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XPS AND SEM-EDX INVESTIGATIONS OF THE DISSOLUTION PRODUCTS OF SEVERAL METALS IN AN ACIDIC BROMINE-CONTAINING LIXIVIANT

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INTRODUCTION

Waste printed circuit boards (WPCBs) contain metals with various ranges of concentrations, including Cu, hazardous elements (Pb, As, Cd, Hg), base (Sn, Pb, Zn, Ni, Fe) and precious (Au, Ag, Pd) metals. For a sustainable environment and resources re-utilization, the leaching of metals from WPCBs and their subsequent recovery are regarded as major challenges nowadays. A previous research demonstrated the ability of the acidic Br^-/Br_2 leaching system to remove the exposed metallic parts from different models of computer motherboards, with cathodic and anodic mean current efficiencies of around 43.6% and 58.4%, respectively (Dorneanu, 2017). Fast leaching rate, low-toxicity and applicability over a wide range of pH values (from acidic to neutral) are important characteristics of the bromide leaching system (Melashvili et al., 2014).

In the present work, the dissolution products developed on the surface of the main metals (Cu, Sn, Pb and Zn) found in WPCBs, after their initial exposure to the acidic Br^-/Br_2 leaching system were studied by XPS and SEM-EDX techniques.

EXPERIMENTAL

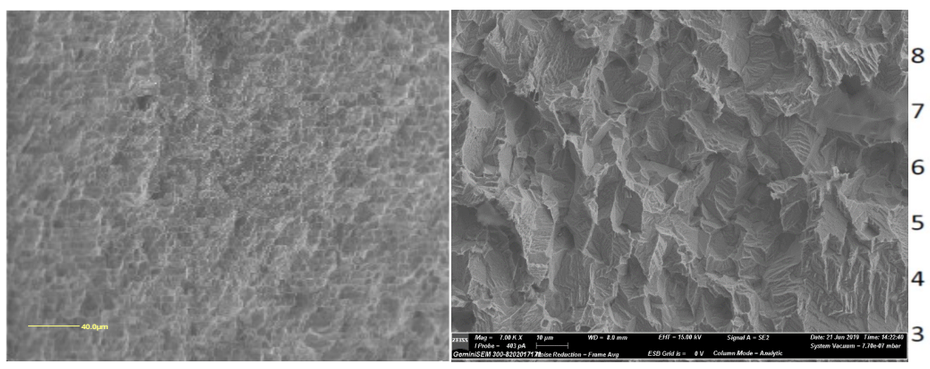
Leaching solution: 2 M KBr + 0.5 M HBr (pH=0.3) + 0.01 M Br_2

Electrodes: Cu; Zn; Sn; Pb

Immersion times: 60 min for Cu, Sn and Zn; 120 min for Pb

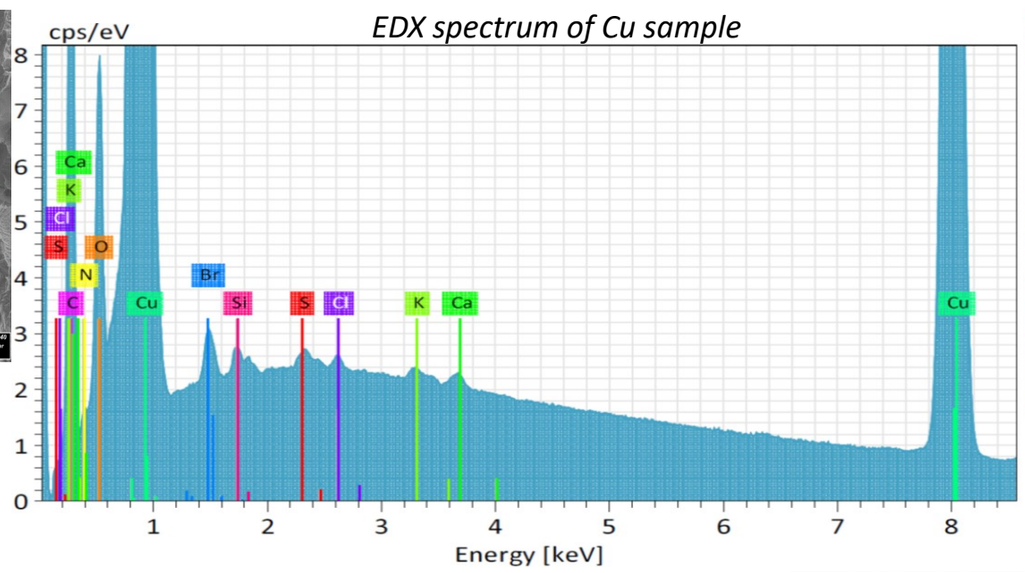
SEM-EDX and XPS measurements – custom built ESCALAB 250 Xi XPS (Thermofisher) spectrometer equipped with a scanning electron microscope and an X-ray detector for EDX data acquisition

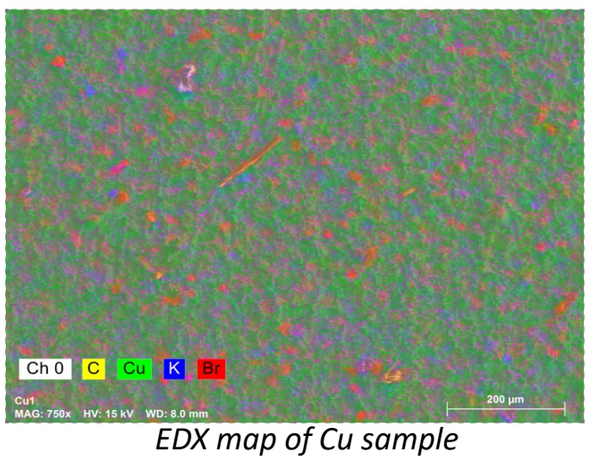
RESULTS AND DISCUSSION



SEM images of Cu sample

EDX spectrum of Cu sample





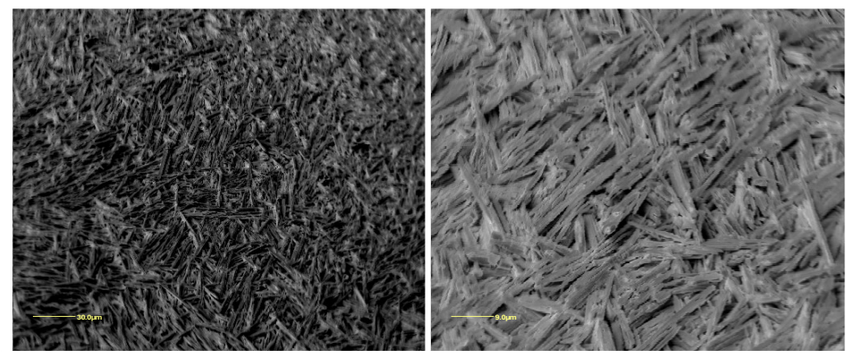
EDX map of Cu sample

Table 1. $Cu2p_{3/2}$ fit parameters referenced to the adventitious carbon C1s peak at 285.1 eV

Peak component	B.E. (eV)	FWHM (eV)	Oxidation state
Cu $2p_{3/2}$ oxide A	932.6	2.1	Cu (I)
Cu $2p_{3/2}$ oxide B	933.7	3.1	Cu (II)

Table 2. $Sn3d_{5/2}$ fit parameters referenced to the adventitious carbon C1s peak at 285.0 eV

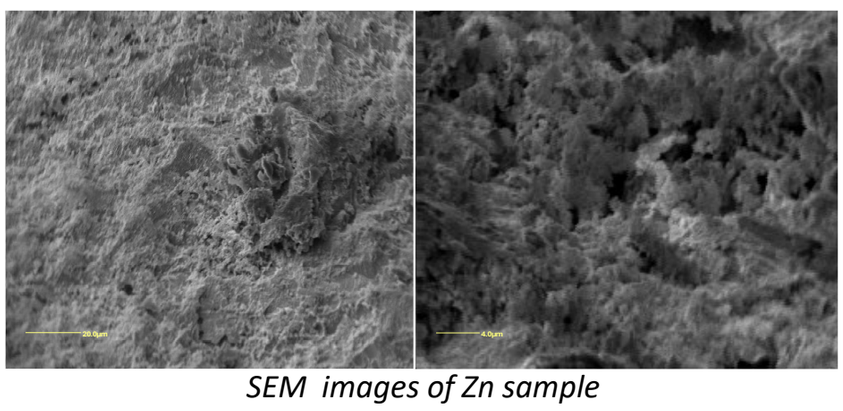
Peak component	B.E. (eV)	FWHM (eV)	Oxidation state
Sn $3d_{5/2}$ metallic	485.0	0.6	0
Sn $3d_{5/2}$ oxidised	486.6	1.2	4+



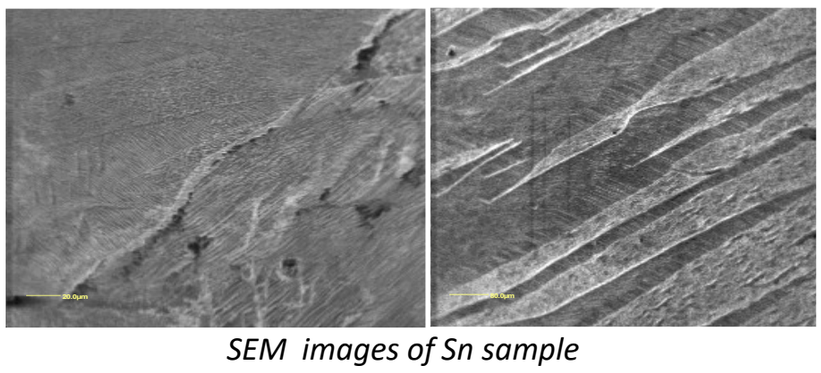
SEM images of Pb sample

Table 3. $Pb4f_{7/2}$ fit parameters

Peak component	B.E. (eV)	FWHM (eV)	Oxidation state
Pb $4f_{7/2}$ metallic	137.0	1.0	0
Pb $7f_{7/2}$ oxidised	139.0	1.1	2+



SEM images of Zn sample



SEM images of Sn sample

Table 4. B.E. and K.E. values for Zn peak contributions / oxidation states

Peak	B.E. (eV)	K.E (eV)	FWHM (eV)	Oxidation state
Zn $2p_{3/2}$	1021.8	-	1.0	metallic
Zn $2p_{3/2}$	1022.5	-	1.4	Zn^{2+}
Zn LMM	-	991.9	1.2	metallic
Zn LMM		987.5	3.0	Zn^{2+}

CONCLUSIONS

- SEM investigations revealed marked differences between the surface textures of the analysed samples.
- XPS chemical assessment allowed the identification of the dissolution products formed on the metallic surfaces in the initial stages of the dissolution process. They consist mainly of metallic oxides in the case of Cu, Zn and Sn samples, while the presence of a layer of $PbBr_2$ was noticed on Pb surface.

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