained values were about 40 mV dec^{-1}. Value of the anode Tafel slope, measured using Ni is 60 mV dec^{-1}. Although the value of standard Ni potential is at $E^{\ominus}$ (Ni^{2+}|Ni) = −0.250 V, the standard

Table 2
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

potential of oxide formation was $E^{\ominus}$ (NiO|Ni) = +0.110 V. Therefore, Ni passes rapidly into the pre-passivation region during determination the anode polarization curves in acid solutions, consequently, the linear dependence E–logj_a was obtained only in a narrow region of current densities (Fig. 2). Kinetics of anode dissolution of Ni can be explained by several dissolution mechanisms [12]. The Tafel slope of anode dissolution of nickel in acid solutions, at stationary measurements, was $b = dE/d(\log j_a) = 40$ mV dec^{-1} and, in this paper at non-stationary measurements, the obtained value was $dE/d(\log j_a) = 60$ mV dec^{-1}.

Values of the cathode Tafel slopes of Cu and copper bearing anodes were very disseminated, ranged from 90 to 260 mV dec^{-1}, as a result of high overstrain of hydrogen escape. Value of the cathode Tafel slope, measured on Ni is 120 mV dec^{-1}.

3.4. The effect of working electrolyte temperature on mass change the copper bearing anodes

Electrolytic refining process was performed at constant current density of 250 mA cm^{-2}, at two different electrolyte temperatures $T_1 = 63 \pm 2$ °C and $T_2 = 73 \pm 2$ °C during 72 h. Anode masses were measured at the beginning and at the end of refining process. Starting copper bearing anodes had weigh of about 7.00 kg, and total mass loss after refining process, ranged from 18 to 33 mass%. Dissolution of anode material resulted in change of working electrolyte chemical composition, formation of anode slime and cathode deposit. As it was expected, dissolution of the copper bearing anodes was more intensive at higher temperatures as a result of metal solubility increase.

3.5. Change of electrolyte chemical composition

In all experiments of refining copper bearing anodes, the real sulphur acidic waste solution was used as starting electrolyte. Chemical composition of this solution is presented in Table 2.

Table 3
Changes in chemical composition of working electrolyte after 72 h of electrolysis process at different temperatures.

Anode	Cu, mass% compared to the value in starting electrolyte		Ni, mass% compared to the value in starting electrolyte	
	$T_1 = 63 \pm 2$ °C	$T_2 = 73 \pm 2$ °C	$T_1 = 63 \pm 2$ °C	$T_2 = 73 \pm 2$ °C
A$_1$	10.00	3.33	187.80	195.12
A$_2$	13.33	6.67	200.00	209.76
A$_3$	8.33	8.33	178.05	180.49
A$_4$	5.00	6.67	202.44	219.51

Anode	Sn, mass% compared to the value in starting electrolyte		Sb, mass% compared to the value in starting electrolyte	
	$T_1 = 63 \pm 2$ °C	$T_2 = 73 \pm 2$ °C	$T_1 = 63 \pm 2$ °C	$T_2 = 73 \pm 2$ °C
A$_1$	3600	3650	10	7.14
A$_2$	4350	4500	25	28.57
A$_3$	8850	9000	12.5	14.29
A$_4$	2400	2450	18	21.43

Anode	As, mass% compared to the value in starting electrolyte		SO$_4{}^{2-}$, mass% compared to the value in starting electrolyte	
	$T_1 = 63 \pm 2$ °C	$T_2 = 73 \pm 2$ °C	$T_1 = 63 \pm 2$ °C	$T_2 = 73 \pm 2$ °C
A$_1$	10	7.5	80	88.89
A$_2$	35	37.5	86.67	77.78
A$_3$	35	37.5	86.67	75.56
A$_4$	45	50	91.11	71.11

Table 4

Mass percentages of anode slime in relation to the mass of dissolved anode, obtained at the end of electrorefining process ($T_1 = 63 \pm 2\,°C$ and $T_2 = 73 \pm 2\,°C$).

Anode	A1	A2	A3	A4
Working electrolyte temperature, °C			$T_1 = 63 \pm 2$	
Slime from anode, mass%	0.55	0.59	0.73	0.28
Slime from the bottom of the cell, mass%	3.99	10.95	11.95	2.46
Total, mass%	4.54	11.54	12.67	2.74
Working electrolyte temperature, °C			$T_2 = 73 \pm 2$	
Slime from anode, mass%	0.52	1.30	1.78	0.26
Slime from the bottom of the cell, mass%	1.29	3.58	5.26	2.35
Total, mass%	1.82	4.88	7.04	2.61

Changes in chemical composition of electrolyte were observed at different electrolyte temperature ($T_1 = 63 \pm 2\,°C$ and $T_2 = 73 \pm 2\,°C$) during 72 h, and the obtained results that were compared with the starting values for the characteristic elements, are given in Table 3.

As it could be seen in Table 3, using the all copper bearing anodes during the electrolysis process, Cu concentration in electrolyte was decreased at the end of the process. Comparing the values for Cu in mass% (Table 3) at two different temperatures, it was observed that Cu concentration in working electrolyte is always higher at lower temperature; while the concentration of all other components is always lower at the same temperature. At the end of A4 anode refining process, conducted at $T_1 = 63 \pm 2\,°C$, the lowest Cu concentration, of 5 mass% compared to starting value is obtained. The lowest realized value of copper concentration of 3.33 mass%, was registered at the end of A1 anode refining process, at temperature $T_2 = 73 \pm 2\,°C$. The Pb content of the A1 and A4 anodes was the same, while Sn and Sb content of A1 anode was twice higher than the same elements content of A4 anode.

During the conventional refining process, aiming to obtain the cathode copper according to the requirements of BS 6017 Standard for placement on the LME, the Cu concentration in electrolyte increased over time. These experiments, where the copper bearing anodes of non-standard chemical composition were used for the refining process, aiming to the copper recovery from the anode and the sulphur acidic waste solution, as well as Ni concentrated into the working solution, showed that Cu concentration in working solution was decreased at the end of the process.

By refining of A1 anode, with the same Pb content as of A4 anode and the lowest total amount of Sn and Sb, the lowest value of Cu concentration in the electrolyte after the 72 h process duration, was obtained. These values of Cu concentration in working electrolyte could not be observed separately, but regarding to the obtained changes of the other elements concentration in the working electrolyte.

During the process of electrolytic dissolution of copper bearing anodes, Cu and the other metals dissolve at the anode and enter the electrolyte. In all realized experiments (Table 3), the higher value of Ni concentration was obtained in process conducted at higher electrolyte temperature. The highest value of Ni concentration in working electrolyte after process ending has been obtained during A1 anode refining. Comparing to starting value, the maximum increase of Ni concentration at $T_1 = 63 \pm 2\,°C$ was about 102 mass%, nevertheless at electrolyte temperature of $T_2 = 73 \pm 2\,°C$ this value was about 122 mass%, after 72 h of the process duration. The highest increase of Sn concentration in working electrolyte was obtained during the refining process of A3 anode that contains the highest total content of ingredients (Pb + Sn + Sb), whereas the lowest increase was realized during refining of A4 anode with the lowest content of Sn and other ingredients. The change of Pb concentration is not discussed, because Pb formed insoluble salt $PbSO_4$ immediately after its dissolution and become part of the anode slime.

The decreasing in SO_4^{2-} ion concentration occurred due to formation of low soluble sulphate salts. This is supported by decrease in concentration of some elements in working electrolyte.

In Table 3 is presents that using the all copper bearing anodes Sb content after 72 h of process duration is decreased, to minimum value of approximately 7 mass% compared to the starting value, at temperature $T_2 = 73 \pm 2\,°C$. As concentration is decreased in all experiments regarding to the starting value and the high-

Table 5

Chemical analysis of anode slime after 72 h of electrolytic process at different temperatures.

Anode	Cu, mass% in anode slime		Ni, mass% in anode slime	
	$T_1 = 63 \pm 2\,°C$	$T_2 = 73 \pm 2\,°C$	$T_1 = 63 \pm 2\,°C$	$T_2 = 73 \pm 2\,°C$
A_1	34.6	9.1	3.5	3
A_2	32.6	10.9	3.6	3.5
A_3	18.5	3.7	3.8	2.5
A_4	52.6	7.7	0.5	1.4

Anode	Pb, mass% in anode slime		Sb, mass% in anode slime	
	$T_1 = 63 \pm 2\,°C$	$T_2 = 73 \pm 2\,°C$	$T_1 = 63 \pm 2\,°C$	$T_2 = 73 \pm 2\,°C$
A_1	7.2	10.4	4.6	12.5
A_2	4.5	7.4	5.6	9.6
A_3	14.1	22.1	5	12.3
A_4	4.6	9.8	5.3	11.3

Anode	Sn, mass% in anode slime		As, mass% in anode slime	
	$T_1 = 63 \pm 2\,°C$	$T_2 = 73 \pm 2\,°C$	$T_1 = 63 \pm 2\,°C$	$T_2 = 73 \pm 2\,°C$
A_1	4.7	14.7	5.3	13.2
A_2	5.5	13	6.5	11.3
A_3	4.8	11.9	5.7	11.3
A_4	7.1	16	5.1	8

est decrease is obtained using the copper bearing anodes with the highest Sb content and the lowest Pb content (A1 anode). Decrease of Sb and As concentration in working electrolyte was a result of $2As_2O_5 \cdot 3Sb_2O_3$ complex type formatting. The quantity and form of this complex are in a function of electrolyte working temperature.

3.6. Chemical composition of the anode slime

After the ending of electrolytic refining process of A1, A2, A3 and A4 anodes, a part of anode slime was present on the anode surfaces, at the bottom of electrolytic cell and in a form of the "floating slime". The percentage of anode slime in relation to the mass of dissolved copper bearing anodes was calculated, and the results are present in Table 4.

In Table 4 shows that the highest value of anode slime mass percent was obtained using the A3 anode with the highest quantity of ingredients, whereas the lowest mass percent of anode slime was obtained using the A4 anode, with the lowest quantity of ingredients.

Chemical analysis of the anode slime after 72 h of electrorefining (total sample was prepared of slime from anode surface, bottom of the electrolytic cell and the "floating slime") was done using the ICP method. The results are shown in Table 5.

High copper content in some anode slime samples is the result of copper powder occurring due to oxygen presence in anodes, as well as elementary copper that fell off from cathode surface during the process. Oxygen is present in anodes in a form of copper(I) oxide, Cu_2O which dissolves into electrolyte according to the reaction:

$$Cu_2O + H_2SO_4 \rightarrow CuSO_4 + H_2O + Cu$$

The formed copper powder was incorporated in the anode slime as the result of reaction $Cu \rightarrow Cu^{2+} + 2e^-$ that is slower than reaction $Cu \rightarrow Cu^+ + e^-$. Therefore, the excess of Cu^+ ions is formed interfacial on the anode surface, whose ions are in accordance with the equilibrium equation later separated into Cu^{2+} ion and elementary copper.

Reduction of copper concentration in the electrolyte during 72 h of refining up to 95 mass% in relation to the starting concentration (Table 2), that was observed in all experiments, is the result of occurrence the un-compact cathode deposit. With the Cu concentration decreased, the limiting diffusion current density of copper deposition decreased as well as the copper powder (un-compact cathode deposit) which was disposed to self-shaking occurrence. Significantly low Cu content in anode slime was observed at higher working electrolyte temperature. Limit diffusion current density is temperature dependent and this value is much higher at higher temperatures. Therefore, more compact cathode deposit and less copper powder was obtained at higher temperatures.

Ni content in anode slime was almost constant as the result of incomplete rinsing of the anode slime in which Ni remained in a form of dissolved nickel sulphate salt.

Values of chemical Pb content in copper bearing anodes were identical to the values of chemical Pb content in the anode slime. Lead, dissolved at the anode, immediately reacted with sulphate ions thus forming the insoluble salt, lead sulphate.

Content of Sb and Sn was almost constant at both temperatures, although their content is double higher at higher temperature. The lowest Sn content was in A4 anode, whereas its concentration was the lowest in the electrolyte, and highest in the anode slime (this is applied to both working temperatures). During the electrolysis process, Sn ions could be oxidized to Sn^{4+} ion, which afterwards precipitates as the stannic hydroxide, remaining in the anode slime.

Using the A1 anode, with the highest Sb content, the lowest As concentration was observed in working electrolyte at the end of process as a result of formation of complex $2As_2O_5 \cdot 3Sb_2O_3$, witch
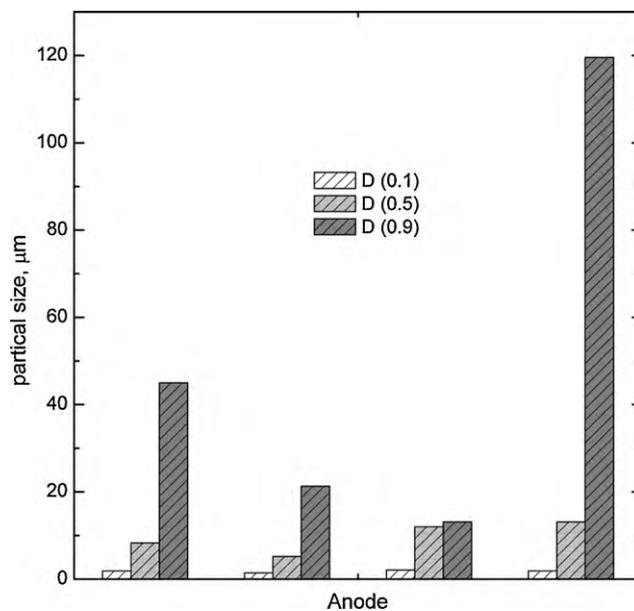

Fig. 3. Particle-size distribution of anode slime obtained at higher electrolyte temperature ($T_2 = 73 \pm 2\,^\circ C$).

solubility degree is a temperature function. Complex of this type have the ability to transfer from soluble into fine dispersive solid state, "floating slime". Using the A1, A2 and A3 anodes with almost similar Sb content of about 0.9%, almost the same values of As content were obtained in anode slime. A4 anode containing the lowest Sb content, had the lowest As content in anode slime, and the highest As concentration in working electrolyte. This phenomenon was observed at both temperatures, although As content in the slime was higher at higher temperatures.

Analyzing of anode slime chemical composition has pointed out that the anode slime composition depends on anodes composition, electrorefining conditions, as well as that it follows the changes of working electrolyte composition during the process.

3.7. Anode slime particle-size distribution

Anode slime formed during the electrorefining process, included the particles of various configuration, size and chemical composition. Particle-size distribution of anode slime obtained at higher electrolyte temperature ($T_2 = 73 \pm 2\,^\circ C$) is present in Fig. 3.

High values of anode slime particle diameter were the result of presence of the elementary copper self-shaking from the cathode surface during the electrorefining process.

The lowest value of the anode slime particle size, Fig. 3, was obtained using the A3 anode, which contains the highest ingredients content (Table 1). The highest value of copper concentration in working electrolyte at the end of refining process (Table 3) was obtained using A3 anode. Also, the limiting diffusion current density of Cu deposition was higher than, as well as the copper content in anode slime had the lowest value (Table 5).

Mass proportion of single fractions, obtained using A3 anode at $T_2 = 73 \pm 2\,^\circ C$:

1.	Fraction + 106 μm:	7 mass%
2.	Fraction + 75 μm:	2 mass%
3.	Fraction + 38 μm:	1 mass%
4.	Fraction + 20 μm:	2 mass%
5.	Fraction − 20 μm:	88 mass%

The value of apparent density was $0.414\,g\,cm^{-3}$. Average values of the anode slime particle sizes, obtained during the electrorefining process at $T_2 = 73 \pm 2\,^\circ C$, were lower than the values obtained in the refining process at $T_1 = 63 \pm 2\,^\circ C$, what could be explain by
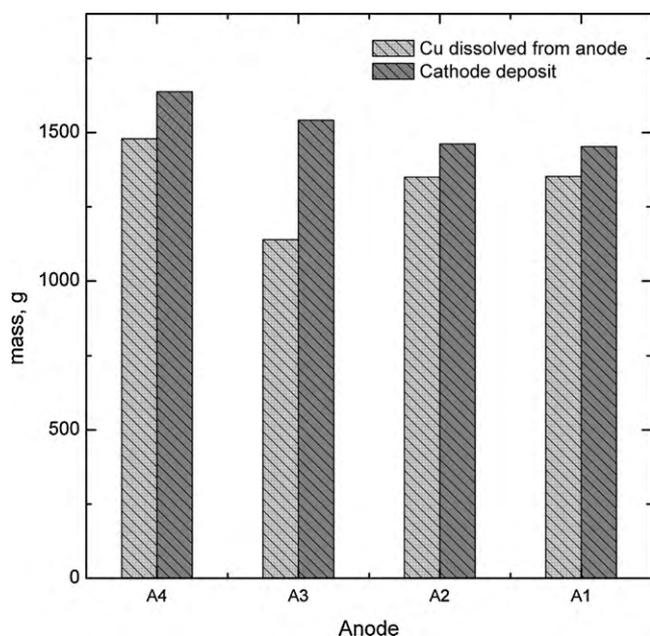
Fig. 4. Copper mass dissolved from anode ratio to cathode deposit, $T_1 = 63 \pm 2\,°C$.

a phenomenon that at higher temperatures and equal copper concentrations in working electrolyte, region of limit diffusion current density of copper deposit, was reached later.

3.8. Dissolution of anode material during the constant galvanostatic pulse

During the process of constant galvanostatic pulse, by observing the changes in chemical composition of electrolytes, using the chemical analysis of anode slime and chemical analysis of obtained cathode deposit, it was pointed out that all chemical elements from copper anodes dissolved while only Cu is deposited on the cathode.

All standard potential values of elements in copper bearing anodes were more negative than the standard potential of the basic, most present elements that is copper. Considering thermodynam-
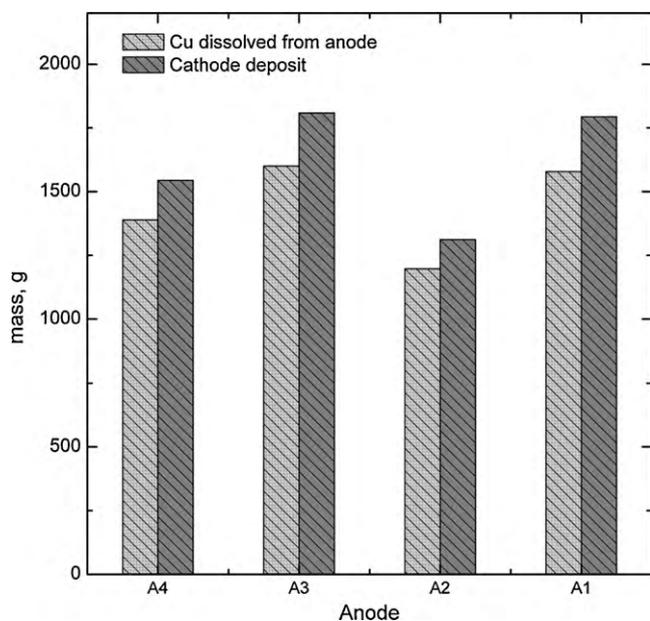

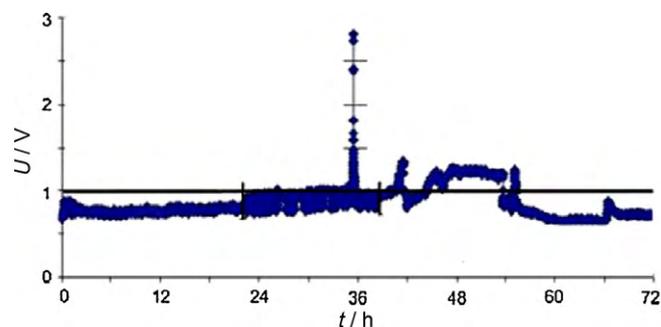Fig. 5. Copper mass dissolved from anode ratio to cathode deposit, $T_2 = 73 \pm 2\,°C$.

Fig. 6. Cell voltage changes during the electrolysis process for A2 anode, $T_1 = 63 \pm 2\,°C$.

ically aspect, copper and all elements in the anode either dissolve into the electrolyte. After the end of electrorefining process, a part of anode slime was present on anode surface. After slime rinsing from the anode surface, small holes indicating dissolution of material were distinguished. It means that some parts of anode were dissolved more actively, while the other parts were blocked by passivation, but total anode surface was active during the whole electrorefining process.

Ni concentration in the electrolyte constantly increased, while there were no Pb ions. As copper bearing anodes dissolved during the electrorefining, Pb in the copper matrix also dissolved, entering the electrolyte and instantly forming the low soluble salt, $PbSO_4$, which become part of the anode slime. Although, the constant increase of Sn ions in the working electrolyte was obtained, a part of Sn was present in the anode slime as well, because it could oxidize into unstable Sn^{4+} form, which can afterwards hydrolyze into Sn(IV) hydroxide. It is a gel-like form of the compound that remains into anode slime. After dissolving, Sb ions could also form the low soluble antimony–arsenate compounds, such as $Sb_2(SO_4)_3$, $SbAsO_4$, etc. and become a part of anode slime. These compounds would partly adhere on the anode surface and make difficulties during electrolysis and in the processing of anode slime, and partly fall on the electrolytic cell bottom.

3.9. Mass ratio of dissolved copper from anode and cathode deposit

The experimental results, where the copper mass dissolved from anode was compared with the mass of cathode deposit at $T_1 = 63 \pm 2\,°C$ are present in Fig. 4, and the suitable results obtained at $T_2 = 73 \pm 2\,°C$ are present in Fig. 5.

The mass of the cathode deposit was higher than the copper mass dissolved at the anode for the both analyzed temperatures (Figs. 4 and 5). This difference was higher when copper that become a part of anode slime by the self-shaking from cathode surface during the electrolysis process, was added to the mass of cathode deposit. The increased Cu mass percentage in cathode, regarding to the starting Cu content in anode, could be explained by the insight into the results from Table 3, Cu concentration in working electrolyte at the end of the electrolysis process (Table 3) was lower than Cu concentration in starting electrolyte (Table 1). It means, that complete amount of Cu dissolved at the anode as well as the complete Cu amount from starting working electrolyte was spent for obtaining the cathode copper.

Cathode deposit was partly in a compact form, and partly in a form of powder. The form of deposit depends on technological parameters and the highest effect has the limit diffusion current density of copper deposition that is the function of concentration the copper ions in working electrolyte and electrolyte temperature. Chemical analyses of compact cathode deposit, obtained by refining the A1, A2, A3 and A4 anodes, has pointed out that Cu content was

Table 6
Characteristic cell voltage changes during the electrolysis process at different electrolyte temperatures.

	Copper bearing anode			
	A1	A2	A3	A4
$T_1 = 63 \pm 2\,°C$				
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
Anode potential, V	0.212	0.55	0.165	0.567
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
Anode potential (max), V	0.358	0.777	0.217	0.618
The first occurrence of full passivation				
Time, h	27:03	35:30	28:25	No
Cell voltage, V	2.457	2.809	2.189	No
Anode potential, V	0.768	2.592	1.887	No
$T_2 = 73 \pm 2\,°C$				
The end of stable and the beginning of oscillation phase				
Time, h	32:36	No	35:58	35:36
Cell voltage, V	0.406	No	0.348	0.346
Anode potential, V	0.133	No	0.175	0.159
The end of oscillation phase				
Time, h	39:16	No	59:13	50:18
Cell voltage (max), V	0.53	No	0.487	0.509
Anode potential (max), V	0.221	No	0.192	0.184

minimum 99.92 mass% in all samples, and Ni, Sb, As, Pb and Sn content was under the detection limit of the ICP method for each element separately.

3.10. Cell voltage and anode potential

During the electrolysis process of copper bearing anodes with non-standard chemical composition, the value of cell voltage was measured (Fig. 6).

Several characteristic changes of cell voltage were marked in Fig. 5. The cell voltage was measured at every 10 s. Assuming that the required time period to establish the electrolysis process is about 6 h, the period when the cell voltage oscillates no more than 0.2 V is called the stable phase, whereas the oscillation phase is the period when the change is higher than 0.2 V. If the cell voltage change occurs suddenly during the electrolysis process, the peaks appeared in a diagram (Fig. 6), could be explained as the anode passivation peaks. All characteristic cell voltage changes are explained in Table 6.

The data from Table 6, as well as from Fig. 6, present that the usage of A1, A2 and A3 copper bearing anodes resulted in occurrence of full passivation in a very short time period of only few seconds, at $T_1 = 63 \pm 2\,°C$, whereas there was no passivation on A4 anode.

Generally, total passivation did mot occur at higher temperatures. The values for the cell voltage and anode potential, during the electrolysis process, slightly increased at both electrolyte temperatures. The time period of anode passivation was very short, a few seconds, nevertheless it did not enable full dissolution of copper anodes, Fig. 6. At higher temperature, this occurrence was not observed.

Many factors have effect on anode passivation: anode chemical composition, working electrolyte chemical composition, electrolyte temperature, current density, electrolytes mixing, etc. Since every anode was prepared with the increased Ni content (7.5 mass%) and increased Pb, Sn and Sb contents (maximum 3%), the anode passivation occurred due to the formation of low soluble compounds such as: $Sb_2(SO_4)_3$, $SbAsO_4$, etc. The compounds adhered to the surface of anode, causing its passivation. It should be pointed out that passivation was disturbed by breaking the adhesive layer from the anode surface whereas the process of electrorefining of anodes continued.

4. Conclusions

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 bearing anodes were prepared with increased Ni content of approximately 7.5 mass%, and the alloying elements, Pb, Sn and Sb (total content was up to 3 mass%) were added for prevention the passivation of copper bearing anode in working electrolyte, and they dissolve simultaneously with As from electrolyte, forming the unsoluble slime.

It was confirmed that using the copper bearing anodes with non-standard chemical composition on electrochemical treatment the real waste solution was possible, what is confirmed with active dissolution of anodes during the tests. It was also observed that it was possible to use current densities ($>250\,mA\,cm^{-2}$) grater than those used for conventional refining process. Copper concentration in the solution was decreased (more than 96 mass% at $T_2 = 73 \pm 2\,°C$) and cathode copper, suitable to the market requirements, was obtained. The concentration of As ion was significantly decreased in the solution (more than 92 mass%), and Ni concentration was increased (about 122 mass%), so Ni could be recovered using the appropriate chemical or electrochemical process from the waste solution. On the other hand, the quality of the final product, cathodic copper, was satisfactory, therefore economically justified.

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