ELECTROCHEMICAL pH CONTROL FOR THE PROCESS OF METALS RECOVERY FROM WASTE PRINTED CIRCUIT BOARDS

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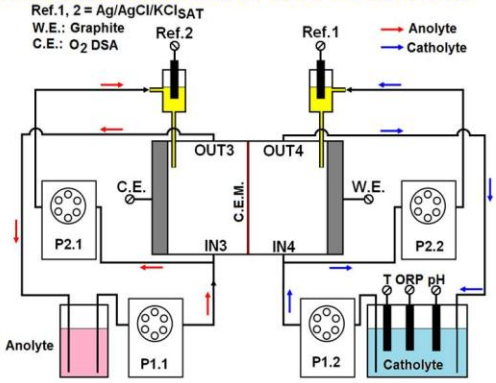
INTRODUCTION

The waste printed circuit boards (WPCBs) represent only 3-5% from the global amount of waste electric and electronic equipment (that will exceed 50 Mt in 2018 [1]), but concentrate more than 40% from the value of the recoverable metals [2]. Therefore, pyrometallurgical, hydrometallurgical and physico-mechanical processes were developed for metals recovery from WPCBs (MRWPCBs), all of them being energy intensive and/or highly polluting [3]. Our preliminary results [4] revealed that the electrochemical MRWPCBs based on the Br_2/KBr leaching system represents an economical and eco-friendly recycling alternative, but requires a carefully pH control in order to avoid the precipitation of the dissolved metals.

AIMS

Study of the on-site electro-generation of HBr (EGHBr) as pH adjusting agent and of Br_2 ($EGBr_2$) as raw material for EGHBr in order to avoid the permanent addition/consumption of fresh reagents.

EXPERIMENTAL SETUP AND CONDITIONS



✓ **Electrochemical cell:** MicroFlowCell® divided filter-press reactor (DFPR) equipped with Nafion® 324 membrane and PVC tubes Luggin capillaries;

✓ **Experimental techniques:** Hydrodynamic linear scan voltammetry (HLSV) @ 5 mV/s; Galvanostatic/potentiostatic EGHBr and $EGBr_2$ tests; Computer controlled automatic titration of HBr and Br_2 with 0.1 N KOH and 0.1 N $Na_2S_2O_3$.

✓ **Working electrode (W.E.):** Graphite bloc of 10 cm² active area (A.A.);

✓ **Counter electrodes (C.E.):** DSA-O_2 & Ni for EGHBr & $EGBr_2$, respectively (10 cm² A.A.);

✓ **Reference electrodes (Ref.):** Ag/AgCl/KCl$_{SAT}$;

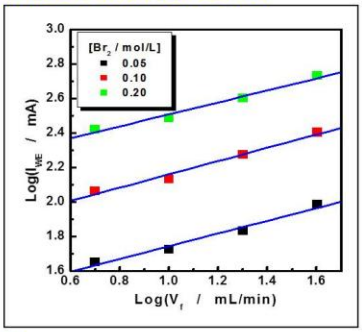
✓ **Anolytes:** 2 M H_2SO_4 and 2 M KBr for EGHBr and $EGBr_2$, respectively;

✓ **Catholytes:** For EGHBr & HLSV: 2 M KBr + 0.05, 0.1 and 0.2 M Br_2; For EGHBr: leaching solution (2 M KBr + 0.08 M $FeBr_3$ + 0.16 M $CuBr_2$ + 0.1 M Br_2); For $EGBr_2$: 0.1 M KOH;

✓ **Equipments:** Computer interfaced: P/G-stat DXC236 (Datronix Computers, Romania); Peristaltic pumps Reglo-Analog & Reglo-Digital (Ismatec, Switzerland); Insulated high-impedance voltmeters C863 (Consort, Belgium).

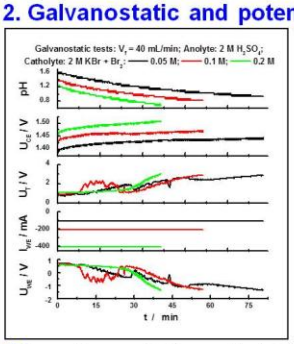
RESULTS AND DISCUSSIONS

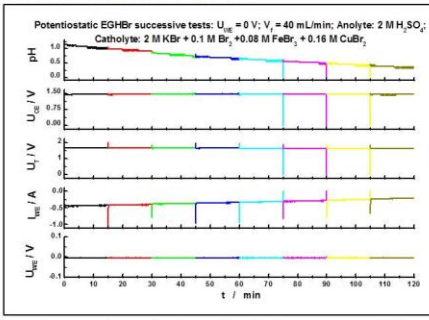
1. HLSV tests for EGHBr

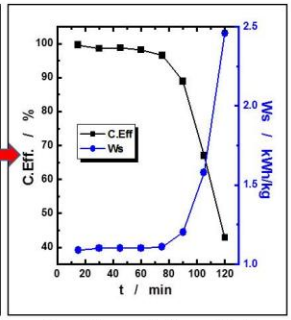


➲ In the used V_f range, a 0.35 slopes mean value for the $Log(I_{WE})$ *vs.* $Log(V_f)$ linear correlations indicates a turbulent flow of "thin layer" type.

2. Galvanostatic and potentiostatic EGHBr tests







➲ In galvanostatic mode, high values of I_{WE} induce fast decrease of U_{WE}, favoring H_2 evolution (HE).

➲ The presence of the Fe^{2+}/Fe^{3+} and Cu^{+}/Cu^{2+} redox coupes in catholyte and the potentiostatic process control allow the EGHBr with diminished occurrence of HE.

➲ The final pH value of ~0.3 is adequate for the successful leaching of base metals from WPCBs.

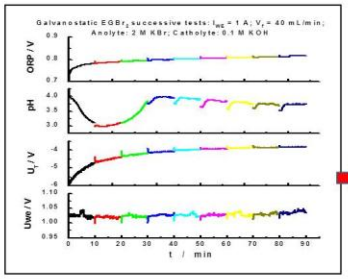
➲ The current efficiency (C.Eff.) and specific energy consumption (Ws) for the EGHBr process present acceptable values for obtained HBr concentrations less than 0.5 M.

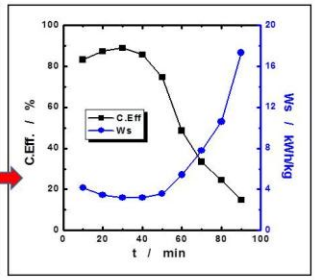
3. Galvanostatic $EGBr_2$ tests

➲ In order to avoid the handling of the extremely toxic and corrosive liquid Br_2, studies concerning its in-situ $EGBr_2$ are also performed in the DFPR equipped with electrodes on graphite and Ni as anode and cathode, respectively.

➲ The C.Eff. and Ws for the $EGBr_2$ process preserve acceptable values for resulting Br_2 concentrations less than 0.1 M. This value determines a high efficiency for the EGHBr process and an ORP of around +0.8 V, highly enough to assure the base metals leaching from WPCBs.

➲ Simultaneously with the $EGBr_2$ process, a concentrated solution of KOH is generated, useful for the metals ions separations.





CONCLUSIONS

✓ Controlling adequately the operational parameters, HBr can be efficiently generate electrochemically in-situ and used as pH control agent during the electrochemical process of metals recovery from WPCBs.

✓ The electrochemical oxidation of bromide to bromine in a divided filter-press reactor offer a reliable raw material source for the EGHBr process and generate additionally a concentrate alkaline solution useful for the leached metals ions separation.

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