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# PARTICULATE BED CATHODE FOR COPPER ION REMOVAL FROM WASTE WATERS
## Part I: An optimization study of operational parameters

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***ABSTRACT.*** The electrode parameters of a cell equipped with a particulate electrode for the recovery of copper ions at low level concentrations from waste waters are described. The influence of current feeder type, electrolysis time, current intensity, sulphuric acid on the recovery efficiency in order to set the optimal working parameters, were studied.

## INTRODUCTION

The direct discharge of metal-contaminated waters from industrial plants and mining sites rises a serious environmental threat, especially in industrial area. In 1986 Amendments of the Clean Water Act (CWA) and Safe Drinking Water Act (SDWA) [1] specified 13 metals including copper, lead, cadmium and mercury, as main pollutants and established the maximum discharge level for the most of these metals to ppm range. That is why, the safe-release level and the costs for treatments of waste waters, involve growing burden to nearly all metals processing industries. Efficient removal and recovery of heavy metals from industrial waste waters prior to discharge are major challenges.

Commonly, the large-scale treatment of waste waters has been carried out by chemical methods: precipitation of metal ions and processing the sludge for metal recovery [2-4]. It is clear that, these procedures are not a final solution of contamination problems because of difficulties of methods: specific reagents for sludges processing, large quantities of residues.

Also, chemical methods are inefficient in treatment of waste waters with low levels of metallic ions.

One strategy for a long-term and economical clean-up of waste waters is based on the use of electrochemical methods. Electrochemical treatment of waste waters satisfies two major requirements: pollutants can be selectively and quantitatively removed. Moreover, it offers the advantage to be used as final process at sites of continuous waste waters treatment.

The classical electrochemical methods use planar electrodes that have the disadvantages of a low active area per unit of volume and low mass transfer rate at small ions concentrations. Consequently, the residual concentrations will be reached only in long time operations with prohibitive electricity costs.

Therefore, it was necessary to consider an alternative option, namely increasing the electrodes active area per unit of volume. In that purpose, were used extended area electrodes [5-7] with different shapes: plates, rods or gauzes. However, despite of their ingenious design, these electrodes have a rather low active area. A way of overcoming this limitation is the use of three-dimensional electrodes, which are represented by [8]:

- continuous electron-conducting porous structure, with electrolyte flowing through the pores (porous electrodes);
- individual conducting particles in the form of a fixed or fluidized bed, flow through by the electrolyte (particulate electrode);
- individual electron conducting particles circulated as a slurry (circulating electrodes).

In this paper the electrochemical behavior of particulate electrodes, used for copper recovery from waste waters was studied.

## EXPERIMENTAL

To investigate the electrochemical behavior of cathodic particulate bed, as electrolytes were used waste waters from S.C. Phoenix S.A., one of the greatest copper ores processing plant from Baia Mare. The electrolyte flows from the bottom to the top of a three electrodes cell, made of a glass tube with 6 cm inner diameter and 25 cm length. Was processing 1.5 l electrolyte with basic composition presented in Table 1:

**Table 1.**

Composition of the used waste waters

| Symbol of electrolyte | Concentration of metallic ions g/l | | | Concentration of sulphuric acid, g/l |
|---|---|---|---|---|
| | $Cu^{2+}$ | $Zn^{2+}$ | $Pb^{2+}$ | |
| I | 0.2 | 0.12 | traces | - |
| II | 0.2 | 0.12 | traces | 25 |

It passes the cathodic bed which consists of a package of copper particles and powder. The bed was supported by a steel sieve at the bottom of the cell. In Table 2 are presented the specific parameters of cathodic bed. For a clearly representation, we express the dimensions of particles and powders colligate with sieves apertures, not in mesh as usually.

**Table 2.**

Physical properties of cathodic bed

| Size range | Cooper particles | | | Copper powder | | |
|---|---|---|---|---|---|---|
| | 0.6-0.4 cm | 0.2-0.125 cm | 0.125-0.016 cm | 0.6-0.4 cm | 0.2-0.125 cm | 0.125-0.016 cm |
| Specific area $cm^2/g$ | 105 | 218 | 412 | 625 | 1305 | 1427 |
| Physical aspect | plate | wire | wire | crust | granular | dust |

Copper particles and powders were pretreated by cleaning in dilute nitric acid, rinsing in water and drying in an oven. Before use they were rinsed in dilute sulphuric acid to remove any oxide coating.

The electrolytes flow rate measured by of rotameter, was adjusted with a pump for every dimenssion range to bring the bed at the desired level of expansion.

Cathodic polarization of bed was performed using two types of current feeder, described in Table 3.

The anode, placed at the upper part of the cell was a stainless steel circular plate of 3 cm diameter.

A calomel electrode, functioning as reference electrode, was placed above the bed. A potentiostat HA 320 from Hokuto Penko Ltd. was used to supply electric power and to control potential difference between working and reference electrode.

**Table 3**.

Characteristics of current feeder:

| Symbol of current feeder | Aspect |
|---|---|
| A | copper wire placed in the center of the cathodic bed |
| B | copper sieve placed at the bottom of the cathodic bed |

In all experiments, metallic ions concentrations were periodically monitored by a AAS Perkin-Elmer Spectrometer, model 3300/5100 PC.

The experiments were repeated in the same conditions by three times. Was observed changed in all tests carried out between 0-2% and the final results represent an average of particular results.

## RESULTS AND DISCUSSIONS

### Influence of specific area:

High specific area is an important condition in the choice of a particulate electrode. Considering data from Table 2, the first choice for experiments was a copper powder of 0.125-0.016 cm size range, with specific area 1427 $cm^2/g$. Preliminary experiments have been affected by two aspects:

- at low electrolyte velocity (< 0.5 cm/s), the powder particles turn off into sludge who agglomerates the surface of the current feeder and the cell becomes hard to operate;

- at high electrolyte velocity (> 0.5 cm/s), the powder particles easily flow-by, reach the anode and are dissolved, increasing the copper concentration of the electrolyte (Figure 1).

Thus, because of inappropriate behavior of range copper powders 0.125-0.016 cm size range, for the other experiments, have been chosen the next size range with high specific area. According to Table 2, this one belongs to copper powder 0.2-0.125 cm (specific area1305 $cm^2/g$).

As expected, the experiences performed with the others size ranges both particles and powders, presented in Table 2, having specific areas lower that of 0.2-0.125 cm size, give us unsatisfactory results.

Preliminary experiments with copper powder by 0.2-0.125 cm size, have been made with different bed weights in range 2-12 g. The most significant results of copper recovery efficiency was obtained at bed weights in range 8-12g.

The electrolyte flow rate was adjusted in limits 1.5 - 2.3 cm/s to get both packed and fluidized bed.

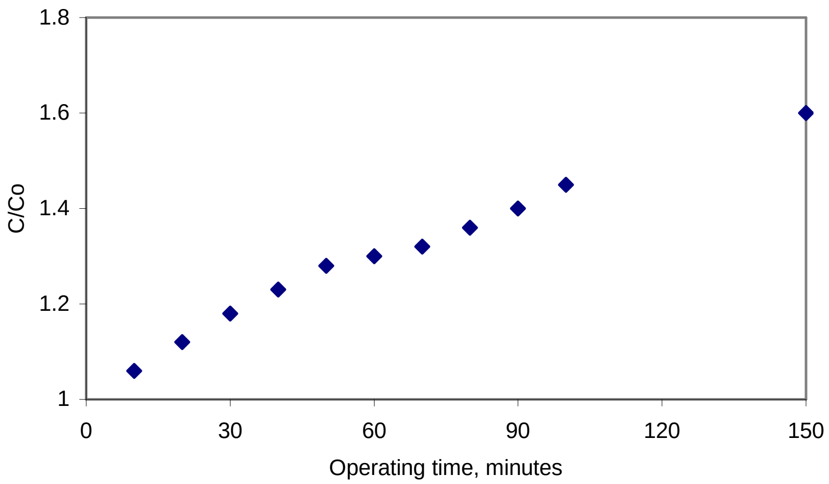


Figure 1. The increase of copper concentration with operating time; copper powder of 0.125-0.016 cm size range (Table 2); bed weight = 8g; current intensity = 2A; current feeder type A (Table 3); electrolyte I (Table 2); $C_0$ – initial concentration of $Cu^{2+}$ (0.2 g/l); C – [ $Cu^{2+}$] at the considered moment; fluidized bed at electrolyte flow rate 0.8 cm/s

**Influence of current intensity on the copper recovery efficiency**

In all cases, copper recovery increase with current intensity but not in an uniform way, as can be observed in Figure 2. Comparing the percentage of Cu recovery for each current intensity, it can be observed

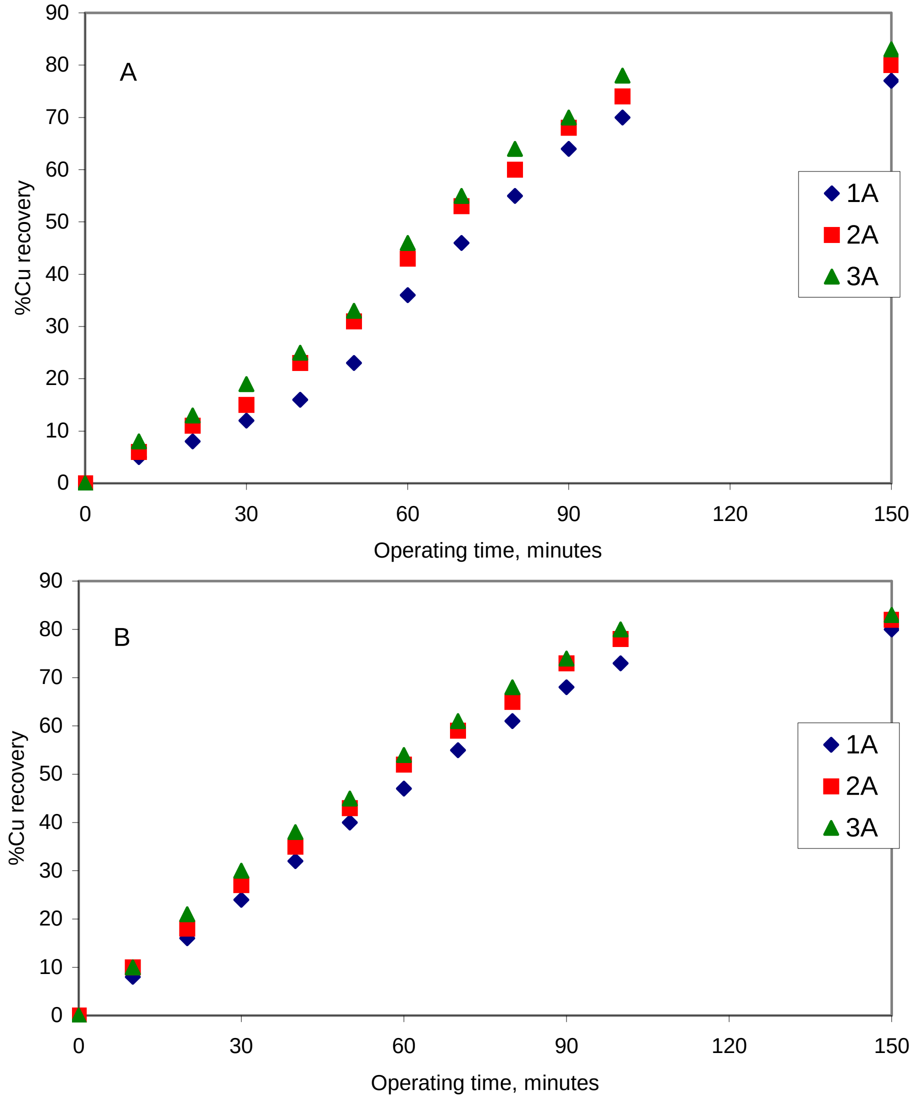


Figure 2. The influence of current intensity and operating time on efficiency of copper recovery at two bed weights; electrolyte I (Table 1); copper powder at 0.2-0.125 cm size range (Table 2); current feeder type A (Table 3); packed bed at 1.5 cm/s electrolyte flow rate; A - 8 g bed weight; B - 10 g bed weight

that the optimal behavior is at 2A. For example, for a 10g bed weight and 100 minutes operating time, an intensity increase from 1A to 2 A determines an recovery efficiency gain of 5% (from 73% to 78%). At the same time of electrolysis, passing from 2A to 3A, the gain is only 2% (from 78% to 80%). Experimental data showed that optimal current intensity, is 2A.

**Influence of the bed weight**

High specific area of powders at 0.2-0.125 cm size range (Table 2), allows us to conclude, at first sight, that a higher bed weight, equivalent with a higher electrochemical active area, improve the copper recovery efficiency. The experiments made with different bed weights led to the results presented in the Table 4.The Cu recovery efficiency increases with bed weight being higher at 12g bed weight.

A detailed analysis of data from Table 4 shows that %Cu recovery enhances are more clearly when bed weight increases from 8g to 10g rather from 10g to 12g.

**Table 4.**

The influence of bed weight and operating time on %Cu recovery; copper powder at 0.2-0.125 cm size range (Table 2); packed bed at 1.5 cm/s electrolyte flow rate; I=2A; current feeder type A (Table 3); electrolyte I (Table 1);

| Operating time minutes | %Cu recovery | | |
|---|---|---|---|
| | 8 g | 10g | 12g |
| 0 | 0 | 0 | 0 |
| 10 | 6 | 10 | 12 |
| 20 | 11 | 18 | 20 |
| 30 | 15 | 27 | 28 |
| 40 | 23 | 35 | 36 |
| 50 | 31 | 43 | 43 |
| 60 | 43 | 52 | 54 |
| 70 | 53 | 59 | 60 |
| 80 | 60 | 65 | 66 |
| 90 | 68 | 73 | 73 |
| 100 | 74 | 78 | 79 |
| 150 | 80 | 82 | 83 |

For example, after:

- 10 minutes of electrolysis can be noticed a gain of 4% (from 6% to 10%) when bed weigh increases from 8g to 10 g, comparing with 2% (from 10% to 12%) when bed weight become 12g.

- 50 minutes, the increase is 12%, from 31% at 8g to 43% at 10g, comparing with 0% (43% at both 10g and 12g).

- 100 minutes, the gain is 4%, from 74% at 8g to 78% at 10g and only 1% when bed weight increases with 2g (from 78% at 10g to 79% at 12g).

The small gains of recovered copper obtained at bed weight increase from 10g to 12g, comparing with those from 8g to 12g, allow us to conclude that 10g is the optimal bed weight.

**Influence of current feeder**

The key point of the electrochemical behavior of particulate bed is the effective solid conductivity. It has been found that in the normal direction the current feeder, the most active regions are near the current collector. As long as the contact between current collector and particulate bed is better, the charge transfer is enhanced.

In case of copper recovery experiments, the shape of the current feeder was an important parameter. A large contact area between current feeder and copper powder and an uniform current distribution determine a higher efficiency for feeder B than A (Table 3). This conclusion is supported by experimental data presented in Figure 3.

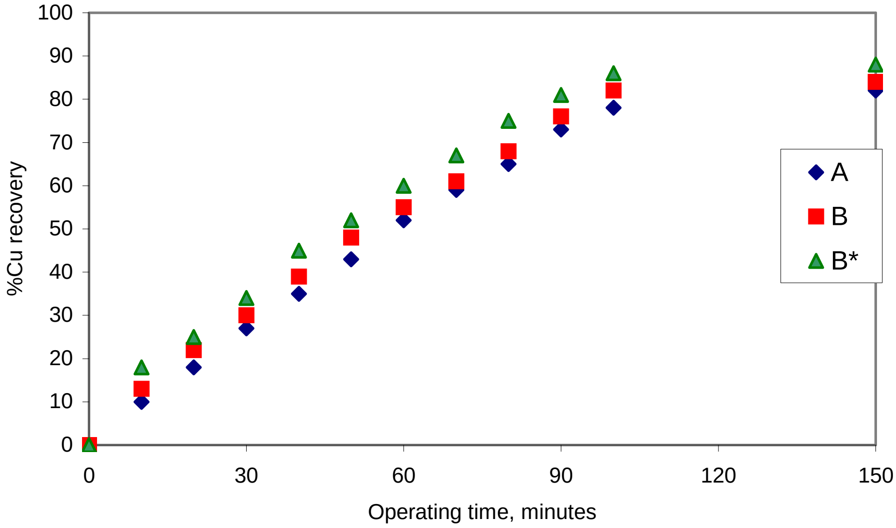


Figure 3. The variation of %Cu recovery with operating time; copper powder at 0.2-0.125 cm size range (Table 2); I = 2A; packed bed at 1.5 cm/s electrolyte flow rate; bed weight = 10g; A, B – current feeders A, B (Table 3), electrolyte I (Table 1); B* - current feeder B (Table 3), electrolyte II (Table 1);

Also, an improvement of charge transfer can be obtained using an acidified electrolyte (Figure 3). The quantity of sulfuric acid added to electrolyte should be not too high, in order to avoid the formation of a cuprous oxide layer on the surface of the electrode which will passivate the metal [9] (also, hydrogen evolution on particulate bed surface will be observed, in detriment of copper deposition).

Resuming the partial conclusions, we can say that for the packed bed cathode, the optimal operating parameters are the following:

*bed weight 10g; current intensity 2A; type of current feeder B (Table 3); acidified electrolyte (Table 1).*

**Influence of fluidization**

Mass transfer of active species plays an important role in the electrodeposition of metals, especially when the concentration of active species is low.

As we observed in previous experiments, low mass transfer rate can be only partially compensated by enhancing the other technical parameters of the process, as current intensity, bed weight, current feeder type, etc.The obtaining of high values of Cu recovery is conditioned by longer operation time at a low current efficiency. Therefore, the necessity to improve the mass transfer by increase of electrolyte flow rate is evident (Figure 4). As can be seen from Figure 4, the effect of electrolyte rate is opposite for the two cases. The rise of electrolyte velocity up to 2 cm/s, increases the copper recovery efficiency. Over this value, at 2.3 cm/s for example, the efficiency of the electrolysis decreases.

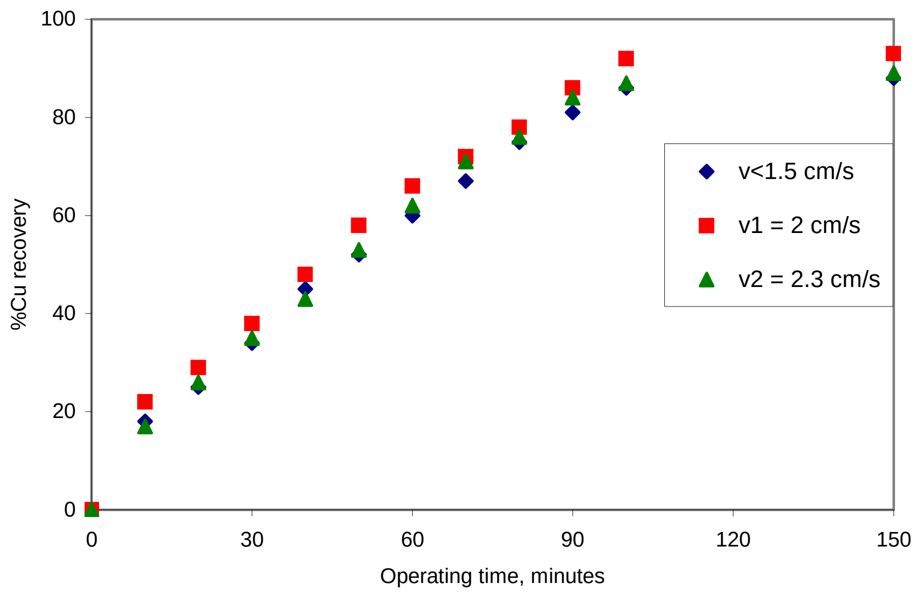


Figure 4. The influence of operating time and electrolyte flow rate on %Cu recovery; copper powder at 0.2-0.125 cm size range (Table 2); bed weight = 10g; electrolyte II (Table 1); current feeder type B (Table 3); I = 2A; v < 1.5 cm/s - packed bed; v > 1.5 cm/s - fluidized bed;

This behavior can be explained considering both the collision and conductive mechanisms proposed to explain the electrodeposition on particulate bed [10]. The particles of the bed are charged while contacted with current feeder or with others charged particles and are discharged because of electrochemical reactions. The slightly increasing of bed expansion by faster circulation of electrolyte, from 1.5 cm/s to 2.0 cm/s, develops the current feeder-particles and particles-particles collisions with enhanced charge transfer and copper recovery efficiency.

The raise of electrolyte rate, from 2 cm/s to 2.3 cm/s, determines of high degree of expansion in the bed. Each particle of the bed becomes free to move about in a random manner, losing touch with one to another and reducing the area in contact with the current feeder.

As the possibility of contacts between particles and current feeder is lower, the ratio of bipolar particles [10] in the fluidized bed will be increased and the %Cu recovery will be decreased.

The aspects presented above are supported by Figure 5. As shown, the current intensities in bed increases as electrolyte flow rate from 1.5 cm/s to 2.0 cm/s. At the lowest bed expansions, a large fraction of the current is carried by particulate phase, so-called “electronic transport”, and used for copper electrodeposition. At high bed expansions are very few conducting particles within the bed and most of the current is carried by the electrolyte -“ionic transport”. At circulation rates of electrolyte higher

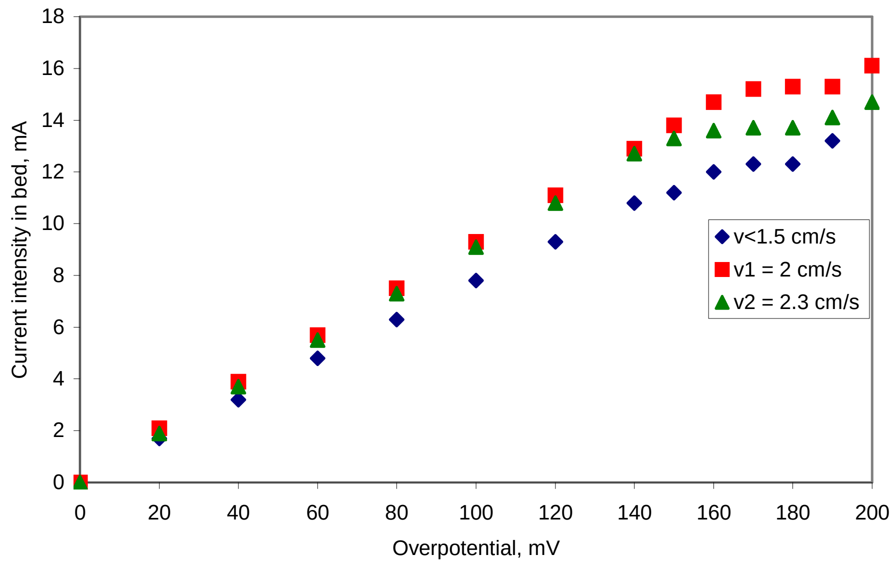


Figure 5. Current intensity in bed against the applied overpotential at different electrolyte flow rates; copper powder 0.2-0.125 cm size range (Table 2) ; bed weight = 10g; electrolyte II (Table 1); current feeder type B (Table 3); current intensity 2A; v < 1.5 cm/s- packed bed; v > 1.5 cm/s - fluidized bed;

than 2.0 cm/s, ionic transport of electric charges becomes more important than electronic transport. Thus, only a small part of the total current is used for electrochemical reaction, and the copper recovery efficiency decreases.

## CONCLUSIONS

Particulate bed cathode considered in this paper showed some good performance for the recovery of copper ions from waste waters. A high efficiency is conditioned by :

- high specific area, satisfied by powders with low size (-0.2 + 0.125 cm size range);

- improved mass transfer rate, realized by fluidization of particulate bed (optimal circulation rate of electrolyte 2 cm/s);

- improve of charge transfer by using a large active area current feeder and a acidulate electrolyte;

Correlation of these requirements allows, after 100 minutes of electrolysis, a 93% Cu recovery efficiency.

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