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PURIFICATION OF THE METALLURGICAL WASTEWATER FROM COPPER MINING AND SMELTING COMPLEX BOR

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ABSTRACT
This paper addresses on purification of wastewater produced by metallurgical activities in Copper Mining and Smelting Complex Bor (RTB-BOR) by using the combination of electrochemical and neutralization process in order to develop remedial technology for prevention of the regional water resources contamination.
Metallurgical wastewater is mixture of wastewaters from Electrolyte regeneration plant, Copper Refining plant and Precious metals plant and this is waste with high content of copper and sulphuric acid. The content of other impurities in this wastewater is a function of impurities content in each of this waste solution.
Researching of electrochemical process is curried out on semi-industrial apparatus with rectangular undisolved lead anodes. The value of cathode current density was 220 A/m^2. Few parameters like current, cell voltage, electrolyte temperature, electrolyte flow rate, level of electrolyte were monitored during the experiments. The copper content after electrolytic decopperization process of wastewater was 0.69 g/dm^3.In the second step, the wastewater obtained after the electrochemical process was purification with 20 % NaOH.
Obtained results have been given and discussed in the paper. Application of combination of these methods enables the satisfactory results for removing the impurities from metallurgical wastewater and possibility to join to regional water resources.
Keywords: metallurgical wastewater, electrochemical method 2, neutralization method

1. INTRODUCTION

In this paper is presented only one part of much wider research work of solving environmental pollution problems with solid and liquid wastes [1].
The sulphide ores are the most important copper bearing ores that are commercially available. Exploitation of these ore deposits along with metal extraction that follows causes severe environmental pollution problems in the area, related to contamination of soil and surface, groundwater.
The final stage of copper production is purification of blister copper mainly by electrolytic refining that produces copper of 99.95-99.97% purity. During the whole copper production cycle, large amounts of solid, liquid and gaseous wastes are generated. The waste interacts with the local environment resulting in serious impacts on eco-system.
In a case where wastewater contain valuable metals there is also an additional economic interest to recover those metals and recycle them as secondary raw materials in various production routes.
The main problem is finding out the suitable technology for wastewater treatment before discharge. In recent years various electrochemical and hydrometallurgical processes, alternative to chemical precipitation, have been developed. Electrochemical removal of metals from metal-bearing wastewater has been extensively investigated during the last decades [2,3,4]. Electrochemical processes are applied for recovery a wide range of metals from acidic/alkaline wastewater with high

metal concentrations [5,6,7,8,9] and selective metal electro recovery from mixed wastewater [10,11]. The increased interest for electrochemical removal of metals from wastewater and the wastewater variety resulted into development of several electrochemical reactors, with advanced operating design [2,4].
According to this, electrolytical treatment is selected treatment for research wastewater decopperization. Neutralization process with 20% NaOH was used as an additional treatment in the aim of obtaining the water with maximum quantity of dangerous substances classified by certain regulation on water classification.

2. EXPERIMENTAL

The aim of this research was to study the possibility of real metallurgical wastewater purification by combination of electrochemical and neutralization process. The wastewater which was used for the investigation was combination of wastewaters from Electrolytic Refinery Plant. The experiments are conducted in semi-industrial conditions on the apparatus which is specially constructed for the Project INTREAT (Integrated treatment of industrial wastes towards prevention of regional water resources contamination**)** financed by EU.

2.1. Chemical Characterization of Real Metallurgical Wastewater

Total volume of this water is evaluated based on planned copper production of max 50 000 t/year for the next ten year. This value is 1.875 m^3/h; 45 m^3/day ; 14 850 m^3/year.
Chemical composition of real metallurgical wastewater is presented in Table 1, as well as the analytical methods. pH value of this solution was 0.27.

Table1. Chemical composition of real metallurgical wastewater (Copper Electro Refining Plant, Precious Metal Plant and Electrolyte Regeneration Plant.)

Element	Concentration, g/dm^3	Analytical method
Cu	8.33	AAS
Ni	0.66	AAS
As	0.63	AAS
Se	0.26	ICP-AES
Fe	0.086	AAS
Sb	0.075	ICP-AES
Te	0.068	ICP-AES
Al	0.04	ICP-AES
Zn	0.034	AAS
Bi	0.028	ICP-AES
Si	0.022	ICP-AES
Pb	0.0034	AAS
Mn	0.0011	AAS
Cd	0.0001	AAS
H_2SO_4	120.79	T
Cl^-	0.07	TU

The following elements: Cu, Ni, As, Fe, Zn, Pb, Mn and Cd were analysed by the use of Atomic Absorption Spectrophotometer-AAS (Perkin-Elmer – 403), Se, Sb, Te, Al, Bi, Si by the use of Optical Emission Spectrometer with Inductively Copled Plasma-ICP-AES (SPECTRO), H_2SO_4 by the use of standard titration procedure and Cl^- by the use of turbodimetric procedure.

2.2. Apparatus

The apparatus for electrochemical investigations is consists of collection reservoir with electric heater and chemical pump for electrolyte. Material for reservoir is P.P., working volume 20 dm^3 and heater power is 750 W. Electrolytic cell, from P.P. , working volume 20 dm^3 was used for the electrolytic investigations. Supply tank, also from P.P., working volume 5 dm^3 was used for the electrolyte

circulation. For the Ventilation system with hood and pipe system was used to bring out the evaporation products (gas, aerosol). Piping system made of P.P was used for the connection.
This apparatus is related to rectifier with operating electrical current intensity of 400 A and voltage of 15 V.

2.3. Technical-Technological Parameters

The experiment was done on semi-industrial apparatus, located in Copper Institute Bor. Seven cathodes and eight anodes were inserted into the cell with 30 mm interraxial distance between two various electrodes.
Cathode copper plate, produced in Copper Electrolytic Refinery Bor of the following content (ppm): As < 3; Sb < 2; Bi < 1; Fe < 5; Pb < 2; Ni < 1; Si < 9; Ag < 5; Te < 0.1; Sn < 2; Zn < 5; Al < 10; Se < 0.7 and Cu = 99.96 % was used as starting cathode sheets. The total active surface of all cathodes which were immersed into the cell was 0.428 A/m^2. Lead with 6 % of antimony was used as anode material in a form of rectangular plate. Anode dimensions and active surface were equal to cathode dimensions and surface. Electrode organization was anode – cathode – anode.
Value for cathode current density was 220 A/m^2 and this value is due to value in industrial condition in Copper Refining Plant. Working volume of wastewater in a system was 45 dm^3 and a 45 dm^3/h was wastewater flow rate. Wastewater volume was maintained as a constant by addition of industrial water. The wastewater temperature during process was between 40 and 50^oC.
The value for theoretical decopperization process time is calculated relatively to chemical content of copper in wastewater and current value and this value was 3,52 h**.** Copper and sulphuric acid concentrations were determinate at the end of each hour. During process, the appearance of AsH_3 was visually controlled with 5 % $HgCl_2$ water solution. A part of copper plate was submerged into metallurgical wastewater for 24 hours with the aim to test the electrolyte influence on copper plate.
After decopperization process the waste solution is treated by 20 % NaOH up to pH = 9,96. Obtained sludge is washed and dried. The waste solution is analysed on Cu, Ni, As, Pb, Fe, Se, Sb, Te, Zn, Bi, Cd and Mn and results are presented in Table 2. together with the maximum allowed concentration for the various water class (Low of water, 1989, Serbia).

3. REVIEW OF RESULTS AND DISCUSION

Decopperization process was stopped when the Cu concentration value was under the 1 g/dm^3. Total process time was 4,5 h. Cell voltage was continually measured and the value of average voltage on cell was 2.79 V. Value for copper concentration on the end of the process was 0,69 g/dm^3 and sulphuric-acid concentration 134,78 g/dm^3. Current efficiency was calculated in relation with copper concentration in the electrolyte and this value was about 80 %. Cathode sheet was dark grey from beginning of the process and the cathode deposit was in a powder form. Yellow colour of filter paper with water solution of 5 % $HgCl_2$ was proof to AsH_3 appearance. Surface of copper plate, submerged into metallurgical wastewater for 24 hours was covered with black slime after starting moment.
Copper, tellurium and selenium were basic component in this slime. Behaviour of some elements during the deccoperization process is presented on Figure 1. and 2.

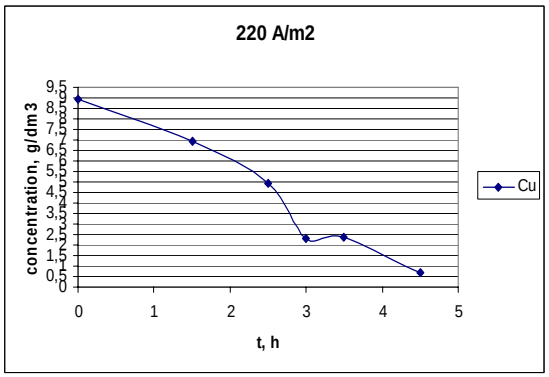

Figure 1. Cu concentration during the process

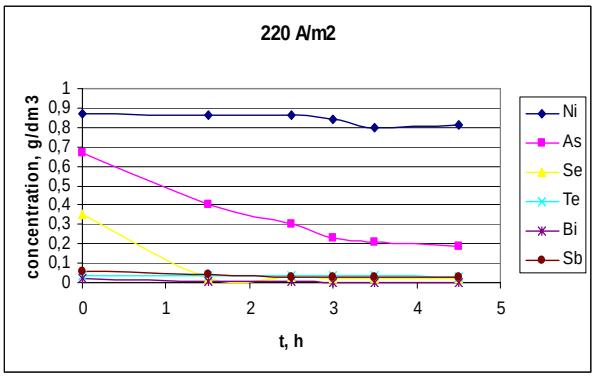

Figure 2. Ni, As, Se, Te, Bi and Sb concentration during the process

Table 2. Chemical composition of solution after neutralization and max allowed concentration for various water class[12],, pH = 9,96

Element	Conc. before neutralization, g/dm^3	Conc. after neutralization, g/dm^3	I, II water class, g/dm^3	III, IV water class g/dm^3
Cu	0.69	0.0016	0.0001	0.0001
Ni	0.84	0.0022	0.00005	0.0001
As	0.36	0.034	0.00005	0.00005
Pb	0.006	< 0.0001	0.00003	0.1
Fe	0.086	0.00014	0.0003	0.001
Se	0.15	0.03	-	-
Sb	0.06	0.009	-	-
Te	0.025	<0.001	-	-
Zn	0.034	0.0001	0.0002	0.001
Bi	0.002	<0.001	-	-
Cd	0.0001		0.000005	0.000001
Mn	0.0014		-	-

4. CONCLUSION

Based on the obtained results, it could be conclude that the combination of electrochemical and neutralization process is given satisfactory results for purification of total metallurgical wastewater. The quantity of 20% NaOH is depending of the concentration of elements in the wastewater and pH value. Neutralization of deccoperized water gives the slime with copper and nickel which recovering could be investigation having in mind the price of those metals and the price of process.

5. ACKNOWLEDGEMENT

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6. REFERENCES

[1] Integrated treatment of industrial wastes towards prevention of regional water resurces contamination INTREAT, (2003), 1st Annual technical report
[2] Juttner, K., Galla, U., Schmieder, H.,: Electrochemical approaches to the environmental problems in the process industry, Electrochemica Acta, Vol.45, 2000.,
[3] Dziewski, J. et al.,: Development and testing electrochemical methods for treating metal salts, cyanides and organic compounds in waste streams, Waste Management, Vol.18., 1998.,
[4] Janssen, L.J.J., Koene, L.,: The role of electrochemistry and electrochemical technology in environmental protection, Chemical Engineering Journal, Vol.85., 2002.,
[5] Orhan, G.et al.,: Recovery of copper from copper sulphate containing rinse waters, IX Balkan Mineral Processing Congress, Istabul., 2001.,
[6] Panda, B., Das, S.C.,: Electrowinning of copper from sulphate electrolyte in presence of sulphurous acids, Hydrometallurgy, Vol.59., 2001.,
[7] Exposito, E. et al.,: Lead electrowinning in an acid chloride medium, Journal of Power sources, Vol. 92., 2001.,
[8] Giannopoulou, I., Panias, D., Paspaliaris, I.,: Electrochemical Recovery of Copper from Spent Alkaline Etching Solutions, Proceedings of the TMS Fall 2002 Extraction and Processing Division Meeting, 16-20 June, Lulea, Sweden., 2002.,
[9] Panias, D., Giannopoulou, I., Paspaliaris, I.,: Copper Electrowinning from the Ammoniacal Etching Effluents of Printed Circuit Boards Industry", Proceedings of the 7th International Symposium on Environmental Issues and Waste Management in Energy and Mineral Production, Cagliari, Sardinia, Italy., 2002.,
[10] Doulakas, L.et al,: Recovery of Cu, Pb, Cd and Zn from synthetic mixture by selective electrodeposition in chloride solution, Electrochemica Acta, Vol.46., 2000.,
[11] Sapari, N. et al,: Total removal of heavy metal from mixed plating rinse wastewater, Desalination, Vol. 106., 1996.,
[12] Low of water, Serbia, 1989.