Brazilian Journal
of Chemical
Engineering

ISSN 0104-6632
Printed in Brazil
www.abeq.org.br/bjche

Vol. 26, No. 04, pp. 649 - 657, October - December, 2009

RECOVERY OF TIN AND COPPER BY RECYCLING OF PRINTED CIRCUIT BOARDS FROM OBSOLETE COMPUTERS

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(Submitted: March 12, 2009 ; Revised: June 22, 2009 ; Accepted: June 22, 2009)

Abstract - This paper presents the experimental results for the leaching of printed circuit boards (PCB) from obsolete computers for extracting and recovering tin and copper by means of leaching followed by precipitation. Printed circuit boards were dismantled, cut into small pieces, and fed into a cylinder mill. The powder obtained was leached by using the aqueous solutions 2.18N H_2SO_4, 2.18N H_2SO_4 + 3.0N HCl, 3.0N HCl, and 3.0N HCl + 1.0N HNO_3. The lowest values for the percentage of metal extraction were obtained with 2.18N H_2SO_4 (2.7% for Sn and lower than 0.01% for Cu), while the 3.0N HCl + 1.0N HNO_3 leach system exhibited an extraction of 98% for Sn and 93% for Cu. Precipitates were obtained at different pH values by neutralizing the leach liquors using NaOH. The 3.0N HCl + 1.0N HNO_3 leach system presented the highest recovery values from the powder feed (84.1% for Sn and 31.9% for Cu), as well as from the leach liquor (85.8% for Sn and 34.3% for Cu).
Keywords: Tin; Copper; Recycling; Electronic scrap; Hydrometallurgy.

INTRODUCTION

Tens of millions of computers have been installed over the past two decades in Brazil. As new and more efficient computers come onto 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, encourages 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 (Veit et al., 2005, 2006; Menetti et al., 1995, 1996).

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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 (Habashi, 1999). In extractive metallurgy, it is the process of dissolving minerals from an ore or a concentrate, or dissolving constituents from metallurgical products.

Lead, tin, and indium were successfully recovered from alloy wire electronic scrap through acid/alkali leaching (Barakat, 1998). The scrap material was leached using a 5M HCl-HNO_3 solution at 80^0C for 1.45 hours, and an NaOH solution was added to the leach liquor for metals precipitation. Under these experimental conditions, the percentages of metal recovery were 94.7% for Pb, 99.5% for Sn, and 99.7% for In.

Barakat (1998) investigated metal recovery from zinc solder dross used in PCBs by means of leaching using a 3.0% H_2SO_4 solution at 45^0C for 1 hour. Zinc and aluminum entered the solution, whereas lead and tin remained within the residue. Aluminum was selectively precipitated as a calcium aluminum carbonate by treating the sulfate leachate with limestone at pH 4.8. The zinc sulfate solution was either evaporated to obtain zinc sulfate crystals or precipitated as a basic carbonate at pH 6.8. The undissolved lead and tin were leached by using a hot 5.0M HCl solution. The majority of the lead chloride (73%) was separated by cooling the leached products down to room temperature. From the soluble fraction, tin was recovered as tin oxide hydrated by means of alkalinization with caustic soda at pH 2.4. The recovery efficiency of the metal salts was 99.1% for Zn, 99.4% for Al, 99.6% for Pb, and 99.5% for Sn.

Lee et al. (2003) investigated the recovery of valuable metals and the regeneration of the expended PCB nitric acid etching solutions. Nitric acid was selectively extracted from the expended etching solution using tributylphosphate (TBP), whereas a pure nitric acid solution was extracted using distilled water. After nitric acid extraction, pure copper metal was obtained through electrowinning, and tin ions were precipitated by adjusting the pH of the solution with $Pb(OH)_2$. Lead, with a purity of 99%, was obtained by cementation with an iron powder.

Some researchers have also been working on the recycling of electronic scrap in Brazil. Menetti and Tenório (1995) 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 by using comminution procedures followed by pyrometallurgical, hydrometallurgical, electrochemical, and biotechnological techniques.

Menetti and Tenório (1996[a]) depicted the steps 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.

Menetti and Tenório (1996[b]) investigated gold and silver recovery from the physical treatment of electronic scrap to produce metallic concentrates. Gold and silver present in a sample of electronic scrap were solubilized with 1.0N HNO_3 solution. The leached pulp was treated with a 1.0N H_2SO_4 solution to cause gold sulfate precipitation. The remaining solid residue was melted at 1085ºC in the presence of Na_2CO_3, producing small pellets of gold.

Veit et al. (2005) 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 fraction concentrated 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. (2006) 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 with a mechanical processing.

This experimental work presents the results for tin and copper recovery from treated PCBs from

obsolete computers using a hydrometallurgical approach. A block schematic diagram with the hydrometallurgical route adopted in this work is shown in Figure 1. It is 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) different acidic leach systems using 2.18N H_2SO_4, 3.0N HCl, 2.18N H_2SO_4 + 3.0N HCl, and 3.0N HCl + 1.0N HNO_3 aqueous solutions were studied for tin and copper extraction. Tin-copper bearing precipitates were obtained from the leach liquor at different initial pH values through neutralization using NaOH. All precipitates obtained were subjected to metal content determination by atomic absorption spectrometry (AA). Tin and copper content for the PCB powder and precipitates obtained from the experiments were determined by means of a mass balance of samples solubilized in an aqua-regia (3.0N HCl + 1.0N HNO_3) solution, followed by analysis by atomic absorption spectrometry (AA). The concentrations of tin and copper in the aqueous solution samples of the leaching liquor obtained from the experiments were also analyzed by AA.

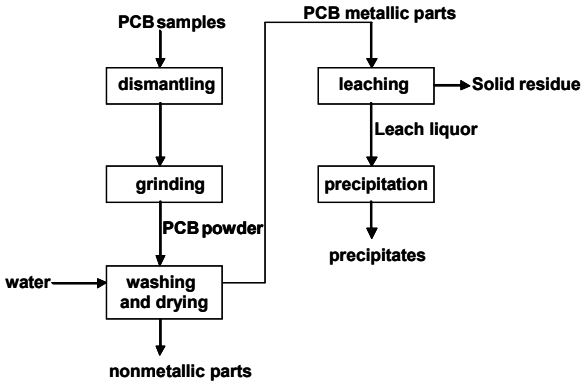

Figure 1: Schematic block diagram of the process route used in the experimental work

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; 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 1.6 kg 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 and precipitation stages. The non-metallic parts floated on the water and the metallic parts sank, remaining at the bottom of the washing flask. Samples of the PCB washed powder collected from the bottom of the washing flask were characterized by X-ray diffraction (Philips Difratometer, model PW1710, USA), to identify inorganic species, and X-ray fluorescence spectrometry (Philips X-ray fluorescence spectrometer, model PW2400, USA) to identify metal elements. The metal content in the samples was determined by atomic absorption spectrometry (Perkin Elmer, model Analyst300).

Samples of PCB washed powder collected from the bottom of the washing flask containing the metallic parts were leached by using different acidic solutions (2.18N H_2SO_4, 3.0N HCl, 2.18N H_2SO_4 + 3.0N HCl, and 3.0N HCl + 1.0N HNO_3) to determine the best leach system for maximum tin and copper extraction. The leach systems studied in the experimental work were selected based on preliminary tests and consulting the literature dedicated to solubilization of metals. The concentration of inorganic acids used in these tests was determined by carrying out exploratory experiments and took into consideration avoiding the use of high concentrations because the experimental costs would also be very high.

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±2ºC, and the temperature was measured by a mercury thermometer (-10ºC/110ºC). Samples of the leach liquor were collected at intervals of 10, 30, 60, and 120 minutes during the experiment.

Leach liquor samples were collected, filtered and sent for chemical analysis to determine tin and copper concentration in aqueous solution through AA. The solid leaching residues from the experiments were centrifuged (laboratory bench

centrifuge, Fanen, model 206-Baby II) and dried in an oven (Fanen, model 320-SE) at 60ºC for 24 hours. The solid leaching residues were cooled to room temperature, and the mass was measured on an analytical balance (Metler, model AE200). Next, the solid leaching residues were sent for characterization by X-ray diffractometry and X-ray fluorescence. Samples of the solid leaching residues were dissolved in acidic aqueous solutions and tin and copper contents were determined through AA.

The percentage of metal extraction of the leaching stage (see Table 2) was determined by dividing the mass of metal dissolved in the leach liquor by the initial mass of the metal present in the PCB washed powder which was fed in the leaching stage. The mass of metal dissolved in the leach liquor was provided by chemical analysis through AA from samples collected at the end of the leaching. The solid leaching residue was collected at the end of the leaching. Then, it was filtered, dried, the mass measured on an analytical balance and completely dissolved in acidic aqueous solution. Samples of this aqueous solution were analyzed through AA to determine the concentration of tin and copper.

The mass of metal from the PCB washed powder was determined by dissolving the material with concentrated HCl at 150ºC in a Teflon cylindrical closed vessel for 18 hours. All PCB washed powder was dissolved and copper and tin concentration was determined by AA.

Some experiments were carried out with the solid leaching residue of the initial leaching as feed material for the secondary leaching. This stage was performed because the metal content in the solid leaching residue was still considered to be high. The experimental conditions used in the secondary leaching process were the same as in the initial leaching process.

The leach liquor treatment for tin and copper compound precipitation was carried out in an experimental unit similar to the leaching experiments. Experiments were performed in duplicate, at least, at room temperature and under an intense magnetic stirring of the aqueous solution. Solid NaOH was gradually added to the leach liquor, and the solution pH was monitored by a pHmeter (Quimis, model Q400A) by using a glass reference electrode immersed in the liquor. All precipitates obtained at specific pH values were collected by centrifugation, dried in an oven, weighed, and sent for characterization by X-ray diffractometry and X-ray fluorescence. In addition, the metal content was ascertained by means of AA.

RESULTS AND DISCUSSION

Table 1 presents the chemical composition of the washed powder obtained from the PCBs from obsolete computers. The highest content of metals present in the samples included Al, Sn, and Cu. With regard to Sn and Cu, the content percentage values were higher than those found in most Sn and Cu ores (Anuário Mineral Brasileiro, 2006; Davenport et al., 2002; Habashi, 1999; Sevryukov et al., 1977). Due to the high metalic content, as seen in the results shown in Table 1, this experimental work focused solely on Sn and Cu recovery.

Table 1: Percentage of metal content in washed powder from the processing of printed circuit boards from obsolete computers

Metals	Percent (%)
Cu	2.85 ± 0.01
Al	3.71 ± 0.02
Zn	0.09 ± 0.005
Sn	3.09 ± 0.15
Ti	<0.1
Ni	0.05 ± 0.002

Table 2 shows the experimental results for the percentage of Sn and Cu extraction versus leaching time for the different acidic solutions (2.18N H_2SO_4, 3.0N HCl, 2.18N H_2SO_4 + 3.0N HCl, and 3.0N HCl + 1.0N HNO_3) used in the experiments. The results for percentage of metal extraction shown in Table 2 represent the amount of copper and tin initially present in the PCB washed powder dissolved by the leaching process.

Comparing the results for Sn and Cu extraction after 120 minutes obtained with the various leach systems, 3.0N HCl + 1.0N HNO_3 exhibited the highest percentage values for simultaneous Sn and Cu extraction (98.1%Sn and 93.2% Cu). The results for tin extraction are similar to those obtained by Barakat (1998). The poorest results were produced by the 2.18N H_2SO_4 system (2.7% Sn and <0.01% Cu). The secondary leaching of the 2.18N H_2SO_4 + 3.0N HCl system reached a level of 90% Sn extraction and only 12.3% Cu extraction from the primary leaching residue. The 3.0N HCl system gave 89.1% Sn and 33.2% Cu extraction. Based on the experimental results, secondary leaching proved to be efficient in reaching a higher percentage of tin extraction as compared to those leach systems performed in only one stage.

Tables 3 and 4 show the main results obtained from X-ray diffraction and X-ray fluorescence of precipitates generated through the neutralization of

leach liquors by adding NaOH. The presence of Cu, Ca, Sn, Al, Zn, Fe, Ni, Ti and their inorganic compounds in the PCB powder fed into the leach systems were detected by X-ray fluorescence and X-ray diffraction. It is important to note that the powder analyzed was generated from the metal parts of the PCBs and these metals were found freely in the powder in crystal form. According to Ewing (1972), the detection of tin, copper, and other metals by X-ray diffraction was expected under these conditions.

Tin oxide was detected in all precipitates obtained from the 2.18N H_2SO_4 and 2.18N H_2SO_4 + 3.0N HCl leach systems. On the other hand, zinc and iron oxide species were detected only in precipitates obtained from the 2.18N H_2SO_4 + 3.0N HCl leach system. No chloride species were detected in the precipitates from that leach system.

Inorganic species containing tin were not identified in the 3.0N HCl and 3.0N HCl + 1.0N HNO_3 systems. This may have occurred because some other organic materials may have been present in the powder feed in the leaching experiments. It is possible that some organic species actually solubilized when they came into contact with acid reagents, which in turn may have influenced the precipitation reactions during the neutralization of the leach liquors. This interference can in fact modify the precipitate structure, turning it into an amorphous material insensitive to identification by X-ray diffraction. Due to this limitation, X-ray fluorescence characterization was also performed.

Copper species were mainly detected by X-ray diffraction in the precipitates obtained from the 3.0N HCl and 3.0N HCl + 1.0N HNO_3 leach systems. Some copper species were detected in the precipitate obtained at pH=8.9 from the 2.18N H_2SO_4 system and at pH=3.0 and pH=8.5 from the secondary leaching in the 2.18N H_2SO_4 + 3.0N HCl system.

The X-ray fluorescence analysis of the precipitates obtained by neutralization of the leach liquors (Table 4) showed that tin species were detected in all precipitates, except in the precipitate obtained at pH=0.5 for the 2.18N H_2SO_4 leach system. Copper species were detected in higher content in the precipitates from the 3.0N HCl and 3.0N HCl + 1.0N HNO_3 leach systems. Most copper species detected in precipitates from other leach systems were in lower content. Combining the results obtained from Tables 3 and 4, it is possible to conclude that the 3.0N HCl and 3.0N HCl + 1.0N HNO_3 leach systems were the most appropriate to recover tin and copper simultaneously.

Table 2: Percentage of tin and copper extraction versus time of leaching for different leach systems studied

Leach systems	Time of leaching (minutes)	Tin extraction (%)	Copper extraction (%)
2.18N H_2SO_4	10	1.3±0.04	<0.01
	30	1.8±0.03	<0.01
	60	2.2±0.04	<0.01
	120	2.7±0.04	<0.01
2.18N H_2SO_4 + 3.0N HCl (primary leaching)	10	31.6±1.4	4.4±0.2
	30	38.9±1.5	5.5±0.2
	60	58.8±2.6	6.4±0.2
	120	59.3±2.3	8.9±0.4
2.18N H_2SO_4 + 3.0N HCl (secondary leaching)	10	90.5±3.0	4.2±0.1
	30	90.5±3.1	7.1±0.3
	60	90.5±3.1	10.1±0.4
	120	90.5±3.0	12.3±0.4
3.0N HCl	10	58.8±2.5	13.0±0.3
	30	67.8±3.3	22.3±0.8
	60	81.4±3.0	29.5±0.7
	120	89.1±3.5	33.2±1.1
3.0N HCl + 1.0N HNO_3	10	78.0±3.1	67.1±2.1
	30	86.1±3.4	79.2±2.7
	60	93.3±4.1	86.0±3.2
	120	98.1±3.3	93.2±2.4

Table 3: Main results for X-ray diffraction of the precipitate samples obtained by neutralization of the leach liquors under pH control

Leach systems	Precipitate obtained by neutralization with pH control	Main species identified
2.18N H_2SO_4	0.5	Na_2SO_4, SnO_2, $CaSO_4$, CaO
	4.6	Na_2SO_4, SnO, $CaSO_4$, CaO
	8.9	Na_2SO_4, SnO_2, $CaSO_4$, CaO, Cu_2O
2.18N H_2SO_4 + 3.0N HCl (primary leaching)	3.0	SnO_2, ZnO, CaO
	4.3	SnO_2, ZnO, CaO
	8.5	SnO_2, ZnO, Fe_3O_4
2.18N H_2SO_4 + 3.0N HCl (secondary leaching)	3.0	SnO_2, CaO, CuO_2, Fe_3O_4
	8.5	SnO, $CaSO_4$, SnO_2, CuO_2
3.0N HCl	1.8	NaCl, $(CuNi)_2Cl(OH)_3$
	3.0	NaCl, $(CuNi)_2Cl(OH)_3$
	4.2	NaCl, $(CuNi)_2Cl(OH)_3$
3.0N HCl + 1.0N HNO_3	2.6	$Cu_7Cl_4(OH)_{10}H_2O$, NaCl
	3.3	$Cu_7Cl_4(OH)_{10}H_2O$, NaCl
	4.2	$Cu_7Cl_4(OH)_{10}H_2O$, NaCl, $NaNO_3$

Table 4: Main results for X-ray fluorescence of the precipitate samples obtained by neutralization of the leach liquors under pH control

Leach systems	Precipitate obtained by neutralization with pH control	Higher intensity	Lower intensity
2.18N H_2SO_4	0.5	Ca, Na, Al	Mg, Zn
	4.6	Sn, Al, Na, Ca	Zn, Fe, Pb
	8.9	Sn, Al, Na, Ca,	Zn, Fe, As, Cu
2.18N H_2SO_4 + 3.0N HCl (primary leaching)	3.0	Sn, Pb, Al	Cu, Ca, Zn, Mg, As
	4.3	Sn, Fe, Ca, Al, Na	Pb, Zn, As
	8.5	Sn, Al, Na	Pb, Zn, As
2.18N H_2SO_4 + 3.0N HCl (secondary leaching)	3.0	Sn, Cu, Al	Pb, As
	8.5	Sn, Pb, As, Cu	Ca, Fe
3.0N HCl	1.8	Sn, Cu, Al	Zn, Pb
	3.0	Sn, Cu, Al	Zn, Pb, Fe
	4.2	Sn, Cu, Al	Zn, Pb, Fe, As
3.0N HCl + 1.0N HNO_3	2.6	Sn, Cu, Al	Sr, Fe, Pb, Fe
	3.3	Sn, Cu, Al	Zn, Pb, Fe
	4.2	Sn, Cu, Al	Zn, Pb, Fe, As

Table 5 presents the experimental results for tin and copper contents in the precipitates obtained from the neutralization of the leach liquors. The percent of tin and copper shown in Table 5 represents the amount of metal present in the precipitate. It was calculated by dividing the mass of metal (tin or copper) by the total mass of the precipitate.

All experiments were carried out in duplicate, at least. The results for mass of precipitate, mass of Cu and Sn recovered and percent of metal extraction represent the average value. The experimental error related to the results was estimated by calculating the deviation of the result from the average value. The experimental error related to the results was lower than 5% and usually considered acceptable from the statistical point of view.

The larger mass of precipitate obtained in this study (33.8 g) was for pH=4.3 from the primary leaching with 2.18N H_2SO_4+ 3.0N HCl. However, only 1.5% Sn and 0.2% Cu were recovered. The precipitate obtained at pH=1.8 from the 3.0N HCl leach system contained a larger mass of tin (1.20g) than did the precipitate produced at pH=2.6 from the 3.0N HCl + 1.0N HNO_3 leach system (0.79 g). With regard to copper, the precipitate obtained at pH=4.2 from the 3.0NHCl + 1.0NHNO_3 leach system showed a larger mass of copper (0.27g) in the precipitate.

Table 6 shows the results for tin and copper recovery from the washed PCB powder fed into the leaching stage, as well as from the leach liquor, for each system under study. The results for percent of metal recovered from the PCB powder feed presented in Table 6 were calculated by dividing the mass of metal in the precipitate by the mass of the respective metal in the PCB powder feed. The results for percent of metal recovered from the leach liquor were calculated by dividing the mass of metal in the precipitate by the mass of the respective metal dissolved in the leach liquor.

Table 5: Tin and copper content in the precipitates obtained by neutralization of leach liquors for the different systems

leach system	initial pH of precipitation	mass of precipitate (g)	%Sn	mass of Sn recovered (mg)	%Cu	mass of Cu recovered (mg)
2.18N H2SO4	0.5	1.48±0.06	<0.01	-	<0.01	-
	4.6	10.45±0.04	0.23±0.01	24±0.9	<0.01	-
	8.9	2.46±0.1	0.52±0.02	13±0.6	<0.01	-
2.18N H2SO4+ 3.0N HCl primary leaching	3.0	13.0±0.4	2.5±0.1	325±14.6	0.4±0.02	52±2.4
	4.3	33.8±1.5	1.5±0.07	507±20.2	0.2±0.01	67±3.0
	8.5	1.2±0.06	0.100±0.005	1,00±0.05	0.1±0.005	1.2±0.04
2.18N H2SO4+ 3.0N HCl secondary leaching	3.0	16.3±0.07	1.2±0.06	196±9.8	0.5±0.02	81±3.6
	8.5	13.2±0.06	0.8±0.04	106±4.7	0.3±0.01	39±1.5
3.0N HCl	1.8	10.1±0.4	12±0.04	1200±5	0.2±0.01	20±0.8
	3.0	16.4±0.6	1.0±0.05	164±8	0.1±0.005	16±0.6
	4,2	1.3±0.06	<0.1	-	10.1±0.5	13.1±0.6
3.0N HCl + 1.0N HNO3	2.6	25.6±0.8	3.1±0.1	793±9	0.4±0.02	10.2±0.4
	3.3	5.1±0.2	4.3±0.2	219±8	1.3±0.05	66±2.6
	4.2	22.3±0.8	1.3±0.06	290±6	1.2±0.06	267±8.4

Table 6: Percentage of Sn and Cu recovered in the precipitates from the powder feed (*) in the leach stage and from the leach liquors of the systems under study

Leach system	Sn recovered (%)		Cu recovered (%)	
	powder feed	leach liquor	powder feed	leach liquor
2.18N H_2SO_4	<0.02	<0.01	<0.01	<0.01
2.18N H_2SO_4/3.0N HCl	79.6±3.5	96.3±2.0	18.4±0.9	29.8±1.1
3.0N HCl	87.3±3.3	98.2±1.3	6.4±0.3	20.0±0.9
3.0N HCl/1.0N HNO_3	84.1±2.9	85.8±2.1	31.9±1.4	34.3±1.7

(*) 1.54 g Sn and 1.41g Cu in the powder feed

Comparing the results for each leach system, 2.18N H_2SO_4 presented the lowest values for tin and copper recovery. The percent of tin recovery for the 2.18N H_2SO_4 + 3.0N HCl leach system approached the values reached by 3.0N HCl and 3.0N HCl + 1.0N HNO_3 leach systems. The recovery values for copper obtained with 3.0N HCl + 1.0N HNO_3 were the highest among all leach systems studied.

Considering tin and copper recovery from the PCB powder feed, the 2.18N H_2SO_4 leach system exhibited the lowest results. The highest results for tin recovery were obtained for the 3.0N HCl leach system, with 87.3%, followed by the 3.0N HCl + 1.0N HNO_3 leach system with 84.1%. Regarding copper recovery, the highest result was reached by the 3.0N HCl + 1.0N HNO_3 leach system, with 31.9%, followed by the 2.18N H_2SO_4 + 3.0N HCl with 18.4% and 3.0N HCl with just 6.4%.

The simultaneous recovery of tin and copper in the precipitates from the PCB powder feed and leach liquors reached significant values mostly for the 3.0N HCl + 1.0N HNO_3 system. Taking into consideration the experimental results obtained herein, concentrates of tin and copper can be recovered from the PCBs of obsolete computers by using a hydrometallurgical approach based on acidic leaching, followed by the precipitation of tin and copper inorganic species.

It was not the scope of this paper to obtain copper and tin as separated metals. However, an electrowinning process for copper recovery is used in the extractive metallurgy of copper. In this process, copper oxides are solubilized by inorganic acids, such as sulfuric acid or aqua regia. The leach solution is used as electrolyte in an electrolysis cell with a set of electrodes (anode and cathode) and direct electric current. Copper metal is electrodeposited on the cathode and it can be refined, reaching a purity grade of 99.9% (Veit et al., 2006).

Concerning tin metal recovery, stannic oxide (SnO_2) is quickly dissolved in hot HCl solution. This leach solution is used as electrolyte in an electrochemical cell where tin metal can be electrodeposited onto stationary stainless steel electrodes (Scott et al., 1997).

CONCLUSIONS

The main conclusions obtained from the results of this experimental work were:

1) Taking into consideration only the combined results for X-ray diffraction and X-ray fluorescence analysis, it is possible to conclude that the 3.0N HCl and 3.0N HCl + 1.0N HNO_3 leach systems were the most appropriate to recover tin and copper simultaneously.
2) Tin and copper content in the powder generated by the processing of PCBs from obsolete computers, i.e., 3.1% Sn and 2.85% Cu, can be considered to be highly significant when compared to the content found in primary mineral sources.
3) The percentage of tin and copper extracted in the 2.18N H_2SO_4 leach system showed the lowest results among the leach systems under study, while the 3.0N HCl + 1.0N HNO_3 system presented the highest results for simultaneous tin and copper extraction (using one stage leaching). The secondary (stage of) leaching for the 2.18N H_2SO_4 + 3.0N HCl system extracted 90% of the tin from the solid residue from the initial leaching. This value was close to that reached by the 3.0N HCl system, the second highest extraction value.
4) The precipitates obtained through the neutralization of the leach liquor from the 2.18N H_2SO_4 system exhibited the lowest results for tin and copper recovery from the powder feed and from the leach liquor. The 3.0N HCl + 1.0N HNO_3 system presented the highest values for simultaneous tin (84.1% from the powder feed and 85.8% from the leach liquor) and copper (31.9% from the powder feed and 34.3% from the leach liquor) recovery.
5) The 3.0N HCl system showed percentages of tin recovered from the powder feed (87.3%) and the leach liquor (98.2%) higher than those from the 3.0N HCl + 1.0N HNO_3 system. However, the respective results for copper recovery were much lower (6.4% from the powder feed and 20% from the leach liquor).
6) The precipitate obtained at the initial pH of the neutralization of the leach liquor from the 3.0N HCl system presented the most significant mass of tin recovered (1.2g) among all precipitates produced in this experimental work. The precipitate containing the largest mass of recovered copper (0.26g) was obtained at an initial pH=4.2 of the neutralization of the leach liquor from the 3.0N HCl + 1.0N HNO_3 system. (1)

ACKNOWLEDGMENTS

The authors wish to thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq-Brazil) and Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG-Brazil) for providing financial support for this project.

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