

TIN RECOVERY BY RECYCLING OF PRINTED CIRCUIT BOARDS FROM OBSOLETE COMPUTERS IN BRAZIL

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Abstract

This paper presents the preliminary experimental results for recycling of printed circuit boards (PCB) from obsolete computers in Brazil aiming at tin recovery by electrowinning. Printed circuit boards were disassembled, cut off in small pieces and fed into a cylinder mill. The powder obtained was leached using aqueous solutions 2.18N H₂SO₄. The leaching liquor obtained was 2.0g.L⁻¹ of Sn.

Tin electrowinning tests were performed using 100mL of synthetic aqueous solutions with chemical composition similar to the H₂SO₄ leaching liquors of PCB.

A statistical approach was applied using a planning of experiments by the full factorial design method for three variables at two experimental levels. Variables studied were electrolyte temperature, time of electrowinning and cathodic current density.

The optimum experimental conditions determined by the statistical approach adopted to reach 97.5% of tin recovery were 300A.m⁻² for cathodic current density, 35 minutes of electrowinning and 32.5°C for the temperature of the electrolyte.

Keywords: tin, PCB, recycling, electrowinning, hydrometallurgy

1. INTRODUCTION

Tens of millions of computers have been installed over the past two decades in Brazil. As new and more efficient computers come into the market, significant numbers of old computers are being scrapped. Likewise, the number of obsolete computers has also been growing in Brazil. One microcomputer company alone estimates that about three million obsolete computers are discarded each year in Brazil. Due to the lack of specialized companies working with the recycling of obsolete computers in Brazil, such equipment is commonly scrapped in inappropriate disposal areas, together with domestic garbage, with no specialized recycling processes.

Printed circuit boards used in computers are composed of different materials, such as polymers, ceramics, and metals, which render the process even more difficult. The presence of metals, such as tin and copper, encourage recycling studies from an economic point of view. However, the presence of heavy metals turns this scrap into dangerous residues. This, in turn, demonstrates the need for solutions to this type of residue so as to dispose of it in a proper manner without harming the environment.

The recycling of printed circuit boards from obsolete computers is, at present, a fairly new activity in Brazil although opportunities are available for expansion in this area. For instance, gold, silver, tin, and copper, among other metals, can be recovered by means of the hydrometallurgical treatment of printed circuit boards (PCB) from obsolete computers [1, 2, 3, 4].

Most hydrometallurgical treatments use leaching as one of the main stages. Leaching is the process of extracting a soluble constituent from a solid by means of a solvent. In extractive metallurgy it is the process of dissolving minerals from an ore or a concentrate, or dissolving constituents from metallurgical products.

Some researchers have also been working on the recycling of electronic scrap in Brazil. Menetti and Tenório [3] presented a short

bibliographic review on metal recovery processes to treat electronic scrap arising from several different sources. Emphasis was given to the initial treatment of residues using comminution procedures followed by pyrometallurgical, hydrometallurgical, electrochemical, and biotechnological techniques.

Menetti and Tenório [4] depicted the steps of a research project for gold, silver, copper, iron, aluminum, tin, and zinc recovery from electronic scrap. The authors researched methods to obtain metallic concentrates from three types of electronic scrap using physical treatments. Special attention was given to comminution, electrostatic, and magnetic concentration procedures.

Veit et al. [1] used PCBs from obsolete or defective personal computers, which represent the largest source of technological waste in Brazil for metal recovery. In the first stage, mechanical processing and comminution were used, followed by size and magnetic and electrostatic separation. A concentrated fraction in metals (mainly Cu, Pb, and Sn) and another fraction containing polymers and ceramics were obtained. The copper content reached a mass of more than 50% in most of the conductive fractions. A significant content of Pb and Sn could also be observed. In the second stage, the fraction concentrated in metals was dissolved with aqua regia or sulfuric acid and treated in an electrochemical process to recover the metals separately, especially copper. The results demonstrate the technical viability of recovering copper by means of mechanical processing followed by an electrometallurgical technique. The copper content in the solution decayed quickly in all the experiments, and the copper obtained by electrowinning was found to be above 98% in most of the tests.

Veit et al. [2] studied metals recovery from printed circuit boards through mechanical processing, such as crushing, screening, as well as magnetic and electrostatic separation. The results obtained demonstrate the feasibility of using these processes to separate metal fractions from polymers and ceramics. A fraction concentrated in metals containing more than 50% on average of

copper, 24% of tin and 8% of lead was obtained. It is important to observe that there is no copper separation from tin using a mechanical processing.

Castro and Martins [5] studied the tin and copper recovery from PCB of used microcomputers using a hydrometallurgical approach. This approach consisted of leaching of PCB powder with inorganic acids followed by precipitation of tin and copper inorganic salts from aqueous solutions using pH adjustment.

This experimental work presents the results for tin recovery by electrowinning from synthetic aqueous solution with tin concentration similar to the leach liquor of treated PCBs from obsolete computers. The hydrometallurgical route used in this work to determine the tin concentration into the leach liquor for PCB dissolution was based on the following steps: (1) PCB samples were taken apart; (2) the metal parts were ground; (3) the nonmetallic parts were removed by washing components in distilled water, followed by drying; and (4) acidic leach systems using 2.18N H_2SO_4 aqueous solution for tin extraction. Aqueous solution with tin content was used as electrolyte of an electrowinning cell with a rectangular lead anode and an aluminum cathode connected to a continuous current power supplier. The mass of metal deposited on the cathode was measured using an analytical scale. Experiments were performed based on a planning of experiments using a full factorial method design for three variables at two experimental levels.

2. MATERIALS AND METHODS

The PCBs from obsolete computers used in the experiments were donated by the computer maintenance sector of the Federal University of Minas Gerais (Brazil). All chemicals used in the experiments were of analytical reagent grade and all glassware was made of borosilicate glass.

Five PCBs from obsolete computers were dismantled, separating all non-metallic parts. The metallic parts were cut into small pieces and fed into a ball mill (Pavitest mill, model

I-4227, Brazil). The powder produced after 8 minutes of milling was 1.6kg of material finer than a 0.208mm particle size. Milling exploratory tests with the PCB material and the ball mill showed that 90% of the material was finer than 0.208mm particle size even for milling times higher than 8 minutes. This particle size is considered satisfactory for many leach systems used in hydrometallurgy. This powder was washed with 3.0L of distilled water, aimed at removing the residual non-metallic materials that could affect the subsequent leaching stage. Samples of PCB washed powder collected from the bottom of the washing flask containing the metallic parts were leached with 2.18N H_2SO_4 aqueous solution. All leaching experiments were carried out in duplicate, at least, using 50g of washed PCB powder and 500mL of leaching solution in a 1,000mL cylindrical glass vessel mounted over a heating plate (Fisaton, model 752A). A magnetic rod was used for stirring. The experiments were carried out at $60 \pm 2^\circ\text{C}$, and the temperature was measured by a mercury thermometer ($-10^\circ\text{C}/110^\circ\text{C}$). The leaching liquor obtained was 2.8g.L^{-1} of Cu and 2.0g.L^{-1} Sn.

The electrowinning tests used a cell with two parallel electrodes, were carried out in a borosilicate glass beaker, which square section was 2.6cm (side) and 5.0cm (height). The cathode was an aluminium plate, and the anode a lead one. The distance between electrodes in the electrowinning cell was 1.5cm. Both had 2.0cm x 7.0cm x 0.2cm. The electrodes were connected to a power supplier (MPL, model 1303, Brazil). The electrolyte used was 100mL of pure aqueous solution with 0.20g of tin solubilised in 2.18N H_2SO_4 solution. Aqueous solutions were prepared by direct weight in analytical scale of the appropriate mass of SnSO_4 , and further dissolution in distilled water. The electrowinning cell was mounted over a heating plate (Fisaton, model 752A). A magnetic rod was used for electrolyte stirring. Some experiments were carried out at $40 \pm 2^\circ\text{C}$ and others at room temperature ($20 \pm 2^\circ\text{C}$) according to the matrix of experiments of the factorial design method. The temperature was measured by a mercury thermometer ($-10^\circ\text{C}/110^\circ\text{C}$).

A statistical approach using a replicated full factorial method design for three variables at two levels and the ascendant path optimisation statistical method [6, 7] were adopted in order to evaluate the behaviour of some operational variables on the electrowinning performance for tin recovery. Table I shows the variables and experimental

levels adopted for the experiments. The experimental response obtained was mass of tin electrodeposited on the cathode. The mass of metal deposited on the cathode was calculated by the difference between the mass of the cathode before and after each experiment.

Table I – Statistical planning of experiments according to the full factorial method for mass of tin deposited on the cathode by electrowinning

Variables	upper level (+)	lower level (-)
A- Cathodic Current Density (A/m ²)	200	100
B-Time of Electrowinning (min)	20	10
C-Electrolyte Temperature (°C)	40	20

3. RESULTS AND DISCUSSION

Table II shows the experimental results for the tin mass deposited on the cathode of the electrowinning cell. Each experiment was

carried out in replicate. The experimental results from Table II allowed building the Yates Algorithm according to the replicated full factorial design method.

Table II - Block matrix for 8 replicated experiments for the tests of tin mass deposited on the cathode by electrowinning using a full factorial design statistical method

Test	A	B	C	Notation	Sn (g)	
1	-	-	-	T	0.15	0.15
2	+	-	-	A	0.06	0.06
3	-	+	-	B	0.09	0.08
4	+	+	-	AB	0.14	0.13
5	-	-	+	C	0.06	0.04
6	+	-	+	AC	0.20	0.20
7	-	+	+	BC	0.18	0.20
8	+	+	+	ABC	0.18	0.20

Table III shows the results obtained for the calculation of the statistical influence of variables and their interactions on the

experimental responses and the respective statistical significance on the mass of tin recovery by electrowinning.

Table III – Statistical influence of variables, interactions and their significance on the mass of copper and tin recovery by electrowinning

Variable/ Interaction	Sn	
	Statistical Influence (*)	Statistical Significance
T	-	-
A	7.5	S
B	10.0	S
AB	20.0	S
C	12.5	S
AC	12.5	S
BC	7.5	S
ABC	1.25	NS

NS - no significant S – significant (*) Test t-Student calculated value

According to the Table III and for the tin recovery system, it is important to note that all individual variables and interactions were considered significant at 95% statistical confidence level. The exception was the ABC interaction. It means that all variables had significant influence on the tin mass deposition on the cathode. However, the variable C, electrolyte temperature showed the highest influence on the experimental response. The time of the electrowinning had the second highest influence on the mass of tin deposition, while the cathodic current density parameter exhibited the lowest effect on the experimental response. This evaluation is valid only for the experimental levels adopted in this work.

Based on the experimental results and on the calculations of the ascendant path optimization statistical method, the optimum conditions for tin recovery (0.19 g of tin deposited or 97.5% of tin recovery) are 300 A.m⁻², 35 minutes for time of electrowinning and 32.5°C for the electrolyte temperature.

The experimental results showed that it is possible to recover tin by recycling of printed circuit board from obsolete microcomputers using relatively simple electrometallurgical methods.

4. CONCLUSIONS

According to the electrowinning experimental results for tin recovery from printed circuit boards of used microcomputers, all three variables studied (cathodic current density, time of electrowinning and temperature of the electrolyte) were statistically significant on the tin mass deposition on the cathode. However, the temperature of the electrolyte showed the highest influence on the experimental response.

The experimental conditions to be adopted to reach the optimum tin recovery (0.19 g of tin deposited on the cathode or 97.5% recovery) by electrowinning were 300 A.m⁻² of cathodic current density, 35 minutes for time of electrowinning and 32.5°C for the electrolyte temperature.

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