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RECYCLING ELECTRONIC WASTE. STUDY FOR THE RECOVERY OF PRECIOUS METALS

BY

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Abstract. This paper presents the results obtained in recovering precious metals from electronic waste (printed circuit board - PCB) by using simple mechanical and chemical procedures. Collected PCBs were disassembled and the components were separated, using density and magnetic separation method. After the chemical recycling processes, the samples were examined by EDAX and SEM, the analysis showing the presence of silver in a mass percentage of 5.29%.

Keywords: gold; silver; printed circuit board; waste management.

1. Introduction

Electrical and electronic waste comes from the equipment that runs on electric currents or electromagnetic fields and the outfit for the generation,

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transfer and measurement of such currents and fields. This category includes refrigerators, televisions, appliances, computers, also mouses and keyboards, classic or mobile phones (Vats and Singh, 2015).

Among the most used electronic products, mobile phones and computers have the most spectacular technological development. With an estimate of over 4 billion phones worldwide (Geraldes, 2010; Ghosh *et al*., 2015) and the advancement of technology, the amount of waste produced from used mobile phones is expected to grow rapidly (Delfini *et al*., 2011; Robinson, 2009). Computers have evolved a lot in the early 20^{th} century, starting with the use of the first microchip. Modern computers have become inseparable from our daily life (Ceruzzi, 2003).

Besides the growth of the human life quality, all of these, have, as a negative effect, the increasing of electronic waste, because the general tendency of people is to purchase all that is new in terms of electronics, because, usually, the novelty is closely related to a better performance of the product (He *et al*. 2006; Ramesh *et al*., 2007). Now, the society must find economic and safe recovery ways for the materials that are incorporated into these products.

Typically, computers, laptops, mobile phones have printed circuit boards (PCB), used as mechanical and electrical support for the electronic components. A conductive circuit is generally made of copper, although sometimes other metals are used such as aluminum, nickel, chromium, etc. The PCB is the platform on which microelectronic components, such as semiconductor chips and capacitors, are mounted. The PCBs, along with epoxy resins and fiberglass, contain copper, nickel, iron, aluminum and a certain amount of precious metals, such as gold and silver. It may also contain hazardous materials such Gallium, Arsenium, Antimony, Beryllium (Goosey and Kellner, 2002; Park *et al*., 2015; Sohaili *et al*., 2012). These materials and metals used as electronics parts are attached to the board with a solder containing lead and tin. Many research papers have revealed that the amount of metals, ceramics and plastics in PCBs could reach 40%, 30% and 30%, respectively (He *et al*., 2006; Veit *et al*., 2006). According to the literature, the concentration of precious metals, such as gold and palladium in PCB waste are richer than in natural ores, which makes their recycling very important from both economic and environmental perspectives (Hageluken and Corti, 2010; Yuan *et al*., 2007; Zhou and Qiu, 2010; 2007; Zhang *et al*., 2012).

Due to their characteristics, including complex structure, high metal content and potential hazards to the environment, printed circuit boards are considered to be the most difficult type of waste submitted to recycling (Zeng *et al*., 2012). Therefore, the issue has attracted much attention from researchers and industry in recent years.

Normally, energy consumption for recovering precious metals from electronic waste is much lower than for the primary ore mining (Vats and Singh, 2015) and this justifies all the measures taken to recover them. Currently, only

12.5% of electronic waste is recycled. For example, for every 1 million cell phones that are recycled, 16000 kg of copper, 350 kg of silver, 34 kg gold, and 14 kg of palladium can be recovered (Budhraja, 2016).

2. Experimental

Fig. 1 shows a block diagram regarding the steps required for recycling electronic waste in order to recovery materials. Recovery method for PCBs content consists of three stages, namely: dismantling, mechanical recycling procedure and chemical recycling process (Hanafi *et al.*, 2012; Chatterjee, 2012; Kaya, 2018; Robinson, 2009).

The samples of electronic waste for the present study are obtained from one product brand DELL (laptop end of life).

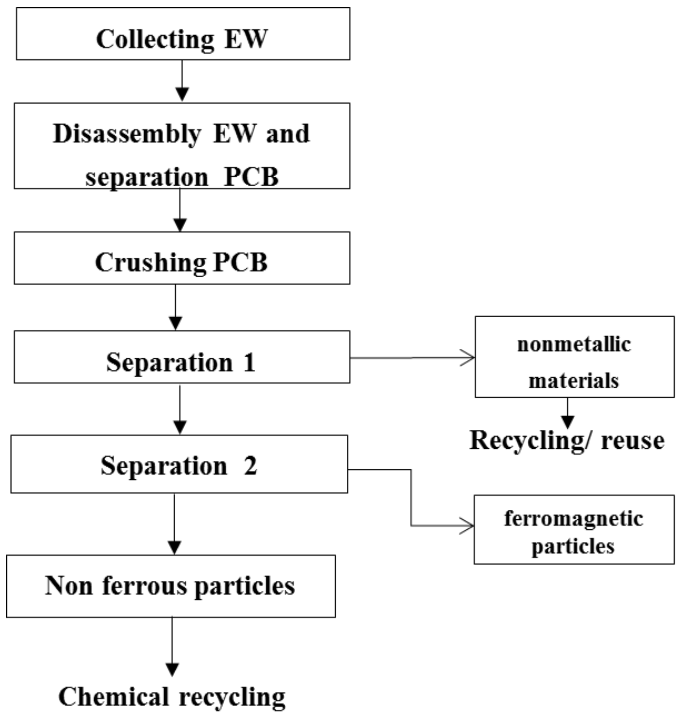


Fig. 1 − PCB recycling process.

Dismantling

In a first step, the IT equipment was disassembled manually, using screwdrivers, an angle grinder and the drilling machine. Components that results were manually sorted into categories of materials: glass, plastic, metal, etc. From these components the printed circuit boards (PCB) are extracted.

The crushing of printed circuit boards has a great importance, because the separation and the results obtained are closely related to the shredding and the size of cuts. PCBs contain copper foil, are reinforced with fiberglass, so the rigidity of these components is high. This feature makes them difficult to cut into small pieces. The analyzed sample was crumbled by cutting, crushing, using the tools in the mechanical workshop (guillotines, pliers, cutters, etc.). The obtained fragment size is between 1 and 4 mm (Fig. 2). The parts of the PCB that have not been properly shredded were removed because their presence would have made the separation process difficult.

Fig. 2 − PCB sample after coarse and fine grinding.

Mechanical recycling procedure

For most of the recycling processes, separation is necessary as a first step in the concentration of materials. The difference in physical properties (such as electrical conductivity, magnetism, or density) underlies separation steps. Currently, there are several methods of separation: electromagnetic, based on conductivity, based on density, etc.

In a first phase, the objective of this process is to separate the metal and non-metal pieces. To do this, the difference of density for the two types of materials has been used. The metal particles are heavier than the non-metal particles, so it is not difficult to separate them. Separation based on the difference of density was performed in a device similar to the one used by Mou (Mou *et al*., 2004). According to the different properties of the composite materials, non-metallic materials from wasted printed circuit board could be used to form new composite materials (Kanchanapiya *et al*., 2015).

For an advanced separation, a magnetic method has been applied. In this stage were separated the metals with magnetic properties from the metals with non - magnetic properties. Magnetic separation was performed manually using a magnet placed over the sample, in a Petri dish. After this final stage of separation, results a material that is supposed to contain precious metals, such as Ag, Au, Pd.

The dismantling and the mechanical treatment of waste printed circuit boards, in order to separate valuable metals components, will produce large amounts of glass fiber, resin powder (ie, non-metallic powders), which has become the problem of world's electronic waste disposal (Kanchanapiya *et al*., 2015; Youssef *et al*., 2012).

Chemical recycling process

Regarding the experimental procedure used to solubilize the sample containing precious metals, in order to analyze them, Fig. 3 shows a block diagram of the-chemical-main steps:

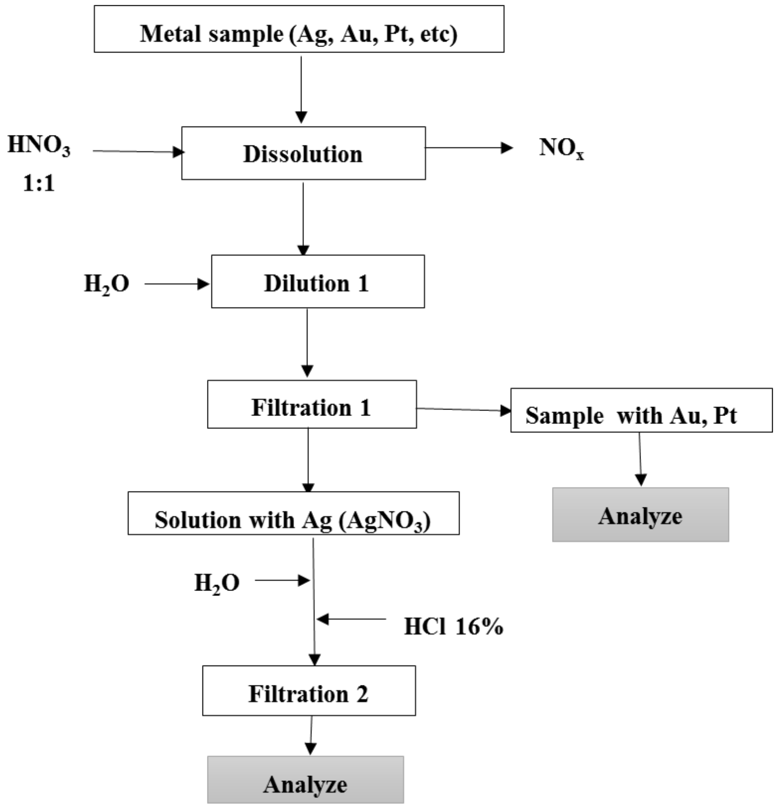


Fig. 3 − PCB chemical recycling process.

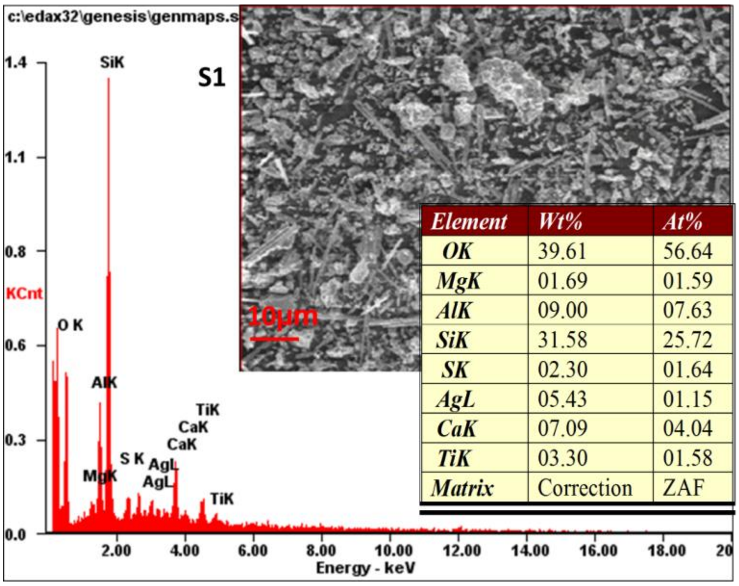
The chemical recycling method is accomplished by dissolving 50 g of sample, with a concentrated nitric acid (1:1, 52.8 mL) placed in a 500 mL Berzelius flask, under continuous stirring. After all the gaseous substances have been evaporated, the stirrer was turned off and the solution was kept still for 5 min, until there was no more vapors of NO_x.

After cooling, the solution was diluted with distilled water, at a ratio of 1: 3 and filtered to separate the solid material containing Au and Pt. The filtrate, containing the silver nitrate is quantitatively collected and diluted again with distilled water (1:3). For the precipitation of silver, 16% hydrochloric acid solution was added, and the mixture was left for 24 h at room temperature. Next, the suspension is filtered and the silver precipitate is collected. This stage is complete after washing the solid with hot water, collected it on filter paper and drying it at room temperature for 24 h.

Both samples, the one containing Ag and the solid obtained after the filtration 1 (see Fig. 2) are analysed in order to identify precious metals. If that show the presence of Au / Pt, experimental work will continue with a separate study for the recovery of these metals.

3. Results and Discussions

The precipitates were analyzed to identify the presence of noble metals, especially silver. The EDAX spectra and the electron microscopy images for sample 1, supposed to contain silver, are shown in Fig. 4. The EDAX measurements were performed with a Quanta 200 3D electron microscope, connected with EDS Ametek/EDAX equipment). The EDAX results show the presence of silver in the analyzed samples. The scanning electron microscopy images show the morphology of the obtained materials, indicating that they are polydispersed and nonhomogeneous.



Element	Wt%	At%
OK	39.61	56.64
MgK	01.69	01.59
AlK	09.00	07.63
SiK	31.58	25.72
SK	02.30	01.64
AgL	05.43	01.15
CaK	07.09	04.04
TiK	03.30	01.58
Matrix	Correction	ZAF

Fig. 4 − EDAX and SEM analysis for sample 1 assumed to contain silver.

Fig. 4 shows the presence of two types of materials some of them are long acicular - prismatic wires, and other amorphous agglomerations, sometimes grouped as spherical aggregates. The same way the organization is showed in Figs. 5 and 6, showing the prismatic aggregates (Fig. 5) and the other amorphous agglomerations (Fig. 6).

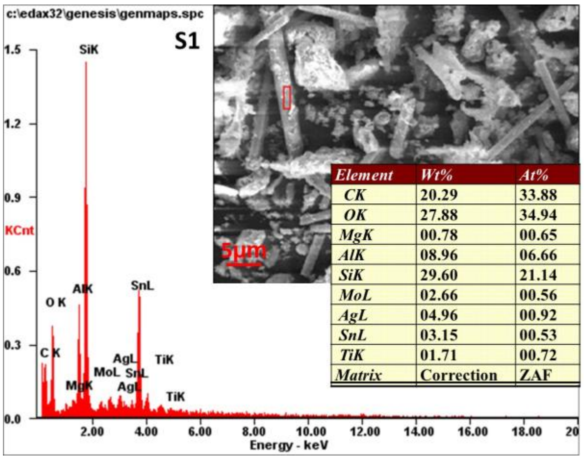


Fig. 5 − EDAX and SEM analysis for sample 1 assumed to contain silver (area 1).

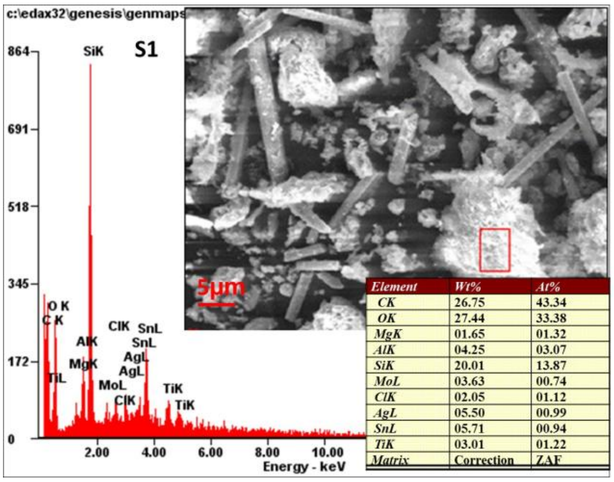


Fig. 6 − EDAX and SEM analysis for sample 1 assumed to contain silver (area 2).

For all samples analysed by SEM, the percentage composition was determined by dispersive energy X-ray spectroscopy, the results being also presented in Figs. 4-6. In order to minimize the error due to atomic number (Z), the absorption of X-rays in the specimen (A), and the fluorescence caused by other X-rays generated in the specimen (F), the ZAF correction was applied. The amount of silver found by EDAX was 5.43Wt% (Fig. 3), 4.96 Wt% (Fig. 5) and 5.50 Wt% (Fig. 5), with an average of 5.29 Wt% (1.02 At%).

The EDAX and SEM results for the solid obtained after filtration 1 are shown in Figs. 7-8. SEM images show the same non-homogeneity as the previous precipitate analysis, with long wires, about 1 µm diameter and 10-20 µm length. The average diameter of the microspheres was 3-4 µm. The EDAX measurement reveals the Ag presence only in some regions (wires), but in much smaller quantities (1.94 Wt%).

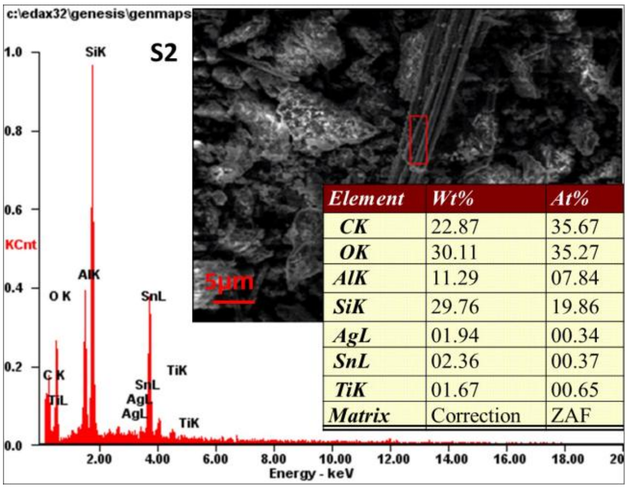


Fig. 7 − EDAX and SEM analysis for sample 2 - solid obtained after filtration (area 1).

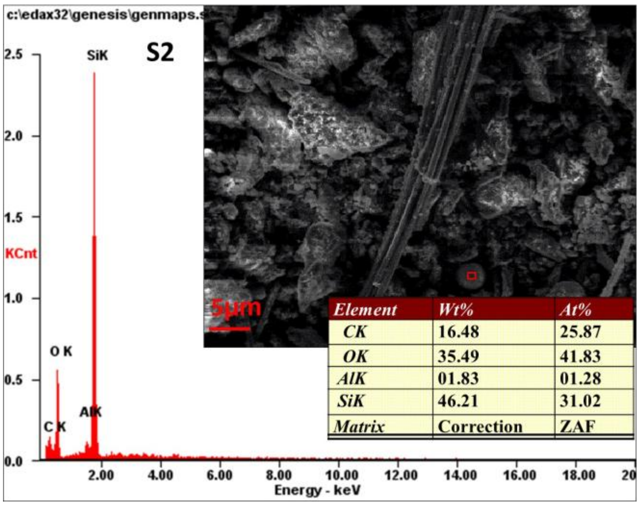


Fig. 8 − EDAX and SEM analysis for sample 2 - solid obtained after filtration (area 2).

The advanced development of the electrical and electronic manufacturing industries led to the generation of large quantities of electronic waste. The profitability of processing electronic waste consists in the recovery of silver, gold and other noble metals which, although present in a concentration of 0.03%, represents approx. 80% of the profit resulting from metal recovery (Budhraja, 2016).

4. Conclusions

E-waste represents a challenging recycling problem for several reasons. First, the material complexity of the product– a combination of precious metals (Au, Ag) with hazardous ones, such as Pb and Hg, and low value plastics – makes its diversion from landfills an important consideration and one that will continue to drive the development of environmentally sound recycling processes. Second, it is a widely distributed and diverse range of consumer products with highly variable rates of obsolescence and failure. This means that it is hard to predict whether particular collection program types will be cost effective in a given region and how much volume will be generated. The next few years will see considerable growth in the volume of electronic products being retired and an entire reverse supply chain will have to be developed around them. This will lead to challenges and opportunities for diverse disciplines and companies.

Since electronic waste contains different and uneven quantities of precious metals that can be extracted by different techniques, we consider that the percentage of silver obtained by this recovery method is satisfactory.

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RECICLAREA DEŞEURILOR
ELECTRONICE. STUDIU PENTRU RECUPERAREA METALELOR
PREȚIOASE

(Rezumat)

Deșeurile electrice și electronice provin de la echipamentele care funcționează pe bază de curenți electrici sau câmpuri electromagnetice și de la echipamentele pentru generarea, transferul și măsurarea unor astfel de curenți și câmpuri. Această categorie include frigidere, televizoare, electrocasnice, computere, telefoane clasice sau mobile. Această lucrare prezintă rezultatele obținute în procesul de recuperare a metalelor prețioase din deșeurile electronice (plăci de circuit imprimate - PCB), prin utilizarea unor proceduri mecanice și chimice simple. PCB-urile colectate au fost dezasamblate și componentele au fost separate, folosind metode de separare pe baza densității și a proprietăților magnetice. După procesele de recuperare a substanțelor chimice, probele au fost examinate prin EDAX și SEM, analizele indicând prezența argintului într-un procent de masă de 5,29%.