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SELECTIVE ELECTROEXTRACTION OF BASE METALS FROM LEACHING SOLUTIONS OBTAINED DURING THE RECYCLING OF WASTE PRINTED CIRCUIT BOARDS. III. PRELIMINARY TESTS FOR IRON, NICKEL AND ZINC ELECTROEXTRACTION

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ABSTRACT. This paper presents the results of our research concerning the feasibility of the Fe, Ni and Zn electroextraction from partially treated spent leaching solutions resulting from the waste printed circuit boards recycling process using the bromine/bromide system. The first tests, performed in a real sample of spent leaching solution and using a Pt Fisher type cathode, led to inacceptable results due to the intensive hydrogen evolution. To find a feasible industrial solution, systematic preliminary tests were performed by hydrodynamic cyclic voltammetry in synthetic solutions using small diameter (3 mm) rotating disk electrodes (RDEs) of carbon paste (CP) and 304 type stainless steel (304 SS), resulting in theoretical current efficiencies of up to 95.8%. Further, to prove the feasibility of the pure Zn and Zn alloys electroextraction, long duration (0.15÷8 h) experiments were done by potentiostatic chronoamwperometry using RDEs on CP and 304 SS of large diameters (38 and 29 mm, respectively). The obtained results proved that, depending on the electrolyte's composition and pH, and on the imposed potential, high purity Zn (over 98%) or Zn-Fe-Ni alloy deposits can be obtained at current efficiencies between 20 and 96% and specific energy consumptions between 2 and 17 kWh/kg of alloy.

Keywords: *waste printed circuit boards recycling, selective electroextraction, iron, nickel and zinc recovery, iron-nickel-zinc alloy electrodeposition*

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INTRODUCTION

During the last decades, due to the environmental and economic implications, intensive research has been carried out regarding the development and optimization of technologies for the recovery of metals and other materials from the waste printed circuit boards (WPCBs). [1-4] As an alternative to the traditional pyrometallurgical methods [5,6], exhaustive studies concerning the valuable metals leaching by hydrometallurgical [7,8], bio-hydrometallurgical [9, 10], and electrochemical [11,12] processes have been conducted. For the latter, electrochemically regenerable leaching systems based on the Fe^{3+}/Fe^{2+} [13], Cu^{2+}/Cu^{+} [14] or Br_2/Br^- [15] redox couples can be successfully used, requiring only minimal pre-treatment of the WPCBs. Noticeably, compared to the chloride containing systems, the Br_2/Br^- one is extremely efficient, allowing a fast leaching of the base metals (BM, e.g. Cu, Sn, Pb, etc.) [16] or even noble metals (e.g. Ag, Au) [17], and the complete recovery of other WPCBs components.

From another point of view, it’s worth noting that, in the great majority of published studies, the recovery of leached metals from WPCBs is focused only on metals with a high market value or those with high toxicity, applying methods such as cementation [18], precipitation, extraction [19,20] or electrodeposition. [21,22] Unfortunately, the recovery of the other metals left in the solution, such as Zn, Al, Fe, Ni, is extremely little discussed [23,24] because of their low market value and high extraction costs. [25,26] A possible solution to these problems can be the electrodeposition of binary and/or ternary alloys of Zn, Fe and Ni. This process has been intensively studied on various cathode materials, both in potentiostatic [27] or galvanostatic [28] mode, but the main goal of these studies was to obtain films with good mechanical and anti-corrosion properties. [29-31] Generally, to improve the quality of the obtained deposits, different additives (e.g., acidity correctors, leveling agents, gelatin, etc.) were used. [32,33] Unfortunately, the presence of these additives in the solutions used for leaching metals from WPCBs can interfere significantly with the recovery of target metals and with the reagent’s electrochemical regeneration processes.

In the previously mentioned context, this paper presents our main results concerning the feasibility of Fe, Ni and Zn electroextraction from leaching solutions obtained during the process of BM electrochemical recovery from WPCBs. The first set of measurements, performed in a real sample of spent leaching solution and using a traditional Pt Fisher electrode, revealed that Pt is inadequate because it favors the hydrogen evolution reaction (HER). Consequently, the next experiments were performed using rotating disc electrodes (RDE), made of carbon paste (CP) and 304 type stainless steel (304 SS). The results obtained by hydrodynamic cyclic voltammetry (HCV) and potentiostatic chronoamperometry (PCA) confirmed the possibility of advanced and efficient recovery of these metals, as well as the creation of premises for the total recovery of the initial leaching solution.

RESULTS AND DISCUSSION

Electroextraction test on Pt Fisher electrode

Aiming to rigorously evaluate the quantities of Fe, Ni and Zn that can be extracted from the leaching solutions obtained during the BM recovery from WPCBs, a series of experiments were started using as catholyte the solution resulted after the previous tests concerning the potentiostatic selective electroextraction of Cu, Sn and Pb.[22] Moreover, the same experimental setup (equipped with the Pt Fisher electrode) was used and similar protocols were applied. The evolutions of electrolyte pH and of the main electrical parameters recorded during these tests are presented in Figure 1, whereas a summary of the main experimental parameters and results is presented in Table 1. Also, three examples of the obtained deposits photographs, indicated in Table 1, are presented in Figure 2.

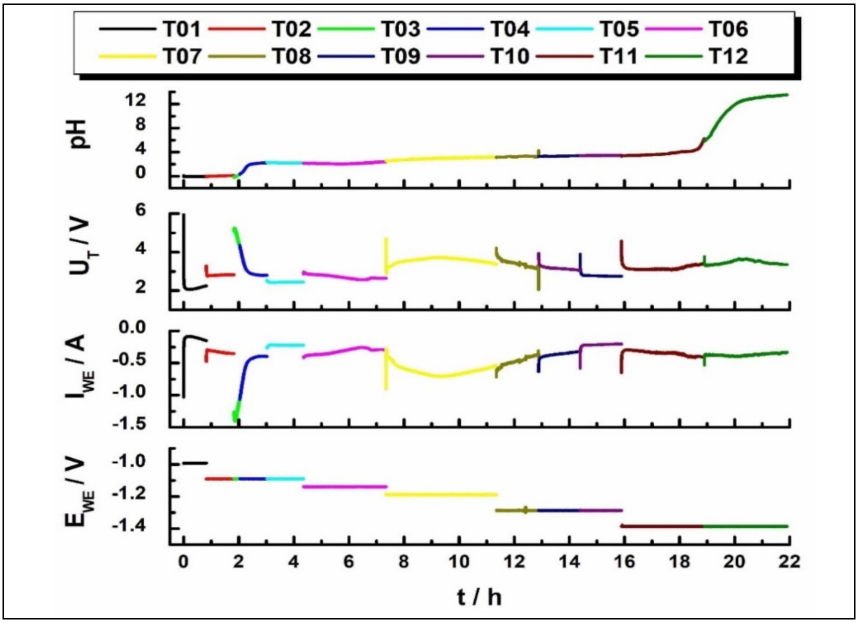

Figure 1. Evolutions of the electrolyte pH and of the main electrical parameters during the potentiostatic electrodeposition of Fe, Ni and Zn from a real sample of leaching solution using the Pt Fisher type electrode

Table 1. Main experimental conditions and results for the tests of Fe, Ni and Zn potentiostatic electrodeposition from a real sample of leaching solution on the Pt Fisher type electrode

Test	Deposit	E_{WE} (V/RE)	t (h)	pH_M	m_D (mg)	[Fe] (%)	[Ni] (%)	[Zn] (%)	[Imp] (%)	C.E. (%)	W_S (kWh/kg)
T01	**D1**	-1.00	0.8	-0.05	131	1.37	1.93	75.0	21.7	93.4	1.96
T02÷04	**D2**	-1.10	2.2	0.62	127	0.21	0.17	69.7	30.0	6.74	42.4
T05	**D3**	-1.10	1.3	2.22	70	10.8	1.63	52.3	35.2	13.0	16.0
T06	**D4**	-1.15	3.0	2.16	112	51.1	0.47	36.4	12.0	9.37	26.2
T07	**D5**	-1.20	4.0	2.94	112	27.7	0.56	7.34	64.4	1.49	224
T08÷10	**D6**	-1.30	4.5	3.35	503	14.4	2.21	0.17	83.2	5.07	60.1
T11	**D7**	-1.40	2.0	3.86	1464	6.69	0.69	0.06	92.6	13.3	30.5
T12	**D8**	-1.40	4.0	11.5	17	18.7	3.64	0.57	77.1	0.17	971

In Figure 1, E_{WE} represents the potential of the working electrode (WE) in respect to the reference electrode (RE) of Ag/AgCl/KCl_{SAT} type, I_{WE} is the current through the WE and U_T represents the voltage at the terminals of the electrochemical reactor (ECR). Also, in Table 1, t is the duration of each successive test (T01 to T12), pH_M represents the mean value of the electrolyte pH, m_D is the mass of the obtained deposits (D1 to D8), [Fe], [Ni] [Zn] and [Imp.] represent the percentages of metals and impurities in the deposit (calculated based on flame atomic absorption spectrometry analysis), and C.E. and W_S are the current efficiency and the specific electricity consumption, respectively. The last two parameters were calculated using the relations:

$$C.E.= \frac{z^*F^*m_D^*(\frac{[Fe]}{A_{Fe}}+\frac{[Ni]}{A_{Ni}}+\frac{[Zn]}{A_{Zn}})}{1000^* \int_0^t I_{WE}{}^*dt} \quad [\%] \qquad (1)$$

$$W_S = \frac{1000^* \int_0^t I_{WE}{}^*U_T{}^*dt}{36^*m_D{}^*([Fe]+[Ni]+[Zn])} \quad [kWh/kg] \qquad (2)$$

where z is the number of transferred electrons (2 in the case of Fe, Ni and Zn), F is the Faraday constant (96480 A*s/E_g), and A_{Fe}, A_{Ni} and A_{Zn} represent the atomic masses of the metals, respectively.

As can be seen from Figure 1, at the start of Test 1 (T01), conducted at E_{WE} of -1.0 V/ER, we observed a very large current impulse, corresponding to HER, which is highly favored by the Pt cathode matrix and the electrolyte's acidity. Fortunately, as the Fisher electrode is increasingly covered with a Zn layer, HER is strongly inhibited and Zn deposition is subsequently favored, resulting in a smooth and compact deposit (see picture D1 in Figure 2).

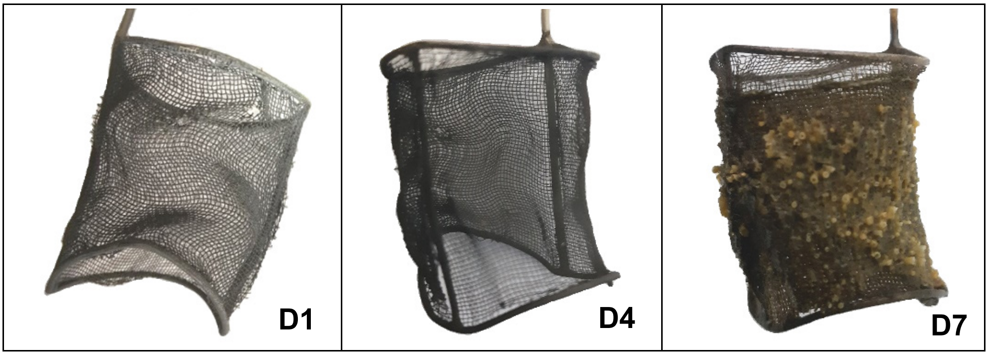

Figure 2. Examples of deposits obtained on the Pt Fisher type electrode

Correlating the data from Table 1 and Figures 1 and 2, it can be observed that, by using a relatively low E_{WE} (-1.0 V/ER), Zn can be extracted with an acceptable purity (over 95%), with an overall C.E. of approximately 93% and a W_S value less than 2 kWh/kg of deposit.

From the data acquired and the performance parameters evaluated from tests T02 – T04, we can conclude that the attempting to speed up the electrodeposition process by increasing the E_{WE} value to -1,1 V/ER has a negative effect on the metals' electroextraction, achieving C.E and W_S values under 6.7% and over 42 kWh/kg, respectively. Additionally, the massive hydrogen evolution during test T04 led to a significant pH rise, over the value of 2. In these new conditions, during T05 and T06, Fe and Ni start to be co-deposited together with Zn as adherent and compact deposits as exemplified in picture D4 from Figure 2.

The following tests (T07 – T12), performed at increasingly negative potentials (between -1,2 and -1,4 V/ER) have shown pronounced pH rises and apparent increases of the deposit's masses. Analyzing the obtained deposits, we found that, in fact, the evaluated quantities of Zn, Fe and Ni were very low, leading to extremely low C.E. and exaggerated W_S values. This paradox can be attributed to the fact that, at elevated pH values, the deposits attached to the Fisher electrode (see Picture D7 from Figure 2) consist preponderantly in oxy-hydroxides of the BM present in the WPCBs leaching solutions, where, besides Fe, Ni and Zn, we also detected high amounts of Cr, Al, Bi and Mn.

The results of this first set of tests suggest that, by using an inadequate cathodic matrix and unoptimized process parameters, we cannot obtain promising results regarding the possibility of Fe, Ni and Zn electroextraction from WPCBs leaching solutions. Consequently, we decided to perform additional tests aimed at finding technical solutions able to ensure the more advanced electroextraction of Fe, Ni and Zn from leaching solutions.

Preliminary electroextraction tests by HCV using small diameter RDE of CP and 304 SS

Before starting new long duration electroextraction test, we decided to perform preliminary HCV experiments to evaluate the electrochemical behavior of other candidates (CP and 304 SS) as cathodic material. Concretely, to evaluate the feasibility to recover Fe, Ni and Zn from synthetic ternary solutions (2 M KBr + 0.5 M HBr + 10 g/L Fe + 10 g/L Zn + 1 g/L Ni), at different pH values (adjusted to 0, 1, 2 or 3), and returning potentials (E_{RET}), two small dimeter (3 mm) RDEs of CP and 304 SS were used, a few examples from the recorded curves being presented in Figure 3.

As can be observed in Figure 3.A and 3.B, at pH = 0, on both materials, the electrodeposition of Fe-Ni-Zn alloys is strongly inhibited, the shape of the anodic redissolution peaks indicating that the obtained deposits, at all tested E_{RET} values, are predominantly composed of Zn. Contrarily, at pH = 2 (Figures 3.C and 3.D), the obtained deposits start to include increasing amounts of Fe and Ni in parallel with the progressive shift of E_{RET} to more negative values. The phenomenon is less evident for CP due to its low electrical conductivity, which leads to significant voltage drops and, implicitly, pronounced alteration of the imposed voltage at the WE's surface.

To find the optimal conditions for Fe, Ni and Zn electroextraction, we evaluated, for all tested conditions, the electrodeposition efficiency (E.E.) as the ratio between the electrical charges recorded during the anodic and cathodic processes, the calculated values being presented in Table 2.

The data presented in Table 2 reveals that, for both materials and at all tested pH values, an E_{RET} value of -1.0 V/RE is too positive to start de electrodeposition process and values more negative than -1.1 V/RE are required. Further, for CP and 304 SS, the maximal E.E. values, of 95.8 and 86.8%, are obtained at pH values of 3 and 2, and E_{RET} values of -1.3 and -1.2 V/RE, respectively. These E.E. values revealed that, theoretically, by adequately choosing the electrode material, solution pH and applied potential, Fe, Ni and Zn can be efficiently extracted by electrodeposition from the spent leaching solutions resulting from the WPCBs recycling process.

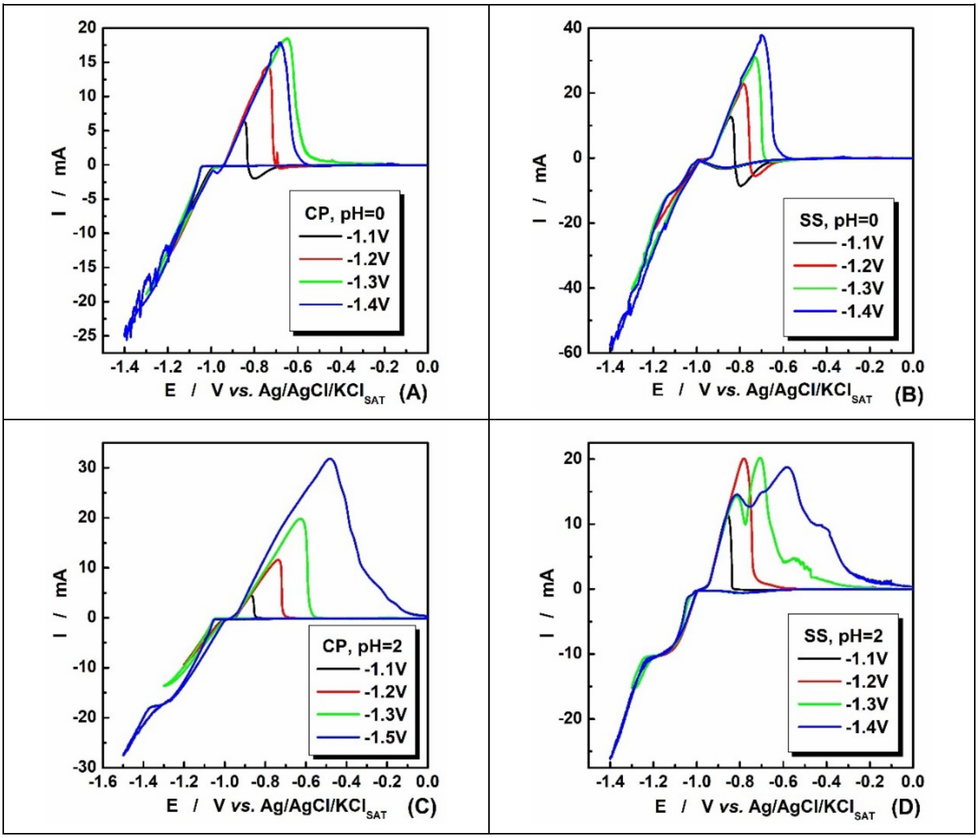

Figure 3. Examples of voltammograms recorded using HCV on RDE of CP (A and C) and 304 SS (B and D) in synthetic ternary solution (2 M KBr + 10 g/L Fe + 10 g/L Zn + 1 g/L Ni) for different values of E_{RET} (indicated in legends) and pH values of 0 (A and B) and 2 (C and D) (ω = 1000 rpm; v = 10 mV/s)

Table 2. Electrodeposition efficiency (%) evaluated through HCV for the Fe, Ni and Zn electrodeposition on RDE of CP and 304 SS in the ternary synthetic solution (2 M KBr + 10 g/L Fe + 10 g/L Zn + 1 g/L Ni) for different E_{RET} and pH values

E_{RET}	**WE = CP**				**WE = 304 SS**			
(V/RE)	**pH=0**	**pH=1**	**pH=2**	**pH=3**	**pH=0**	**pH=1**	**pH=2**	**pH=3**
-1	0	0	0	0	0	0	0	0
-1.1	47.6	51.9	38.9	72.1	32.8	63.5	68.2	73.4
-1.2	66.5	86.5	81.4	89.1	39.4	81.2	86.8	80.8
-1.3	66.6	87.6	90.8	95.8	32.7	68.6	84.4	85.8
-1.4	30.9	80.1	91.1	95.5	27.0	67.5	81.2	72.7

Long-duration PCA tests on RDE of CP and 304 SS

The first sets of long duration electroextraction tests by PCA were performed in an original compartmented ECR (see Experimental section), using a CP RDE of 38 mm diameter and ternary synthetic solutions (2 M KBr + 0.5 M HBr + 10 g/L Fe + 10 g/L Zn + 1 g/L Ni), at different pH and E_{WE} values. The corresponding evolutions of pH and main electrical parameters are presented in Figure 4, a synthesis of the main experimental parameters and the obtained results is presented in Table 3, and a few examples of the obtained deposits photographs are presented in Figure 5.

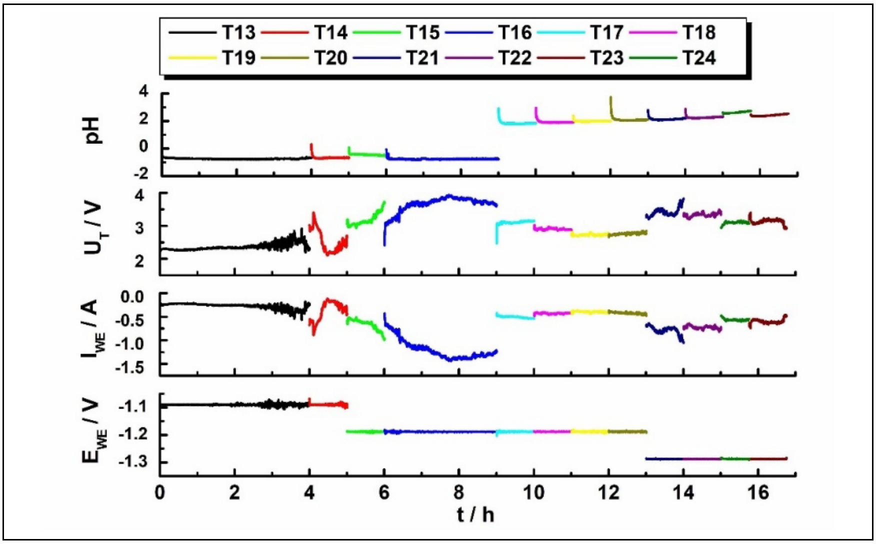

Figure 4. Evolution of the pH and main electrical parameters during the potentiostatic electrodeposition of Fe, Ni and Zn from samples of synthetic leaching solution (2 M KBr + 0.5 M HBr + 10 g/L Fe + 10 g/L Zn + 1 g/L Ni) using the CP RDE of 38 mm diameter

Very interestingly, as can be seen from Figure 4 and the first four lines of Table 3 (T13 ÷ T16), the pH recorded in the ternary solution of metals (Fe + Zn +Ni) containing 2 M KBr and 0.5 M HBr presented exaggerated negative values (generally, under -0.5 pH units). We also recorded this abnormal behavior in similar solutions, even without the BM ions [34], most probably due to the ions' interactions in solutions with very high ionic strength. [35,36] In these conditions, as can be seen from the first two lines of Table 3 (T13 and T14), when the CP RDE was polarized at -1.1 V/ER, no deposits were obtained. Contrarily, in the same solution, decreasing the E_{WE} to -1.2V/ER (T15 and T16) allows the deposition of high purity Zn with an C.E. of around 50% and W_S of 6 kWh/kg. Moreover, as can be seen in Figure 5, deposit D12 is relatively compact, allowing it to be easily detached and analyzed. These first two experiments prove the fact that, by choosing the adequate polarizing potential, Zn can be recovered from the leaching solution without diminishing its acidity, which allows for the direct recirculation of the leaching solution in the process.

Table 3. The main experimental parameters and obtained results for the PCA electrodeposition tests of Fe, Ni and Zn from synthetic ternary solutions (2 M KBr + 0.5 M HBr + 10 g/L Fe + 10 g/L Zn + 1 g/L Ni) using the CP RDE of 38 mm diameter

Tests	**Deposit**	**E_{WE} (V/RE)**	**t (h)**	**pH_M**	**m_D (mg)**	**[Fe] (%)**	**[Ni] (%)**	**[Zn] (%)**	**[Imp.] (%)**	**C.E. (%)**	**W_S (kWh/kg)**
T13	**D9**	-1.1	4	-0.74	-	-	-	-	-	-	-
T14	**D10**	-1.1	1	-0.66	-	-	-	-	-	-	-
T15	**D11**	-1.2	1	-0.45	560	0.05	0.18	68.8	31.4	48.1	5.53
T16	**D12**	-1.2	3	-0.76	2450	0.12	0.04	89.8	10.1	50.6	6.02
T17	**D13**	-1.2	1	1.84	590	1.08	0.14	83.0	16.0	80.3	3.20
T18	**D14**	-1.2	1	1.93	500	1.34	0.20	84.8	14.0	83.4	2.88
T19	**D15**	-1.2	1	1.98	420	1.92	0.18	94.7	3.59	84.5	2.68
T20	**D16**	-1.2	1	2.10	500	5.45	0.52	80.8	14.3	85.8	2.69
T21	**D17**	-1.3	1	2.13	960	17.9	1.55	63.3	20.3	86.1	3.42
T22	**D18**	-1.3	1	2.25	940	29.4	3.35	45.1	28.8	88.5	3.31
T23	**D19**	-1.3	1	2.42	790	35.5	3.85	37.2	31.1	89.9	3.11
T24	**D20**	-1.3	0.75	2.62	670	44.2	4.32	13.7	46.5	91.2	3.14

Further tests, conducted at pH values of around 2, indicate the fact that, depending on the imposed E_{WE} and the depletion degree of the leaching solution, mixed deposits of Fe-Ni-Zn in varying proportions can be obtained, with C.E. values between 80 and 91% and W_S values between 2.7 and 3.4 kWh/kg. Additionally, as can be seen from the example included in Figure 5 (D14), the deposits are compact, facilitating their removal.

The results of the long-duration PCA tests, performed on the CP RDE at pH = 2, suggest the fact that, when the leaching solution is almost entirely spent (excessively loaded with Fe, Ni, Zn and other metals), the operator can opt for the advanced electroextraction of Fe, Ni and Zn, followed by the strong alkalinization of the solution for complete removal of BM ions and total regeneration of the leaching solution.

Encouraged by the previously obtained results and conclusions, we decided to perform another set of measurements, using once again a 304 SS RDE, but with an increased diameter of 29 mm, which is going to allow the advanced electroextraction of Fe, Ni and Zn from highly acidic spent leaching solutions (pH under 0). The evolution of pH as well as the main electrical parameters recorded during this new set of experiments is presented in Figure 6, and a synthesis of the main experimental parameters and obtained results is presented in Table 4.

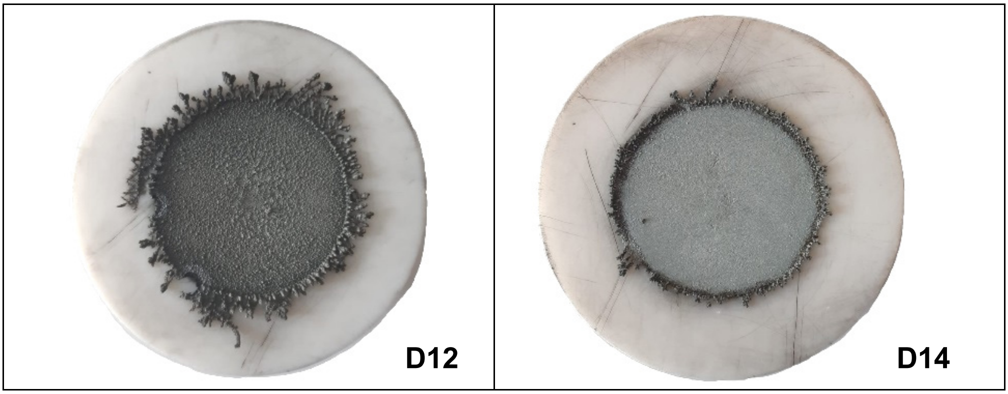

Figure 5. Examples of the Fe-Ni-Zn deposit pictures (see Table 3) obtained by PCA on CP RDE with a diameter of 38 mm in synthetic ternary solutions (2 M KBr + 0.5 M HBr + 10 g/L Fe + 10 g/L Zn + 1 g/L Ni).

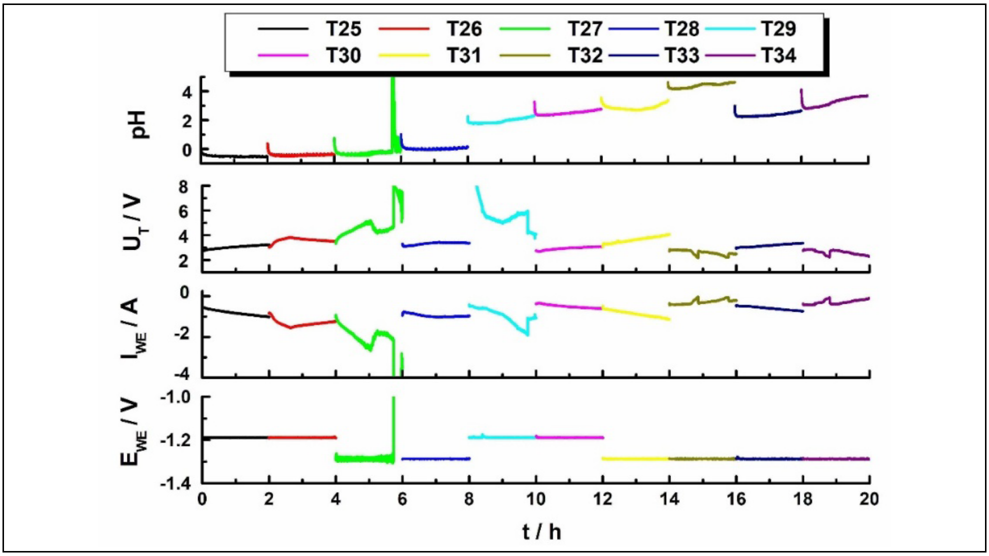

Figure 6. Evolution of the pH and the main electrical parameters during the electrodeposition of Fe, Ni and Zn from samples of synthetic spent leaching solution (2 M KBr + 0.5 M HBr + 10 g/L Fe + 10 g/L Zn + 1 g/L Ni) using the 304 SS RDE with a diameter of 29 mm

As can be seen from the first two lines of Table 4 (T25, T26), when the 304 SS RDE was polarized at -1.2 V/ER in the ternary solution of pH under 0, there is the risk that HER will dominate, which is going to lead to the impossibility of forming a Zn film on the electrode and, implicitly, the impossibility of forming a deposit.

Table 4. Experimental parameters and obtained results during the electrodeposition of Fe, Ni and Zn from samples of synthetic spent leaching solution (2 M KBr + 0.5 M HBr + 10 g/L Fe + 10 g/L Zn + 1 g/L Ni) using the 304 SS RDE with a diameter of 29 mm

Tests	Deposit	E_{WE} (V/RE)	t (h)	pH_M	m_D (mg)	[Fe] (%)	[Ni] (%)	[Zn] (%)	[Imp.] (%)	C.E. (%)	W_S (kWh/kg)
T25	**D21**	-1.2	2	-0.49	800	0.04	0.04	99.12	0.79	41.6	6.07
T26	**D22**	-1.2	2	-0.42	1	1.53	1.53	20.67	76.28	0.01	40737
T27	**D23**	-1.3	2	-0.11	1780	3.39	3.39	74.06	19.16	26.3	16.8
T28	**D24**	-1.3	2	0.03	360	3.45	4.08	81.93	10.54	20,8	13.6
T29	**D25**	-1.2	2	1.95	590	1.25	0.15	91.39	7.20	27.8	16.7
T30	**D26**	-1.2	2	2.50	500	1.74	0.20	94.91	3.15	54.0	4.52
T31	**D27**	-1.3	2	2.87	420	1.44	0.18	95.03	3.35	26.4	11.5
T32	**D28**	-1.3	2	4.39	500	5.45	0.52	89.78	4.25	73.3	3.02
T33	**D29**	-1.3	2	2.37	960	17.49	1.55	74.12	6.84	76.7	3.52
T34	**D30**	-1.3	2	3.26	94	29.35	3.35	27.05	40.25	88.1	2.71

On the contrary, in the same solution, decreasing the E_{WE} to -1.3V/ER (T27, T28) allows for the deposition of mixed Zn-Fe-Ni with a modest C.E. (under 26%) and W_S of 13 kWh/kg. In these conditions, as can be seen in Figure 7, the D23 deposit has a granular and dendritic structure, with weak adherence to the cathodic matrix, which allows its facile extraction from the reactor as a powder.

The subsequent tests were performed starting from an initial pH of 2 and for identical durations (120 minutes), with imposed E_{WE} of -1.2 and -1.3 V/ER (T29-T34). Using these parameters, a series of mixed Fe-Ni-Zn deposits were obtained, with acceptable C.E. and W_S values of 26 and 88% and 2.7 and 16.7 kWh/kg, respectively.

Regarding the structure of the obtained deposits, as can be seen in the example D27 from Figure 7, they have a pronounced granular and powdery aspect, with weak mechanical properties and an accentuated tendency of fragmentation and detachment from the electrode. This apparent disadvantage can be exploited for the continuous detachment of the deposit from the electrode by using a scraper fixed in the proximity of the electrode's surface if it's of RDE or rotating cylinder electrode (RCE) type.

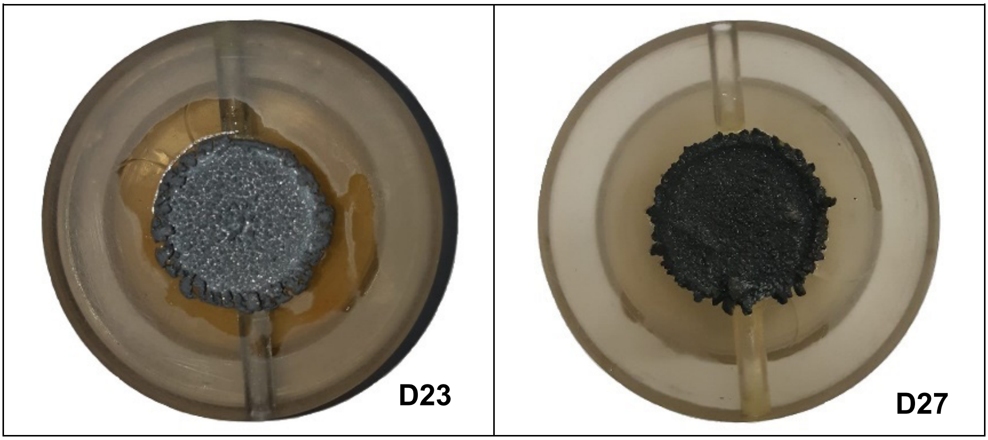

Figure 7. Examples of the Fe-Ni-Zn deposits obtained by PCA on CP RDE (D12/D14) and examples of Fe-Ni-Zn deposits obtained by PCA on 304 SS RDE with a diameter of 29mm in synthetic ternary solutions (2 M KBr + 0.5 M HBr + 10 g/L Fe + 10 g/L Zn + 1 g/L Ni)

From another point of view, the highly dispersed values of the deposit composition, C.E. and W_S can be associated with uncontrolled pH variations due to the HER and due to the proton migration through the ceramic membrane. Considering these factors, we appreciated that the electroextraction process of Fe, Ni and Zn can be significantly improved by the constantly monitoring and adjusting of pH. Additionally, the implementation of analytical techniques able of permanently monitoring the concentration of metallic ions in solutions is crucial when it comes to making a decision regarding the continuation of the electroextraction process or moving on to the complete purification of the leaching solutions by alkalinization and removal of the resulting precipitates.

CONCLUSIONS

Literature provides an extremely large number of research articles regarding the recovery of metals from WPCBs, but most of these papers are focused only on the recovery of precious metals (Au, Pt, Ag, Pd etc.) and of those with a high market value (Cu, Sn, Pb etc.). Unfortunately, the separation, extraction and valorization of other metals which are found in smaller quantities or have a lower market value (Fe, Ni, Zn, Al etc.) but which are present, regardless, in the specific fluxes of WPCBs recycling processes, is insufficiently studied. In this context, our studies focused on evaluating the feasibility of the electroextraction process of Fe, Ni and Zn, both from synthetic and real leaching solutions corresponding to the final steps of BMs recovery process from WPCBs. The performed experiments and the obtained results allowed us to draw the following conclusions:

- Using a Pt Fisher electrode is inadequate for the sequential electroextraction of Fe, Ni and Zn from real samples because of the intense HER on this substrate.
- The tests performed by HCV in synthetic solutions and using RDEs with a reduced diameter (3 mm) made of CP and 304 SS, indicate the fact that, by carefully selecting the pH and the imposed cathode potential, Zn can be selectively electroextracted, as well as its alloys with Fe and Ni, with hypothetical C.E. values between 17.5 and 95.8%.
- The long-duration (0,15 ÷ 8 h) experiments, performed by PCA in synthetic samples and using large diameter RDEs on CP (Ø = 38 mm) and 304 SS (Ø = 29 mm), have shown that, by adequately polarizing the cathode and carefully adjusting the solution pH, high purity Zn deposits (>98%) can be obtained, as well as Fe-Ni-Zn alloys.
- Even though CP RDEs are extremely useful and versatile in laboratory studies, their exploitation at an industrial level is not feasible. A potential solution to this deficiency is using 304 SS cathodic matrices, which led to extremely promising results.
- The composition of the Fe-Ni-Zn alloys is highly dependent on experimental parameters, as the electrolyte solution composition and imposed E_{WE}, the obtained C.E. and W_S values varying between 20 and 96% and 2 and 17 kWh/kg of alloy, respectively.
- Using a 304 SS RDE allows the selective electroextraction of Zn (even from highly acidic solutions), and their direct recirculation in the process.
- A pH value of 2 creates the conditions needed for the advanced recovery of Fe, Ni and Zn as alloys and allows for the easy and total regeneration of the leaching solutions.

EXPERIMENTAL SECTION

Reagents

Reactants such as KBr, HBr, KOH, Fe, NiO, ZnO were purchased from Fluka and Sigma-Aldrich.

As pointed in our previous study[22], after the selective electrodeposition of Cu, Sn and Pb, the concentration of the main metallic ions left in the real leaching solution were: 3 mg/L Cu; 20 mg/L Sn; 14 mg/L Pb; 0.2 g/L Cr; 7.5 g/L Zn; 5.1 g/L Fe; 0.62 g/L Ni; 6.9 g/L Al. This solution was used as catholyte for the electroextraction experiments that used the Pt Fisher type electrode.

For all other experiments, the synthetic solutions used as catholyte were prepared by dissolving adequate amounts of Fe, NiO and ZnO in a KBr 2 M + HBr 0.5 M solution. Where necessary, the pH of the solutions was adjusted to the required values by adding 10 M KOH or 48% HBr. The anolyte was prepared by dissolving 238 g KBr in double-distilled water and adding HBr until the pH reached 2, for a final volume of 1L. Main metal concentrations in the synthetic ternary solution were 30 g/L Fe. 3 g/L Ni and 30 g/L Zn.

Equipment and methods

For the tests concerning the selective potentiostatic electrodeposition of Fe, Ni and Zn from the real spent leaching solution using the Pt Fisher type electrode, the experimental setup already presented in our previous paper [22] was used. Moreover, the same protocols were used for the cathode cleaning and weighing, and for the mineralization and analysis of obtained deposits.

The HCV experiments were performed using a computer-controlled multi-channel potentiostat (DXC240, Datronix Computer, Romania) and a glass electrochemical cell of 50 mL, equipped with a Pt wire (Ø = 0,5 mm, L = 10 cm) as counter-electrode, an Ag/AgCl/KCl$_{SAT}$ system as reference electrode (RE) and the two small diameter (Ø = 3 mm) RDEs of CP and 304 SS. All HCV measurements were performed at a scan rate of 10 mV/s.

For the long-duration PCA experiments, as can be seen in Figure 8, to assure a uniform current distribution on the large diameter RED surface, an original ECR, divided with a horizontal ceramic membrane, was used.

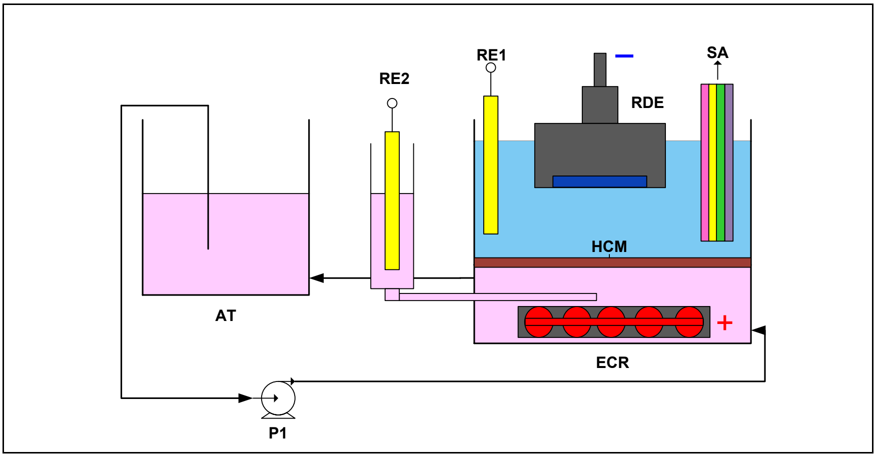

Figure 8. Schematic of the experimental setup used for the PCA experiments: AT – anolyte tank; ECR – electrochemical reactor; HCM – horizontal ceramic membrane; P1 – peristaltic pump; RE1,2 – Ag/AgCl/KCl$_{SAT}$ reference electrodes; RDE – rotating disk electrode; SA – sensor array (pH and temperature).

0.75 L samples of 2 M KBr + 0.5 M HBr solution, adjusted at pH = 2, and 0.45 L samples of ternary synthetic leaching solutions were used as anolyte and catholyte, respectively. The ECR electrodes and the sensor array (pH and temperature) were connected to a computer controlled electrochemical station (DXC236, Datronix Computer, Romania).

At the end of the PCA experiments, all performed at a rotation speed of 400 rpm, the obtained deposits were detached from the RDE surface, cleaned, weighed and mineralized, and the resulting solutions were analyzed by flame atomic absorption spectrometry using an AVANTA-PM spectrometer (GBC, Australia).

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