# Preliminary Study for Copper Recovery in WEEE Leachate by Using Ionic Liquids Based on Choline Chloride

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The rapid development of the global economy and intense use of electric and electronic equipments lead to the increase of the waste quantity (electrical and electronic wastes, WEEE). Due to their high toxicity, these materials have become one of the major environmental risks. The necessity for the treatment of WEEE results from the large quantities generated and the content of valuable metals (as Cu, Sn, Zn, Pb etc.). Globally, the recovery of WEEE contained metals is a subject which has generated numerous studies, leading to the development of some technologies based on combining the classical pyro- and hydrometallurgical methods, specific for obtaining metals. Since copper is an important metal for industries, development of Cu recycling processes is an important issue. The aim of this paper is to recover Cu by using from the multicomponent alloy obtained by pyro-metalurgic technology from WEEE. We aim to develop a novel ecological technology for the recovery of metals from WEEE by leaching and electrodeposition using ionic liquids based on choline chloride (ChCl). For obtaining the leaching state we used mixtures of ChCl-X (X=Urea, Malonic acid and CuCl<sub>2</sub>×2H<sub>2</sub>O). Metallic copper and tin were then electrochemically recovered from the ionic liquids in the electrowinning stage. It was found that the peak potentials for Cu ions reduction are very similar using either Pt or glassy carbon as counter electrode. The electrochemical study allowed determining the mechanism for  $Cu^{2+}$  reduction in ChCl-X (X=Urea, Malonic acid and CuCl<sub>2</sub>×2H<sub>2</sub>O) ionic liquids, which appears to be a two steps mechanism for copper probably involving copper chloride complex. Finally the obtained metallic deposits on the copper/steel cathode (were subject of determination of XRD and microscopy in order to evidence the deposits structure and morphology).

Keywords: metals recovery, ionic liquids, electrodeposition, waste recovery

The recycling of electronic equipment is important from both economical and environmental viewpoint. The existence of big quantities of hazardous residues demands for an adequate treatment whereby valuable materials are regained. The life cycle of electronic equipment is composed of several steps: raw material, production, commercialization, consumption and management of the rejected parts. The treatment of this kind of residue includes chemical, mechanical and thermal processes. In first instance the metal fraction is separated here from the polymer fraction and the heat released is used as fuel into the process, at least partly. Hydrometallurgical processes make use of specific solutions to dissolve metals and to separate them in this way from the other constituents of the printed circuit boards (PCB). Then, the metals are separated in their pure form. The aqueous solutions most commonly used in industry for this purpose are mixtures of acids such as:  $H_2SO_4$ ;  $H_2SO_4$ + $H_2O_2$ ;  $HNO_3$ +HCl (aqua regia). The latter is the most efficient. In another way the ionic liquids (ILs) can be used as well in the recycling of metals from electronic waste. The treatment of electric and electronic waste (WEEE) is a problem which receives ever more attention, because an inadequate treatment results in harmful products ending up in the environment. According to the procedure of using ionic liquids we intend to investigate the possibilities of an alternative route for recycling of metals from printed circuit boards (PCBs) obtained from rejected computers. The process is based on deep eutectic solvents or aqueous solutions composed of an etchant, and a quaternary ammonium salt (quat salts) such as choline chloride [(2-hydroxyethyl)trimethylammonium chloride=ChCl]. These solutions are reminiscent of deep eutectic solvents (DES) based on quats. The *ionic liquid analogues* called *deep eutectic solvents* (DES) are produced by mixing ChCl with a hydrogen bond donor such as urea, malonic acid or ethylene glycol. It can be argued the H-bond donor forms some kind of anion complex with Cl, but in general DES are not considered as constituted of true ions and are thus not regarded as *ionic* liquids. Besides the separate terminology, ILs and DES behave very much in a similar manner and they have parallel properties. A remarkable difference between genuine DES and ILs is the addition of rather large quantities of water. It is shown the presence of water has a lot of advantages on the leaching of metals, while the properties typical for DES still remain.

We used these solvents in order to recover copper and tin from the multicomponent alloy obtained by pyrometalurgic technology from WEEE using a new more ecological technology by leaching and electrodeposition using ionic liquids based on choline chloride (ChCl).

Ionic medium based on ChCl is characterized by a minimal impact on the environment, recyclable, biodegradable and non-harmful and was proved to be an electrolyte/solvent particularly attractive for applications in electrodeposition of metals [1-6].

## Experimental part

## Materials and methods

All reagents were used as purchased without recrystallization or drying, in order to simulate a more appropriate technological process for future industrial use:

Choline chloride (ChCl, Sigma Aldrich >99%), urea (Sigma Aldrich >99%), malonic acid (Fluka >98%), dehydrate copper chloride (CuCl<sub>2</sub>×2H<sub>2</sub>O Merck >98% and CuCl<sub>2(and</sub>) Merck >99%) were used. Popular DESs that are used throughout this work are Reline200 and Maline200, which are formed by mixing and heating ChCl with urea or malonic acid in a molar ratio corresponding to eutectic at 80°C until homogenous and colorless liquid was formed. Another solvent for the leaching process was obtained my mixing ChCl with 0.2 M CuCl<sub>2</sub>×2H<sub>2</sub>O in different concentrations and a green liquid was obtained. The oxidizing capacities of Cu(II) stem from the existence of a stable Cu(I) component in quat based DES and thus the leaching stems from the activity of the Cu(II)/Cu(I) redox couple. This opens perspectives for regeneration of the etching solution. For qualitative and quantitative determination of metals dissolution, the atomic absorption, UV-Vis spectrophotometry, XRD and micrographic images were used. In order to determine the mechanism of metals electrodeposition we used cyclic voltammetry (CV). The equipment used for measurement was PARSTAT 2273 potentiostat with a special soft Power Sine. The cell contained a platinum wire as stationary working electrode (WE) directly immersed in the electrolyte, a glassy carbon (GC) as a counter electrode (CE) and a silver wire as quasireference electrode (QRE) [7, 8]. All three electrodes were from Radiometer Analytical. The working electrode was polished mechanically with alumina oxide paste, washed with bi-distilled water and dried prior to measurement. Electrochemical experiments were performed via a 100 mL jacketed cooling glass cell. The cell was linked to a thermostated bath. The voltammograms were drawning at room temperature (~25 C) and 80 °C using scan rates of 10-200 mV×s<sup>-1</sup>. Supplementary voltammetric measurement was performed for determining the electrochemical window of the above solvents.

## **Results and discussions**

Taking in account the composition of the multicomponent alloy obtained by pyro-metalurgic technology from WEEE, which consists of 69.13 % Cu, in this paper the leaching of copper was studied as a function of solvent used. We used directly electrochemical measurements for determining the mechanism of electrodeposition of cooper from Reline 200 and Maline 100 electrolytes.

Figure 1 presents comparative cyclic voltammogrames for ChCl-Urea and (ChCl-Urea) + CuCl<sub>2</sub>. In comparison with other ionic liquids the potential window of the ChCl-urea deep eutectic solvent was found to be relatively narrow (-1.1 to +1.0 V vs. Ag quasireference) [2,6]. The cyclic voltammogram of (ChCl-Urea)+CuCl<sub>2</sub> from figure 1 reveals two pairs of peaks as two distinguishable steps of reduction and oxidation representing Cu(II)/Cu(I) and Cu(I)/Cu(0) redox couples. It is very clearly that all waves that occur in the background voltammogram (for ChCl-Urea) do not interfer with the waves of the electroactive copper species. As in the case of the supporting electrolyte (ChCl-Urea), we attributed the large increase of anodic current on the ChCl-urea-CuCl, voltammogram, between 1.0 V and 1.5 V, to the irreversible oxidation due to the conversion of Cl ion into Cl<sub>a</sub> gas. It was found that the peak potentials for Cu(II) ions réduction are very similar using either Pt or glassy carbon as counterelectrodes. All cyclic voltammetry results for Cu(II)/Cu(I) and Cu(I)/Cu(0) couples obtained in the described conditions are in very good agreement with literature [2, 9-11]. The reversibility of the electrodeposition and dissolution of copper on platinum electrode was

conveniently evaluated by the authors *via* continuous CV and EIS [2, 3]. For 10 cycles at 200 mV×s<sup>-1</sup>, the obtained voltammograms were completely overlapped and such a good reproducibility was also seen at different scan rates. Thus, it is confirmed that copper deposition on Pt electrodes in both aqueous chloride solutions and ionic liquids occurs by electroreduction of Cu(II) ions through the well known two stage mechanism, although the anodic and cathodic peak potentials and currents are significantly different. The CV observations confirm that Cu(II) ions existing in ChCl-Urea ionic liquid can be electrochemically reduced up to metallic copper by two consecutive steps.



 $\label{eq:states} \begin{array}{l} \mbox{Fig.1 Comparative cyclic voltammogrames } (v=200\ mVs^{-1})\ for $ChCl-Urea $ and $ChCl-Urea-0.05M\ CuCl_{_2}$ at $80\ ^{\circ}C,v=200\ mV\times s^{-1};$$ $[Red1=Cu(II)/Cu(I);\ Red2=Cu(I)/Cu(0);$$ $Ox1=Cu(0)/Cu(I);Ox2=Cu(I)/Cu(II)]$} $$ 

We also made deposition experiments for Cu on steel substrate from ChCl-Urea, molar ratio 1/2, at different current densities and time. The XRD pattern on the obtained deposits proved the deposition of Cu. Best results were obtained for 100 mV×s<sup>-1</sup> and 30 min, but as the electrolyte foams abundantly during electrolysis, the Cu deposits are not very homogenous, which was confirmed by micrographic images. Figure 2 presents the XRD spectrum and SEM image of Cu deposit obtained in ChCl-Urea, showing a rough and dull deposit.



Fig.2 XRD (a) and SEM(b) for the copper deposit obtained from ChCl-Urea-CuCl, (1:2:1)M

For the deposition of copper from ChCl-Malonic acid, electrochemical experiments gave the results presented in figure 3. One can see from this figure that the copper deposition mechanism is almost the same as in the ChCl-Urea. Cyclic voltammogram showed redox couples corresponding to cathodic deposition and anodic dissolution of Cu in two steps: Cu(II)/Cu(I) and Cu(I)/Cu(0) and vice versa. Their cathodic peak currents increase with square root of scan rate, thus proving a diffusion controlled electrode process. The heights of the cathodic and anodic peak for the Cu(I)/Cu(0) process are direct proportional to the potential scan rate. We also remarked the increase of DEp by (separation between anodic and Cathodic peaks) increasing scan rates. This behavior suggests rather a quasireversible deposition/dissolution response of Cu<sup>+</sup> ions, with a certain degree of irreversibility. It is possible that CuCl and CuCl, to dissolve in ChCl-MA forming a complex, as CuO does forming  $[Cu_{0}O \times m(NH_{0})CO \times nCl]^{n}$ . A general simple expression of a possible mechanism for the process of disproportionation which takes place during the electrolysis can be:  $2CuCl \rightarrow CuCl_{+} + Cu$ ,  $CuCl_{-} \rightarrow CuCl_{+} 1/$ 2Cl<sub>2</sub>. So we can conclude that the mechanism of the electro-deposition of Cu<sup>2+</sup> is not an ideal one, but the redox reaction is coupled with a reversible chemical reaction with complex ions formation. For this non-ideal process the diagnostics power of cyclic voltammetry is most useful. Figure 4 presents the XRD and micrographic images for the best deposits of copper obtained from ChCl-Malonic acid at 0.05  $A\times cm^{-2}$  and 20 minutes deposition time. An adherent and uniform deposit with a small granulation was obtained. Two zones, of which one lighter at the upper part at the electrolyte interface are present due to foaming. Calculated thickness of the copper layer was  $d \sim 5.9 \, \mu m$ and elementary crystalline cell parameter was a=0.3619(5) nm.



Fig.3 Cyclic voltammogram for ChCl-Malonic acid-CuCl $_{2(anh)}$  (1:2:1 molar ratio), v=25mV/s

The dissolution of copper in an aqueous solution of 0.2M  $CuCl_2 \times 2H_2O$ -ChCl was also tested. The objective of this preliminary work was to study the influence of the choline chloride ChCl concentration on the dissolution of copper, in order to determine the optimal concentration and leaching rate of copper. Therefore, aqueous solutions were prepared with 0.2M  $CuCl_2 \times 2H_2O$  in 0-90wt% ChCl at 25 °C and 80°C. In these solutions we tried to see the solubilization



Fig.4 XRD pattern (a) and micrographic image with magnification x400 (b) for the copper deposit obtained from ChCl-Malonic acid-CuCl<sub>2</sub> (1:2:0.2)M

of Cu with agitation and some times with adding HCl or  $H_2O_2$ . Best dissolution results were obtained for 30 wt% ChCl concentration for 25°C and 80°C. The solution of 0.2M CuCl<sub>2</sub>×2H<sub>2</sub>O-30wt% ChCl is clearly green and transparent. For studying the dissolution of Cu metal in this solution metallic copper (Riedel de Haen) was added into a 40mL solution at 25°C and was agitated with 650 rpm. The solution turns in green-turquoise with a specific colour for CuCl<sub>2</sub>×2H<sub>2</sub>O and then as the more amount of copper dissolves, it becomes greenish yelow opaque specific for CuCl. After a duration more than 1h the solution becomes more opaque and dark green because the presence of a big quantity of Cu(II) in the solution, which comes from the copper dissolution and formation of a Cu(I) precipitate. At 80 °C, the dissolution is more faster.

Figure 5 show the piece of copper used for experiment (fig. 5a) and the results of Cu disolution in different states (fig.5 b-d). At 120 min of leaching at 25°C, an amount of ~0.56 g of Cu was dissolved while at 80°C ~0.71 g dissolved. In order to investigate the possibility to regenerate Cu(II) species the solution with Cu(I) obtained after dissolution of Cu in 0.2M CuCl<sub>2</sub>×2H<sub>2</sub>O-30 wt% ChCl was treated with H<sub>2</sub>O<sub>2</sub> or HCl solutions. When H<sub>2</sub>O<sub>2</sub> was added the solution becomes blue due to the presence of Cu<sup>2+</sup>, while when HCl was added a black powder was formed demonstrating the passivation of copper particles.

Figure 6 shows images of all solutions immediately after Cu dissolution and after 48 h. It can be seen that for copper dissolution a blue precipitate like floaters appears after



Fig.5 Piece of copper (a) and dissolution of copper in the IL solution in initial (b) and final stages (c,d).

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a)

- b)

c) d) http://www.revistadechimie.ro



Fig.6 IL solution of 0.2M  $CuCl_2\times 2H_2O+30$  wt % ChCl after adding Cu in the initial stage (a) and after 48 h(b).



Fig.7 A comparison of cyclic voltammograms of 0.2M  $CuCl_2 \times 2H_2O + 30$  wt % ChCl (1) and  $[0.2M CuCl_2 \times 2H_2O + 30$  wt% ChCl]+0.2M CuCl\_2(2) at 80°C with 200 mV×s<sup>-1</sup> scan rate.



Fig.8 Dissolution of the multicomponet alloy (having mainly Cu in composition) in the aqeueous ionic liquid 0.2M CuCl<sub>2</sub>×2H<sub>2</sub>O+30 wt %ChCl solution at 80°C in the initial stage (a) and after adding  $H_2O_2$  solution (b).

>24 hours. This are troublesome Cu(I) precipitates formed with Cu(II) leaching solutions.

Finally we performed cyclic voltammetry for dissolution of CuCl, in the aqueous ionic liquid solution formed by 0.2M CuCl,  $\times$  2H,O+30 wt % ChCl at 80°C. In figure 7 it can be observed the copper electrodeposited at about -0.62 V vs. Ag QRE by a two steps mechanism. The peak corresponding to Cu(II)/Cu(I) couple did not appear. The nucleation related to the deposition of metals is confirmed by stripping peak in the anodic reversal scan.

In order to test the good behaviour as leachate of this aqueous ionic liquid solution we made test for dissolution of the multicomponent alloy obtained by pyro-metallurgic technology from WEEE which has mainly Cu in composition. Images of the results are presented in figure 8. The tests were done with 950 rpm agitation and increasing temperature up to 80 °C. It finds that the alloy is almost completely dissolved. If we add 3.1 mL H<sub>2</sub>O<sub>2</sub> (30%) solutions the total dissolution occurs (fig.8b).

## Conclusions

We demonstrated the possibility of copper recovery in WEEE leachate by using ionic liquids based on choline chloride (as ChCl-Urea and ChCl-Malonic acid) as long as by using aqueous ionic liquids based on choline chloride (as  $0.2M \text{ CuCl}_2 \times 2H_2\text{O} + 30\text{wt\%}$  ChCl). Future electrochemical experiments correlated with XPS characterization are necessary in order to complete this study.

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