

In memory of prof. dr. Simion Gocan

ELECTROCHEMICAL RECYCLING OF WASTE PRINTED CIRCUIT BOARDS IN BROMIDE MEDIA. PART I: PRELIMINARY LEACHING AND DISMANTLING TESTS

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ABSTRACT. In the context of the large and increasing interest for an efficient and ecological recycling of the Waste Electrical and Electronic Equipments (WEEEs), we decide to evaluate the feasibility of an electrochemical recycling process for waste printed circuit boards (WPCBs) based on bromine-bromide leaching system. For this preliminary study, a perforated rotating drum chemical reactor (RDCR), interconnected with a divided electrochemical reactor (DER) in a closed hydraulic loop, was successfully used to dismantle consecutively three computer motherboards (CMB) after a minimal mechanical pre-treatment. Essentially, the base metals were leached at the RDCR level and the bromine-bromide system was regenerated at the DER level, simultaneously with the partial electrodeposition of dissolved metals. Even if the operating parameters were not optimized, each CMB was completely dismantled in around 18 h, with cathodic and anodic mean current efficiencies of 43.6% and 58.4%, respectively. Notably, grace to the proposed process, the remaining undissolved parts (fiberglass reinforced epoxy boards, electronic components, plastics, etc.) preserve their original shape and structure, allowing an easier consequent separation-classification and a more efficient and profitable recycling.

Keywords: *Waste printed circuit boards, metals recovery, electrochemical recycling, bromine-bromide leaching system, environmentally friendly process*

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INTRODUCTION

At this hour, the quantity of generated WEEEs exceeds 45 Mt/year and tends to increase with 4% each year [1]. Moreover, the traditional linear production philosophy (“take-make-dispose”) increases resource scarcity, causes great environmental costs and endangers human health. As a solution, the concept of circular economy has been introduced and generally accepted, maximizing the utility and value of components and materials [2]. In this context, for the recycling of WEEEs and, especially, of WPCBs, many researchers have studied and proposed various processes, e.g. physico-mechanical [3], hydrometallurgical [4], pyrometallurgical [5], pyrolytic [6] biometallurgical [7] or by combination of thereof as presented in several reviews [8 - 12]. In spite of an intense research activity, proved by the increased number of published papers [13], many of the proposed technologies present serious disadvantages, e.g. extremely low speed for the bioleaching processes and, for the other mentioned processes, high energy and materials consumption, leak of selectivity and generation of toxic or unusable supplementary waste fluxes. The electrochemical recycling of metals from WPCBs represents a feasible alternative and allows the minimization of the drawbacks mentioned before. Several regenerable leaching systems were proposed and tested, e.g. electro-generated Cl_2 in HCl solution [14], $\text{FeSO}_4/\text{H}_2\text{SO}_4$ [15], $\text{Fe}_2(\text{SO}_4)_3/\text{H}_2\text{SO}_4$ [16], FeCl_3/HCl [17 - 19], SnCl_4/HCl (for solder stripping) [20]. Unfortunately, the electrochemical regeneration of chloride based leaching agents presents the risk of chlorine evolution, requiring well sealed equipments. Also, the presence of sulfate induces a low rate of the solder alloy dissolution if large amounts of Pb are present. The Br_2 based lixiviants can be also used, but some authors suggest that these are unattractive due to the high vapor pressure of Br_2 (ex. 28 kPa at 35 °C) [21]. Contrarily, other researchers indicate that the use of the adequate complexing agents like bromide or organic ammonium perhalides can resolve this problem [22].

In this context, during the present work, we test the ability of the aqueous Br_2/KBr leaching system to remove all exposed metallic parts from different models of computer motherboards (CMB), simultaneous with the electrochemical lixiviants regeneration and the partial electrodeposition of the dissolved metals. The experimental setup has included a perforated rotating drum chemical reactor (RDCR) and a divided electrochemical reactor (DER), connected in an electrolyte closed loop. The resulting setup was successfully used for the consecutive dismantling of three different CMB after a minimal mechanical pre-treatment. Even if the operating parameters were not optimized, each CMB was completely dismantled in around 18 h, with cathodic and anodic mean current efficiencies of 43.6% and 58.4%, respectively, and a cumulated specific electric energy consumption of 0.65 kWh/kg of treated WPCB. Finally, it is worth to note that, after the leaching tests, the remaining

undissolved parts (fiberglass boards, electronic components, plastics, etc.) preserve their original shape and structure, allowing an easier consequent separation/classification and a more efficient recycling.

RESULTS AND DISCUSSION

Before the leaching experiments, several components were manually removed from the used CMB: the Li batteries, aluminium heat sinks, Cr/Ni plated bronze screws from the peripheral interfaces (RS232, WGA, LPT1, etc.) and the cylindrical aluminium electrolytic capacitors. This minimal mechanical pre-treatment, which lasted less than 2 min. for each CMB, was compulsorily in order to avoid few unwanted problems:

- risk of explosion when the extremely reactive inner of the Li batteries came in contact with the leaching solution;
- risk of leaching solution contamination with extremely toxic polychloride-biphenyls presented in some cylindrical aluminium electrolytic capacitors;
- increased total time of leaching due to the high thickness of the mentioned screws;
- significant and unjustified consumption of leaching agent for the Al dissolution due to the small commercial value of Al and the difficulty of Al recovery from the resulting solution. Moreover, the reaction between Al and the aqueous solutions of bromine generates high amount of gaseous hydrogen and is extremely vigorous and exothermic, increasing the risk of explosion.

After the mechanical pre-treatment of the CMB, the resulted components were weighted separately and each board was broken in few pieces in order to full fit the dimension of the rotating drum from the RDCR. Subsequently, the fragments of the first CMB (model PIII-GA-60XT, designed as CMB1) were introduced in the rotating drum, the RDCR and DER were interconnected and filled with 3.4 L of KBr 2 M. Only before the first test (designed as Test1), 38 mL of liquid bromine and 350 mL of HCl (32%) were added to the leaching solution, resulting concentrations of around 0.25 M and 1 M for bromine and HCl, respectively. In order to allow the reaction between the initial added bromine and the metals from the CMB1, the drum was rotated for 1 h without the DER energising and the solution was circulated between reactors at a flow rate of 250 mL/min. During this period, the solution colour change from intense orange to light green, indicating the complete consumption of the initial bromine.

After this preliminary step, we started effectively the Test1, that was divided in 10 successive short experiments, completed at different combinations of current (I_{WE}) and electrolyte flow rate (V_F) values, presented in

Table 1, where t_{START} , t_{STOP} and t_{NET} represent the experiment starting, ending and net time, respectively, and S_{CAT} stands for the cathode surface. During the measurements, the values of the voltage at the DER terminals (U_{CELL}), working electrode potential (U_{WE}), counter-electrode potential (U_{CE}) and I_{WE} were recorded, the corresponding concatenated data being presented in Figure 1.

Table 1. Experimental parameters used during Test1

Parameter	t_{START} [min]	t_{STOP} [min]	t_{NET} [min]	I_{WE} [A]	V_{F} [mL/min]	S_{CAT} [cm ²]
Test1-Exp.1	0	50	50	-2.0	100	298
Test1-Exp.2	50	200	150	-2.0	250	298
Test1-Exp.3	200	339	139	-3.5	150	192
Test1-Exp.4	339	403	64	-3.5	150	192
Test1-Exp.5	403	439	36	-3.5	150	192
Test1-Exp.6	439	477	38	-3.5	150	192
Test1-Exp.7	477	601	124	-4.0	100	192
Test1-Exp.8	601	746	145	-4.5	50	192
Test1-Exp.9	746	847	101	-4.0	100	192
Test1-Exp.10	847	1103	256	-4.0	25	192

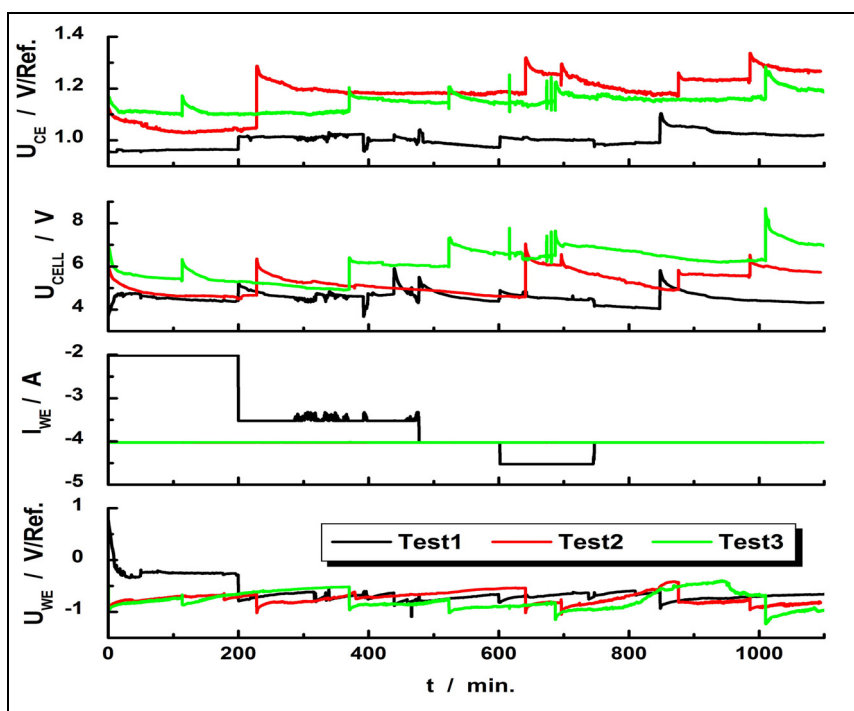


Figure 1. Evolution of the electric parameters recorded at the DER level during the three successive tests of metal leaching using the bromine-bromide system

Correlating the data from Table 1 and Figure 1 with the visual observation concerning the quality and quantity of the obtained deposits, we conclude that the combination of $I_{WE} = 4$ A and $V_F = 100$ mL/min represents an acceptable compromise in respect to the electric energy consumption, leaching rate and quantity of the electrodeposited metal. It is worth to note that for all the tested experimental parameters combinations, pulverulent deposits, consisting mainly of Cu, were obtained. After each short experiment, the content of the rotating drum was inspected, revealing that all the accessible thin metallic parts (thickness less than 0.5 mm, e.g. pins, foils, chip terminals, solder points and balls, etc.), were completely dissolved after around 18 hours. The undissolved metallic parts resulted from the CMB1 include only 6 surface mounted MOS-FET power transistors and few pieces of thick enameled copper wires ($\phi > 0.5$ mm).

At the end of Test1, the content of the rotating drum was discarded, washed with distilled water, dried, manually sorted and weighted. Also, the pulverulent metal deposit was collected by suction from the DER cathodic compartment, decanted, filtered, washed with distilled water and acetone, fast dried and weighted. In order to evaluate the metallic composition of the obtained deposit, samples of 1-2 g were re-dissolved in aqua regia and analyzed by flame atomic adsorption spectroscopy (FAAS). The final concentrations of the dissolved metals in the leaching solution were also evaluated by FAAS.

Following the protocol described before, other two CMB (both of AMD-DURON - Socket 462 type) were mechanically pre-treated and successively leached using the same electrolyte solution. For Test2 and Test3, identical experimental parameters ($I_{WE} = 4$ A and $V_F = 100$ mL/min) were used, the recorded data being also presented in Figure 1.

As can be seen in Figure 1, during the Test2 and Test3, the recorded electrical parameters are similar with those of Test1, with a small increase of the U_{CELL} and U_{CE} . A more accurate comparison can be made base on the calculated mean values, presented in Table 2, where the total consumed electric charge (Q_T) and power (W_T) values are also included.

Table 2. The averaged values of the electrical parameters recorded during the three successive CMB leaching tests ([†]Standard deviation)

Parameter	Test1	Test2	Test3
$U_{WE, MEAN}$ [V]	$-0.62 \pm 0.21^{\dagger}$	-0.74 ± 0.11	-0.78 ± 0.17
$I_{WE, MEAN}$ [A]	-3.59 ± 0.81	-4.02 ± 10^{-3}	-4.02 ± 10^{-3}
$U_{CELL, MEAN}$ [V]	4.56 ± 0.26	5.26 ± 0.49	6.17 ± 0.69
$U_{CE, MEAN}$ [V]	1.01 ± 0.03	1.18 ± 0.08	1.15 ± 0.03
Q_T [A*s]	$238 \cdot 10^3$	$264 \cdot 10^3$	$267 \cdot 10^3$
W_T [W*s]	$1.09 \cdot 10^6$	$1.38 \cdot 10^6$	$1.65 \cdot 10^6$

The data from in Table 2 indicate small differences between the averaged values of the electrical parameters recorded during the three successive tests, excepting W_T that increase constantly. This fact suggests that the same solution can be used for repetitive leaching processes.

Based on FAAS analyses, we evaluated, for all three tests, the amount of the electrodeposited (m_{DEP}) and dissolved (m_{DIS}) base metals and the current efficiency for the cathodic ($r_{f, CAT}$) and anodic ($r_{f, ANOD}$) processes, the corresponding data being presented in Table 3.

Table 3. Amount (in g) of the electrodeposited and dissolved base metals and the current efficiencies (in %) for the three successive CMB leaching tests

Metal / Efficiency		Test1		Test2		Test3	
		m_{DEP}	m_{DIS}	m_{DEP}	m_{DIS}	m_{DEP}	m_{DIS}
Cu		52.62	62.31	53.44	50.60	52.90	54.60
Ni		0.14	4.70	0.32	3.00	0.63	2.80
Zn		0.05	14.10	0.08	15.50	0.67	9.50
Sn		12.63	17.16	19.20	16.20	22.75	22.00
Pb		2.10	8.34	7.20	7.20	10.73	8.10
Fe		0.04	16.33	0.12	8.30	0.06	6.50
$r_{f, CAT}$	$r_{f, ANOD}$	43.36	42.73	45.75	73.52	41.78	59.03

The data presented in Table 3 reveal very important information:

- The great dispersion of the measured m_{DIS} values indicate large differences between the compositions of the leached CMBs.
- For all three tests, the major component of the deposits is Cu (around 53%) and its amount remains quasi-constant, suggesting that this metal can be efficiently recovered by electrodeposition if the operational parameters are optimized.
- The amount of electrodeposited Sn and Pb increase constantly, indicating their accumulation in the leaching solution and the necessity of their constant extraction from the electrolyte.
- The quantities of Ni, Zn and Fe are extremely small (less than 1%), suggesting that, using optimal operational parameters, their capture in the Cu deposits can be eliminated.
- The simple recirculation of the leaching solution on the route RDCR - cathodic - anodic induces very low values of the current efficiency, for both $r_{f, CAT}$ and $r_{f, ANOD}$. This fact can be explained by the electrochemical short-circuit due to the presence of the Cu^+/Cu^{2+} , Fe^{2+}/Fe^{3+} and Br_2/Br^- reversible redox couples on all three compartments. To overcome this drawback, the setup must be re-designed in order to separate the anodic and cathodic fluxes.

Based on the cumulated m_{DEP} , m_{DIS} values and amounts of parts separated mechanically for all three tests, we elaborated the mass balance and the flowchart of the global process, presented in Figure 2.

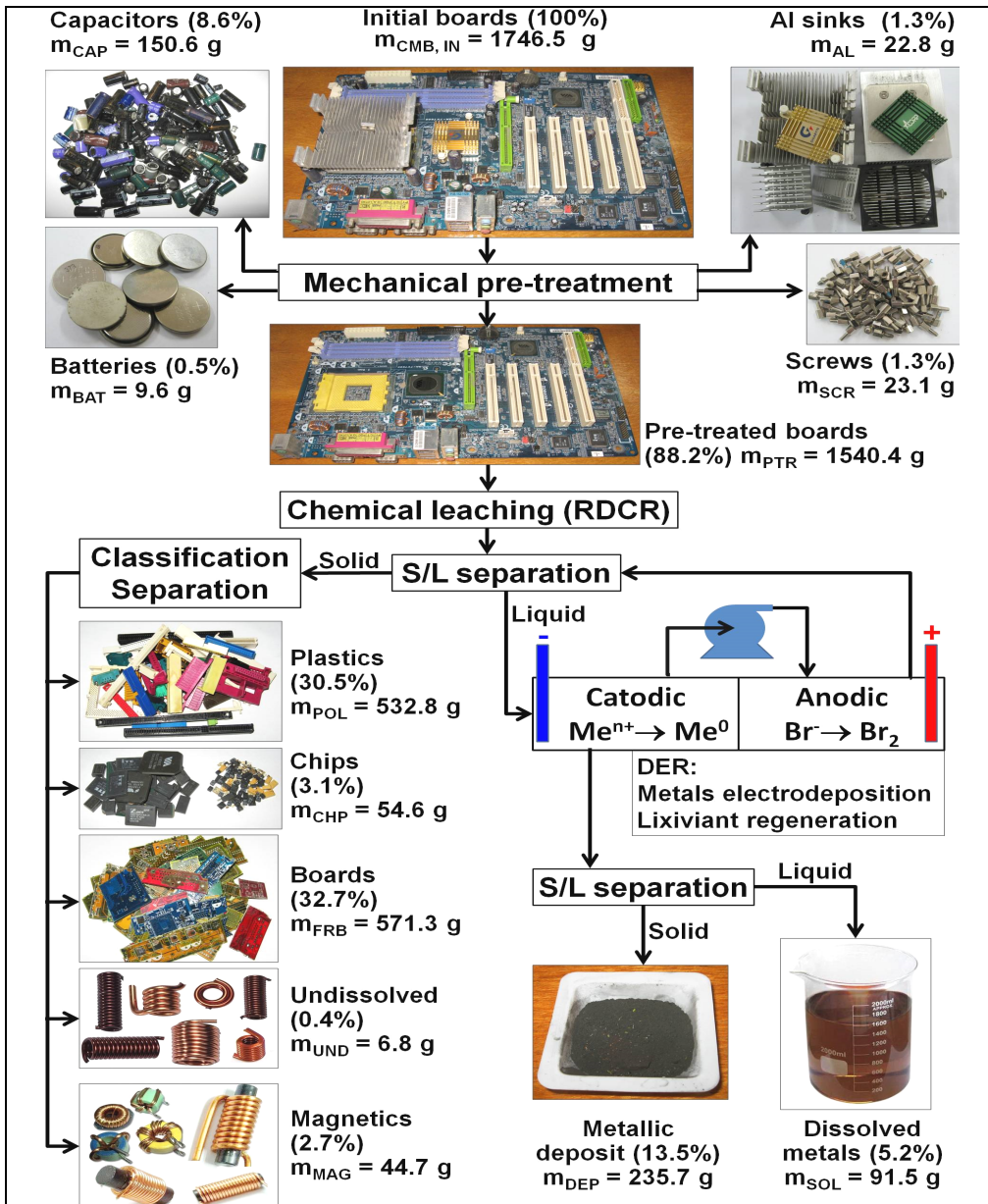


Figure 2. Mass balance and flowchart of the global dismantling process

For Figure 2, the designed names, corresponding weight symbols and compositions of the resulted fractions after the mechanical pre-treatment and leaching steps are summarized in Table 4.

Table 4. Designed names, weight symbols and compositions of separated fractions from CMB by mechanical pre-treatment and leaching

Fractions designed names	Weight symbol	Composition of the fractions
Initial boards	$m_{\text{CMB, IN}}$	Untreated boards with all components
Batteries	m_{BAT}	Button cell Li-batteries for CMBs clock
Al sinks	m_{AL}	Aluminium heat sinks
Capacitors	m_{CAP}	Al based cylindrical electrolytic capacitors
Screws	m_{SCR}	Ni/Cr plated screws from peripheral connectors
Pre-treated boards	m_{PTR}	Mechanically pre-treated CMBs
Boards	m_{FRB}	Fiberglass reinforced epoxy boards
Magnetics	m_{MAG}	Ferrite or iron coil cores, CPU locking levers
Plastics	m_{POL}	Polymer based extruded/injected parts
Chips	m_{CHP}	Electronic chips and small surface mounting devices (SMD), all without terminals
Undissolved	m_{UND}	Undissolved metallic parts like high power SMD-MOS-FETs and thick enameled cooper wires
Dissolved metals	m_{SOL}	Dissolved metals remained in lixiviant

The mass balance presented in Figure 2 indicate that the direct leachable metals represents 18.7% from the total weight of CMBs and, for the used operational parameters, at least 72% from the dissolved base metals can be recovered by electrodeposition in one stage.

Finally, based on the cumulated values of W_T , m_{DIS} and $m_{\text{CMB, IN}}$ (see Table 2 and Figure 2), the global specific electricity consumptions were calculated, values of 0.65 and 3.5 kWh/kg being obtained in respect to the mass of treated CMBs and recoverable metals, respectively. Taking into account the market value of the leached base metals, the composition of the deposits and the price of electric energy, we conclude that the expenses for the consumed electricity during the leaching process can be covered by the value of the recovered base metals. In this conditions, the high value of the precious metals presented on the CMB, neglected during this study, can increase significantly the process profitability.

CONCLUSIONS

The main conclusion of the present study consists in the certitude that the electrochemical regenerable Br_2/Br^- leaching system can be successfully

used for the dismantling of WPCBs and the recovery of the base metals from wasted CMBs. The proposed process requires only a minimal mechanical pre-treatment, and its profitability can be increased significantly by recovering and valorising the precious metals from the WPCBs.

Finally, it is very important to note that the proposed and tested process allows to preserve the original shape and structure of the remaining undissolved parts (fiberglass boards, electronic components, plastics, etc.), facilitating a more easier and profitable classification, separation and recycling of these secondary waste fluxes.

EXPERIMENTAL SECTION

The leaching tests were performed in a RDCR made from HD-PP, the volume of the drum and reactor being of 1.5 and 3 L, respectively. The DER, of rectangular shape, was constructed also from HD-PP, divided in two chambers by a ceramic porous membrane. A peristaltic pump (model TC, Medorex, Germany) was used to transfer the electrolyte from the cathodic to the anodic compartment of DER. Both DER compartments were connected with RDCR following the principle of communicating vessels, assuring an uniform circulation of the electrolyte in the whole system. The anode was a rectangular graphite block ($H*W*D = 80*70*20 \text{ cm}^3$), immersed 6.5 cm in solution. The "brush" shape cathode consisted in 30 or 20 cylindrical bares of spectral graphite ($\phi = 0.5 \text{ cm}$, $H = 10 \text{ cm}$), immersed 6 cm in solution. The U_{WE} and U_{CE} were measured and reported in respect to two reference electrode of Ag/AgCl/KCl_{SAT} type ($\varepsilon = +0.197 \text{ V/SHE}$).

Before the Test1, the reactors were filled with 3.5 L of solution containing 2 M KB, 0.25 M Br₂ and 0.2 M HCl that was reused during Test2 and Test3. A computer controlled P/G-stat (model DXC236, Datronix Computers, Romania) was used to impose the current through DER and measure the resulting potentials. A data acquisition board (model PCI-6221M, National Instruments, USA) and dedicated LabView 2015 (National Instruments, USA) applications were used to control the P/G-stat operation and acquire data. The FAAS analyses were performed using an AVANTA-PM spectrometer (GBS, Australia) in air/acetylene flame mode. The weights of the initial CMBs and all the other separated fraction were measured using a laboratory electronic balance (model PLJ-510-3m, KERN&SOHN GmbH, Germany).

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