ELECTRODEPOSITION OF COPPER AND PRECIOUS METALS FROM WASTE SULFURIC ACID SOLUTION

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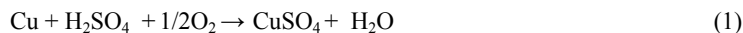**[2] TMF Belgrade, Karnegijeva 4, 11 000 Belgrade, Serbia**

ABSTRACT
The aim of this work was to determine the optimum parameters of electrochemical deposition of Cu, Rh, Pt and Pd from waste sulfur acid solution. These solutions are geting decopperizing anode slime from the electrolytic refining of anode with increased content of PGMs dilute sulfuric acid (5-10%) with the addition of oxidative agents. Experimental laboratory studies were perfomed at different current denstities (135±5, 270±5,405±5 A/m^2) on copper cathodes with insoluble lead anodes. At all current densities achieved are high efficiency of metal (from 99.72 to 99.99%).
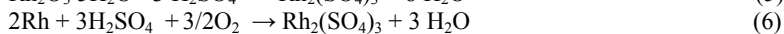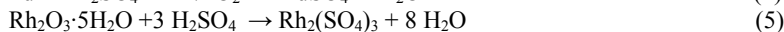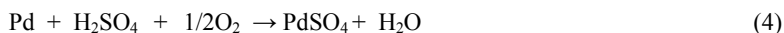**Key words**: *electrolytic deposition, metals, PGMs, insoluble lead anodes*

1. INTRODUCTION

Platinum group metals have become indispensable in many of today´s key technologies: automotive catalysts, chemical and oil refining catalysts, electronics, electroplating, glass manufacturing, dental applications, fuel cells, high fashion jewelry and others [1].
Dissolution of copper is carried out according to the following reactions [2]:

$$Cu + H_2SO_4 + 1/2O_2 \rightarrow CuSO_4 + H_2O \qquad (1)$$
$$Cu + H_2SO_4 \rightarrow CuO + SO_2 + H_2O \qquad (2)$$
$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O \qquad (3)$$

According to the literature data , the platinum metals, generally, are not solvent in deluted sulfuric acid, experimentaly it is possible to a certain low concentration: up to $0.001 g/dm^3$ for Pt, 0.015 g/dm^3 for Pd, while Rh concentration reaches 2 g/dm^3. Dissolution of paladium and rhodium can be described by the following reactions [3,4,5]:

$$Pd + H_2SO_4 + 1/2O_2 \rightarrow PdSO_4 + H_2O \qquad (4)$$
$$Rh_2O_3 \cdot 5H_2O + 3 H_2SO_4 \rightarrow Rh_2(SO_4)_3 + 8 H_2O \qquad (5)$$
$$2Rh + 3H_2SO_4 + 3/2O_2 \rightarrow Rh_2(SO_4)_3 + 3 H_2O \qquad (6)$$

Platinum is slightly soluble only at elevated temperatures [6]:

$$Pt + 2H_2SO_4 + O_2 \rightarrow Pt(SO_4)_2 + 2 H_2O \qquad (7)$$
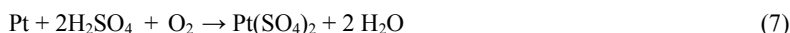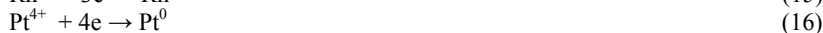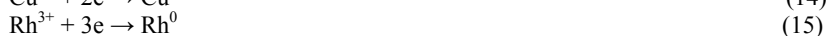
To minimize the loss of platinum metals to less than 1% and carry out regeneration of copper, separation of these metals was accomplished by electrochemical deposition using copper cathode and insoluble lead anode. During the electrodeposition of copper and platinum metals from waste acidic solution from decopperization, the following reactions may occure [6]:

- **processes in solution:**

$$CuSO_4 \rightarrow Cu^{2+} + SO_4^{2-} \qquad\qquad (8)$$
$$Rh_2(SO_4)_3 \rightarrow 2Rh^{3+} + 3SO_4^{2-} \qquad\qquad (9)$$
$$Pt(SO_4)_2 \rightarrow Pt^{4+} + 2SO_4^{2-} \qquad\qquad (10)$$
$$PdSO_4 \rightarrow Pd^{2+} + SO_4^{2-} \qquad\qquad (11)$$
$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-} \qquad\qquad (12)$$
$$H_2O \rightarrow 2H^+ + O^{2-} \qquad\qquad (13)$$

- **at the cathode:**

$$Cu^{2+} + 2e \rightarrow Cu^0 \qquad\qquad (14)$$
$$Rh^{3+} + 3e \rightarrow Rh^0 \qquad\qquad (15)$$
$$Pt^{4+} + 4e \rightarrow Pt^0 \qquad\qquad (16)$$
$$Pd^{2+} + 2e \rightarrow Pd^0 \qquad\qquad (17)$$

- **at the anode:**

$$O^{2-} - 2e \rightarrow \tfrac{1}{2} O_2 \qquad\qquad (18)$$

2. EXPRIMENTAL PART

Electrodeposition experiments were performed in laboratory scaled electrolizer. This apparatus consisted of electrochemical cell, dosing vessel and rezervoar for electrolyte recirculation equipped with submersible pump and heater. A group of six copper cathodes and seven lead anodes, alternatively sorted, was housed in the electrolitic cell. The shape and dimensions of electrodes were identical and amounted 180x170mm, and the total cathode surface area on which metals were deposited, was $0.3672m^2$.

The experiments were performed at three different current densities, while the initial amount and chemical composition of waste solution, working temperature and rate of electrolyte circulation were the same in each experiment run. These parameters are listed below:

- Volume of waste solution: 47.7 dm^3
- Chemical compozition of waste solution (g/dm^3):
  Cu – 36.3564, Rh – 1.3041, Pt – 0.0036, Pd – 0.0111, H_2SO_4 – 78.1504
- Operating temperature: 50 ± 2 °C
- Electrolite circulation: 50 dm^3/h
- Current density and cell voltage for each experiment:
  First experiment: 405 ± 5 (A/m^2); 3 ÷ 3.3 (V)
  Second experiment: 270 ± 5 (A/m^2); 2.6 ÷ 2.9 (V)
  Third experiment: 135 ± 5 (A/m^2); 2.1 ÷ 2.4 (V)

The content of copper in the solution before the electrodeposition was determined by electrogravimetry. Concentration of sulfuric acid was determined by volumetric neutralization method. Content of platinum metals before, during and after the electrodeposition, as well as copper content after electrodeposition, were determined using ICP-AES Inductively coupled plasma atomic emission spectrometer (model Spectro ciris visio).

3. RESULTAT AND DISCUSSION

Based on the obtained data on the concentrations of Cu, Rh, Pt, Pd and H_2SO_4 in the electrolyte, during the experiments done at three different current densities, graphics are designed and shown in Figure 1 a), b), c), d), e).
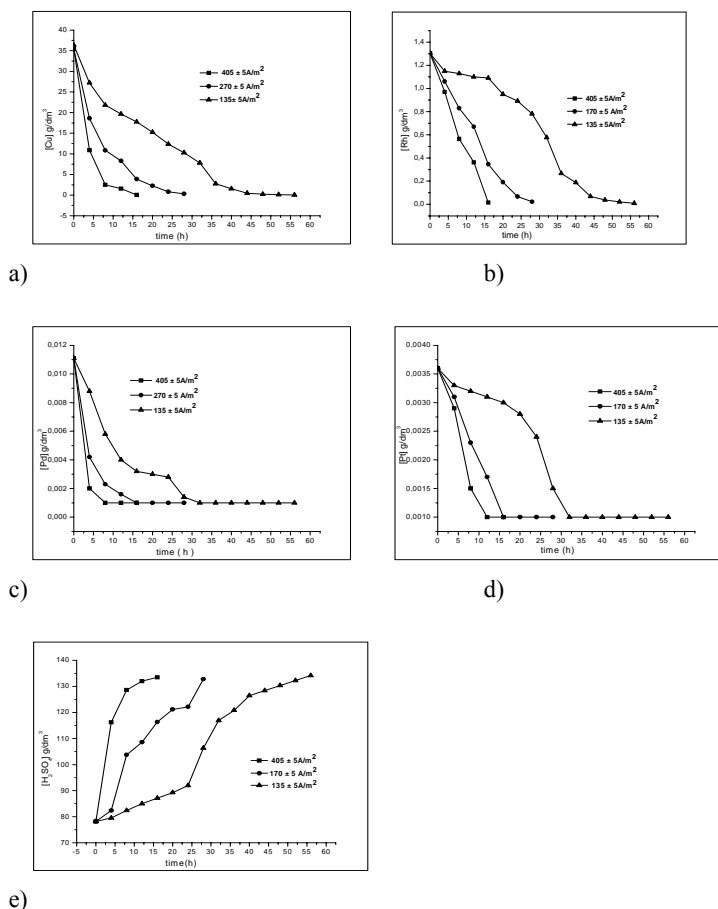
Figure 1. The change in the concentration of a) Cu, b) Rh, c) Pd, d) Pt, e) H_2SO_4 in electrolyte vs duration of cathodic electrodeposition at three current densties: 405 ± 5 A/m^2, 270 ± 5 A/m^2, 135 ± 5 A/m^2.

4. CONCLUSION

Study presented in this paper, confirmed the possibility of platinum metals (Pt, Pd and Rh) and copper separation from waste sulphur-acid solution, by electrochemical deposition on copper cathodes. Thus obtained cathode deposit is returned to the pyro In spite of PGMs low concentration in this solutions (Rh – 1.3041 g/dm^3, Pt – 0.0036 g/dm^3, Pd – 0.0111 g/dm^3), regarding their price and stringent regulations about discharging heavy metals into water courses, these amounts of PGMs are not negligible, particulary at high production in the electrolysis. Due to this fact, electrochemical treatment of these solutions, investigated in this work, is essential as well as cost effective. The results of electrodeposition experiments, done at three different current densities: 405 A/m^2, 270 A/m^2 and 135 A/m^2, indicate that described electrochemical process is most efficient at 405 A/m^2. Under the experimental conditions, achieved metal recovery were in range of 99,72 ÷ 99,99%.

5. ACKNOWLEDGEMENTS

6. LITERATURE

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