ABSTRACT. This article presents our results concerning the feasibility of selective electroextraction of copper from leaching solutions obtained during base metals recycling from waste printed circuit boards. The researches were focused on the intensive copper electrodeposition as a potential parallel paired process for the electrochemical regeneration of the leaching solutions. Preliminary tests, performed by cyclic voltammetry on 316 stainless steel disc electrode in synthetic solutions of CuBr₂, SnBr₂ and PbBr₂, indicate the possibility of selective electroextraction of Cu if the electrodeposition potentials of Sn and Pb are not exceeded. Therefore, selective and intensive Cu electrodeposition tests were accomplished in galvanostatic mode, in a real sample of leaching solution, using also 316 stainless steel sheets cathodes. The experimental results demonstrate that the selective electrodeposition of Cu is possible in a wide range of current densities, between 200 and 600 A/m², if the concentration of Cu in solution of at least 12 g/L is maintained. Under these conditions, the purity of the obtained Cu deposits can attain 99.6%.

Keywords: waste printed circuit boards, selective electroextraction, copper recovery, electrochemical parallel paired processes

INTRODUCTION

As a result of the rapid growth of the world economy and improvement of living standards, the production rate of waste electrical and electronic equipment (WEEE) strongly increases [1], becoming two to three times higher...
than for other urban wastes [2]. In the past two decades, WEEE has become a worldwide major pollution problem [3] with estimated quantities of about 50 million tons in 2020 [4] and over 52.2 million tons in 2021 [5]. The global shift towards sustainable resource management and the continuous depletion of high-quality virgin ore resources increase the need to develop strategies for the cyclical use of metals found in WEEE, as well as for the safe disposal of residues after recovery of the desired materials [6,7]. The recycling of WEEE also represents a strategy to avoid environmental pollution, although landfilling is still a notorious way of disposing this solid waste in emerging countries [8]. The WEEE recycling process also offers a valuable source of raw materials for the electronics industry [9].

The printed circuit boards (PCBs) are the most used items in almost all electronic devices [10] and/or represent their core component [11]. Usually, PCBs contain thin layers of precious metals over the metal contacts [12], significant amounts of Cu [13], but also traces of highly toxic ones, like Pb and Cd [14].

Currently, various technologies have been developed for the metals recycling from waste printed circuit boards (WPCBs), such as physical-mechanical, pyrometallurgical, hydrometallurgical, bioleaching methods or combinations of these approaches [15]. The hydrometallurgical methods present many advantages over the pyrometallurgical ones, including lower energy consumption, reduced capital costs and low toxic gas emissions [16]. However, conventionally, hydrometallurgical processes consume large amounts of chemicals and generate large volumes of waste waters [17]. As an alternative to the traditional PCBs recycling methods mentioned before, the electrochemical recovery of metals from WPCBs gains more and more attention, due to the high environmental compatibility [18], high energy and economic efficiency [19], minimal involvement of auxiliary materials [20] and better recovery of valuable materials [21].

Starting from the very promising results of our previous researches [21-23], the present work aimed to check the feasibility of the copper selective electroextraction from the extremely complex solutions obtained during the recovery of base metals from WPCBs using the KBr/HBr/Br₂ leaching system. The studies were focused on the possibility to use the intensive (high rate) copper electrodeposition as a potential parallel paired process for the electrochemical regeneration of the leaching solutions which will be performed, obviously, in a divided reactor [21], simultaneously with the obtention of pure and easy valorisable Cu deposits. Before the galvanostatic experiments concerning the intensive Cu electrodeposition from the real leaching solution, preliminary tests were accomplished by cyclic voltammetry (CV) on a 316 stainless steel (SS) disc electrode in synthetic mono-component solutions of CuBr₂, SnBr₂.
and PbBr₂. CV results indicate that Cu can be electroextracted selectively if the electrodeposition potentials of Sn and Pb are not exceeded. Finally, the Cu deposits obtained by galvanostatic electrolysis were cleaned, dried, detached from the 316 SS sheet cathodes, mineralized with aqua-regia, and analysed by ICP-OES. The obtained results demonstrate that valuable and high purity Cu deposits (up to 99.6%) can be obtained using current densities between 200 and 600 A/m² and maintaining the Cu concentration in solution higher that 12 g/L.

RESULTS AND DISCUSSION

The results of the preliminary tests performed by CV on the 316 SS disc electrode of 3 mm diameter, in synthetic mono-component solutions of CuBr₂, SnBr₂ and PbBr₂, are presented in Figure 1.

![Voltammograms recorded by CV on 316 SS disc electrode in synthetic mono-component solutions containing 2 M KBr + 0.5 M HBr + CuBr₂ (A), SnBr₂ (B) and PbBr₂ (C) of different concentrations (see inset)](image)
It is worth to note that the CV applied to study the process of metals electrodeposition/electrodissolution offers less accurate quantitative data, the peaks amplitude and position being strongly influenced by many factors like deposit morphology, electrode-deposit compatibility, vertex potential, etc. However, the CV remains a powerful tool for qualitative comparisons. Consequently, for a rigorous estimation of the Cu, Sn and Pb electrochemical behaviours, we decided to evaluate the electrodeposition potential, \( E_{DEP} \), where the process start effectively. As exemplified in Figure 1.C, \( E_{DEP} \) corresponds to the intersection of the linear extrapolations associated with the \( \mathrm{Cu}^{2+} \) to \( \mathrm{Cu}^{+} \) reduction process and the effective electrodeposition process. The evaluated \( E_{DEP} \) values are presented in Table 1.

Table 1. Evolution of \( E_{DEP} \) corresponding to the \( \mathrm{Cu}^{2+} \), \( \mathrm{Sn}^{2+} \) and \( \mathrm{Pb}^{2+} \) ions electrodeposition on 316 SS electrode from solutions containing different concentrations of \( \mathrm{CuBr}_2 \), \( \mathrm{SnBr}_2 \) and \( \mathrm{PbBr}_2 \).

|               | Cu       |                  | Sn       |                  | Pb       |                  |
|---------------|----------|------------------|----------|------------------|----------|------------------|
| \( [\mathrm{CuBr}_2] \) (mM) | \( E_{DEP} \) (V/Ref.) | \( [\mathrm{SnBr}_2] \) (mM) | \( E_{DEP} \) (V/Ref.) | \( [\mathrm{PbBr}_2] \) (mM) | \( E_{DEP} \) (V/Ref.) |
| 16            | -0.407   | 10               | -0.491   | 5                | -0.541   |
| 32            | -0.383   | 20               | -0.485   | 10               | -0.532   |
| 48            | -0.366   | 50               | -0.476   | 20               | -0.526   |
| 64            | -0.355   | 100              | -0.472   | -                | -        |

As it can be seen from Figure 1 and Table 1, for all three studied ions, the modification of concentration values induces only minor changes of \( E_{DEP} \) in good agreement with the Nernst equation. Moreover, for the worst scenario, corresponding to the minimal \( \mathrm{Cu}^{2+} \) concentration (16 mM \( \cong \) 1 g/L) and maximal concentration of \( \mathrm{Sn}^{2+} \) (0.1 M \( \cong \) 10 g/L), substantial \( E_{DEP} \) gap, of \( \sim \)70 mV, occurs for Cu and Sn. Similarly, for the highest Pb concentration (20 mM \( \cong \) 4 g/L), the \( E_{DEP} \) gap increase at \( \sim \)120 mV. Considering these \( E_{DEP} \) gaps values and that, usually, the concentration of Cu, Sn and Pb ions in the spent leaching solutions vary between 300 and 600 mM, 50 and 90 mM, and 0.2 and 40 mM [23], respectively, we concluded that the selective electroextraction of Cu can be performed successfully on 316 SS electrodes if the operational parameters are rigorously controlled.

As stated before, the selective Cu electrodeposition tests from real leaching solutions were performed in galvanostatic mode, at current values \( (I_{WE}) \) imposed through the working electrode \( (WE) \) between -0.08 and -0.4 A, corresponding to current densities \( (i_{WE}) \) between 200 and 1000 A/m². Practically, using the experimental parameters indicated in Table 2, five distinct experiments were performed for similar quantities \( (Q) \) of electric charge (excepting the last
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test), the corresponding Cu deposits being coded as D1 ÷ D5. In addition, in
Table 2 are also presented the most important parameters evaluated from the
experimental data: the current efficiency (CEF), the specific energy consumption
(WS), the average values of the WE potential (E_{WE,M}) and of the oxidation/
reduction potential (ORP_M). CEF, WS, E_{WE,M} and ORP_M were evaluated using
the main electrical parameters recorded during the experiments, presented
in Figure 2, where E_{WE}, U_T, E_{CE}, pH and ORP represent the instant values of
the WE potential, voltage at the terminals of the electrochemical cell, the counter
electrode (CE) potential, pH and of the oxidation/reduction potential, respectively.

Table 2. The experimental parameters for the selective electrodeposition of Cu
from a real leaching solution and the main evaluated parameters

| Deposit | i_{WE} (A) | t (min) | i_{WE} (A/m²) | Q (A*h) | CEF (%) | WS (kWh/kg) | E_{WE, M} (V/Ref) | ORP_M (V/Ref) |
|---------|------------|---------|---------------|---------|---------|-------------|--------------------|---------------|
| D1      | -0.40      | 127     | 1000          | 0.847   | 50.5    | 0.389       | -0.363             | 0.047         |
| D2      | -0.32      | 158     | 800           | 0.843   | 54.6    | 0.292       | -0.346             | 0.031         |
| D3      | -0.24      | 211     | 600           | 0.844   | 92.8    | 0.133       | -0.343             | 0.020         |
| D4      | -0.16      | 316     | 400           | 0.843   | 90.8    | 0.105       | -0.311             | 0.018         |
| D5      | -0.08      | 316     | 200           | 0.421   | 89.0    | 0.086       | -0.287             | 0.032         |

As can it be seen in Table 2, the current efficiency varies between
50.5 and 92.8%, considering that the Cu electrodeposition process occurs
predominantly mono-electronic, described by the reaction:

\[
\text{CuBr}_2^- + \text{e}^- \rightarrow \text{Cu}^0 + 2\text{Br}^- \quad (1)
\]

Unfortunately, in parallel with this main process, a series of secondary
processes take place, described by the reactions:

\[
\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}^0 \quad (2)
\]

\[
\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+ \quad (3)
\]

The intensity of the processes described by the equations (2) and (3)
depends on the Cu^{2+} ion concentration and, especially, on the ratio between
the Cu^{2+} and Cu^{+} ion concentrations, which significantly influence the solution
specific ORP value. From another point of view, it is important to note that,
during the break between experiments and, especially, during them (when
the solution is stirred), the Cu^{+} ions are permanently oxidized to the Cu^{2+} ions
due to the presence of atmospheric oxygen, according to the reaction:

\[
4\text{Cu}^+ + \text{O}_2 + 4\text{H}^+ \rightarrow 4\text{Cu}^{2+} + 2\text{H}_2\text{O} \quad (4)
\]
This parasitic process is confirmed by the evolution of ORP throughout all experiments, which starts permanently, as illustrated in Figure 2, from a high value, and then decreases as Cu$^{2+}$ ions get reduced to Cu$. The presence of the atmospheric oxygen has a negative effect on the Cu electrodeposition process, increasing Cu$^{2+}$ concentration and favouring the secondary processes described by equations (2) and (3).

**Figure 2.** Evolution of the main electrical parameters during the experiments concerning the galvanostatic electrodeposition of Cu from the leaching solution.
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Inherently, as illustrated in Figure 3, the applied current density has a significant effect on the morphology, structure and appearance of the obtained deposits.

Figure 3. Images of the Cu deposits 
D1 ÷ D5
For an $i_{\text{WE}}$ of 1000 A/m², the lowest $C_{\text{EF}}$ and the highest $W_S$ values were evaluated, simultaneously with the highest values for $E_{\text{WE},M}$ and ORP$_{M}$, indicating clearly that the secondary processes (2) and (3) predominate during the experiment. Additionally, the resulting D1 covers only a small part of the cathode and has an accentuated dendritic structure, which induces high risk of detachment from the electrode surface.

For an $i_{\text{WE}}$ of 800 A/m², the values of $C_{\text{EF}}$, $W_S$, $E_{\text{WE}, M}$ and ORP$_{M}$ improve to a small extent, indicating a reduction in the ratio between Cu$^{2+}$ and Cu$^+$ ion concentrations. In these conditions, it can be stated that the secondary processes (2) and (3) still predominate during the experiment. However, the aspect of the resulting D2 changes from an accentuated dendritic structure to a granular one. Also, in this case, D2 covers only a small part of the cathode.

At the $i_{\text{WE}}$ of 600 A/m², the best value for $C_{\text{EF}}$ (≈ 93%), a much lower value for $W_S$ (0.133 kWh/kg) and acceptable values for $E_{\text{WE}, M}$ and ORP$_{M}$ were obtained, indicating that, in this case, the predominant process becomes the mono-electronic electrodeposition of Cu. Under these conditions, D3 covers most of the cathode and has a predominantly granular structure, with a much-diminished edge effect.

For an $i_{\text{WE}}$ of 400 A/m², the obtained results in terms of $W_S$, $E_{\text{WE}, M}$ and ORP$_{M}$ are improved in comparison with D3. Unfortunately, the $C_{\text{EF}}$ value presents a small decrease, suggesting that the rates of parasitic processes start to increase. In these conditions, D4 covers almost entirely the cathode surface and has a finer granular structure, but with a more evident edge effect than D3.

Finally, to avoid excessive experiment duration (more than 10.5 h), we decided to halve the Q value used for the $i_{\text{WE}}$ of 200 A/m². In these conditions, the best value for $W_S$ (0.086 kWh/kg) and an acceptable value for $C_{\text{EF}}$ (89%) were obtained. This fact indicates that, although, in this case, the mono-electronic electrodeposition of Cu is the predominant process, the oxidation process with atmospheric oxygen is accentuated. As it can be seen in Figure 3, D5 completely covers the cathode with a smooth and compact film, but it has an accentuated edge effect.

In addition to the information concerning the $C_{\text{EF}}$, $W_S$, $E_{\text{WE}, M}$ and ORP$_{M}$, and those related to the deposits appearance, the establishment of optimal operating conditions must also take into account the purity of the obtained deposits. In this respect, the deposits were subjected to mineralization in aqua regia, and the concentrations of the metallic impurities were evaluated by ICP-OES. The results obtained from these analyses are summarized in Table 3 and represent the percentage concentration (w/w) relative to the mass of the deposits.
Table 3. Cu content and the percentage of the metallic impurities from the Cu deposits obtained by selective electrodeposition from real leaching solutions

| Deposit | Cu (%) | Sn (%) | Pb (%) | Fe (%) | Ni (%) | Zn (%) | Ag (%) |
|---------|--------|--------|--------|--------|--------|--------|--------|
| D1      | 98.93  | 0.60   | 0.10   | 0.01   | 0.02   | 0.21   | 0.10   |
| D2      | 99.40  | 0.21   | 0.05   | 0.01   | 0.01   | 0.21   | 0.08   |
| D3      | 99.67  | 0.09   | 0.03   | 0.00   | 0.00   | 0.15   | 0.05   |
| D4      | 99.67  | 0.06   | 0.03   | 0.01   | 0.00   | 0.19   | 0.04   |
| D5      | 99.68  | -      | 0.04   | 0.01   | 0.00   | 0.22   | 0.04   |

As it can be seen in Table 3, excepting the D1 case, for all other experiments, the purity of the obtained Cu deposits exceeds 99%, reaching 99.68% in the case of D5. The weaker results in case of D1 are justified by the fact that, at the beginning of the experiment, $E_{\text{WE}}$ drops to values of -0.8 V/Ref, favouring the massive electrodeposition of impurities. Contrarily, at the lowest current density ($i_{\text{WE}} \approx 200$ A/m$^2$), the concentration of impurities is minimal, but the electrodeposition rate becomes extremely low.

Corroborating the results presented in Figures 2 and 3, and Tables 2 and 3, it is obviously that the current density represents the key factor in the selective electroextraction of Cu. Practically, the increase of the current density induces more negative $E_{\text{WE}, M}$ values, increasing the risk of the other base metals co-deposition.

Based on these observations, we suppose that an improved selective electrodeposition can be achieved using a variable profile for the current density, starting from low values in order to cover the cathode surface with a layer of compact and pure Cu, and continuing with increasing current densities, up to 600 A/m$^2$.

CONCLUSIONS

Based on the experimental results concerning the intensive electrodeposition of Cu on 316 SS electrodes from real solutions, we concluded that the selective Cu electroextraction can be successfully and efficiently used as the parallel paired process for the electrochemical regeneration of the leaching solutions based on the KBr/HBr/Br$_2$ system. High purity Cu deposits, up to 99.6%, can be obtained by maintaining the concentration of Cu ions in the leaching solution over 12 g/L and imposing cathodic current densities between 200 and 600 A/m$^2$. 

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Increased purity of the deposits and better process efficiency can be achieved by using variable current profile, avoiding oxidation of the solution with atmospheric oxygen and increasing the thickness (mass) of the deposit.

**EXPERIMENTAL SECTION**

**Chemicals**

Reagents as: KBr, HBr, CuBr₂, SnBr₂, and PbBr₂ are purchased by Fluka and Sigma-Aldrich.

For the CV measurements, synthetic sample solutions are prepared by dissolving appropriate quantities of CuBr₂, SnBr₂, and PbBr₂ in 2 M KBr + 0.5 M HBr solution.

The real leaching solution was obtained by mixing equal samples from different solutions resulted by the leaching of the exposed metals from 10 PC motherboards in 2.2 L of 2 M KBr + 0.5 M HBr + 1 M Br₂ solutions [22]. The ORP of the resulting mixture (1 L) was lowered by placing it over 2 kg of WPCBs, after which the solution pH was adjusted to 0.1 by addition of HBr 47%. The concentrations of the main metallic ions in the solution were: 12 g/L Cu; 6.9 g/L Sn; 4.4 g/L Pb; 9 g/L Zn; 5.6 g/L Fe; 0.8 g/L Ni.

**Experimental methods**

Cyclic voltammetry was performed using a computer-controlled multi-channel potentiostat (DXC240, Datronix Computer, Romania). The electrochemical glass cell (50 mL) was equipped with a 316 SS disc (ϕ = 3 mm) as WE, a Ag/AgCl/KCl_sat as reference electrode (Ref.) and a Pt wire (ϕ = 0.5 mm, L = 10 cm) as CE. All the CV measurements were performed using a scan rate of 50 mV/s.

In order to preserve the electrolyte composition, the selective Cu electrodeposition experiments in galvanostatic mode (from real leaching solution) were performed in an undivided polypropylene electrochemical cell with a volume of 1 L, in which 400 mL of previous described real leaching solution was introduced. For the same reason, a 3 cm x 8 cm Cu plate with a thickness of 0.5 mm was used as CE (soluble anode). The cell was equipped with one 2 cm x 2 cm plate WE made from 316 SS sheet with a thickness of 0.2 mm, the face non-exposed to the CE being insulated. WE, CE and 2 reference electrodes of Ag/AgCl/KCl_sat type were connected to a computer controlled potentiostat (DXC236, Datronix Computer, Romania). Additionally, 2 laboratory multi-meters (Consort C863, Consort, Belgium) were used as galvanically insulated electrochemical interfaces with high input
impedance between the data acquisition board (NI6221, National Instruments, USA) and the pH and ORP sensors (SP10T and SO50X, respectively, both from Consort, Belgium). During the experiments, the electrolyte was stirred using a magnetic stirrer (FB 15001, Fischer Scientific). Before each test, the WE was polished using emery paper (1200 and 2000), washed with double-distilled water and dried under nitrogen jet. After each experiment, the SS electrode was removed from the electrochemical cell and the obtained Cu deposit was washed with 2 M KBr + 0.5 M HBr mixture (to avoid the precipitation of Cu, Sn and Pb ions), cleaned with double-distilled water and dried with pure acetone and pure nitrogen jet. Finally, the Cu deposits were detached from the SS cathode, weighed with an analytical balance, and mineralised with 28 mL of aqua-regia. The resulted solutions were analysed by ICP-OES method, using a SPECTRO CIROS CCD spectrometer (SPECTRO Analytical Instruments, Germany). The concentrations of the dissolved metallic ions from the leaching solutions were measured by flame atomic adsorption spectroscopy (FAAS), using an AVANTA-PM spectrometer (GBC, Australia).

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