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REMOVAL OF As FROM THE SULPHUR ACIDIC WASTE SOLUTION OBTAINED IN THE ELECTROLYTIC COPPER REFINING PROCESS

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ABSTRACT
The aim of this paper was to examine the possibility of electrolytic treatment of the sulphur acidic waste solution with high content of copper, nickel and arsenic. This waste solution is product of the conventional electrolytic copper refining process.
The copper bearing anodes with non-standard content of nickel, lead, tin and antimony were specially prepared for the refining process. During the process, the change of electrolyte chemical composition as so as the content of copper, arsen, antimony and tin in anode slime, was monitored for the different electrolyte temperatures, T_1= 63±2 °C and T_2= 73±2 °C.
The results are shown that by using the anode with the highest content of tin and antimony, the concentration of As in solution is significantly reduced, more than 92 wt. %.
Key words: electrorefining, waste solution, As

1. INTRODUCTION

The commercial anodes with copper content from 98.0 to 99.5 wt. % and the sulphate-acidic 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, 2].

The process is developed under the force of an applied direct current such as Cu ion dissolves at the anode and then deposit onto the cathode.

Except the copper as the base metal, 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.

Chemical and electrochemical properties of selected alloying elements were not such to significantly reduce the solybility of anode material in order to reduce or prevent the formation of Ni oxide, which causes anode passivation and to remove As from the working electrolyte.

2. EXPERIMENTAL

Copper bearing anodes, used in the process of electrorefining, were prepared from pure metal components. In all anodes, nickel content was approximately 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 is a difference up to 100 wt %.

Induction furnace (Balzers), power of 15 kW and a graphite crucible 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 ^{o}C, only when the oxygen content was under 200 ppm.

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

During the electrolysis process, values of the following parameters were measured: the direct current (A), cell voltage (V), anode potential (V) and electrolyte temperature (^{o}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 and reference electrode was made of electrolutic copper.

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). The MALVERN - particle size analyzer was used for the particle size analysis.

3. RESULTS AND DISCUSION

Table 1. Chemical composition of copper bearing 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

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

In Tab. 3 is shown that the highest value of anode slime wt. 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.

Table 3. Chemical analysis of the anode slime after 72 h on diferent electrolyte temperature

anode	Cu wt. % in anode slime		Ni wt. % in anode slime	
	T_1 = 63± 2 ^{o}C	T_2 = 73± 2 ^{o}C	T_1 = 63± 2 ^{o}C	T_2 = 73± 2 ^{o}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 wt. % in anode slime		Sb wt. % 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 wt. % in anode slime		As wt. % 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

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. 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 has been obtained at higher temperatures.

Ni content in anode slime is 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 are identical to the values of chemical Pb content in anode slime. Lead, dissolved at the anode, immediately reacts with sulphate ions thus forming the insoluble salt, lead sulphate.

Content of Sb and Sn is almost constant at both temperatures, although their content is double higher at higher temperature. The lowest Sn content is in A4 anode, whereas its concentration is the lowest in electrolyte, and highest in 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, which remains 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 the result of formation the complex $2As_2O_5 \cdot 3Sb_2O_3$,witch 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, has the lowest As content in anode slime, and the highest As concentration in working electrolyte.

The lowest value of anode slime particle size was obtained using the A3 anode, which contains the highest ingredients content.

Mass proportion of single fractions, obtained using A3 anode at T_2=73 ±2 °C:

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

The value of apparent density is 0.414 g cm^{-3}. Average values of the anode slime particle sizes, obtained during the electrorefining process at T_2=73 ±2 °C, are lower than values obtained in refining process at lower temperature.

4. CONCLUSIONS

Treatment of waste sulphur acidic solution, obtained in the process of conventional copper refining process, with increased concentrations of Ni and As, was the aim of these investigations.

Therefore, the copper bearing anodes were prepared with increased Ni content and the alloying elements, Pb, Sn and Sb were added for prevention the passivation of copper bearing anode in working electrolyte, and they reacted simultaneously with As from electrolyte, forming the unsoluble slime.

It was confirmed that using the copper bearing anodes with non-standard chemical composition 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.

The importance of this work is in a fact that the use of copper bearing anodes of non-standard chemical composition for treatment the waste solutions from conventional copper refining is ecologically justified and economically recognizable.

5. REFERENCES

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