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ELECTROLYTIC RECOVERY OF COPPER FROM HIGHLY CONTAMINATED WASTEWATERS

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ABSTRACT

The EU-financed INTREAT Project (Integrated treatment of industrial wastes towards prevention of regional water resources contamination) addresses the environmental pollution associated with solid and liquid wastes/effluents produced by complex sulphide ore mining and metallurgical activities. The results concerning an electrolytic recovery of copper from wastewaters formed after mixing of the streams from Copper Refining, Precious Metals Plant and Electrolyte Regeneration will be shown. These wastewaters are characterized by low pH value due to the high content of residual sulphuric acid and heavy metals, such as Cu, Ni, Bi, As, Sb. The majority of these wastewaters flow untreated into the natural water streams and through the network of the existing rivers, which end up in the river Danube. The influence of a current density and flow rate of synthetic solutions with a content closed to wastewaters during an electrolytic recovery in a cell with two rotating discs on the copper deposition rate and quality of metals was studied. An electrolytic recovery represents pre-treatment of wastewater for the subsequent treatment in a cascade line.

Key words: Copper, wastewaters, purification, electrolytic recovery, current density

INTRODUCTION

Exploitation of complex sulphide ores is one of the most dynamic industrial sectors in Serbia. Actually, sulphide ores are the most important copper bearing resources that are commercially available. Their exploitation is accomplished either by open pit or underground mining. During the whole copper production cycle, large amounts of solid, liquid and gaseous wastes are generated. These wastes interact with the local environment resulting in serious impacts for the local eco-system [1]. Many types of wastewaters/effluents are produced from pyrometallurgical treatment of copper bearing mixed sulphide ores [2]. These wastewaters are characterized by low pH due to a high content of residual sulphuric acid and heavy metals, such as Cu, Fe, Ni, Mn, Zn etc. The majority of these wastewaters flow through the network of the existing rivers up to the River Danube [3].

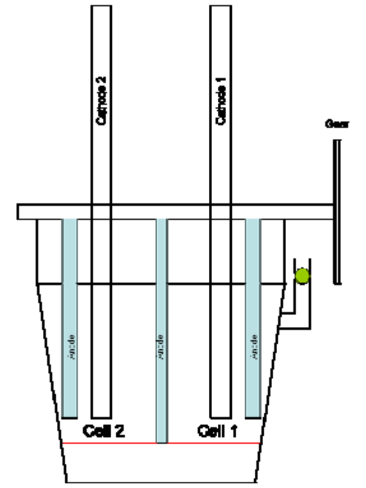
Industrial uses of water generally lead to deterioration in quality and, in most instances, wastewater must be collected and given effective treatment before being released to the environment. The conventional method for heavy metal removal from industrial wastewater generally involves a chemical precipitation process of the various treatment methods employed to remove heavy metals [4, 5]. Hydroxide precipitation is the most common and economically sound treatment technology. Metal precipitation is primarily dependent upon two factors: the concentration of metals in wastewaters and the pH of the water [6]. Heavy metals are typically removed by adding alkali such as caustic, lime or soda ash to adjust the wastewater pH to points where the individual metals exhibit their minimum solubility. Then the precipitates are removed by a proper solid-liquid separation technique such as sedimentation and filtration. However, a much larger quantity is produced by electrolysis from aqueous solutions. Electrolytic metal powder occurs mainly as a dendrite electrodeposits, which can spontaneously fall off or can be removed from the cathode by tapping or by other similar ways. Electrometals Technologies Limited EMEW®, Australia simplifies the process of recovering metals by electrowinning. This process is capable of direct electrowinning of high-grade copper cathode or powder directly from industrial pickling solution and similar waste products with continuous control of copper concentration below 3000 ppm [8]. The use of this continuous acid technology allows the direct and efficient recovery of nearly 90 % of the copper product, which takes place in conventional depletion technology. Also the purification of the wastewaters with 20-40 mg of copper was performed using of three dimensional cathode in packed bed layer [9]. EnViro-cell Umwelttechnik GmbH, Germany has at the present moment optimal electrolysis modules for all applications solvable by electrolysis [10].

In this paper a continuous process of an electrolytic recovery of copper was carried out in an electrolytic cell with rotating discs in order to achieve a deposition of copper from wastewater. The used synthetic metal-bearing solution had a chemical composition as similar as possible to the wastewaters formed after mixing of the streams from Copper Refining, Precious Metals Plant and Electrolyte Regeneration (RTB-Bor, Serbia). Also the real wastewaters from Bor were investigated. The main aim of this paper was to study the influence of a current density and flow rate of a synthetic solution on the copper removal rate.

EXPERIMENTAL

Experimental part was performed using an electrolytic cell (Fig. 1) as main component of the equipment shown in Fig. 2. The cathodes (rotating discs) with diameter of 30 cm were made by stainless steel. Anode were made from titanium coated with platinum. The source chemicals were analytical grade $CuSO_4$x $5H_2O$ and 96 % (w/w) sulphuric acid. The composition of initial synthetic solution was constant in all cases. The synthetic solution of copper sulphate and sulphuric acid was used for the investigation. Using two pumps the initial solution was transported from the canister into the first cell and later to the second cell. The laser sensor was used for the control of solution level in the electrolytic cell. The copper was deposited at the rotating discs. After an electrolytic recovery of copper the solution was transported to the second cell for the second recovery process and later moved to the canister. The initial concentration of solution amounted 7.24 g/L Cu and 75.5 g/L H_2SO_4. The experiments were performed at a room temperature. The other experimental conditions were: current density 50-240

A/m^2, flow rate of solution dV/dt= 0.5; 1.0 and 2.0 L/h, current intensity I= 7.5 A, voltage U= 2.3-2.7 V, time t = 11- 20 h; stirring speed v= 2 rotation per minute. The content of solution was determined using the Induced Coupled Plasma ICP analysis.



Technical data for an electrolytic cell:

Length: 34 cm, width: 13 cm, height: 20 cm

Working volume of cell 1 and cell 2: 3 L

Diameter of rotating disc cathode: 30 cm

Stirring speed: 2-10 rpm

total immersed cathode area: 940 cm^2

Anode basket:

Length: 30 cm, width: 2,5 cm, height: 15 cm

Working current density: 50-240 A/m^2

Flow rate of solution: 0.5 -5.0 L/h

Fig. 1. Sketch of the electrolytic cell with rotating discs cathodes at IME, Aachen

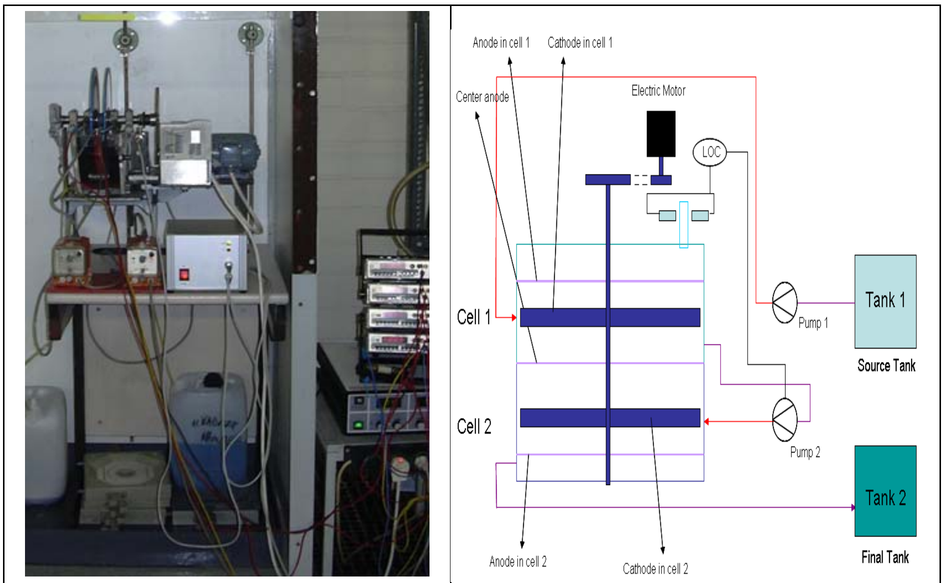


Fig. 2. An equipment for electrolytic recovery at the IME, Aachen (an electrolytic cell with two rotating discs, two pump, two canisters, laser sensor, exhaust system, rectifier)

RESULTS AND DISCUSSION

In the experimental part the influence of a current density and flow rate of a synthetic solution on the copper removal rate was investigated. The obtained results are shown at Figs. 3-6.

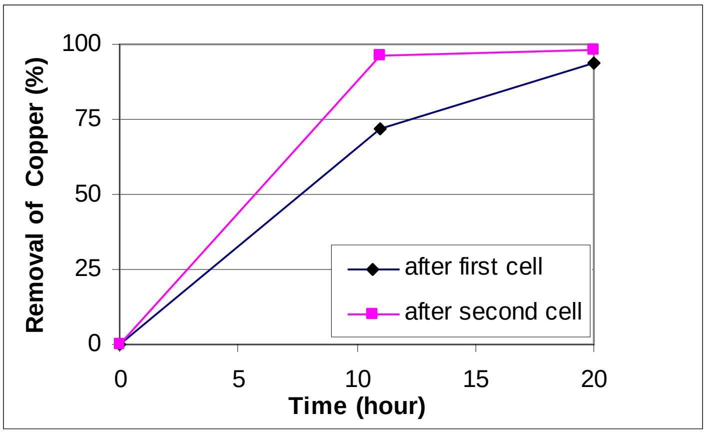


Fig. 3a. The removal degree of copper from the synthetic solution at current density 80 A/m^2, flow rate 0.5 L/h, stirring speed 2 rpm

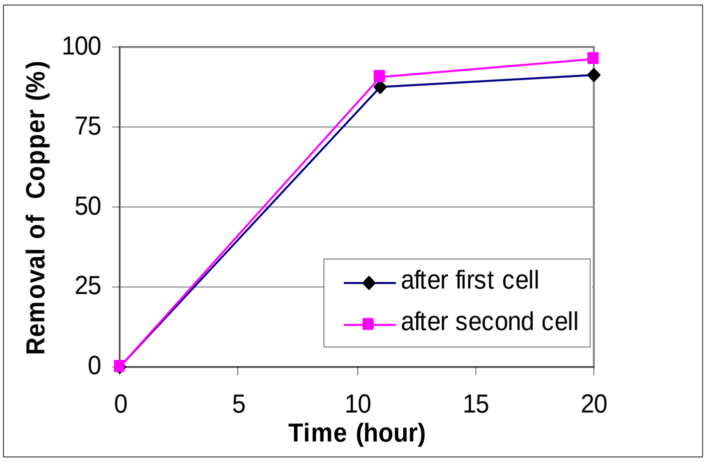


Fig. 3b. The removal degree of copper from the synthetic solution at current density 50 A/m^2, flow rate 0.5 L/h, stirring speed 2 rpm

The removal degree of copper from the synthetic solution increases with time of treatment. After 11 hour the calculated removal degree of copper reached the 71.6 % and 96.3 % in the first and the second cell, respectively. The increase of time from 11 hour to 20 hour increases the removal degree of copper to 94.0 % and 98.2 % in the first and the second cell, respectively (refer with: Fig. 3a). Under same conditions at a current density of 50 A/m^2 the maximal copper removal amounts 96.3 % after 20 h (refer with: Fig. 3b).

The increase of the flow rate of solution from 0.5 L/h to 2 L/h at 80 A/m^2 decreases the removal degree of copper.

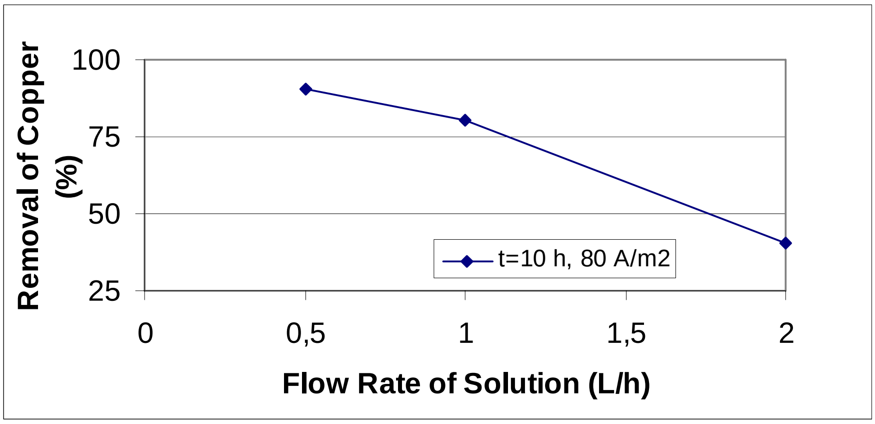


Fig. 4. The removal degree of copper from the synthetic solution at 80 A/m^2 depending on the flow rate of solution

The obtained electrodeposited copper at 80 A/m^2 and 240 A/m^2 is shown at Fig. 5.

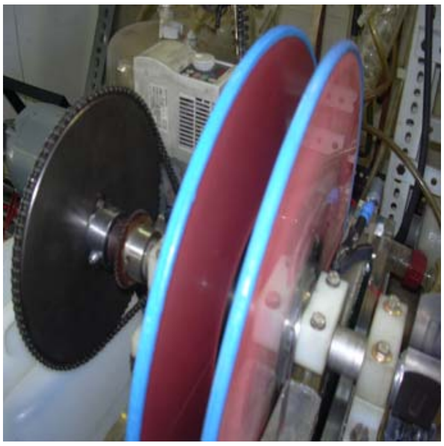
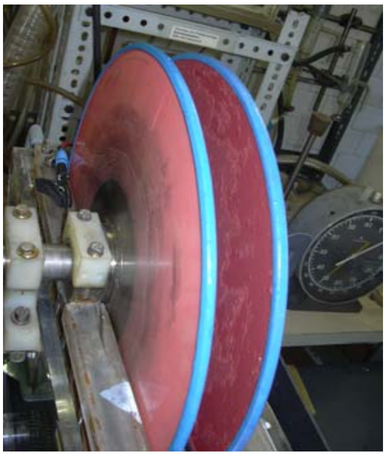
	

Fig. 5.a. Deposited copper at 80 A/m^2	*Fig. 5.b. Deposited copper at 240 A/m^2*

The increase of cell current density changes the electrodeposits morphologies from fine layer (Fig. 5.a) to the non-homogeneous powder deposit (Fig. 5.b) due to the formation of hydrogen. According to the concentration of copper in wastewaters the 0.1 M $CuSO_4$ solution was investigated in order to determine a limited current density for hydrogen formation. Using AMEL INSTRUMENTS Potentiostat/Galvanostat MOD 7060 the potential- current density curves were monitored. The limited current density for hydrogen formation for 0.1 M $CuSO_4$ was experimentally determined and amounts 8 mA/cm^2 (refer with: Fig.6).

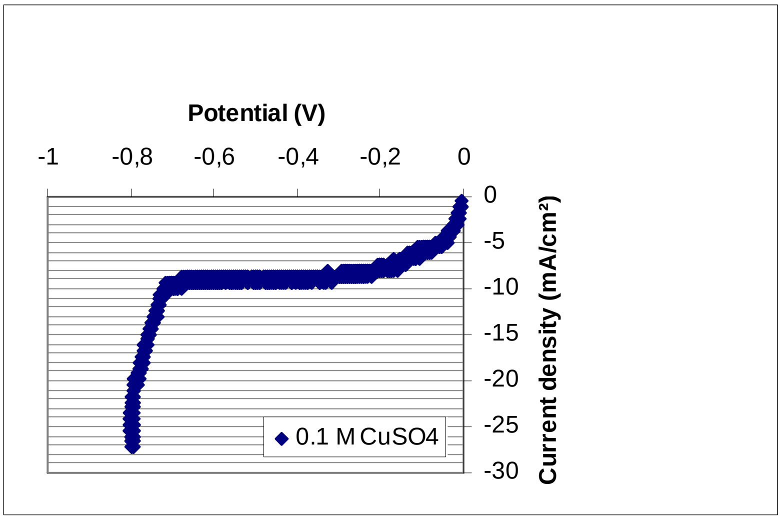


Fig. 6. The potential- current density curve for 0.1 M $CuSO_4$ at the room temperature

Also the experiments were performed at T=20°C, 80 A/m^2, dV/dt=0.5 l/h with real wastewaters following chemical composition in (g/l): 8.33 Cu, 0.66 Ni, 0.63 As, 0.26 Se, 0.09 Fe, 0.08 Sb, 0.07 Te, 0.04 Al, 0.03 Zn, 0.03 Bi, 0.02 Si, 0.07 Cl^-,0.003 Pb, 0.001 Mn, 0.0001 Cd, 117.04 H_2SO_4. The obtained results are shown at Fig. 7.

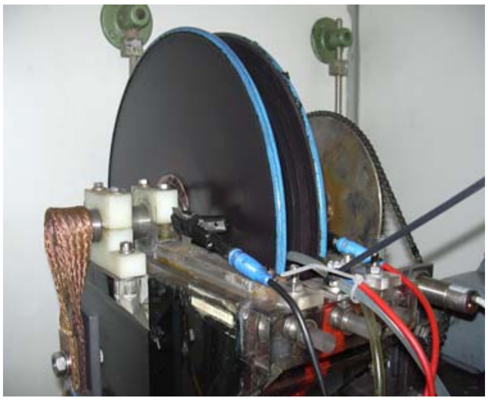


Fig. 7.a. Black powder direct after test start

Fig. 7.b. A dark reddish gray deposition after 60 min

The chemical composition of the obtained cathode deposit contains: 39.0 Cu, 0.15 Ni, 0.11 As, 11.7 Se, 0.25 Fe, 0.21 Bi (values in %), and 68 Mn, 27 Sn, 218 Al, 85 Mg, 307 Ca, 146 Si, 7 Co, 448 Cr, 833 Zn, 128 Sb, 32 Pb (values in ppm). The formation of arsine is not detected.

SUMMARY

At room temperature in an electrolytic cell with two rotating discs copper is deposited from the solution with 7.24 g/L Cu and 75.5 g/L H_2SO_4. Due to the formation of hydrogen the increase of cell current density from 80 A/m^2 to 240 A/m^2 changes the electrodeposits morphologies from fine layer (Fig. 5.a) to the deposit with smooth surface (Fig. 5.b). The removal degree of copper from the synthetic solution increases with time of treatment as expected. Maximal removal degree of copper amounts 98.2 % after 20 h at 80 A/m^2. Under the same conditions the increase of the flow rate of solution from 0.5 L/h to 2 L/h decreases the removal degree of copper. For 0.1M of copper sulphate solution the limited current density amounts 8 mA/cm^2. First real waste water treatment tests prove the principle, require high safety standards due to arsine risk, produces Cu-Se-powders and need to be extended.

THE FUTURE WORK

Electrolytic recovery is only a pre-treatment step and needs further neutralization in the existing cascade line in order to purify such highly contaminated wastewaters. Tests to be continued with real waste water in order to study the influence of current density and flow rate on the deposit characteristics.

The influence of presence of selenium, arsenic, nickel, iron, zinc, antimony on the copper deposition should be considered in order to prevent the formation of very dangerous arsine and stibine and arsenic co-deposition.

ACKNOWLEDGMENTS

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