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DECOPPERIZATION PROCESS OF WASTE SOLUTIONS FROM CONVENTIONAL COPPER ELECTROLYSIS

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ABSTRACT

This paper is adresses on treatment of sulphuric acid waste solutions obtained during the conventional copper metallurgical activities. Mother liquor is a part of this solutions and it is generated during the regeneration process of copper bleed solution. Copper, nickel and sulphuric acid are the main components and the other registered impurities are: As, Se, Fe, Sb, Zn, Bi, Pb, Cl ions. Aim to copper removing from the mother liquor, the decopperization process on the industrial scale equipment, is investigated. Investigation was done using the rectangular insoluble lead anodes alloyed with 6 wt.% of antimony at current value of 13 000 A, identical to the current in a commercial copper refinery plant. A few parameters as so as: current, cell voltage, electrolyte temperature, electrolyte flow rate, level of electrolyte, were monitored during the test. Comparing the values of copper content in the solution before and after the decopperization of copper, it was found that it decreased of about 80 wt. % of the initial value. Chemical characterization of the sludge obtained on cathode has shown that it is a material with copper content of about 90 wt. %..

1. INTRODUCTION

Practically, all human societies depend on the availability and possibility to use the various natural resources. Extraction of copper minerals that is primarily based on mining and metallurgy, in order to obtain the basic and precious metal has a long history in the territory of Western Balkan (1). Also, the fact that thanks to the quantities of confirmed mining reserves of 700 million tons, as so as the reserves of Au and other precious metals, the mining and metallurgical activities at this site could be expected in the future.

A series of copper mining and metallurgical activities begins with mining of copper bearing ore and ends with the production of cathode copper, causes the serious environmental pollutions in this area such as contamination of soil, groundwater and local waterways, the Danube River, air. Mother liquor is a part of the waste solution from the conventional copper electrolysis that is generated during the regeneration process of copper bleed solutions. Copper concentration limit in the mother liquor was in range of values from 9 to 22 g dm^{-3} and H_2SO_4 in range from 323 to 489 g dm^{-3}.

The main problem related to the processing of waste solution is to find the appropriate technology that will be applied before the release of solutions in local waterways. In recent years, the alternative to chemical precipitation process is the electrochemical and

hydrometallurgical processes. Electrochemical processes of metal removal from waste solutions are the special interest of researchers in the last decade [2-4].
In this work, the mother liquor generated during the regeneration process of copper bleed solutions obtained in the conventional process of copper electrolysis are electrochemically treated using the insoluble anodes. Alloying plates of lead with antimony was used as insoluble anode aimed to increase the hardness of alloy, reduce corrosion, improve conductivity and reduce the anodic polarization, a preventive effect on preventing the formation of PbO [5,6].

2. EXPERIMENTAL PART

2.1.1 Equipment parts

Electrolytic copper decopperization from mother liquor was carried out on the industrial scale plant, located in conventional Tank House, whose parts are:
a) *Collecting tank* - working volume is 8 m^3
b) Electrolytic cell –the number of cells is 4 pieces in two groups and the cell volume with the electrodes is ~ 15 m^3
c) *Commercial tank* - the working volume is about 24 m^3
d) Head tank - working volume is about 0.5 m^3
e) Chemical pump - capacity is 45 m^3/h,
f) Plate heat exchanger
g) Piping system
g) Sludge tank - the maximum working capacity is about 3.83 m^3 and the minimum is approximately 0.34 m^3.

2.1.2. Technological procedure

After the electrodes, cathode sheet from the cathode copper and rolled lead sheet with 6 wt. % Sb as anode, were put in the cells, interracial electrode distance of 100 mm was controlled. Rakes and cranes in the Tank House are used to put in the insoluble anodes in the cells, cell voltage was measured before the cells were connecting with current source with working current of 13000 A and determined the chemical composition of the solution. Mother liquor is transported from collecting tank into commercial tank, by gravitational pipeline system. Supplying of the cells with the solution is above, using pump and distribution systems, and the overrun of solution from the cell was over the overflow box. The circulation of solution was ~ 2.5 cell volume changes per hour. After circulation system stabilization, the cells have been included in the electrical circuit. The technological parameters are controlled during decopperization process, the solution working temperature was 55-60 ^oC, and calculated value for process duration was 400 min. Plate heat exchanger was used for solution heating and piping system was used for mother liquid transport from the collection tank to the commercial tank. Solution volume that was transported is regulated by automatic valve. Decopperized solution is discharged from the cell by opening the electrolyte plug, located at the suitable height from the cell bottom and using return pipeline transported into the commercial tank. Pulp of copper sludge is discharged by opening the slime plug, located on the cell bottom and with pipeline for slime, transported into sludge tank. Analysis of copper and sulfuric acid was performed each hour. The process was stopped at the moment of occurrence the toxic gas - AsH_3, by interrupting the circuit. The working volume

solution of ~ 24 m^3 was circulated for about thirty minutes aim to unification the composition and sampling for chemical analysis. Toxic emissions that occur during the process are high. During the process, the appearance of arsine (AsH_3) was qualitatively examined by 5 % solution of mercuric chloride. Volume of solution was not corrected during the process but only at the end. The water evaporation from the cell surface was about 2 kg $m^{-2}h^{-1}$.

Table 1. Technological parameters of mother liquor decopperization process

Working process characteristics			
First cells group, Ia/b cell		Second cells group, IIa/b cell	
Cathode number	34 pcs.	Cathode number,	31 pcs.
Total cathode surface	53.2 m^2	Total cathode surface	48.5 m^2
Cathode current density	244.36 A m^{-2}	Cathode current density	268.04 A m^{-2}
Anode surface for 35 pcs.	47.88 m^2	Anode surface for 32 pcs.	42.41 m^2
Cell volume with electrodes	3.85 m^3	Cell volume with electrodes	3.86 m^3
Measurement during the decopperization process			
First cells group, Ia/b cell		Second cells group, IIa/b cell	
Average cell voltage, I a cell	2.53 V	Average cell voltage, II a cell	2.66 V
Average cell voltage, I b cell	2.6 V	Average cell voltage, II b cell	2.63 V
Average solution temperature	58 ^oC	Average solution temperature	58.5 ^oC

3. RESULTS AND DISCUSSION

3.1. Electrolytic decopperization of mother liquor

The waste solutions that were collected at the facility for the regeneration of copper electrolyte are:

- water generated in places where the industrial water uses (water pump seal, vacuum pumps refrigeration, washing floors, washing unit, filter washing, overflow of cooling tower)
- water obtained during evaporation – acid condensate
- waste copper electrolyte – mother liquor

Waste copper electrolyte – mother liquor, that remains after the copper sulfate production, is the only from the waste solution with a certain amount of copper, sulfuric acid, and harmful and hazardous substances so that these solutions have to previously purified to quality limits corresponding to the current legislation prior to discharge into the local waterways [7]. Copper concentration limit in the mother liquor was in range of values from 9 to 22 g dm^{-3} and H_2SO_4 in range from 323 to 489 g dm^{-3}. Solution density at the beginning of the process is 1.28 g cm^{-3}. Results of chemical characterization of mother liquor before and after decopperization process are present in Table 2. The results present the average composition of the solution followed by a period of 5 years.

Table 2. Chemical characterization of mother liquor before and after decopperization process

Components	Concentration	
	initial, g dm^{-3}	final, g dm^{-3}
Cu	13.14	2.68
H_2SO_4	432.36	440.09
Ni	3.07	3.36

Fe	0.82	0.65
As	0.8	0.56
Cl^-	0.053	0.084
Zn	0.049	0.044
Sb	0.04	0.039
Te	0.029	0.018
Sn	0.009	0.009
Bi	0.0085	0.0022
Pb	0.0012	0.0012
Se	0.002	0.001

Electrolysis of copper using insoluble anodes could be described as the deposition of copper from the copper electrolyte due to the direct current passage.
During the decopperization process, the following reactions take place on the electrodes:

Cathode: $Cu^{2+} + SO_4^{2-} + 2e = Cu + SO_4^{2-}$ (1)

Anode: $2OH^- = ½\ O_2 + 2H^+ + 2e$ (2)

During the process, oxygen is separated at the anode and the excess hydrogen ions remain in the solution and react with sulfate ions that in the anode space come with the help of direct current, with result in the generation of sulfuric acid. This means, that the separation of each equivalent of copper deposited on the cathode, creating the equivalent of sulfuric acid and releases the equivalent of oxygen at the anode, due to the reaction:

$(Cu^{2+} + SO_4^{2-}) + H_2O = Cu^o + 2H^+ + SO_4^{2-} + ½\ O_2$ (3)

Table 3. Measurements after mother liquor decopperization process

Duration of experiment, h	6.66
Deposit character	Cathode sheet is covered with black slime, which is removable
Cu content in copper sludge, wt. %	91.17
Solution density, g cm^{-3}	1.27
Cathode current efficiency based on the analysis of electrolytes, %	~ 60
Consumption of ampere hours, Ah	346320
The specific power consumption, kWh/tCu	3513

During the decopperization with insoluble anodes (Pb +6 wt. % Sb), copper concentration is constantly decreasing, and H_2SO_4 increases. Copper is deposited to the cathode sheet, all the time in the area of limiting diffusion current deposition. According to this fact, cathode deposit is in a powder form with a possibility of self shaking. Parallel with the reaction of copper deposition, the copper concentration in the working solution decreases and the reaction of hydrogen evolution is carried out [8,9,10,11]. Arsenic from the electrolyte in the presence of hydrogen chemically reacts to form toxic gas arsine (AsH_3). Achieved effects of treatment the mother liquor using insoluble anodes are: reducing of copper concentration is up to level of nickel concentration (12) and production of cathode powder deposit that falls from the cathode surface during the decopperization process on the bottom of the cells.

Physical and chemical characterization of the obtained cathode deposit- sludge is shown in Table 4.

Table 4. Chemical and physical characterization of cathode deposit –sludge

Chemical characterization		Physical characterization	
Element	Content, wt. %	Particle size, μm	Wt. %
Cu	91.17	+250	13.64
Pb	0.31	- 250+75	50.24
As	0.18	- 75+45	16.4
Se	0.15	- 45	18.6
Sb	0.075		
Si	0.031		
Fe	0.019		
Te	0.014	Apparent density, g cm^{-3}	2.46

The results of X-ray analysis showed that the elemental copper and cuprites are present in the sample of copper sludge sample. Duration of decopperization process and limiting copper concentrations in solution were conditioned by the appearance of arsine (AsH_3) at working area. Qualitatively, the presence of arsine was observed from the beginning of the process by reaction with a solution of $HgCl_2$ and by analysis of solution on Cu and H_2SO_4 is controlled the decopperization degree of mother liquor. The decreasing of Cu concentration is resulted in increased hydrogen evolution at the cathode; arsine occurrence was the reason for the process interruption.
Based on data on the initial and final Cu concentration as well as solution working volume, was calculated the decopperization degree of the mother liquor which amounts to 80 wt. %.
Calculation of the cathode current efficiency, which was based on differences of copper concentration in solution, provided the values of about 60 %.
Analysis of copper sludge composition indicates a high copper content and low content of accompanying elements.

4. CONCLUSION

During the process of electrolytic decopperization the mother liquor, the copper sludge with copper content over 90 wt. % was obtained. Based on data on the initial and final Cu concentration, as well as solution working volume, was calculated the decopperization degree of the mother liquor which amounts to 80 wt. %. Calculation of the cathode current efficiency, which was based on differences of copper concentration in solution, provided the values of about 60 %. Copper sludge and decopperized solution could be used for further chemical treatment in the aim to copper and nickel salts production.

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