ELECTROLYTIC TREATMENT OF HIGHLY CONTAMINATED EFFLUENTS FROM COPPER SMELTERS

S.R. Stopic, K.B. Friedrich, and A.W .Widigdo
IME Process Metallurgy and Metal Recycling
Intzestrasse 3
Aachen, Germany
sstopic@ime-aachen.de

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 the electrolytic recovery of copper from effluents formed after mixing of streams from Copper Refining, Precious Metals Plant and Electrolyte Regeneration in the Balkan Area will be shown. The waste water is characterized by low pH values and high contents of heavy metals, such as Cu, Ni, Bi, As, Sb. The majority of these waste water flow untreated into the natural water streams and through the network of existing rivers, which end up in the river Danube. The influence of current density and flow rate on the deposition rate, the quality of copper and the process efficiency will be presented. The full continuous process is based on cells with rotating disc cathodes and represents a pre-treatment step before common neutralisation in a cascade line.

INTRODUCTION

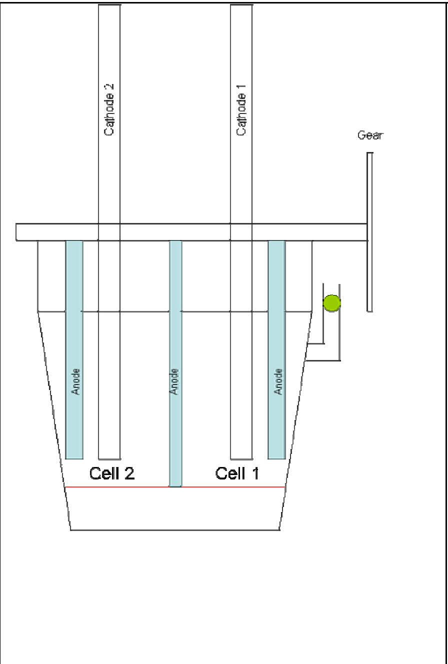
Exploitation of complex sulphide ores is one of the most dynamic industrial sectors in Serbia. Actually, sulphide ores are the most important copper bearing resources that are commercially available. Their exploitation is accomplished either by open pit or underground mining. During the whole copper 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 waste water/effluents are produced from pyrometallurgical treatment of copper bearing mixed sulphide ores [2]. This waste water is 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 waste water 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; waste water must be collected and given effective treatment before being released to the environment. The conventional method for heavy metal removal from industrial waste water 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 waste water 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 waste water 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 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 waste water 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 waste water. The used synthetic metal-bearing solution had a chemical composition as similar as possible to the waste water formed after mixing of the streams from Copper Refining, Precious Metals Plant and Electrolyte Regeneration (RTB-Bor, Serbia). The first experiments were performed with a synthetic solution in order to establish the optimal parameter for an investigation with real waste water from Bor. Also the main aim of this paper was to study the influence of a current density and flow rate of a synthetic and real 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. Anodes 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; rotating speed v = 2 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

Figure 1- Sketch of the electrolytic cell with rotating discs cathodes at IME, Aachen [11]

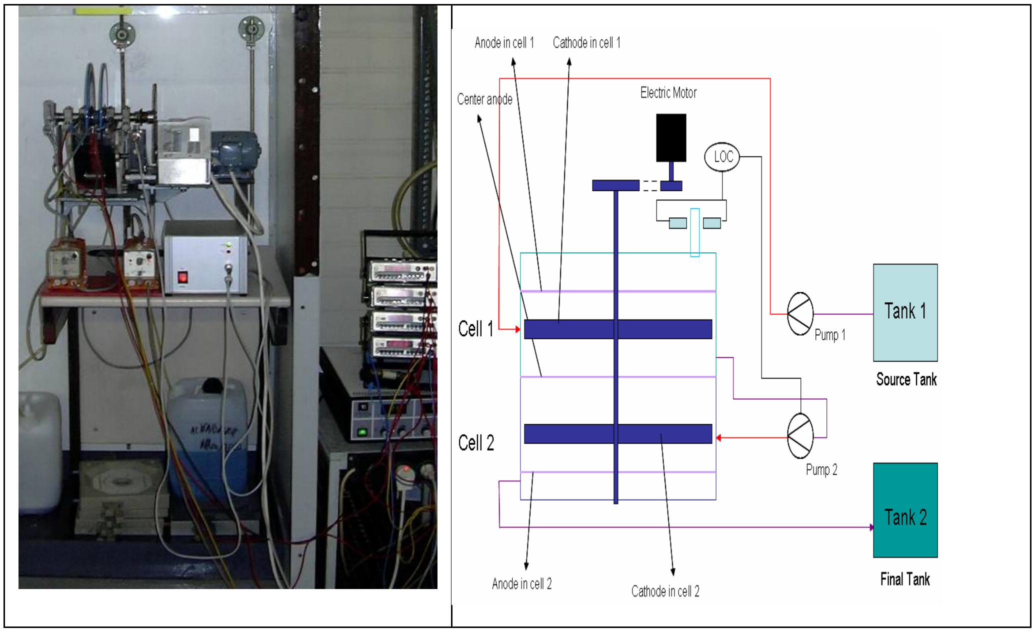


Figure 2- An equipment for electrolytic recovery at the IME, Aachen (an electrolytic cell with two rotating discs, two pump, two canisters, laser sensor, exhaust system, rectifier)

Content of real waste water amounts (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 waste water was filled into the source tank, and than was pumped into the first cell. The first pump is in charge of flow rate parameter of the process. In the first cell, the first step of extraction takes place. The other important parameter of this process is the current density. The current flows into the cathode through the axis of the rotating discs. The current density is measured inside the cell continuously. The waste water was pumped into the second cell after reaching a certain level. The solution level in the first cell was monitored by a pair of laser beam, which have operated the second pump to prevent over flooded. The second extraction step in the second cell was aimed to get the rest of copper substance after the first extraction. The process is finish after the solution arrives in the final tank. The duration of the whole process depends on the flow rate of the waste water into the cell and the volume of waste water in the source tank. The experiments divided into two series, using synthetic solution and real waste water. In difference to the traditional electrolytic recovery of copper this treatment was performed at room temperature in order to spare energy for the heating.

An X-ray diffractometer (Siemens D 5000) and a scanning electron microscope (ZEISS DSM 982 Gemini) were used for the characterization of the obtained copper powders. SEM images were used to observe the surface morphology of particles formed at different parameter sets. The qualitative characterization of the impurity level was performed by energy disperse spectroscopy (EDS) analysis with a Si(Bi) X ray detector, connected with the SEM and a multi-channel analyzer.

Table 1 –List of Experimental investigations

Experiment No.	current density (A/m^2)	Volume flow (l/h)	solution type
1	240	0.5	Synthetic
2	80	0.5	Synthetic
3	50	0.5	Synthetic
4	80	1.0	Synthetic
5	80	2.0	Synthetic
6	50	0.5	Real
7	80	0.5	Real
8	100	0.5	Real
9	80	1.0	Real
10	80	2.0	Real

RESULTS AND DISCUSSION

Synthetic Solution

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. 3-5.

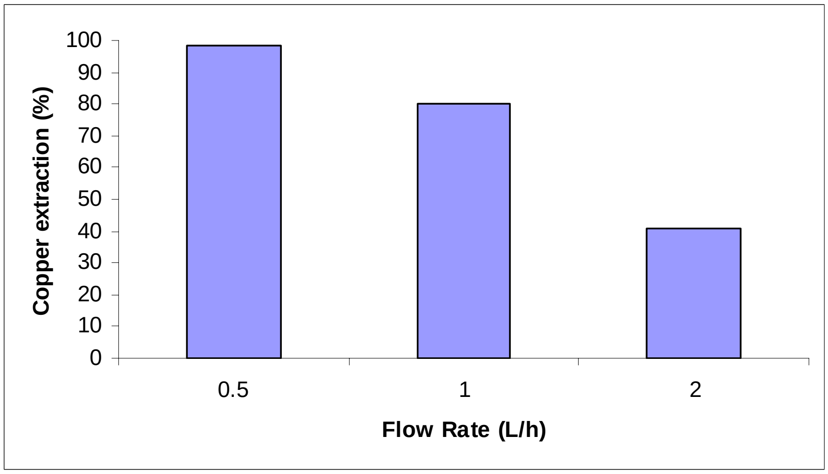


Figure 3a- The removal degree of copper (in %) from the synthetic solution at current density 80 A/m^2, flow rate 0.5 L/h, 1 L/h, and 2 L/h, stirring speed 2 rpm

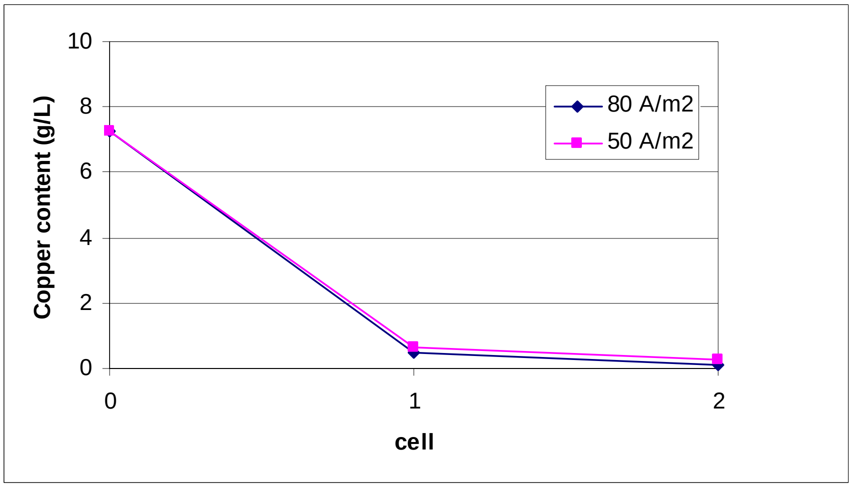


Figure 3b- The removal degree of copper from the synthetic solution at current density 50 A/m^2 and 80 A/m^2, flow rate 0.5 L/h, stirring speed 2 rpm

The removal degree of copper from the synthetic solution decreases with the increase of flow rate. The increase of flow rate from 0.5 L/h until 2 L/h, decrease the copper extraction from 98.2 % to 40.6 %, respectively (refer with: Fig. 3a). Increasing the current density increases the copper removal from the solution, in both of cells (refer with: Fig. 3b).

The increase of cell current density changes the electrodeposits morphologies from fine layer to the non-homogeneous powder deposit due to the formation of hydrogen [11]. According to the concentration of copper in waste water 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. 5)

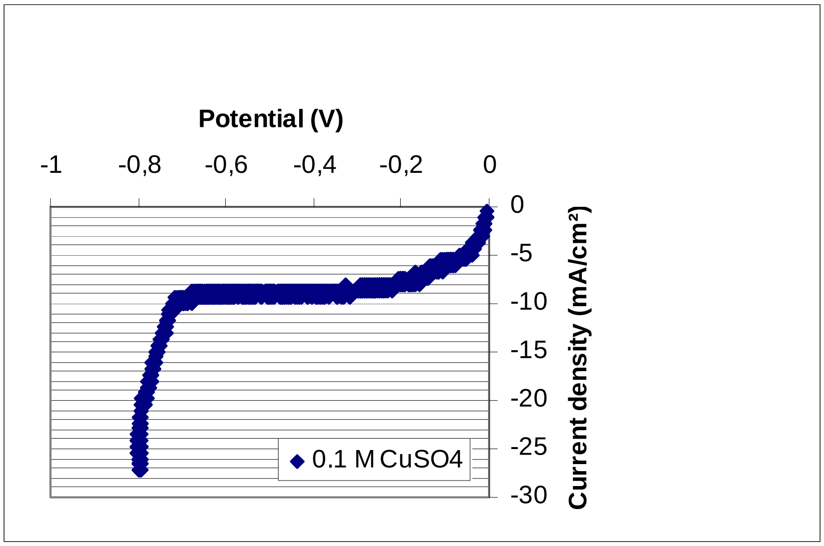


Figure 5- The potential- current density curve for 0.1 M $CuSO_4$ at the room temperature

This value of current density should be investigated in experimental investigation with real waste water.

Real waste water from the Copper Smelter, Bor, Serbia

As to be seen, the content of copper and sulphuric acid is higher than the synthetic waste water. The arsine content is favourably will be extracted from the waste water if no copper content left and/or will react with hydrogen:

$$2\ As^{3+} + 3\ H_2 = 2\ AsH_3 + 6\ e^- \qquad (1)$$

AsH_3 is highly toxic and very dangerous to human life. Therefore its formation must be avoided. Prevention of AsH_3 – formation was done by avoiding hydrogen formation (optimizing current density) and by $FeAsO_4^-$ deposition; as shown:

$$Fe^{2+} - e^- = Fe^{3+} \tag{2}$$

$$As^{3+} - 2e^- = As^{5+} \tag{3}$$

$$Fe^{3+} + 2\,O_2 + As^{5+} = FeAsO_4 + 8e^- \tag{4}$$

Concerning the possibility of arsine formation, the several tests of arsine detection were performed using a Draeger pump, Germany. Arsine tests were conducted on the experiments with current flow variation in l/h (0.5, 1.0 and 2.0), because of the high probability of hydrogen formation. The value of current density of 80 A/m^2 was confirmed as the density limit to avoid hydrogen formation. Depending of different flow rate of waste water the content of metals at 80 A/m^2 was amounted:

Table 2- The change of metal concentration
during an electrolytic treatment for 10 l waste water at 80 A/m^2

Content (g/l)	Initial	0,5 l/h	1 l/h	2 l/h
Cu	8,33	3,79	2,86	3,54
As	0,63	0,54	0,49	0,52
Se	0,26	0,0089	0,0613	0,0862
Zn	0,034	0,0358	0,032	0,0337

The obtained results show that this electrolytic treatment was successful in a case of copper and selenium. The concentration of arsenic was slight changed. At the beginning of the process the deposition of selenium took place. Then the deposition of copper was started after most of the selenium extracted. The increase of the current density from 80 A/m^2 to 100 A/m^2 increases the removal degree of copper.

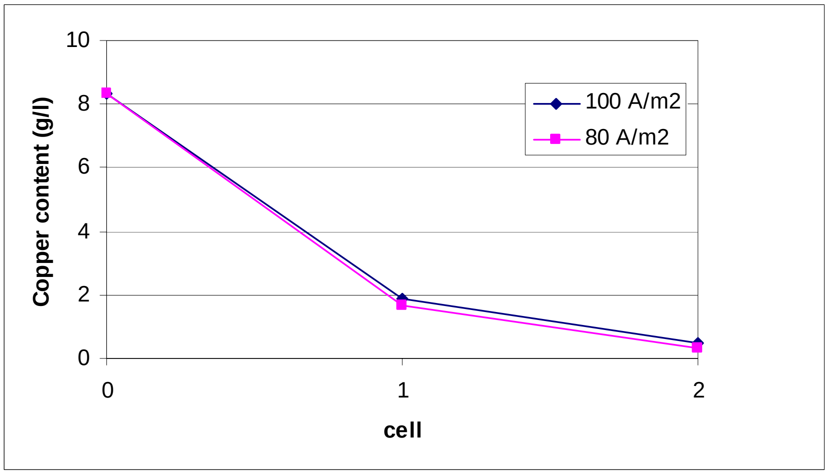


Figure 6a- The influence of the current density on copper removal

Removal degree of copper at 80 A/m^2 after cell 1 and cell 2 amounted 77.2% and 93.8%, respectively. The increase of current density on 100 A/m^2 increases the removal degree of copper: after cell 1 and cell 2 amounted 78.2% and 96.6%, respectively.

Under the same current density of 80 A/m^2 the increase of flow rate from 0.5 L/h until 2 L/h, decrease the copper extraction from 94.3 % to 57.5 %, respectively (Fig. 6b).

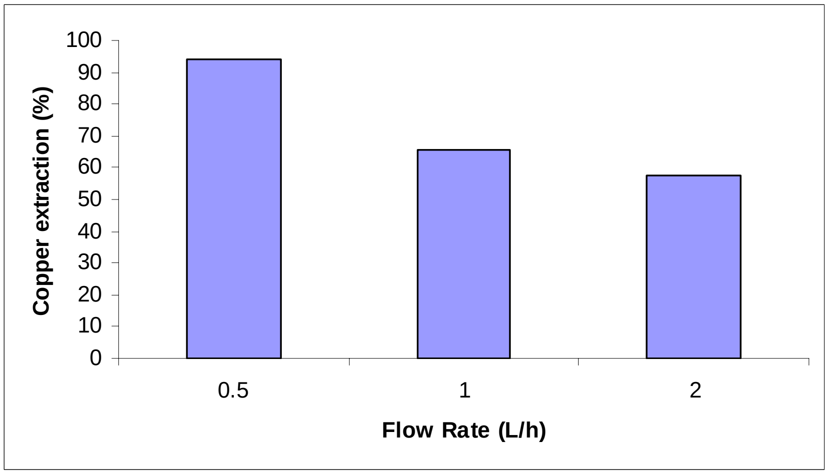
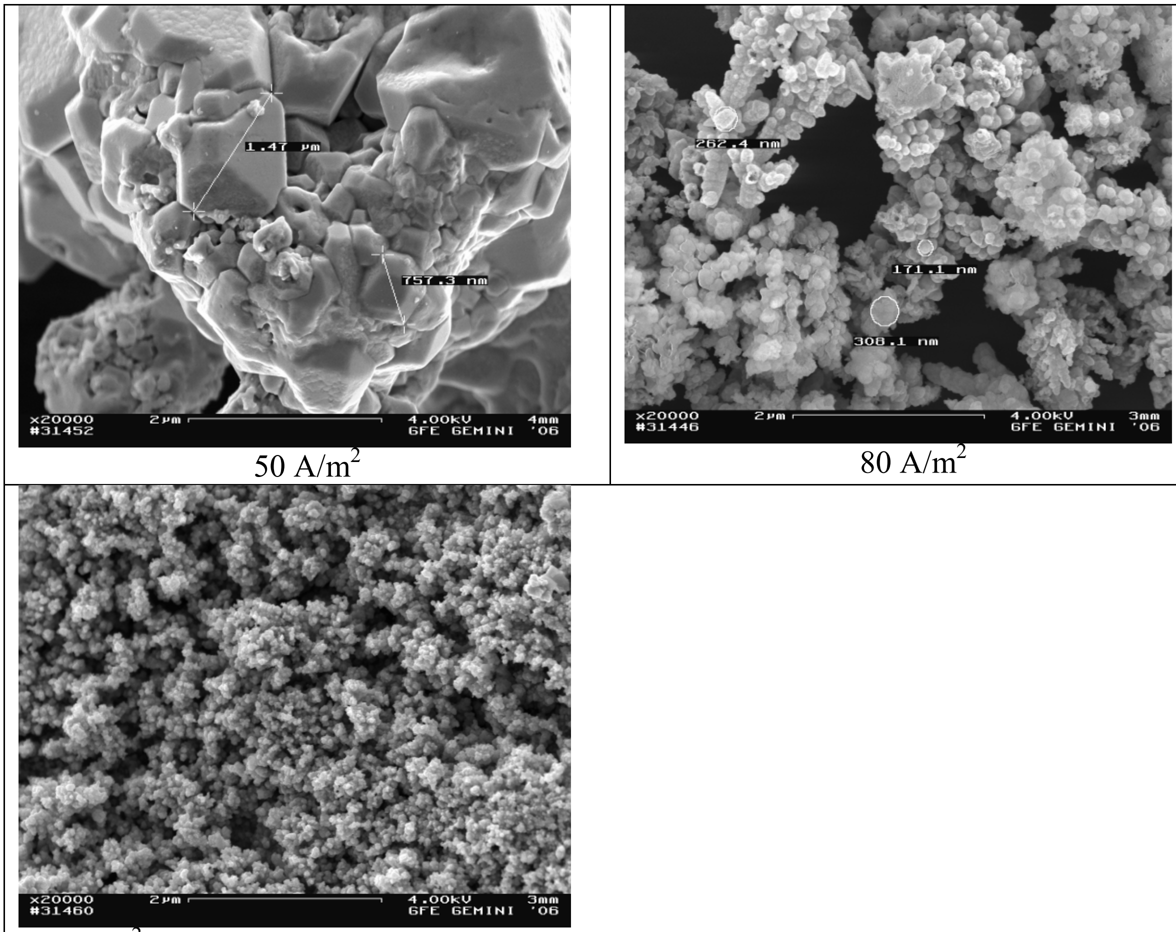


Figure 6b- The influence of the flow rate on copper removal

The SEM analysis of obtained powder using a flow rate 0.5 l/h was amounted at Figure 7.



50 A/m^2

80 A/m^2

100 A/m^2

Figure 7- SEM Analysis of obtained powder

It seems that the increase of current density may reduce the agglomeration possibility, therefore decrease the particle size. The obtained particles are agglomerated and irregular shape. EDS analysis of obtained powder show the presence Cu, Se, S, Cl.

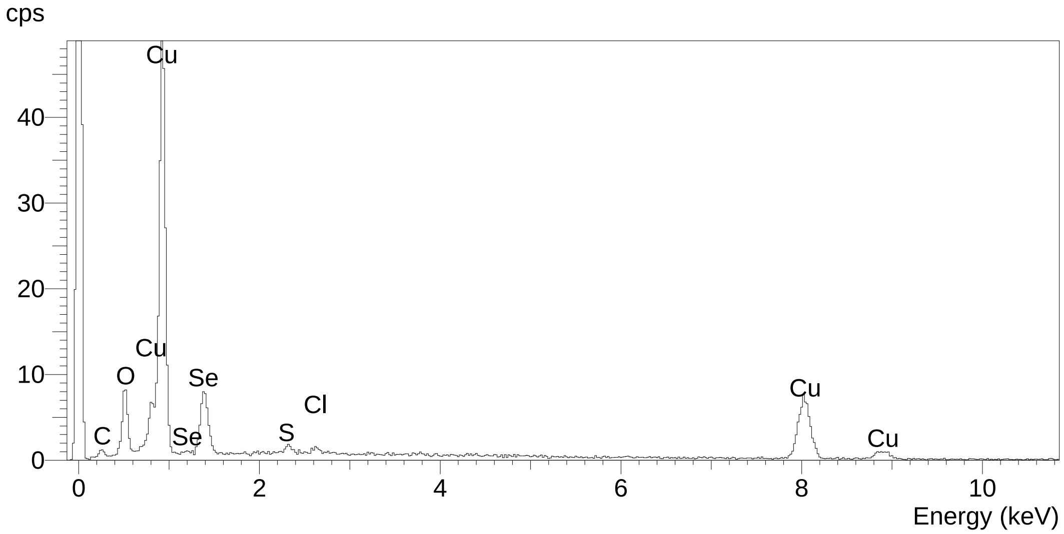


Fig. 7- EDS Analysis of obtained powder

Typical ICP analysis of obtained powder amounts in (%): 80 Cu, 0.7 Ni, 5 As, 3 Se+Te, 0.2 Fe, 0.5 Sb, 0.1 Bi , 0.1 Zn, and in (ppm): 200 Al, 300 Ca+Mg, 400 Cr, 400 Pb.

CONCLUSION

Copper was successfully removed from the synthetic solution with 7 g/l Cu and 75 g/l H_2SO_4 also from real waste water with 8.3 g/l Cu and 117.9 g/l H_2SO_4 in an electrolytic cell with two rotating discs at room temperature. The suitable operation parameters according to the conducted experiments are 0.5 L/hour flow rate and current density of 80 A/m^2 (safety issue). The rotating cathode electrolysis is suitable for removal of Cu and Se without extracting Zn, As, Ni from waste water. The obtained solution after an electrolytic treatment could be used for a cascade neutralization treatment in order to decrease of copper concentration up to 1 mg/L.

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