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Recovery of copper from printed circuit boards scraps by mechanical processing and electrometallurgy

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Abstract

The constant growth in generation of solid wastes stimulates studies of recycling processes. The electronic scrap is part of this universe of obsolete and/or defective materials that need to be disposed of more appropriately, or then recycled. In this work, printed circuit boards, that are part of electronic scrap and are found in almost all electro-electronic equipments, were studied. Printed circuit boards were collected in obsolete or defective personal computers that are the largest source of this kind of waste. Printed circuit boards are composed of different materials such as polymers, ceramics and metals, which makes the process more difficult. However, the presence of metals, such as copper and precious metals encourage recycling studies. Also the presence of heavy metals, as Pb and Cd turns this scrap into dangerous residues. This demonstrates the need to search for solutions of this kind of residue, in order to have it disposed in a proper way, without harming the environment. At the first stage of this work, mechanical processing was used, as comminution followed by size, magnetic and electrostatic separation. By this process it was possible to obtain a concentrated fraction in metals (mainly Cu, Pb and Sn) and another fraction containing polymers and ceramics. The copper content reached more than 50% in mass in most of the conductive fractions and significant content of Pb and Sn. At the second stage, the fraction concentrated in metals was dissolved with acids and treated in an electrochemical process in order to recover the metals separately, especially copper. The results demonstrate the technical viability of recovering copper using mechanical processing followed by an electrometallurgical technique. The copper content in solution decayed quickly in all the experiments and the copper obtained by electrowinning is above 98% in most of the tests.

Keywords: Recycling; Copper; Printed circuit boards; Mechanical processing; Electrometallurgy

1. Introduction

The amount of electro-electronics equipments produced nowadays is very high, and it has been constantly increased due to the short lifetime of this equipments [1].

The number of personal computers discarded globally increases every year [2]. Consequently the amount of obsolete and defective material grows in the same proportion and its disposal becomes necessary. The recycling of this type of scrap is still quite limited due to the heterogeneity of materials present on the product and the complexity in producing these equipments.

Printed circuit boards are part of these equipments and their composition is quite varied, containing polymers, ceramics and metals. The quantity of metals, especially copper, turns the scrap into an interesting raw material according to the economic point of view. Also the lead presence in their composition stimulates studies for recycling according to the environmental point of view.

The existing processes of recycling printed circuit boards use pyrometallurgical [2–5] or hydrometallurgical methods [6–10], which generate atmospheric pollution through the release of dioxins and furans [11] or high volumes of effluents.

This work intends to use mechanical processings [12–18] as an alternative to concentrate the metals in a fraction and the polymers and ceramics in another. The fraction containing metals is processed by electrochemical methods [19–21] in order to

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separate the metals among themselves. This method intends to recycle printed circuit boards without consuming a great amount of energy (pyrometallurgical methods) and also without generating a great amount of effluents (hydrometallurgical methods).

The printed circuit boards scrap used in the magnetic and electrostatic separation were previously comminuted and separated by size in different fractions.

The fractions used in the electrometallurgical process were previously concentrated through the electrostatic separation. These fractions were dissolved with aqua regia or sulfuric acid and then put in an electrochemistry cell in order to recover the metals separately.

Besides studying the recycling of entire printed circuit boards (EPCB), it was also studied the recycling of the electronic components (EC) separately. These components were welded to the substrate of the printed circuit boards and were obtained through a manual separation.

The fractions concentrated on metals were chemically analyzed to identify its contents and the efficiency of this separation.

2. Materials and methods

2.1. Preparation, comminution and size separation

Printed circuit boards scrap used in this work were collected from damaged or obsolete equipments (microcomputers, TVs, video cassettes recorders, etc.). It was used 3 kg of entire printed circuit boards and 4 kg of electronic components. The electronic components used in this work were removed from the substrate where they were welded by heating and consequently melting the Pb–Sn weld. Two types of samples were then obtained:

- EPCB—entire printed circuit boards: 3 kg;
- EC—electronic components: 4 kg (capacitors, resistors, transistors, integrated circuit, etc.);

After doing this previous separation, each sample was comminuted separately in a cutting mill until the fractions reached particle size smaller than 1 mm (to guarantee an excellent degree of metals liberation) [15]. The samples were separated by particle size into three different fractions: $F_1 < 0.25$ mm; $0.25 < F_2 < 0.50$ mm and $0.50 < F_3 < 1.00$ mm.

The chemical composition of this scrap is presented in Table 1 (for the entire printed circuit boards) and in Table 2 (for electronic components).

Table 1
Chemical composition of EPCB after comminution and particle size separation

	EPCB		
	F_1	F_2	F_3
Copper (wt.%)	6.28	23.53	24.34
Iron (wt.%)	0.13	0.13	0.18
Aluminum (wt.%)	3.01	1.55	1.56
Nickel (wt.%)	0.05	0.20	0.20
Lead (wt.%)	0.35	0.95	1.35
Tin (wt.%)	2.51	2.50	2.51

Table 2
Chemical composition of EC after comminution and particle size separation

	EC		
	F_1	F_2	F_3
Copper (wt.%)	9.68	17.25	30.15
Iron (wt.%)	0.28	0.10	0.08
Aluminum (wt.%)	2.06	1.62	0.92
Nickel (wt.%)	0.40	0.31	0.60
Lead (wt.%)	2.34	3.18	2.78
Tin (wt.%)	3.83	4.78	4.92

2.2. Magnetic and electrostatic separation

The three fractions for each sample type were magnetically separated in a dry magnetic separator, using, on average, a magnetic field of 6000–6500 G.

It was obtained in this stage a magnetic fraction and a non-magnetic fraction. The non-magnetic fraction was transported to an electrostatic separator that would separate conducting from non-conducting materials.

The electrostatic separator used was the Model ES1010 produced by Equimag. The operation of the electrostatic separator is presented in Fig. 1. It was obtained a conductive fraction and a non-conductive one in the electrostatic separation. The magnetic and conductive samples were dissolved with aqua regia and after that they were chemically analysed by means of atom absorption spectrometry (AAS). The result is the average of three analysis.

2.3. Electrowinning

After obtaining fractions concentrated on metals through mechanical techniques (comminution, size separation, magnetic and electrostatic separation) it is necessary some other processes in order to obtain the metals separately. It was chosen

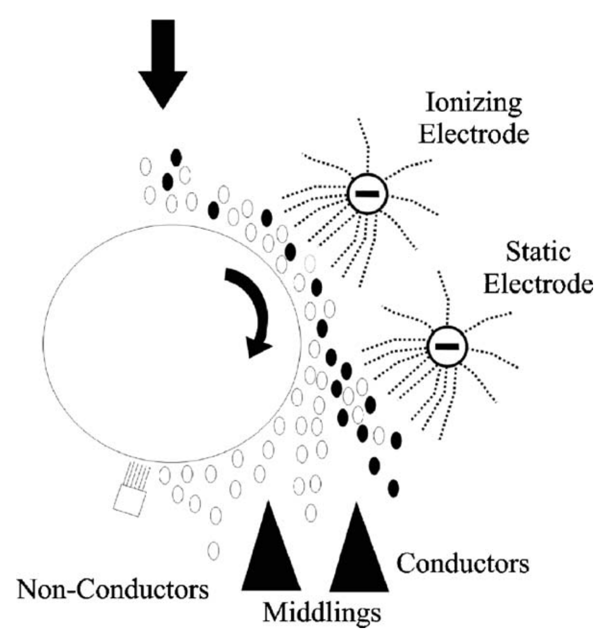

Fig. 1. Operation of an electrostatic separator.

Table 3
Chemical analysis of the samples after magnetic separation

	Copper (wt.%)	Iron (wt.%)	Nickel (wt.%)	Lead (wt.%)
EPCB				
F_1	11.40	43.28	13.02	1.10
F_2	16.22	42.02	17.76	1.88
F_3	17.04	43.81	14.96	4.39
EC				
F_1	10.62	37.62	12.56	1.46
F_2	13.26	45.80	17.76	1.34
F_3	11.40	54.70	16.80	1.52

electrochemical techniques because they are also used in the primary metallurgy of copper, as electrowinning and electrorefining. Copper is found in the nature in sulphides (90% of the ores) or oxides form. In both cases, electrowinning or electrorefining processes are used in the extractive metallurgy of copper.

The electrowinning tests were conducted by a potentiostat EG&G model 362. The electrowinning was made with two real solutions (sulfuric acid 20% and aqua regia 20%) of F_3 of EPCB and two of F_3 of EC. The electrowinning tests were conducted just with fraction F_3 because this fraction has a higher metal content. This happens because there is a higher difficulty in milling metals than polymers and ceramics (more concentrated in the smaller fractions).

Two different solutions were used to conduct the electrowinning:

- With aqua regia: usually employed in laboratories but with difficult industrial use.
- With sulfuric acid: usually employed in the industry, but with a slower dissolution.

The cell was set up using a copper plate (5 cm × 4 cm) as cathode and a platinum plate (5 cm × 2.5 cm) as anode. The distance between electrodes was 4 cm. The electrowinning experiments were conducted in room temperature (±20 °C) applying 40 mA cm^{-2} as current density, value obtained through cyclic voltammetry tests. Three different electrowinning tests duration were evaluated: 30, 60 and 120 min. After each test the electrochemical cell was rebuilt with new solution and new electrodes.

3. Results

The results are divided in three sessions: the first presents the results of mass balance after mechanical processing, the second presents the results of the chemical analysis in the fractions treated mechanically (magnetic and electrostatic separation) and the third part presents the results of the electrowinning stage.

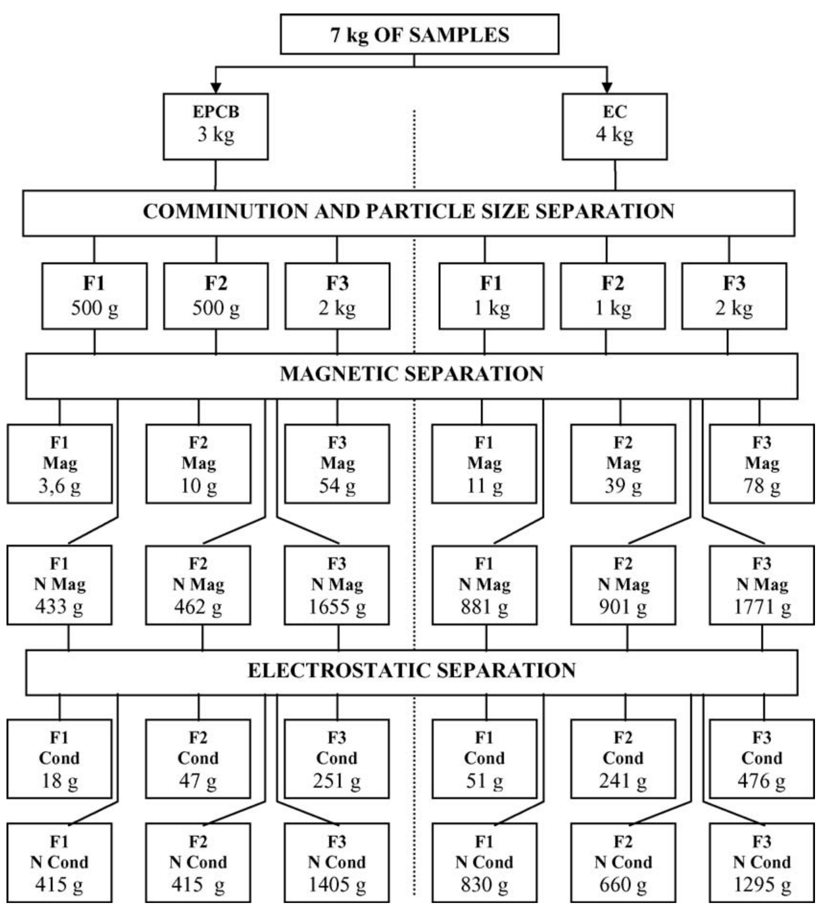

Fig. 2. Flowchart of the printed circuit board scraps recycling process. Mag: magnetic; N Mag: non-magnetic; Cond: conductive; N Cond: non-conductive; EPCB: entire printed circuit board; EC: electronic components; F_1: f < 0.25 mm; F_2: 0.25 < f < 0.50 mm; F_3: 0.50 < f < 1.0 mm.

Table 4
Chemical analysis of the fractions after electrostatic separation

	Copper (wt.%)	Iron (wt.%)	Nickel (wt.%)	Lead (wt.%)	Aluminum (wt.%)	Tin (wt.%)
EPCB						
F_1	36.66	0.78	0.53	5.50	0.84	31.86
F_2	53.21	0.12	0.27	9.67	0.76	20.58
F_3	53.04	0.48	0.43	6.42	0.59	20.22
EC						
F_1	34.42	1.04	0.66	10.96	0.34	29.40
F_2	43.76	0.18	0.18	7.54	0.60	26.86
F_3	59.54	0.26	0.50	6.34	0.66	12.72

3.1. Mass balance

Fig. 2 presents the results of the mass balance after mechanical processing stages (size, magnetic and electrostatic separation). Comparing this figure with Tables 1–4, where the chemical analysis of the fractions are shown, it is possible to verify the influence of the particle size and the magnetic and conductivity properties of materials in the efficiency of mechanical processing as an alternative to the electronic scrap recycling.

First of all, by this comparison it is possible to see that F_3 has the higher metal content. Fig. 2 shows that fraction F_3 has the higher material mass after the comminution step. Tables 1 and 2 show that this fraction has a great metal content. It is than possible to say that fraction F_3 has the higher copper quantity.

At Table 4, it is possible to see that there are no big differences on copper content between fractions F_1, F_2 and F_3. But again, comparing these contents with the mass of each one of the fractions, it is possible to see that fraction F_3 has always the highest copper quantity.

3.2. Magnetic and electrostatic separation

Table 3 presents the chemical analysis of the fraction retained by the magnetic separator. The analyzed elements were chosen in the following way: copper—for being the main element in the printed circuit boards scrap, iron and nickel—for being the magnetic elements of the scrap and lead—for being the main toxicant element in the scrap. All chemical analysis were made by means of atom absorption spectrometry (AAS).

Table 4 presents the results of the chemical analysis in the fractions retained by the electrostatic separator. The analyzed elements were chosen for being the main metals present in the printed circuit boards scrap.

All tables show the results for the main components. The remaining percentages are impurities (polymers and ceramics) or metals present in very small amounts.

3.3. Electrowinning

The results for the electrowinning tests are presented below. Firstly, the results of the chemical analysis of the remaining solution are presented for each electrowinning test, in order to verify how the copper concentration decayed and if the other elements remained constant. For the samples of EPCB dissolved with sulfuric acid the results are presented in Fig. 3 and for the solution with aqua regia in Fig. 4.

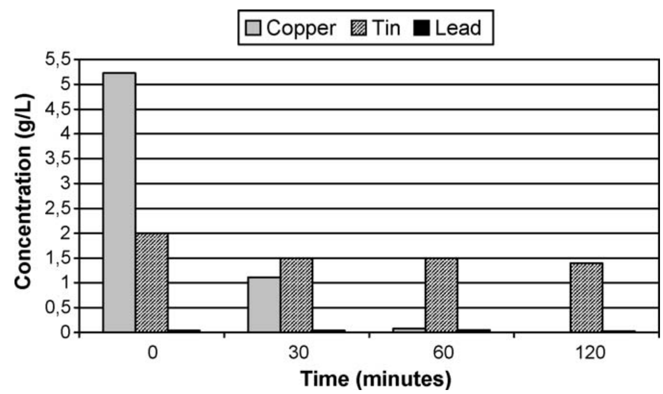

Fig. 3. Variation of copper, tin and lead concentration in relation to time in a real solution of EPCB dissolved with sulfuric acid in the electrowinning test.

For the samples of EC, the results of the electrowinning are presented in Fig. 5, dissolved with sulfuric acid and in Fig. 6, dissolved with aqua regia.

In a second moment, analysis of the deposit obtained on the cathode were made through X-ray Fluorescence, in order to verify the purity of the copper that is being recovered. The results for the sample of EPCB dissolved with sulfuric acid are presented in Table 5 and for the sample of EPCB dissolved with aqua regia in Table 6.

The results for the samples of EC dissolved with sulfuric acid are presented in Table 7 and for the samples dissolved with aqua regia in Table 8.

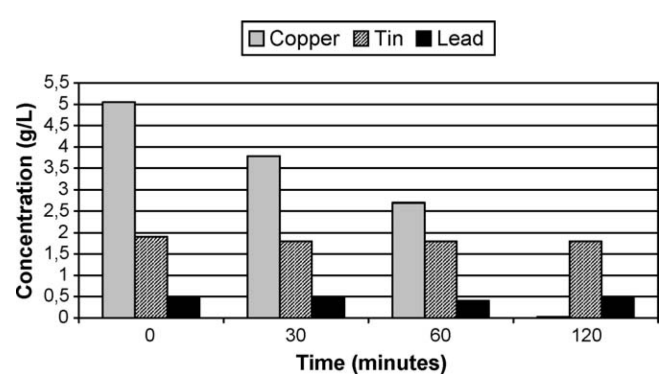

Fig. 4. Variation of copper, tin and lead concentration in relation to time in a real solution of EPCB dissolved with aqua regia in the electrowinning test.

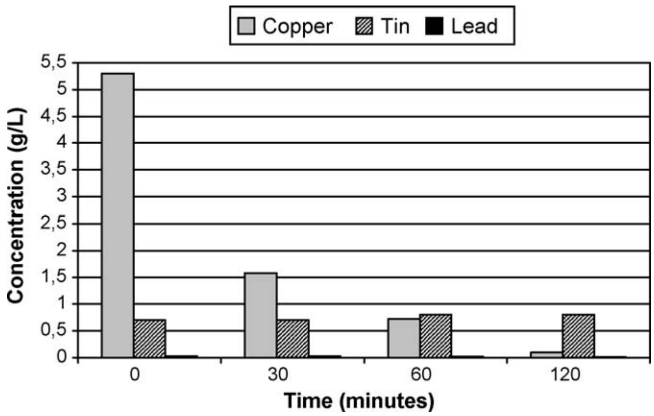

Fig. 5. Variation of copper, tin and lead concentration in relation to time in a real solution of EC dissolved with sulfuric acid in the electrowinning test.

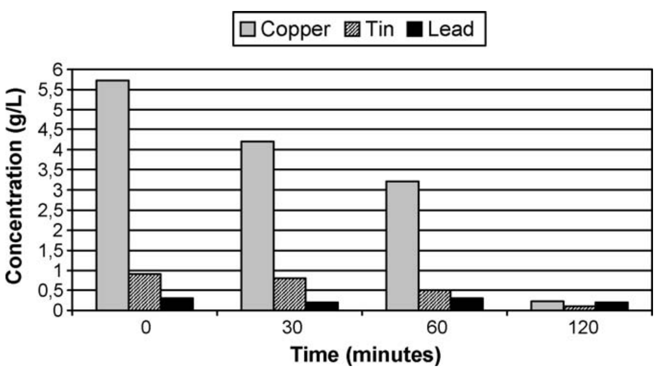

Fig. 6. Variation of copper, tin and lead concentration in relation to time in a real solution of EC dissolved with aqua regia in the electrowinning test.

Table 5
Chemical analysis by X-ray Fluorescence of the deposit obtained by electrowinning for the solution of EPCB dissolved with sulfuric acid, in 30, 60 and 120 min of deposition

	30 min	60 min	120 min
Copper (wt.%)	98.9	99.5	97.3
Tin (wt.%)	0.6	0.1	0.7
Lead (wt.%)	n.d.	0.1	0.4
Iron (wt.%)	0.04	0.04	0.06
Bromine (wt.%)	0.07	0.08	0.1
Zinc (wt.%)	0.3	n.d.	1.2
Nickel	0.02	n.d.	0.05

n.d.: not determinate.

Table 6
Chemical analysis by X-ray Fluorescence of the deposit obtained by electrowinning for the solution of EPCB dissolved with aqua regia in 30, 60 and 120 min of deposition

	30 min	60 min	120 min
Copper (wt.%)	97.6	99.3	95.9
Tin (wt.%)	1.4	0.4	2.2
Lead (wt.%)	0.8	0.1	0.9
Iron (wt.%)	0.07	0.04	0.07
Bromine (wt.%)	0.04	n.d.	0.04
Zinc (wt.%)	n.d.	n.d.	0.6
Nickel (wt.%)	n.d.	n.d.	0.03

n.d.: not determinate.

Table 7
Chemical analysis by X-ray Fluorescence of the deposit obtained by electrowinning for the solution of EC dissolved with sulfuric acid, in 30, 60 and 120 min of deposition

	30 min	60 min	120 min
Copper (wt.%)	98.6	98.6	98.7
Tin (wt.%)	0.2	0.4	0.1
Lead (wt.%)	0.7	n.d	n.d.
Iron (wt.%)	0.06	0.1	0.2
Bromine (wt.%)	n.d.	n.d.	n.d.
Zinc (wt.%)	0.3	0.7	0.8
Nickel (wt.%)	n.d.	0.1	0.1

n.d.: not determinate.

4. Discussion

The results of the magnetic and electrostatic separation were already expected, because iron is the main magnetic element present in printed circuit boards scrap and copper is the main conductive element present in this material. It can be seen in the result of the magnetic separation, that iron was the main element retained in the separator, proceeded by nickel. The presence of non-ferrous metals (Cu and Pb mainly) can be explained due to different particles shapes after comminution process, what can cause the drag of non-magnetic particles [22].

Although the amount of magnetic material present in printed circuit boards is small (Fig. 2), it is interesting to separate it previously, in order to obtain conductive fractions with higher copper content. The largest concentration of iron was obtained for fraction F_3 of EC: 57.4% of samples (Table 3).

The electrostatic separation also obtained great results: It can be seen that copper content reached more than 50% in mass in most of the conductive fractions, as well as an important content of Pb and Sn was also achieved in this fractions (Table 4). The majority presence of these three elements was expected, because these metals are conductors and are present in higher contents in printed circuit boards.

In the electrowinning tests it can be seen that the copper content in solution decayed quickly in all the cases. For the samples dissolved with sulfuric acid (Figs. 3 and 5) this decline happened in a time range smaller than for the samples dissolved with aqua regia (Figs. 4 and 6). This could be explained by the presence of the ion NO_3 in aqua regia solution that can act as an oxidizing agent, decreasing the efficiency of electrowinning

Table 8
Chemical analysis by X-ray Fluorescence of the deposit obtained by electrowinning for the solution of EC dissolved with aqua regia in 30, 60 and 120 min of deposition

	30 min	60 min	120 min
Copper (wt.%)	99.3	96.9	97.7
Tin (wt.%)	0.4	0.7	1.2
Lead (wt.%)	0.2	1.2	0.6
Iron (wt.%)	0.04	0.06	0.3
Bromine (wt.%)	n.d.	n.d.	0.05
Zinc (wt.%)	n.d.	0.4	n.d.
Nickel (wt.%)	0.02	n.d.	0.1

n.d.: not determinate.

[23]. In solution of EPCB with sulfuric acid (Fig. 3), in 60 min the copper content is already near zero, while in solution with aqua regia, in 60 min there is still about 50% of the original copper content.

This same behavior can be seen for the sample of EC. In solution with sulfuric acid (Fig. 5), in 60 min the copper content is already near zero, while in solution with aqua regia (Fig. 6), in 60 min, the copper content is still high.

Besides, it can also be seen that tin and lead contents in samples dissolved with sulfuric acid or aqua regia did not decrease significantly, confirming that only copper ions, that were in solution, are being deposited in the cathode.

In Tables 5–8 it can be seen that the purity of copper deposited in the cathode is very high, reaching 99.5% for the sample of EPCB, in test of 60 min, dissolved with sulfuric acid, confirming once again that manly ions copper are being deposited on the cathode.

It was also possible to calculate the current efficiency of the electrowinning tests. The average was 41% for the sulfuric acid solutions, while in the solutions with aqua regia, the efficiency was 30.5%. These relatively low efficiencies can happen due to low copper concentration in the solutions, on the average 5 g/L and also due to the high concentration of sulfuric acid or aqua regia (20%).

Other metals present in the printed circuit board scrap, mainly lead and tin, can be also recovered by electrowinning process. A future work will evaluate this alternative.

5. Conclusion

The use of magnetic and electrostatic separation was very efficient to obtain fractions concentrated on metals from printed circuit boards scrap. It can be seen that copper content reached more than 50% in mass in most of the conductive fractions and significant content of Pb and Sn.

With the electrowinning tests, it can be seen that it is possible to recover metals separately, especially copper, since the copper content in the electrowinned deposit reached more than 98% in most of the tests, allowing this metal to be used in secondary industries. As well as copper, other metallic elements (Sn and Pb, for example) could be recovered by this method.

The non-conductive fractions (that contain polymers and ceramics) should be evaluated in separate to be appropriately disposed of or to be send to recycling processes of polymers and ceramics.

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