Study the new technological procedure of copper electrolytic refining using non – standard plate electrodes

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This paper presents a new, improved technological procedure of copper electrolytic refining by using non – standard plate electrodes where the electrodes bottom lines are designed along the ellipse line. The aim of electrolytic refining was to get as more as possible, cathode copper of the high purity and anode slime from which precious metals - gold and silver are obtained by its further processing.Three sets of experimental investigations of electrolytic refining of anode copper were carried out in semi-industrial plant under different conditions. The original results are presented in this paper.

1. Introduction

Electrolytic refining of anode copper, which contains more than 90% copper and ingredients of various non-precious (Bi, Sb, As, Fe, Ni, Pb, Se, Sn, Zn ...) and precious (Au, Ag ...) metals, began to apply in the eighties of the nineteenth century.

Anode copper, obtained by pyrometallurgical processing, of copper concentrates, beside the high content of copper (more than 90%), contains many ingredients of base metals and precious metals (Au, Ag ...), which are accompanying minerals of copper ores. Pure cathode copper and anode slime are obtained using electrolytic refining of anode copper. The anode slime contains precious metals (Au, Ag ...), as well as a part of the base metals contained in copper anode [1].

The process of electrolytic refining of anode copper has been applied since the eighties of the nineteenth century. Various factors affecting the electrolytic refining process, were investigated by the time, all with the aim to increase the efficiency of the process [2, 3]. Based on studying the current distribution in electrochemical cells with plate electrodes, it was concluded that besides the main factors which affect the distribution of current density (electrolytic cell geometry, electrolyte and electrode conductivity, activation ie, the polarization or electrochemical resistance and concentration overvoltage), the shape of electrode has influences on the electrolytic refining process, too

The process of electrolytic copper deposition was investigated and shown in numerous works [4-14]. However the impact of different types of electrodes and additives on the electrolytic refining efficiency is less studied.

This paper presents the original results of experimental investigations of electrolytic refining of anode copper in semi-industrial plant, under different conditions:

1. Standard procedure (operating conditions)
2. Electrolytic refining of copper, with the changed shape and number of cathode, the composition of colloids and the addition of the cathode depolarizer.
3. Electrolytic refining of copper with changed shape of anode,, shape and number of cathode, the composition of colloids and the addition of cathode depolarizer and means for the precipitation of selenium.

Electrolytic refining of anode copper is carried out according to the following electrochemical reactions [4]:

$$Cu^{2+} + 2e^- \leftrightarrow CuO \qquad (1)$$

Process is carried out in three stages in acid sulphate systems [6]:

$$Cu2+ + e^- \leftrightarrow Cu+ \quad (\text{slow process}) \qquad (2)$$

$$Cu+ + e^- \leftrightarrow CuO \text{ (fast process)} \qquad (3)$$

According to the results of experimental work [14] it is confirmed that pseudocapacitance of anode and cathode process depends on the current density and time.

In literature sources it is stated that distribution of current density is determined by the geometry of the system, only [2], Experimental studies of electrolytic refining of anode copper are based on these literature sources.

The growth rate, composition, microstructure and properties of an electrodeposited metal or alloy are mainly determined by the potential and current i.e. current density

distribution at the electrode. It is therefore essential to understand the phenomena that determine potential and current distribution in order to control the characteristics of deposited metal.[15]

Fig. 1 shows primary distribution of current density on electrode for different electrode length and distances between electrodes where symbols are following [2]:

j- current density

jx - current density in certain point

L- electrode lenght
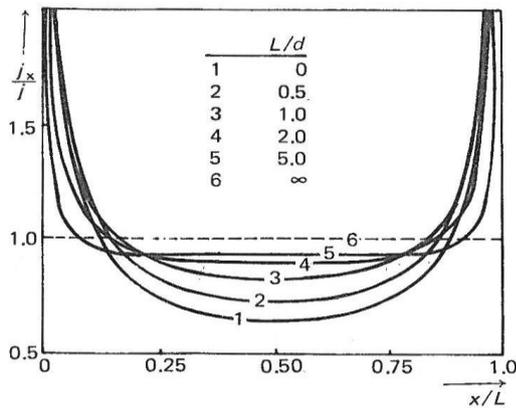
d- distance between electrodes

Fig. 1. Primary distribution of current density at electrode for different electrode length and distances between electrodes.

Fig. 2 shows secondary current density at electrode in reactor with parallel plated electrodes at different rates of length and distance between electrodes. Dimensionless parameter that indicates the degree of inequality of current density distribution is Wagner number Wa. As Wagner number is higher the equality of current density distribution is better [2].
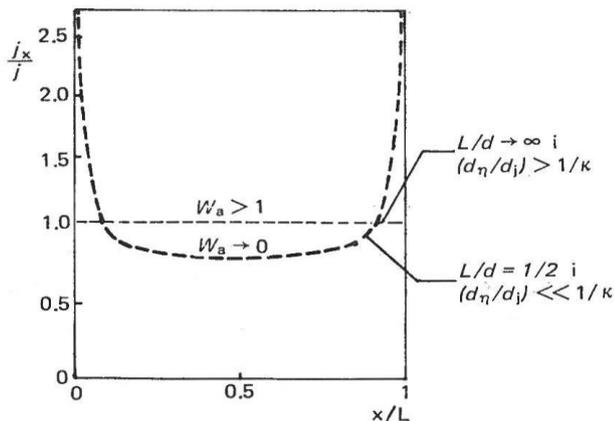

Fig. 2. Secondary current density distribution at electrode for different electrode length and distances.

2. Experimental work

An experimental study of electrolytic refining has been carried out with anode copper taken from the RTB Bor TIR.

Experiments were carried out on semi-industrial plant for electrolytic refining. Fig. 3 shows the pilot plant during the process of electrolytic refining.

Fig. 3. Pilot plant for copper electrolytic refining.

Semi-industrial plant consists of three electrolytic cells, the dispenser, the reservoir for electrolyte circulation (submersible pump is located in it), and the supply of direct current (AC). One ceramic heater for electrolyte heating, was placed in each of the three cells.

Experimental work was carried out in one cell. Electrolytic refining of anode copper was carried out in one cell, the second cell was used only for electrolyte heating (to maintain the temperature of the electrolyte), while the supply of electrolyte, the dispenser in a third cell was closed by a valve (mounted on the pipeline in front of the cell).

Three sets of experimental work of anode copper electrolytic refining were carried out in the above described pilot plant facility under different conditions. The results of experimental work are presented in Table 1.

I experiment- Standard procedure of electrolytic refining of anode copper (industrial conditions)

II experiment- Electrolytic refining of copper with varying form and number of cathodes, the composition of additives and addition of the cathode depolarizer

III experiment- Electrolytic refining of copper with changed shape of anodes, form and number of cathodes, the composition of additives, addition of cathode depolarizer and chemicals for the selenium precipitation.

Fig. 4 a), shows cathode starting sheet and cathode with deposited copper with changed shape where electrodes bottom lines are designed along the ellipse line. Anode, where electrodes bottom lines are designed along the ellipse line is presented in Fig. 4 b).

a)   b)

Fig. 4. a) Cathode starting sheet and cathode with deposited copper - changed shape b) Anode with changed shape.

Table 1. Experimental conditions of work on semi-industrial plant for electrolytic refining of anode coppe.

Number		I experiment	II experiment	III experiment
1.	**Anode**			
1.1.	Shape	Rectangular	Rectangular	Electrode bottom line is designed along the ellipse line
1.2.	Number	3	3	3
1.3.	Total anode mass (kg)	79,7	79,71	72,76
1.4.	Dimensions (m)	0,25×0,37	0,25×0,37	0,15×0,34
2.	**Cathode (starting sheets)**			
2.1.	Shape	Rectangular	Electrode bottom line is designed along the ellipse line	Electrode bottom line is designed along the ellipse line
2.2.	Number	4	8	8
2.3.	Dimensions (m)	0,34×0,4	0,15×0,34	0,15×0,34
2.4.	Total mass of starting sheets			
2.4.1.	I cathode period(kg)	4,14	2,663	2,962
2.4.2.	II cathode period(kg)	3,61	3,286	3,359
3.	**Electrolyte**			
3.1.	C_{Cu}	37-41	37-41	37-41
3.2.	C_{H2SO4}	160-170	160-170	160-170
3.3	C_{Cl^-}	0,025-0,055	0,025-0,055	0,025-0,055
3.4.	Additives	(3g gelatine+3g thiourea)/24 h	(3g gelatine+3g urea)/24 h	(3g gelatine+3g urea)/24 h
3.5.	MnO_2 (depolarizer)	-	1g/8h	1g/8h
3.6..	$K_2S_2O_5$(for selenium precipitation)	-	-	1g/8h
4.	**Current intensity –strenght (cathode current density)**	160 A (210 A/m^2)	140 A (210 A/m^2)	140 A (210 A/m^2)
5.	**Average cell voltage (mV)**			
5.1.	I cathode period (mV)	393,27	362,78	349,2
5.2.	II cathode period (mV)	468,08	450,53	434

Experimental conditions are shown in the Table 1.

3. Results and discussion

All the results of experimental work in the pilot plant for copper refining are shown in Table 2.

Table 2. Experimental results of the work on the pilot plant for copper refining.

Number.		I EXPERIMENT	II EXPERIMENT	III EXPERIMENT
1.	Mass of the cathode deposit (I+II cathode period)	44+19,36=63,9	44,02+25,82=69,84	40,53+23,25=63,78
2.	Retour	14,535 kg (18,24%)	8,64kg (10,84%)[*]	7,436 kg (10,22)[*]
3.	Anode slime mass (kg)	0,2817	0,2913	0,2504
4.	Time of the I cathode period duration	215,33	237	231,15
5.	Time of the II cathode period duration	120	141	145
6.	Energy consumption(kWh/kgCu$_{kat}$)			
	I cathode period	0,3046	0,2729	0,2799
	II cathode period	0,3658	0,3437	0,3453
	Average	0,323	0,2822	0,3039

*Mass of the retour from the II and the III experiment is greater than the actual retour mass due to differences in anode flooding in the electrolyte.

Percentage of the retour at a standard procedure of electrolytic refining of copper (experiment I) is greater than in experiment II and III when process were conducted with electrodes with changed shape (Table 2, item 2)

Dissolution of the anode is carried out from the bottom edge to the upper, during the second and third experiment, while the standard procedure (experiment I) occurs equally around the whole surface.

Changes of the copper concentration during the process of electrolytic refining under deferent conditions of the experimental work are shown by the curves in the Fig. 5. (experiments I, II and III).
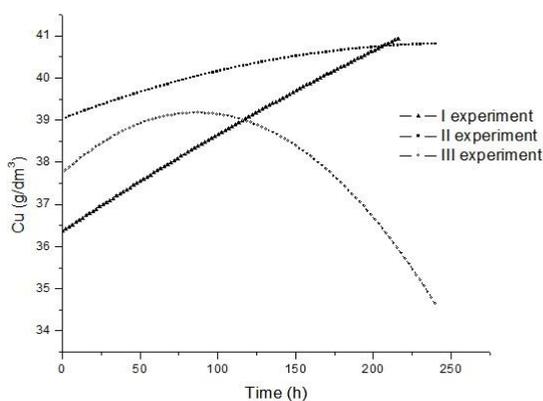
Fig. 5. Changing of the copper concentration in the electrolyte during electrolytic refining under different experimental conditions vs time.

Changes of the sulfuric acid concentration during the process of electrolytic refining under deferent conditions of the experimental work are shown by the curves in the Fig. 6 (experiment I, II and III).
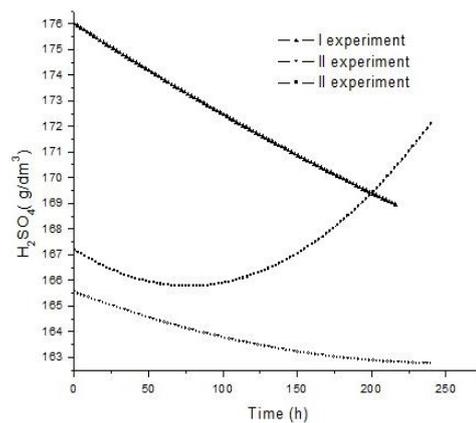
Fig. 6. Changing of the sulfuric acid concentration in the electrolyte during electrolytic refining under different experimental conditions vs time.

Experiments II and III were conducted without the correction of electrolyte. It is because concentration of each component in the electrolyte during the process of copper electrolytic refining, were with allowed limits and slightly varied. Specifically, in experiment I (Fig. 3, curve

I) concentration of copper in the electrolyte has increased with time during electrolytic refining, while the concentration of sulfuric acid decreased (Fig. 5 and 6 - curves I), which is logical (because a part of sulfuric acid reacted with copper forming copper sulfate).

During second experiment – II, (Fig. 5 and 6 - curves II), concentrations of copper and sulfuric acid varied a little, but there was no need to correct the electrolyte.

In the third experiment - III, the concentration of copper and sulfuric acid were nearly constant to the end of the experiment (Figs. 5 and 6 - the curve III).At the end of the experiment, when the most of the anode dissolved, so that the cathode surface were all greater than the anodic area, there was a decrease of copper concentration and increased the concentration of sulfuric acid in the electrolyte (due to an insufficient amount of copper that is dissolved from the anode there to a process of electrolyte decopperization).

Electrical energy consumption per pound of cathode copper is lower than during the standard procedure (Table 2, item 6).

Thickness of cathode deposits vary depending on whether the cathode surface facing the surface of the anode or the opposite.

It is recommended to observe the concentration of manganese in the electrolyte and its impact on the quality of the cathode.

4. Conclusion

The whole study described in this paper represents a new, improved technological procedure of electrolytic refining of anode copper by using plate electrodes with changed shape, where the electrodes bottom lines are designed along the ellipse line.

Percentage of the retour at a standard procedure of electrolytic refining of copper (experiment I) is greater than in experiment II and III (Table 2, item 2)

Dissolution of the anode is carried out from the bottom edge to the upper, during the II and the III experiment, while the standard procedure (experiment I) occurs equally around the whole surface.

Electrical energy consumption per pound of cathode copper is lower than during the standard procedure (Table 2, item 6).

Thickness of cathode deposits vary depending on whether the cathode surface facing the surface of the anode or the opposite.

Appropriate concentration of manganese and its impact in the electrolyte is important for cathode quality.

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