

THERMODYNAMIC STUDY OF LEACHED METALS (Cu, Zn AND Ni) FROM WASTE PRINTED CIRCUITS BY ELECTROCHEMICAL METHOD

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Abstract. A thermodynamic study (Pourbaix type diagrams, using the software Hydra/Medusa) of acid leaching solutions to obtain the electrochemical recovery of Ni, Cu and Zn present in printed circuit boards is reported. Solutions were characterized by atomic absorption spectroscopy at room temperature. The metals were leached in a 0.9237 M H₂SO₄ solution (pH = 1.56) at 313, 323, 333 and 343 K. From this data, the reduction potentials were determined for each metal, finding the values of -0.0024, -1.1274 and -0.5892 V vs calomel for Cu, Ni and Zn, respectively. Displacement in the reduction potential with the increase of the metal concentration in the leaching solution was observed.

Introduction

In some materials, an effective recycling system cannot be implemented spontaneously, which is an issue that concerns technology, planning, economics and environmental regulation [1-5]. Gold, silver, copper, nickel and zinc are examples of elements present in electronic scrap. This basically consists of computer components, printed circuit boards (PCB), cell phones, etc. Specifically, computer circuit boards have a design consistent of a gold layer deposited on a substrate of a non-noble metal such as nickel, zinc and/or copper, which is also inserted into a polymeric base [1, 5]. Obviously, there is a huge potential source of gold and the mentioned base metals, which, currently, are partially recovered or even discarded [1, 2, 4, 5]. An optimum mechanism for the recovery of metal products is to subject them to dynamics acid leaching using oxygen and sulfuric acid to dissolve copper, nickel and zinc for later gold retrieval [1, 2, 4-7]. However, in order to obtain a selective recovery of non-noble metals, the electrochemical methods have been considered as a viable alternative since they are environmentally friendly. Some studies have reported the viability of copper, nickel and zinc electrodeposition from aqueous solutions by electrochemical methods [8-12]; the recovery of the metals mentioned above by such methods was considered. As the first part of this study, leaching of electronic components was made in order to facilitate the ionic presence of the selected metals and the recovery of Au. Once obtained, measurements were made in solutions with the determined non-noble metals and the corresponding thermodynamic study (Pourbaix type diagrams) of the leaching solutions at different temperatures, to obtain the best experimental conditions for the metal recovery (Cu, Ni and Zn).

Experimental

To determine the elements present in the sample, the metal phase present in the PCB was characterized using a JEOL JSM 6300 scanning electron microscope (SEM) with Si and 0.1 resolution coupled to a THERMO NORAN energy dispersive spectroscopy (EDS) device. Several leaching experiments were performed at different temperatures (313, 323, 333 and 343 K) in a 500 mL glass reactor mounted on a hot plate with magnetic stirring at constant pH of 1.56 (by adding a

0.9237 M of H₂SO₄ solution). Oxygen was injected to obtain a pressure of 1 atm. The reaction starting time was set when the product came into contact with the leaching solution. Samples were collected at different times (t) to follow the progress of the reaction. All leaching solutions were characterized using a Perkin-Elmer 2380 atomic absorption spectrophotometer (AAS), at room temperature, to determine the leached elements. The presence of Cu, Ni and Zn with different amounts for each temperature was observed. Concentrations were calculated for each metal in order to produce the data needed in the thermodynamic study using Pourbaix type diagrams, by the Hydra/Medusa software [13] and to evaluate the possibility for the selective metal recovery by electrochemical methods.

Results and discussion

SEM-EDS characterization. Fig. 1 shows an image obtained by SEM that corresponds to the metal portion constituting the PCB. Four areas were taken as reference points to find the elements present in the sample: i) the bottom, in which the metal part is welded to the base polymer, ii) the middle part, which is the body of the metal element, iii) top, which makes contact with other electronic components, and iv) the tips, mostly coated with gold and as the top, they are in contact with electrical items. Table 1 shows the analysis on the EDS results on the characterized zones, and the weight percentage of the present metal elements.

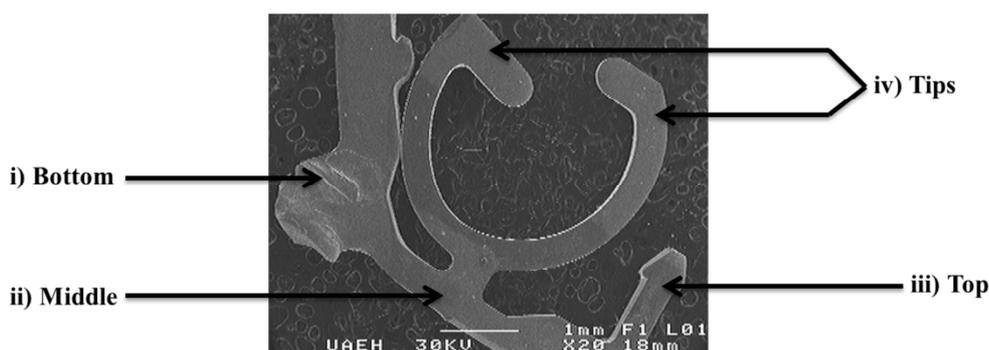


Figure 1. Detail image of the metallic element present in PCB, using SEM.

Table 1. Wt% of the characterized elements.

Element	Wt.% by zones			
	Bottom	Middle	Top	Tips
Cu	1.07	1.99	2.83	3.10
Ni	8.23	30.49	83.60	16.46
Zn	0.11	0.00	0.03	0.18
Au	0.61	0.96	12.26	76.97

Pourbaix diagram study. In order to establish the chemical species in the leached solution and the equilibrium potential for subsequent electrodeposition under our experimental conditions, a thermodynamic study by using Pourbaix type diagrams [9, 13] was performed. The solutions studied come from real liquor of dynamics acid leaching. Speciation of Cu, Ni and Zn in the solution was examined by constructing the distribution pH diagrams of each separated metal. The results concerning Cu are shown in Fig. 2. Under the experimental conditions of this work, the predominant chemical species is CuSO₄, carrying out the following reaction:



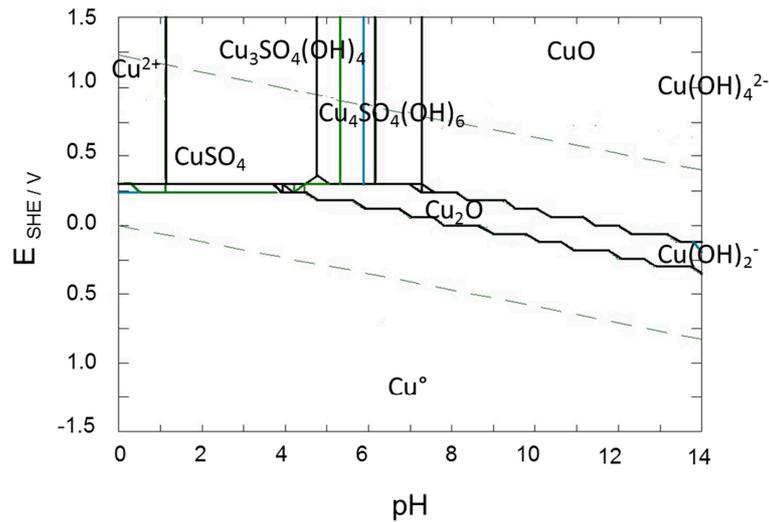


Figure 2. Pourbaix type diagrams of the Cu(II)/Cu(0) systems: (—) $p\text{Cu(II)} = 3.01$, (—) $p\text{Cu(II)} = 2.99$, (—) $p\text{Cu(II)} = 2.19$, (—) $p\text{Cu(II)} = 1.54$ and $p\text{SO}_4 = 0.03$.

The results concerning Ni are shown in Fig. 3. Under the experimental conditions of this work, the predominant chemical species is NiSO_4 , carrying out the following reaction:

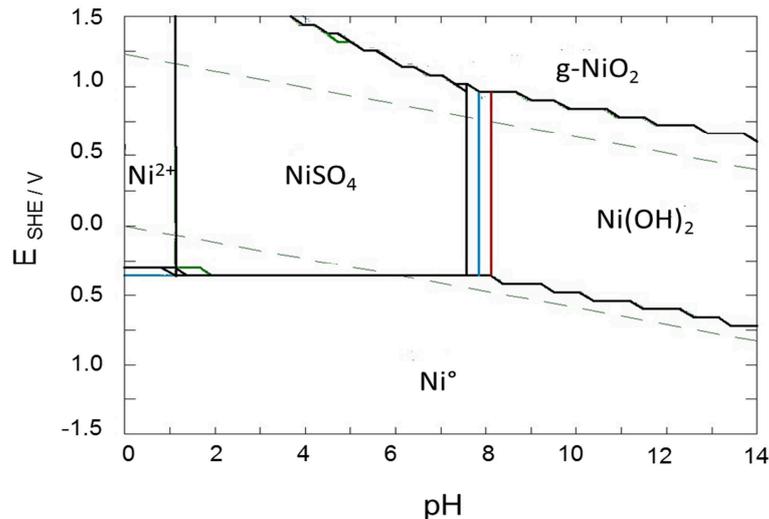


Figure 3. Pourbaix type diagrams of the Ni(II)/Ni(0) systems: (—) $p\text{Ni(II)} = 3.92$, (—) $p\text{Ni(II)} = 3.20$, (—) $p\text{Ni(II)} = 2.64$, (—) $p\text{Ni(II)} = 2.83$ and $p\text{SO}_4 = 0.03$.

The results concerning Zn are shown in Fig. 4. Under the experimental conditions of this work, the predominant chemical species is $[\text{Zn}(\text{SO}_4)_2(\text{H}_2\text{O})_4]$, carrying out the following reaction:



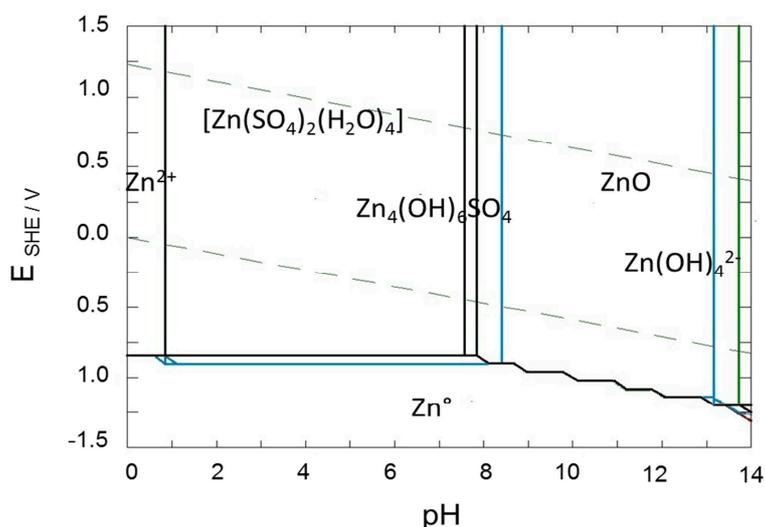


Figure 4. Pourbaix type diagrams of the Zn(II)/Zn(0) systems: (—) $pZn(II) = 3.20$, (—) $pZn(II) = 3.14$, (—) $pZn(II) = 1.79$, (—) $pZn(II) = 1.62$ and $pSO_4 = 0.03$.

From the above diagrams, it was possible to observe the influence of the concentration of each metal on the reduction potential. This concentration was different due to the different temperatures required for leaching, which were: 1) 313 K, 2) 323 K, 3) 333 K and 4) 343 K. In general, a displacement of the reduction potential was observed for each system, thereby allowing to determine the conditions under which the metal deposition requires lower energy cost, making the process cheaper.

Table 2 shows the results obtained from the Pourbaix type diagrams. Note that the potential of the $CuSO_4/Cu$ couple is of the ranges from -0.0024 to 0.0566 V vs calomel. Although there was an increase in concentration with increasing temperature of each system the reduction potential value for the concentration obtained at temperatures of 313 and 323 K was the same (-0.0024 V vs calomel); while at 333 and 343 K there was a positive, displacement of reduction potential (0.0010 and 0.0566 V vs calomel, respectively). In the case of the reduction potential for the $NiSO_4/Ni$ couple with the first two leaching temperatures, the value was the same (-0.5892 V vs calomel), while for the next two temperatures there was another constant value (-0.5371 V vs calomel). Finally, the potential of the $[Zn(SO_4)_2(H_2O)_4]/Zn$ couple was determined in the range of -1.1274 to -1.0753 V vs calomel, having a similar behavior to Cu and Ni. For the first two leaching temperatures, the reduction potential remained constant (-0.0024 V vs calomel), while for 333 and 343 K the value was increased (-1.0753 V vs calomel), being the same for both temperatures.

Table 2. Reduction potential values determined for the electrodeposition of leached metals.

Element	Temperature (K)							
	313		323		333		343	
	[Total] (mM)	E (V)	[Total] (mM)	E (V)	[Total] (mM)	E (V)	[Total] (mM)	E (V)
Cu	0.97	-0.0024	1.01	-0.0024	6.41	0.0010	28.80	0.0566
Ni	0.12	-0.5892	0.62	-0.5892	2.29	-0.5892	1.47	-0.5892
Zn	0.63	-1.1274	0.72	-1.1274	16.0	-1.0753	23.60	-1.0753

Conclusions

In the characterization of PCB prior to leaching, the elemental composition was determined, which consists of a gold layer deposited on a substrate of a non-noble metal such as nickel, zinc and/or copper inserted into a polymeric base. The temperature increase influences dramatically the degree

of the metal dissolution. From the Pourbaix type diagrams, under the experimental conditions of this study, the reduction potential where it is possible to obtain the metal recovery was determined. Furthermore, it was observed that increasing the concentration causes a decrease in the energy cost of the reduction: for Cu, the reduction potential was increased from -0.0024 to 0.0566 V vs calomel; for Zn it changed from -1.1274 to -1.0753 V vs calomel; and for Ni, it increased from -0.5892 to -0.5371 V vs calomel; in all cases, the potential increase was due to the increase of the metal concentration in the solution for the performed study.

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