# POLITECNICO DI TORINO

Department of Environment, Land and Infrastructure Engineering

Master of Science in Petroleum and Mining Engineering

Master Thesis

**STUDY OF METAL RECOVERY FROM PRINTED CIRCUIT BOARDS BY PHYSICAL-MECHANICAL TREATMENT PROCESSES**

**Supervisor**
Paola Marini

**Candidate**
Camila Mori de Oliveira

**Co-supervisor**
Rossana Bellopede

**Torino**
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# ABSTRACT

With the technology advancement of electro-electronic devices, there was an increase in consumption and in the replacement of the equipment in a shorter interval of time. Consequently, the production of waste electrical and electronic equipment (WEEE) has also been increased, becoming not only a sustainability issue but also an environmental problem.

In almost all electronic devices it can be found a printed circuit board (PCB), making it an important component of WEEE. It is usually composed of polymers, ceramic material, and metals, in which the metallic fraction of the PCB can vary between 19% and 40% of its weight. It contains heavy metals that can cause environmental impacts due to improper disposal. But on the other hand, there are elements with added value, such as copper, gold, silver, iron, aluminium and critical raw materials, such tantalum that can be recovered, making PCB scrap an economically attractive for recycling. It conserves natural resources, since it prevents new minerals from being extracted and it is a great contribution to the circular economy, removing the waste from its disposal and reinserts in the production cycle.

Thus, the main objective of this work is to characterize the PCB and study the physical-mechanical processing (through grinding, granulometric, magnetic, electrostatic and gravity separations) in order to concentrate metals, especially copper, identifying the main elements obtained through the processes applied.

For this, initially, studies were carried out on the characteristic composition of printed circuit boards through the electron microscope. Then, the PCB was processed in a cutting mill in order to release the materials, and after the granulometric separation was performed. For each size classification resulted, a magnetic separation was performed.

Subsequently, on the non-magnetic fraction, electrostatic separation was performed, in which the material was separated into conductive, mix and non-conductive fraction, and also it was performed a gravity separation, in which the material was separated into concentrated, middling and tailing. After all the separation processes, the different products obtained were observed with the macroscope to qualitatively assess the metallic content.

In gravity separation, the metal recovery was 64% for the particle size -0.6 + 0.3 mm and 67% for the particle size -1.18 + 0.6mm. In the recovery of metals by electrostatic separation, the efficiencies obtained were 55% for the upper particle size (+1.18mm) and 81% for the lower particle size (-0.3mm). Thus, by the end of this work, it is possible to conclude that physical-mechanical techniques have high potential for the production of a concentrate with high added value.

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# SUMMARY

# CHAPTER 1

## 1. INTRODUCTION

Technology is increasingly present in people's lives. Mobiles, computers and tablets have become indispensable in everyday life and this has happened very quickly and intensely. Companies create more and more innovated products, with better resources than the previous ones and many of them are not made to last. This turnover of electronic products market causes a rapid disposal, making waste all this castoff material (Jianzhi et al. 2004).

An immeasurable amount of these residues has been discharged into the environment, without the necessary care that these materials require. This irregular disposal raises awareness to the environmental issue, since the toxicity of some elements can cause not only risk to the human healthy, but also problems on the quality of several ecosystems. (Jianzhi et al. 2004)

According to The Global E-waste Monitor (2020), in 2019, the global production of electronic waste was 53.6 Mt, an average of 7.3 kg per person. The worldwide e-waste grew by 9.2 Mt since 2014 and is projected to grow to 74.7 Mt by 2030.

Although this growing amount is a challenge for any management system, WEEE also offers a secondary source of raw materials that are readily available for recycling. Recycling processes can recover various components, such as copper and precious metals. However, due to the lack of facilities and high operating costs, and the lack of demanding regulations and legislation, countries tend not to recycle WEEE. Instead, they are landfilled in an improper way (Kumar, 2020).

The properly disposal of electronic waste after its useful life combined with the recovery of materials, generates a great contribution to the circular economy. It closes the loop, removing the waste from its disposal sites, taking into the processing again and reincorporating into the production cycle (Kumar, 2020).

Printed circuit boards (PCBs) are inserted in electronic waste, which are essential elements of most electronic equipment, found in computers, cell phones, TVs, etc. In these boards, typically composed by resin and fiberglass, the electronic components are welded to copper tracks, by a solder. PCBs may vary with the type of equipment, but in general they have the same components (Szałatkiewicz, 2014).

This heterogeneous composition of the PCB makes recycling processes difficult. But in compensation, the presence of common and precious metals makes it an interesting raw material. Therefore, it is essential that studies continue to be carried out in order to make the recycling of metals present in PCBs viable, in a progressive way operationally and economically (Veit, 2002).

The technologies used for recycling PCBs involve processes that can be physical-mechanical, metallurgical. Such processes still lack studies aiming at optimization to improve performance (Veit, 2002). Based on this, the objective of this work is to contribute to finding better ways of recycling electronic waste, quantifying the metals present in printed circuit boards, thus having a lower cost and reducing the environmental impacts.

## 1.1. Aim of the work

The central theme of this work is electric and electronic equipment waste, specifically PCBs, and the main factors involved since its composition, environmental and health problems due to its irregular disposal and the processes used for its recycling.

Thus, the general objective is to establish a scientific understanding of the PCBs as electronic waste and evaluate the different process for recycling, with specific focus on the recovery of metals.

To achieve this objective, the following specific objectives must be achieved:

- ✓ Characterize the composition of the components present on the printed circuit boards;
- ✓ Define the types of processes to be used to recovery;
- ✓ Define the operational conditions and conduct physical-mechanical treatments;
- ✓ Analyse and discuss of the results.

## 1.2. Structure

The present work is structured in seven chapters, organized as follows:

- In Chapter 1, the introduction and motivation of this work is presented;
- Chapter 2 describes the electric and electronic waste;
- In Chapter 3, there is a description of the printed circuit board and its components;
- Chapter 4 presents the necessary theory about the recycling processes;
- Chapter 5 describes the material and the methods used to perform this work.
- In Chapter 6, the results are shown;
- Finally, in Chapter 7, the conclusions about the results obtained and recommendations for future work are presented.

# CHAPTER 2

## 2. ELECTRONIC WASTE

Electrical and Electronic Equipment (EEE) per definition by the WEEE Directive 2012/19/EU, means "equipment which is dependent on electric currents or electromagnetic fields in order to work properly and equipment for the generation, transfer and measurement of such currents and fields and designed for use with a voltage rating not exceeding 1 000 volts for alternating current and 1 500 volts for direct current".

Directive 2008/98/EC of the European Parliament and of the Council on waste define waste as any substance or object which the holder discards or intends or is required to discard. The Article 3(1) of this directive defines the Waste Electrical and Electronic Equipment or WEEE as electrical or electronic equipment, which is waste within the meaning of, including all components, sub-assemblies and consumables which are part of the product at the time of discarding. WEEE is also called E-waste.


Figure 1: Informal processing of electronic waste; discarded central processing units (CPU) for recycling (a), electronic waste dumb in Ghana (b), substandard processing in Shanghai, China (c) discarded electronic waste collection in Guiyu, China (d) (Işıldar, 2016)

The directive also classifies WEEE into four categories (Category 1, Category 2,Category 3, and Category 4):

- Category 1: large household appliances (fridges, washing machines, air conditioners, etc.);
- Category 2: small household appliances (vacuum cleaners, toasters, fryers, etc.);
- Category 3: IT equipment (PCs, tablets, notebooks, smartphones, etc.);
- Category 4: consumer equipment (e.g., TVs, stereo systems, digital cameras, etc.).

The E-waste consists mainly of household appliances, computers, televisions, and other goods that are damaged or broken. Table 1 shows the main typical WEEE and the respective components (He, Y. et Xu, Z.,2014). Due to its hazardous nature, management of WEEE, is of environmental and social concern. Informal recycling of WEEE brings disastrous effects on the population and the environment, as shown in Figure 1 (Işıldar, 2016).

Table 1: Main components of typical WEEE. source (He, Y. et Xu, Z.,2014).

| WEEE | Main components |
|---|---|
| Refrigerator | Tubes, liners, condenser, wires, refrigerant |
| Air conditioner | Heat exchanger, motor, compressor, copper pipe, PCBs, wires, refrigerant |
| Washer | Tub, drain hose, motor, wires, salt waste |
| Television | Deflection yoke, demagnetized coil, speaker, PCBs, wires, CRT, LCD |
| Computer | Speaker, battery, storage medium, PCBs, wires, CRT, LCD |
| Printer/duplicator | Roller, toner, PCBs, wires, toner cartridge |

*CRT: cathode ray tube*
*LCD: liquid crystal display*
*PCB: printed circuit board*

In order for the correct management of WEEE, the directive establishes, the entities involved in the EEE life cycle and in the WEEE management process, such producers, distributors, municipalities, and users, must cooperate with each other, respecting their responsibilities (Işıldar, 2016).

## 2.1. E-Waste generation

Waste electrical and electronic equipment is currently considered one with the fastest growing waste in the world, with an estimated rate of approximately 4% per year (The Global E-waste Monitor, 2020). The decreasing in the lifespan of the equipment plays a role in the increasing of WEEE generation. For example, between the year 2000 to 2010, the lifespan of large EEE decreased from an average of 8 years to 2 years (Guan et al., 2012).

The lifespan has been decreased due to several reasons, among them: the constant launch of more sophisticated devices to the market and at lower prices and the high cost of repairing the equipment compared to the purchase price of new equipment (Guan et al., 2012).

These data presented above reflect the world panorama in relation to the generation of WEEE, and they show that the disposal of these materials increases every year. All of this justifies the significant importance that the management of WEEE has been reported, especially regarding the search for new technologies and improvement of recycling processes for these materials (The Global E-waste Monitor, 2020).

According to Figure 2, the electronics industry generated 53.6 million tons of WEEE in 2019, which represents 5.9 kg of WEEE per inhabitant. The estimate is that by the end of 2030 the mark of 74.7 million tons will be reached worldwide. According to that same source, a total of 82.6% of e-waste generated is uncertain, probably mixed with other waste streams and its where abouts and the environmental impact varies across the different regions.

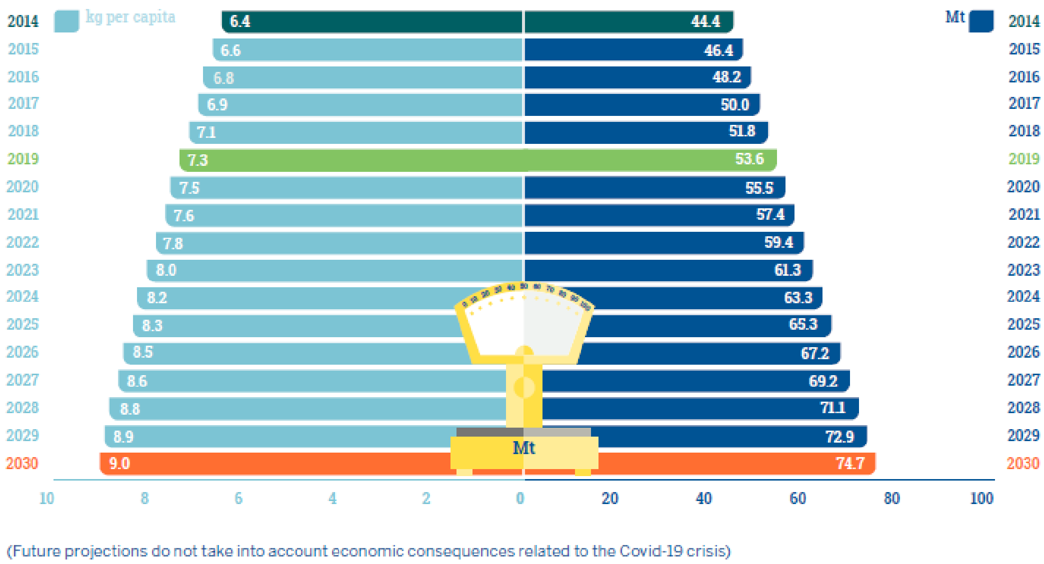



Figure 2: Global e-waste generated by year (The Global E-waste Monitor, 2020).

The Global E-Waste Monitor (2020) also indicates that among all continents of the world, the majority of electrical and electronic waste is generated in Asia, the continent contributed with almost 25 million of tons of WEEE in 2019, representing 46% of the total generated. Followed by Americas with 24% of WEEE generation, and Europe with 22%, as it can be seen in Table 2.

Table 2: Quantity of e-waste generated by continent (Adapted from The Global E-waste Monitor, 2020).

| Continent | Waste Generated [Mt] | kg per capita | % Collected and Properly Recycled |
|---|---|---|---|
| Africa | 2.9 | 2.5 | 0.9% |
| Americas | 13.1 | 13.3 | 9.4% |
| Asia | 24.9 | 5.6 | 11.7% |
| Europe | 12 | 16.2 | 42.5% |
| Oceania | 0.7 | 16.1 | 8.8% |

The properly management of electronic waste is essential to guarantee access for future generations to electronic products, preserve natural resources and human health, protect working conditions to reduce the environmental impacts associated with production, use and disposal of electronic equipment.

## 2.2. E-waste composition

Plenty of research have been carried out in the last years to characterize the electronic waste generated. WEEE encompass up to 69 elements from the periodic table, becoming a diverse and complex type of waste having both hazardous and non-hazardous compounds (The Global E-waste Monitor, 2020).

E-waste is made of wide variety of substances in thousands, as it can be seen in the Figure 3, that all metals represents 60.2%, Plastics 15.2%, Metal-plastic mixture5%, Printed Circuit Boards 1.7%, pollutants 2.7% etc. The author also affirms that iron and steel are almost 50%; copper, aluminium and other metals around 13% ;toxic metals constitute about 1% of and precious metals such as gold 0.1%, silver 0.2% and palladium 0.005%.

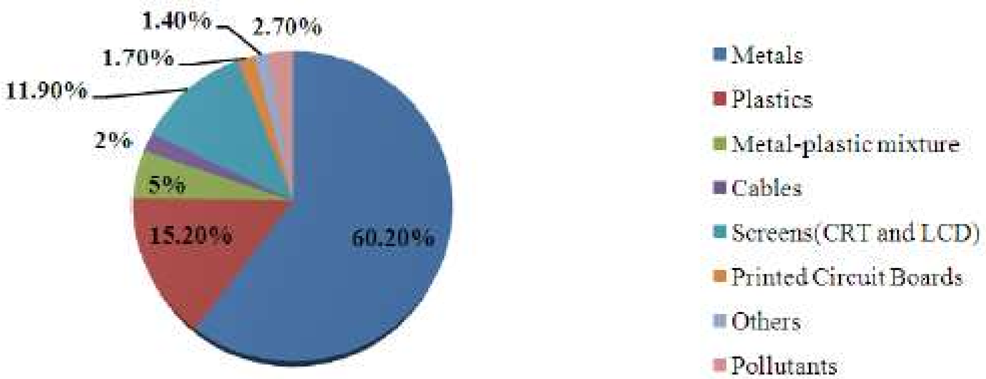



Figure 3: Average composition of materials found in E-waste (Empa, 2005 cited in Vats, 2014)

The presence of precious metals, such gold, silver, makes the WEEE extremely attractive to recovery it. Some elements have concentrations significantly higher than those usually found in corresponding mineral ores (Vats, 2014)

Critical raw materials play an important economic role and a high risk associated with their supply and economic usage. Studies by the Oeko Institut, investigating for four products of e-waste (flat screen, smartphone, notebooks and LED lights) have identified that following Critical Raw Materials:

• Cobalt,

• Gallium,

• Germanium,

• Indium,

• Platinum group metals,

• Rare earths,

• Tantalum

Obviously, the amount these materials can vary widely and according to their type. The recovery of them through recycling of obsolete electronics devices could provide significant prospects in the future (Santucci, 2018).

The presence of heavy metals in e-waste not only impede the biodegradation process but it can damage the environment and the human health also. People engaged in the-waste treatment process are directly exposed to these metals while recycling, recovery processes and they are most affected (Işıldar, 2016).

Table 3 lists some of the most important elements from the toxicologic perspective with their main occurrence in EEE components, some forms of exposure and possible harm to human health. Thus, if the proper disposal is not done, there can be drastic consequences for human healthy and the environment (Kaya, 2016).

Table 3: Hazardous substances in WEEE/EEE (Kaya, 2016)

| Substances | Occurrence in WEEE | Possible adverse effects |
|---|---|---|
| Lead (Pb) | CRT screens, batteries, PCBs | Vomiting, diarrhea, convulsions, coma or even death, appetite loss, abdominal pain, constipation, fatigue, sleeplessness, irritability and headache |
| Mercury (Hg) | Fluorescent lambs, some alkaline batteries, switches | Brain and liver damage |
| Chromium VI ($Cr^{6+}$) | Data tapes, floppy-discs | Irritating to eyes, skin and mucous membranes, DNA |
| Barium (Ba) | Getters in CRT | Brain swelling, muscle weakness, damage to the heart, liver and spleen |
| Cadmium (Cd) | NiCd batteries, fluorescent layer (CRT screens), printer inks and toners | Symptoms of poisoning (weakness, fever, headache, chills, sweating and muscle pain), lung cancer and kidney damage |
| Arsenic (As) | Gallium arsenide in light emitting diodes (LED) | Skin diseases, decrease nerve conduction velocity, lung cancer |
| Americium (Am) | Smoke detectors | Radioactive element |
| Antimony (Sb) | Flame retardants in plastics | Carcinogenic potential |
| Chlorofluoro carbon (CFC) | Cooling units, insulation foams | Deleterious effect on the ozone layer, increased incidence of skin cancer and/or genetic damages |
| Polychlorinated biphenyls (PCB) | Condensers, transformers | Cancer, effects on the immune systems, reproductive system, nervous system, endocrine system and other health effects |
| PBDEs, PBBs | Flame retardants in plastics | Hormonal effects, under thermal treatment possible formation of dioxins and furans |

The risks to human health, according to Yu Welford & Hills (2006), include difficulty to breathing, respiratory irritation, cough, choking, pneumonitis, tremors, neurological problems, seizures, comas and even death.

## 2.3. E-waste as secondary source of raw material

As already mention, EEE has a complex and heterogeny composition. It can contain not only organic components, but also significant concentrations of precious metals (gold, silver, copper), critical raw materials (cobalt, palladium, indium, germanium, tantalum) and noncritical (aluminium and iron). These metals may be available again at the end-of life of the devices. An effective recycling of these materials is essential to keep them available for the manufacturing of new products. In this way the primary resources of metals and energy can be saved for the next generations. For example, it can be found a hundred times more gold in a tonne of smartphones than in a tonne of gold ore (The Global E-waste Monitor, 2020).

In this context, the perspective in waste management has shifted in recently from landfill disposal to the recovery of material from secondary resources. The aim is to highlight the economic feasibility and the environmental damage which can be reduced in a full recycling scenario, this concept is also called as Circular Economy (Işıldar, 2016)

Ellen MacArthur Foundation says that "the circular economy model aims to design out waste and pollution, keep products and materials in use, and regenerate natural systems–therefore ‘gradually decoupling economic activity from the consumption of finite resources". In other words, the waste discarded material is used as a secondary raw materials, being recycled and reintroduced in the manufacturing process, closing the loop.

In 2019, the global e-waste recycling rate of 17.4% recovered a raw material value of $10 billion USD, and 4 Mt of raw materials could be made available for recycling. Iron, copper, and gold that mostly contribute to this value has helped save up to 15 Mt of CO2, comparing emissions resulting from their use as virgin raw materials (The Global E-waste Monitor, 2020).

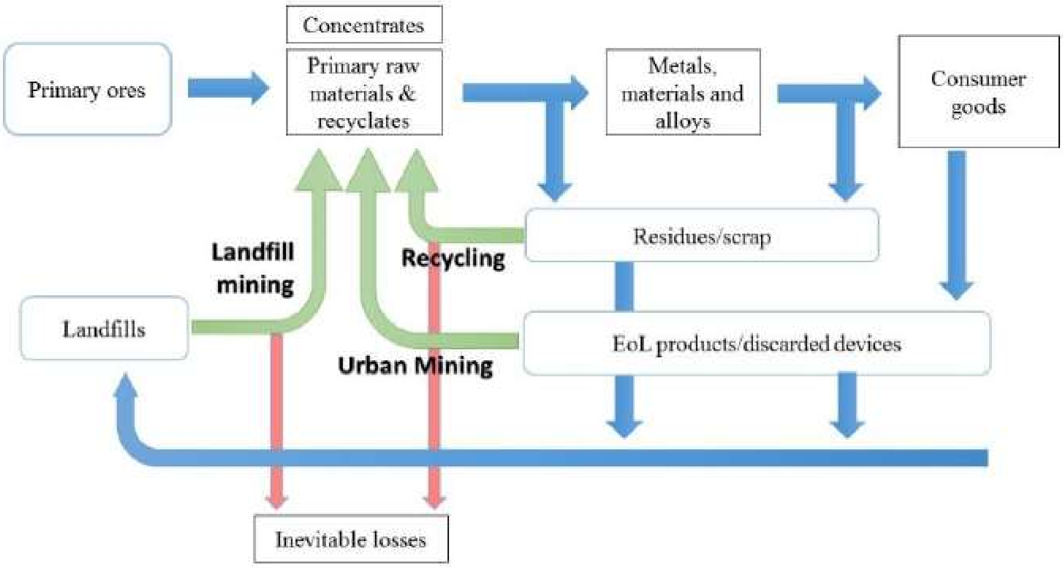



Figure 4: Closing material loops in a circular economy (Işıldar, 2016)

For having an idea of the possible income that can be achieved from different WEEEs: CRT monitors value 25€ /product unit, CRT TVs 18 €/product unit, cell phones 25 €/kg and smartphones value of 19 €/kg  (Cucchiella et al., 2015, as cited in Santucci, 2018)

The implementation of waste management and regulations for recycling can reduce the volume of material to be disposed of in landfills and create a source of secondary raw material for the industrial sector (Işıldar, 2016)

## 2.4. E-waste market

The electrical and electronic waste market for recycling is expanding and showing enormous appreciation, either for the ecological perspective or for the financial point of view side and, the moment is ideal to invest in this market and make money from recycling electronic waste. The companies in this sector aim to give this waste a correct destination, extract metals and minerals and reuse it. In China, for example, one recycling facility already can recovery, in a year, more cobalt than the Chinese mines (EMG, 2019).

Regarding the smartphones market, 1.46 billion were sold in 2017. Each smartphone unit contains electrical components with an estimated price up to $100.49, which represents a lot of value come into the market each year. If just their raw materials are recycled, they could be value around $11.5 billion (EMG, 2019).

E-waste recycling can also generate decent jobs and produce income. In a year, the global waste market sector is estimated to be US$410 billion. A circular-economy model for EEE could reduce the costs for consumers by 7% by 2030 and 14% by 2040 (The Global E-waste Monitor, 2020).

The majority of the e-waste generated is not properly collected and not managed in an environmental sound manner, and in most of the countries, e-waste is treated as the general waste. Moreover, the high cost of recycling e-devices results into generation of high amount of e-waste. Thus, to overcome these challenges, it is essential to keep high attention on e-waste management in global scale.

## 2.5. Regulations

The increase in the amount of e- waste generation has drawn the attention of government agencies and producers. European directives were created with the purpose of solving the problems associated with improper management of WEEE. Created in 2003, the WEEE directive (Waste Electrical and Electronic Equipment) 2002/96/CE defines targets for the collection, treatment, and recycling of electronic products, introducing the concept of “take-back system”. It confers the responsibility of WEEE collection on manufacturers. As mention in the beginning of this chapter, the Directive No.2012/19/EU, which covers any types of EEE, promoting of recycling, recovery, and reuse of WEEE. The RoHS directive (Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment) No. 2002/95/EC, countries member of the European Community must ensure that the electronic equipment does not contain certain substances above the maximum concentration determined in its Annex II. The substances considered in this directive are mercury, lead, cadmium, hexavalent chromium, and two flame retardants (polybrominated biphenyls (PBB), and polybrominated diphenyl ether). The restriction of the use of these substances was suggested to reduce their negative impact on the environment and on the worker's health at recycling facility (Işıldar, 2016). In 2015, the first EU action plan for the Circular Economy is published. This action plan aims to promote the transition to a circular economy, increasing the recycling of the materials. In the end of 2019 EU presented the European Green Deal, a “new growth strategy that aims to transform the EU into a fair and prosperous society, with a modern, resource-efficient and competitive economy” (European Commission)

In the United States (US), there is no national legislation on the management of WEEE but about half of the federal states (25 states) of the US regulate have legislated some form of regulation of it. The laws are varied and cover around 80% of the USA population. In South America, only Brazil and Chile are starting to implement of a formal regulation for e-waste. Brazilian law established a Reverse Logistics System for WEEE, defined as agreements between the government and producers, importers, wholesalers and retailers, seeking to implement shared product lifecycle responsibility (The Global E-waste Monitor, 2020).

On the Asian continent, Japan was one of the pioneers to implement a regulation on e-waste that the manufacturers have the responsibility for the collection and treatment of their products, by the Home Appliance Recycling Law. China's national legislation stablished fourteen types of e-waste (televisions, refrigerators, washing machines, air conditioners, personal computers, range hoods, electric water-heaters, gas water heaters, fax machines, mobile phones, single-machine telephones, printers, copiers, monitors) and regulates their treatment (The Global E-waste Monitor, 2020; Işıldar, 2016).

In Africa, e-waste management legislations basically do not exist. Just few countries, such as South Africa, Morocco, Egypt, Namibia, and Rwanda, have some facilities in place for e-waste recycling in a presence of a large informal sector (The Global E-waste Monitor, 2020).

# CHAPTER 3

## 3. PCB CHARACTERIZATION

Printed circuit boards (PCB) appear as one of the most common materials in this type of waste, present in computers, household appliances, among others. These are particularly rich in copper and precious metals, as well as in toxic substances such as chlorinated and brominated compounds. However, its heterogeneous composition makes its treatment difficult (Vermesan et al. 2019).

The reduction of adjacent environmental damage and the possible financial return have boosted the growth of the PCB recycling market, with benefits ranging from saving raw materials, water and energy, to reducing pollution, waste and of areas degraded by the extraction of these ores (Tanısalı et al. 2020).

Being constituted by a one or more sheet layers of copper between sheet layers of a non-conductive substrate in which conductive tracks are printed or deposited. While the board behaves as a dielectric, the tracks have the function of electrically connecting the various components of a circuit. The components, depending on their function, can be made up of different materials (Szałatkiewicz, 2014).

Printed circuit boards can also be classified according to the number of conductive layers they have. They can be single-sided boards, in which only one side of the board is coated with copper; double-sided in which both sides are covered with copper, or multilayer, in which there are 4 to 16 layers of copper between the layers of fiberglass (Jianzhi et al.,2004; Moraes, 2011).

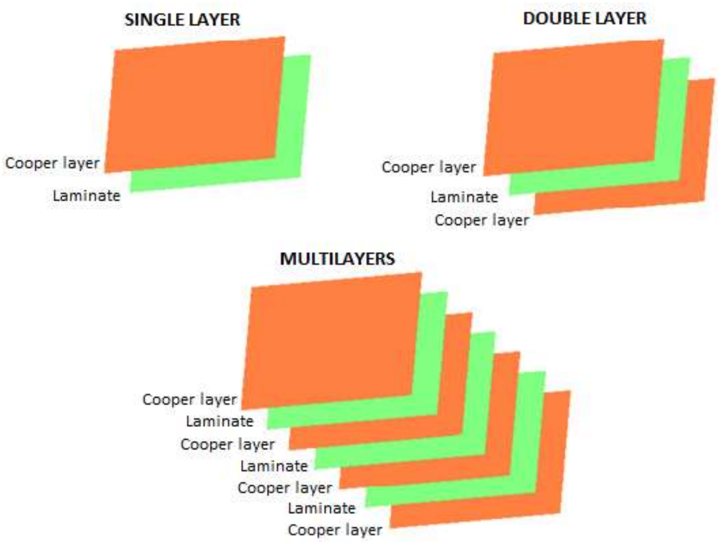



Figure 5: PCB classification scheme (Moraes, 2011)

The first circuit boards produced, used only a copper foil to interconnect all the electronic components of a circuit. As the complexity of the electronic circuits increased, it was necessary to increase it to two layers of copper, one on each side of the substrate (or dielectric). The advent of integrated circuits with a large scale of integration, made it necessary to use multi-layer plates (Kumar, 2020).

The printed circuit board (PCB) already assembled (with the electronic components) has a very heterogeneous composition. The material composition fractions can reach 30% for organic materials, 30% for ceramic and 40% for metallic material, which make this complex and a challenge to the treatment processes and techniques (Vermesan et al. 2019; Ogunniyi et al., 2009).

Figure 6 shows the chemical components that a printed circuit board may contain (considering its electronic components).

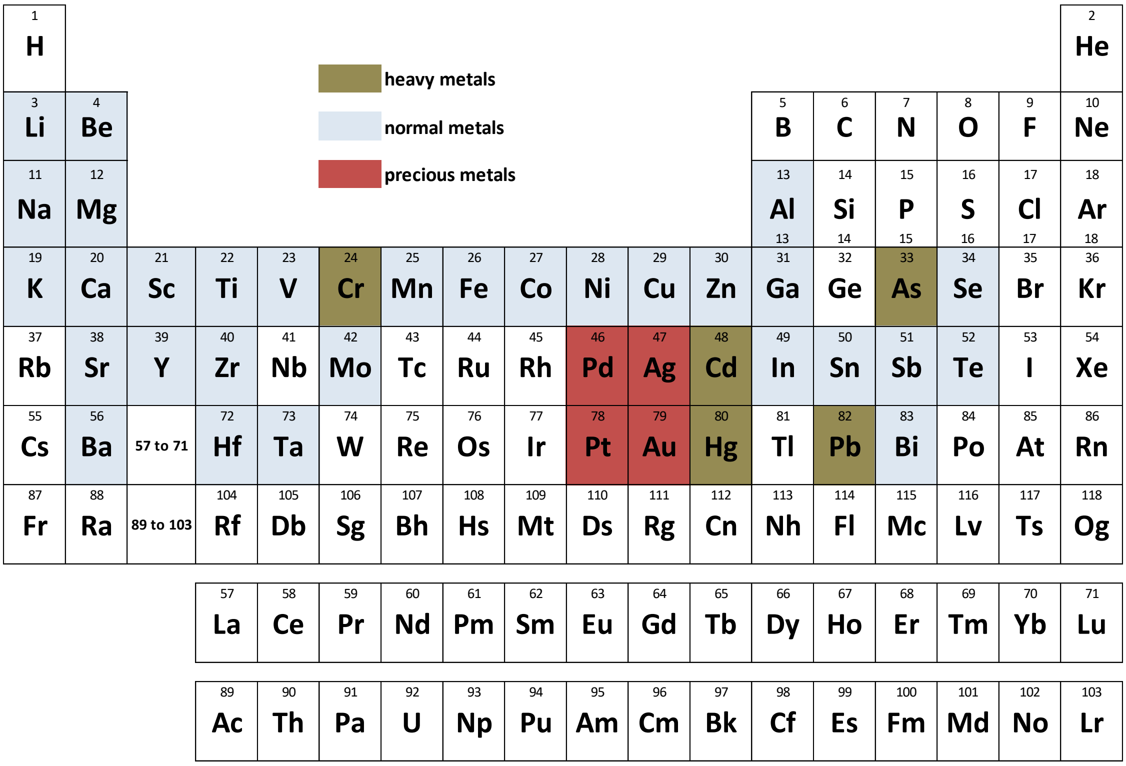



Figure 6: Metals contained in a PCB (adapted from Lu and Xu, 2016)

The organic material is mainly composed of paper and plastics, containing flame retardants. The ceramic material is essentially made up of silica and alumina and may contain mica and barium titanate (Vermesan et al. 2019; Ogunniyi et al. 2009).

Metals, with a PCB typically consisting of more than 20 different types of metals, divided into base metals such as copper, iron, nickel and tin; precious metals such as gold and silver and heavy metals such as lead and zinc (Vermesan et al. 2019).

Table 4 shows, in percentage, the composition of the metallic fraction in the computer PCBs reported by several authors. Since the percentage composition of the PCB constituent materials depends on its age and the function for which the board was designed, it is remarkable the difference among the authors.

Table 4: Representative composition of PCB. (by wt.%).

| Metal content [%] | a | b | c | d | e | f | g | h | i | j | k | l | m | n | o | Average | STDEV | CV |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Al** | 2 | 1.8 | | 2.04 | | 4.7 | 2.46 | 1.32 | 2 | 5 | | | 7.06 | | 2.8 | 3.12 | 1.85 | 0.59 |
| **Cu** | 20 | 20 | 16 | 12.5 | 14.2 | 26.8 | 12.82 | 27.5 | 21 | 16 | 15.6 | 22 | 19.19 | 13.7 | 14.3 | 18.11 | 4.78 | 0.26 |
| **Fe** | 8 | 1.3 | 3 | 0.6 | 3.08 | 5.3 | 3.49 | 1.6 | 0.2 | 5 | 1.4 | 3.6 | 3.53 | 1.97 | 4.5 | 3.10 | 2.06 | 0.66 |
| **Sn** | 4 | 1.8 | 4 | 4 | 4.79 | 1 | 1.23 | 3.43 | 3 | 3 | 3.24 | 3 | 2.03 | | 2 | 2.89 | 1.14 | 0.39 |
| **Au** | 0.1 | 0.024 | 0.03 | | 0.0142 | 0.008 | | 0.006 | | 0.025 | 0.042 | 0.035 | 0.007 | | 0.0566 | 0.03 | 0.03 | 0.87 |
| **Pd** | 0.005 | 0.015 | 0.01 | | | | | | | 0.01 | 0.01 | | | | | 0.01 | 0.00 | 0.35 |
| **Ag** | 0.2 | 0.057 | 0.5 | | 0.0317 | 0.33 | | 0.0026 | | 0.1 | 0.124 | | 0.01 | | 0.0639 | 0.14 | 0.16 | 1.13 |
| **Ni** | 2 | | 2 | 0.7 | 0.41 | 0.47 | 0.47 | 0.4 | 0.2 | 1 | 0.28 | 0.32 | 5.35 | 0.17 | 1.1 | 1.06 | 1.37 | 1.29 |
| **Pb** | 2 | 2.3 | | 2.7 | 2.5 | | 2.37 | | 1 | 2 | 1.35 | 1 | 1.01 | | | 1.82 | 0.67 | 0.37 |
| **Zn** | 1 | 0.27 | | 0.08 | 0.18 | 1.5 | | 2.86 | | 1 | 0.16 | | 0.73 | 0.484 | 0.4 | 0.79 | 0.82 | 1.04 |
| **Cr** | | | | | | 0.05 | | | | | | | | 0.003 | | 0.03 | 0.03 | 1.25 |
| **Ta** | | 0.0007 | | | | | | | | | | | | | 0.0192 | 0.01 | 0.01 | 1.31 |
| **Ba** | | 0.19 | | | | 0.02 | | | | | | | | | | 0.11 | 0.12 | 1.14 |
| **Na** | | | | | 0.48 | | | | | | | | | | | 0.48 | | |
| **Ca** | | | | | 1.69 | | | | | | | | | 2.9 | | 2.30 | 0.86 | 0.37 |
| **Mn** | | | | | 0.0081 | 0.47 | | | | | | | | 0.14 | | 0.21 | 0.24 | 1.15 |
| **TOTAL[%]** | **39.3** | **27.8** | **25.5** | **22.6** | **27.4** | **40.6** | **22.8** | **37** | **27** | **33** | **22** | **30** | **39** | **19** | **25** | **34** | | |

a=Shuey et al. (2006); b= Oguchi, M. et al. (2011); c= Goosey and Kellner (2003); d= Veit et al. (2002); e= Bizzo et al. (2014); f= Zhao et al. (2004); g= Das et al. (2009) ; h= Guo et al. (2011) ; i= Veit et al. (2006); j= Wen et al. (2005); k= Kim et al. (2004); l= Yokoyama and Iji (2002) ; m= Yoo et al. (2009); n= Vasile et al. (2008) ; o= Legarth et al. (1995) Oishi et al. (2007)

## Components

The main components of electronic circuit boards are:

- Capacitors:

Capacitor is a component devoted to the storage of energy by means of an electric field. It is consisted of two electrical conductors separated by an insulator: the conductors are called plates and the insulator is the capacitor's dielectric. Plates are made of thin films of metal and the dielectric can be any insulator like glass, ceramic, air, paper, mica. They are usually named after the material of their dielectric (Rainer, 2019).

Figure 7 shows the main types of capacitors:

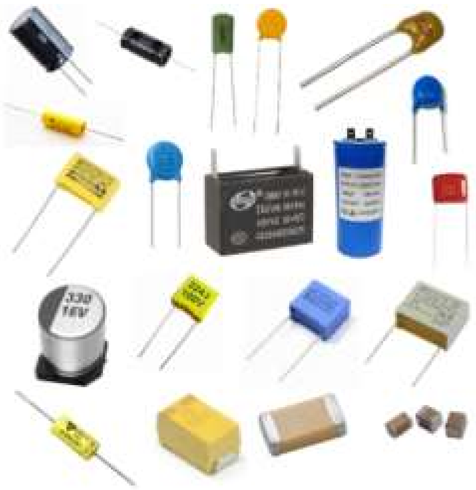


Figure 7: Different types of capacitor (Power Electric Talks, 2019)

- Resistors:

Resistors are electronic components that have the purpose of offering an opposition to the passage of electric current, through its material. We call this opposition electrical resistance. Resistors can be fixed or variable. Resistors can be made of ceramic or carbon. The resistance element of the ceramic composition resistor is a mixture of clay and alumina (Rainer, 2019).

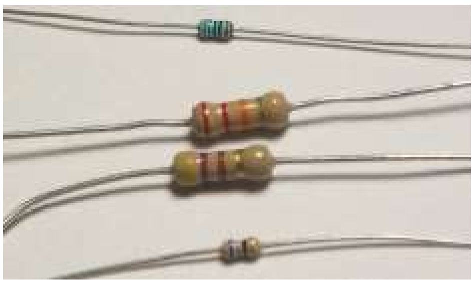


Figure 8: Resistor (Rainer, 2019)

- Semi-conductors:

Semiconductors are basically composed by Silicon or Germanium, being the first one the most used. Figure 9 shows the various types of electronic components that can be built with semiconductors. Among them, integrated circuits, transistors and diodes stand out (Rainer, 2019).

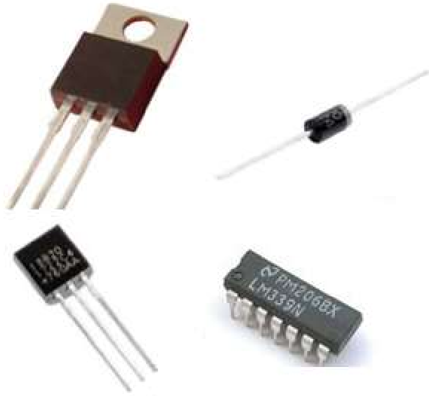



Figure 9: Types of semi-conductors (Rainer, 2019)

- Inductors:

An inductor that is shown in Figure 10 is an electrical device that stores energy in the form of a magnetic field. The inductor can be used in circuits as a filter (Michael, 2015).

Figure 10: Inductors (Rainer, 2019)

An inductor is generally constructed as a coil of conductive material, for example, copper wire. The ferromagnetic material increases the inductance by concentrating the magnetic field force lines that flow through the interior of the turns (Michael, 2015).

- Heatsinks:

A heat sink (Figure 11), is a metal object usually made of copper or aluminium, which, due to the phenomenon of thermal conduction, seeks to maximize, through the presence of a larger area through which a thermal flow can occur, the rate of thermal dissipation. that is, heat, between any surface with which it is in thermal contact and the external environment. Thermal sinks aim to guarantee the integrity of equipment that can be damaged if the significant amount of thermal energy generated during its operation is not removed and dissipated in a timely manner (Goosey, 2003).

Figure 11: Heatsink

- Solder – tin:

The solder is an interesting alloy in electrical and electronic, used to join the printed circuit board and the terminals of the components and/or wires. In the past, the solders were generally consisting of an 60/40 Tin Lead alloy (being 60% of tin and 40% of lead). Nowadays, the solders types are Lead-free. The wire consists in 99%Sn, 0.7% of Copper and 0.3% of Silver. Figure 24 shows a tin roll in Sn99Cu0.7Ag0.3 for electronic soldering (Vermesan et al. 2019).

Figure 12: Tin-lead alloy

# CHAPTER 4

## 4. RECYCLING PROCESSES

Several technologies and processes have been developed, aiming a responsible environmental management, enhanced by the high environmental damage adjacent to this waste, but also by the conservation of non-renewable natural resources inherent in recycling .

Currently, to perform the recovery of metals from electronic waste, technologies associated with metallurgy such as pyrometallurgy, hydrometallurgy, biometallurgy and electrochemical are used, as well as physical-mechanical processes, either individually or combined.

In this chapter, the main processes used to recover metals from PCB scrap residues will be briefly described.

### 4.1. Physical-Mechanical Processes

Physical-mechanical processing uses unitary ore treatment operations as a means of separating and concentrating the existing materials in the waste, considering their physical properties, such as ductility, grain size, magnetic permeability, density and conductivity (Kaya, 2016).

The techniques are, in general, and in sequence: dismantling, comminution, particle size classification, magnetic separation, electrostatic separation and gravity separation (Kaya, 2016).

Since the present work was based on the application of physical-mechanical processes for the recovery of metals in PCB waste, these operations are described in more detail below.

#### 4.1.1. Dismantling

The dismantling of waste electrical and electronic equipment is a physical process that can be performed manually or automated and it precedes any waste treatment in order to improve the following steps in the recycling (Kumar, 2014).

It is essential because it allows to use again some components, to select and remove hazardous components, as well as the selection of specific components of high add value (for example the PCB) (Vermesan et al., 2019).

In the case of PCB scrap, in this first phase there is the manual removal of toxic or valuable components, easily removable (such as batteries and metallic supports) (Vermesan et al., 2019).

### 4.1.2. Size reduction

Size reduction or comminution means the mechanical fragmentation of the PCB, with or without electronic components on the board. The fragmentation equipment usually used to reduce the size of WEEE are normally shredders, hammers, and knife mills (Kumar, 2014).

The reduction in the size of the material, with the different ductility of the polymers, ceramic and metallic components of the PCB, promotes the liberation of grains of metallic material. Therefore, this step is crucial in the efficiency of the physical separation processes (Vermesan et al., 2019).

### 4.1.3. Sieving

After the size reduction, the product is normally classified according to their granulometry. This process aims to separate the material in fractions, according to the geometric size of the particles (Kumar, 2014).

The test consists of piling the sieves from the smallest opening (base) to the largest (top) and depositing the material on the sieve with the largest opening, shaking them vibratory agitator. The smaller particles can pass through the holes, while the larger ones are retained. Subsequently, the retained material is weighed. In some cases, after this step, it is already possible to obtain fractions concentrated with certain materials, which can be separated from the main fraction (Vermesan et al., 2019).

After this step, the material is prepared for separation techniques: magnetic, electrostatic and gravity.

### 4.1.4. Magnetic separation

Magnetic separation uses the magnetic susceptibility characteristic of some metals to separate them from others. This characteristic determines how the material behaves in the presence of a magnetic field, if attracted or repelled, classified it in three categories: (i) ferromagnetic, materials that have high magnetization; (ii) paramagnetic, those that weakly magnetize; and (iii) diamagnetic, are the materials that have negative magnetic susceptibility, which causes repulsion to the field (Suponik, T. 2019).

In the case of printed circuit boards, through this type of separation it is possible to obtain a magnetic fraction rich in iron and nickel and a non-magnetic fraction, which contains the rest of the materials.

Some metals, such as copper, are found in both the magnetic and non-magnetic fractions, because as it is a metal with a high amount in the WEEE PCB, copper ends up being dragged along with the attracted iron and nickel particles. This is also a result of the agglomeration of particles that results in the attraction of some non-ferrous particles being carried by the ferrous fraction (Kaya, M. 2016).

There are several types of equipment that perform the magnetic separation, divided into two groups: dry and wet separators. Dry separators are used for larger particles, while wet separators are used for smaller particles (Veit, 2005).

After the magnetic separation, the non-magnetic product is generally not discarded, it goes on to further treatments, for example, to an electrostatic or gravitational separator.

### 4.1.5. Gravity separation

The separation by gravity or density consists in a method that uses the gravitational forces of a particle moving through a fluid (water or air), to separate due to its different shapes, sizes and densities. The efficiency performance in this process depends on factors such as flow rate, particles size range, difference in fluid-particle density (Vermesan et al., 2019).

There are several types of techniques to perform the gravity separation such as air classifiers, jigs, hydrocyclones, shaking tables, and sin -float (Vermesan et al., 2019). In the present work, the application of the wet shaking table is studied to recovery the metals fraction present in the PCB scraps. It consists of a deck, with rectangular shape, with flexible supports that allow it to take an oscillatory movement. The surface has an adjustable inclination, and a layer of water flows over it, as you can see in Figure 13 (Lins, 2010).

At the top of the table, a tube with holes promotes continuous water distribution, while the material is fed in the corner of the table. The discharge of the resulting products takes place along the opposite sides of the feeding. The surface of the table is made of a material with a high friction, usually rubber or plastic, and is almost entirely covered riffles, oriented parallel to the direction of movement in which thickness decreases from the feeding until they disappear in the opposite side, where it becomes smooth (Lins, 2010).

The asymmetric movement promotes conditions that the riffles transmit the movement to the particles, resulting in a displacement of the particles forward; the small and heavy ones moving more than the coarse and light ones allowing their classification, in terms of size and density (Shariati et al., 2015).

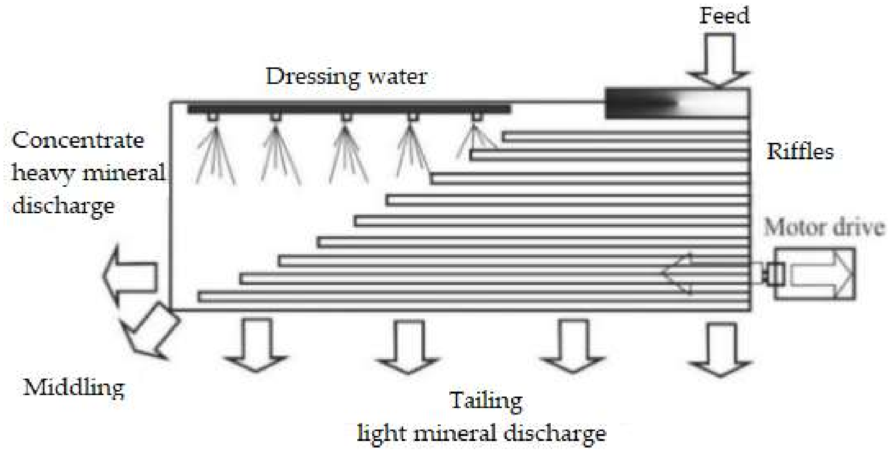



Figure 13: Schematic illustration of the arrangement of a shaking table (Shariati et al., 2015)

The operational parameters that condition a shaking table are its inclination, the water flow, the frequency of the movement, the characteristics of the riffles and the surface of the table (Lins, 2010).

This technology has been applied for several decades in mineral processing industry. However, this process hardly allows the recovery of isolated metals, with high efficiency.

### 4.1.6. Electrostatic separation

Electrostatic separation uses the electrical conductivity that some metals have, in contrast to others that are insulators. In this way, the PCB waste is separated, obtaining a fraction with conductive metals, such as copper, and another one consisting of polymeric and ceramic materials. There are three types of electrostatic separation known, Eddy current separation, triboelectric separation and Corona electrostatic separation (Kaya, 2016).

"The principle of the Eddy-current is that in separation zone gravitational, centrifugal, frictional, and magnetic deflection forces influence the falling particles, but only magnetic force deflects the ferrous particles to a higher degree" (Jianzhi et al., 2004). The Triboelectric separation is performed by contact, separating particles with similar conductivities (Kaya, 2016).

In Corona electrostatic separation, conductive materials are separated from non-conductors materials through induction or high voltage charge and are applied to separate particles that have large difference in conductivities. Since PCB is consisted of a conducting metal layers and non-conducting substrate, corona electrostatic separation is the most used and is due to its great efficiency, environmentally friendly and an economical process (Vermesan et al., 2019).

In this studied, corona electrostatic separation was applied. The scheme of operation is shown in the Figure 14. The material is fed in the vibratory feeder onto the revolving earthed roll. A voltage is applied by the Corona and an electrostatic electrode which generates an electrostatic field as the particles fall onto the roll. Conductive particles (copper) instantly lose their charge are throw off. Insulating particles will keep their charge and remain attached to the roll, eventually falling off into storage bins (Fears, 2020)

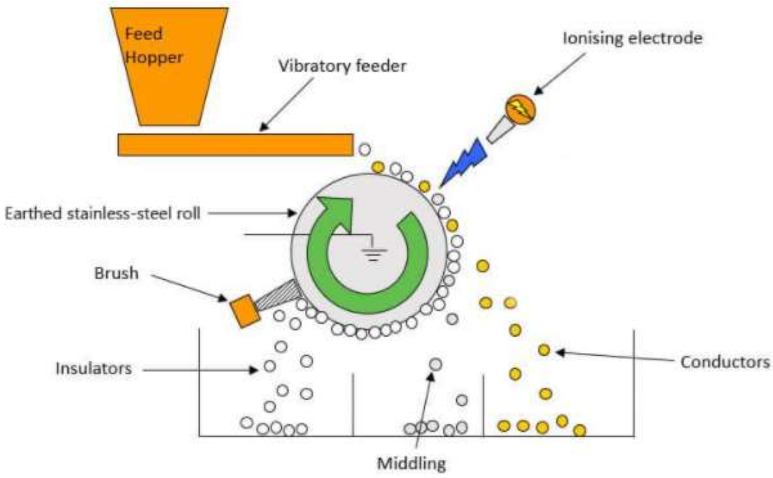



Figure 14: Schematic illustration of corona electrostatic separation (Fears, 2020)

## 4.2. Pyrometallurgical Processes

Pyrometallurgical processes are characterized by incinerating, smelting in a plasma arc furnace or blast furnace, drossing, sintering, melting and reactions in a gas phase at high temperatures. The mechanism is to promote the decomposition and volatilization of organic material at high temperatures, while inorganic charges, metals, withstand these temperatures and remain unchanged or form alloys with metals that have chemical affinity (Gramatyka, 2007)

The main advantage of pyrometallurgical treatment for the recovery of metals from WEEE is its capability to accept any types of scrap. The disadvantages of this process are high cost and hight energy consumption processes and when applied to materials with flame retardants, as the case of PCB, causes the volatilization and emission of toxic compounds, such as dioxins and furans (Kaya, 2016).

## 4.3. Hydrometallurgical Processes

Hydrometallurgical processes are treatments that involves the leaching of metals, present in WEEE, in an acid or alkaline aqueous medium. The metal is recovered from the leachate solution using processes such as precipitation, ion-exchange, solvent extraction, filtration, or distillation (Gramatyka, 2007).

Compared to other metallurgical processes, it requires low capital cost, and it has high rates of metal recovery with lower environmental impact. However, as in pyrometallurgical processes, toxic waste is generated, in this case, acid and alkaline liquid from leachate solution. It is also required grinding to obtain finer particle sizes for efficient dissolution, therefore, mechanical pre-treatment is also preferred before hydrometallurgical treatment (Kaya, 2016).

There are several hydrometallurgical techniques that can be used in the recovery of precious metals, such as chemical leaching with cyanide, halide, thiourea and thiosulfate, involving acid treatment, such as sulfuric acid, hydrochloric acid, nitric acid (Gramatyka, 2007).

## 4.4. Biometallurgical Processes

Biometallurgy uses interactions between microorganisms and minerals to recover valuable metals. It combines the metabolism of microorganisms with the minerals chemical transformations providing simple and efficient applications, in comparison to the physical and chemical processes already existing in the treatment of metals recovery. It uses microorganisms such as bacteria and fungi to mobilize metals from waste (Kaya, 2016).

The biometallurgical processes are attracting interest for metal recovery from waste materials due to their environmental-friendly and low cost. The disadvantages are the long period required for the occurrence of bioleaching, which results in a slower kinetics, when compared with the conventional hydro-metallurgy methods (Kumar, 2020).

## 4.5. Electrochemical Processes

Electrometallurgical processes have electrolysis as their basic principle for obtaining and refining metals. They explore the non-spontaneous redox reactions that occur through aqueous electrolytes or molten salts. Metals such as copper, zinc, cadmium, aluminium, precious metals, among others, can be obtained (Gramatyka, 2007; Vermesan, 2020)

The great advantage of these processes is that they neither have extremely high energy consumption, as in pyrometallurgical processes, nor produce a large amount of effluents, such as hydrometallurgical processes. However, as metals need to be dissolved, leaching operations will always be present and consequently the production of liquid discharges (Vermesan, 2020).

## 4.6. WEEE: Previous Studies Review

On 2002, Veit et al. published a study of metal recovery from obsolete PCB of computers. The boards were comminuted, reducing them to sizes smaller than 1 mm, and after granulometric classification was performed, obtaining 3 different classes - F1: -0.25 mm; F2: -0.5 + 0.25mm; F3: -1.0 +0.5 mm. Regarding the results of grinding and grain size separation, the author also reported that it was possible to obtain a metal concentrate from these stages, noting that only in the grinding followed by the granulometric classification was it possible to reach a concentration of 35% of metals in the coarsest fractions. The metallic fraction was concentrated in the greater granulometry because most metals are less fragile than some polymers and ceramics.

Table 5: Chemical composition for electronic components after comminution and particle size separation (Veit et al., 2002)

| Chemical composition (%) | F1 | F2 | F3 |
|---|---|---|---|
| Copper | 9.68 | 17.25 | 30.15 |
| Iron | 0.28 | 0.10 | 0.80 |
| Aluminum | 2.06 | 1.62 | 0.92 |
| Nickel | 0.40 | 0.31 | 0.60 |
| Lead | 2.34 | 3.18 | 2.78 |
| Tin | 3.83 | 4.78 | 4.92 |

F1 < 0.25mm; 0.25 < F2 < 0.50 mm; 0.50 < F3 < 1.00 mm.

Four years later, Veit (2006) published another study, using, in addition to comminution and granulometric classification, magnetic and electrostatic separation. The non-magnetic fraction was subjected to electrostatic separation, a process that separated conductive and non-conductive materials. In the magnetic separation, the amount of material retained was said to be low, as the amounts of strongly magnetic metals (iron and nickel) are low. Iron was the main element obtained in the magnetic fraction (42%), followed by nickel (15%) and copper (18%). In contrast, the electrostatic separation, was considered efficient, since it resulted in a fraction with about 50% copper, 25% tin and 7% lead.

In the studied carried out by Zhao et al. (2004), mechanical processes were developed in the recovery of copper from waste PCBs. In order to calculate and analyse the liberation degree, the PCB samples were crushed in two-stages. The results indicate that the degree of copper liberation increased with the decreasing in particle size, and optimal liberation particle size from other components was around 0.5 mm. After the crushing and sieving, the material was conducted to electrostatic and pneumatic separation and a comparison in the different separation methods and results were conducted. The results for both techniques are shown in the Table 6and Table 7.

Table 6: Pneumatic separation results under different air velocity (Zhao et al., 2004)

| Particle size mm | Air velocity, m/s | Copper grade | | | Copper recovery, % |
|---|---|---|---|---|---|
| | | Feed, % | Concentrate % | Tailings, % | |
| -1.0+0.5 | 14.14 | 34.53 | 49.08 | 20.37 | 70.11 |
| | 16.97 | 35.00 | 51.96 | 22.65 | 62.56 |
| -0.5+0.25 | 5.94 | 39.62 | 64.01 | 23.14 | 65.15 |
| | 6.51 | 35.45 | 54.66 | 20.91 | 66.42 |
| -0.25+0.125 | 3.11 | 20.74 | 49.54 | 3.09 | 90.76 |
| | 3.68 | 20.70 | 55.50 | 5.23 | 82.51 |
| -0.125+0.075 | 2.38 | 7.77 | 29.98 | 1.93 | 80.35 |
| | 2.60 | 7.81 | 31.67 | 2.70 | 71.54 |
| -0.075 | 1.70 | 2.89 | 26.81 | 2.15 | 27.83 |
| | 1.92 | 2.88 | 26.57 | 2.52 | 13.83 |

Table 7: Electrostatic separation results (Zhao et al., 2004)

| Particle size, mm | Feed | | Concentrate | | | Tailing | | |
|---|---|---|---|---|---|---|---|---|
| | Weight, % | Cu grade, % | Weight, % | Cu grade, % | Cu recovery, % | Weight, % | Cu grade, % | Cu loss, % |
| -1+0.5 | 100 | 25.29 | 45.97 | 53.72 | 97.65 | 54.03 | 1.10 | 2.35 |
| -0.5+0.3 | 100 | 24.93 | 34.08 | 71.61 | 97.88 | 65.92 | 0.80 | 2.12 |
| -0.3+0.15 | 100 | 20.80 | 10.00 | 90.62 | 43.78 | 90.00 | 13.0 | 56.22 |
| -0.15+0.075 | 100 | 8.50 | 3.51 | 90.90 | 37.57 | 96.49 | 5.50 | 62.43 |

Approximately 91% copper recovery was achieved from the -0.25 +0.125 mm feed with the pneumatic separator. More than 97% copper recovery was achieved for -1 +0.3 mm size fraction and he confirmed as an efficient dry separation method for recovering copper from PCBs. particle sizes smaller than 0.075 mm neither the pneumatic nor the electrostatic separation processes resulted a good separation (Zhao et al., 2004).

Burat and Özer (2018) published a study which the focus was to design a physical separation processes to obtain a pre-concentrate prior to metallurgical processes. After crushing and size classification, the PCB were submitted to gravity separation by shaking table, magnetic and electrostatic separation to separate valuable metals from non-metallic fraction. The results of chemical analyses after comminution and sieving show that the content of metals and non-metals are diverse at fractions. The copper content is the highest at -1+0.5; -0.5+0.3, and -0.3+0.1 mm. Alluminium particles are concentrated in the larger size fractions, due to it easily deforms and hardly breaks under the loads. In other hand, the results also show that majority of metals (Fe, Ni, Pb and Ag) are concentrated in the finest fraction, as it can be seen in the Table 8.

Table 8: Metal contents of size fractions determined by AAS (Burat and Özer, 2018)

| Size fraction, mm | Amount, % | Metal grade, % | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Cu | Fe | Al | Ni | Pb | Au | Ag | Total |
| +2 | 17.3 | 6.36 | 0.19 | 10.7 | 0.02 | 0.01 | 0.003 | 0.003 | 17.8 |
| -2+1 | 24.0 | 10.49 | 0.26 | 12.1 | 0.04 | 0.02 | 0.022 | 0.005 | 23.2 |
| -1+0.5 | 13.6 | 20.92 | 0.40 | 12.4 | 0.10 | 0.04 | 0.011 | 0.008 | 34.2 |
| -0.5+0.3 | 10.5 | 23.53 | 1.14 | 4.8 | 0.21 | 0.13 | 0.009 | 0.038 | 30.1 |
| -0.3+0.15 | 10.9 | 19.73 | 2.53 | 2.9 | 0.37 | 0.29 | 0.006 | 0.040 | 25.9 |
| -0.15 | 23.7 | 5.37 | 17.98 | 3.4 | 0.24 | 0.30 | 0.017 | 0.041 | 27.5 |
| Total | 100.0 | 12.36 | 4.80 | 8.1 | 0.15 | 0.13 | 0.013 | 0.021 | 25.8 |

After some tests, the authors affirmed that to enhance the metal concentration, it is very crucial the metallic particles liberation from the PCB pieces, otherwise the selectivity decreases mostly at coarsest fraction, especially because resins and glass fibers adhere to the conductive copper. For this reason, all the fractions +1 mm size fraction were re-ground. After, three size fractions (+1, -1+0.3 and -0.3 mm) were conducted to the separation by gravity. The products obtained were classified as concentrate (heavy), middling and tailing (light). The results of the shaking table process of the metallic components from the PCBs shows a heavy product content about 72% and 77%metal for the fraction +1 mm and -1+0.3 mm, respectively. The total metal content increased to over 90% at finest fraction. The highest grade of copper (73.21%) was found in the sizer fraction -1+0.3 mm. The heavy fraction product obtained from shaking table was conducted to the magnetic separation in order to remove the ferrous alloyed materials and produce a high-quality copper containing concentrate. It was verified, after the magnetic separation that in the finest fraction had an average recovery of approximately 94% Fe in the magnetic product compromising roughly about 18.9% of the feed weight. The middling product from tabling for the size fraction of -1+0.3 mm and -0.3 mm was subjected to electrostatic separation. A conductive product was obtained with 33% Cu content and 98% recovery (Burat and Özer, 2018).

A recent study published by Tanısalı et al. in 2020, focused on the recovery of valuable metals (gold, silver, and copper). A total of 90 kg of waste PCBs were first shredded and sieved with a screen of 2mm. The material product smaller than this was separated and identified as Metal Dense Product (MDP). The product above 2 mm was re-crushed and classified by screening as −4 + 0.5 and −0.5 mm. The metal distributions from comminution, according to fractions, are presented in the Figure 15. It was verified that after crushing, about 23.3% of the total feed was obtained as MPD.

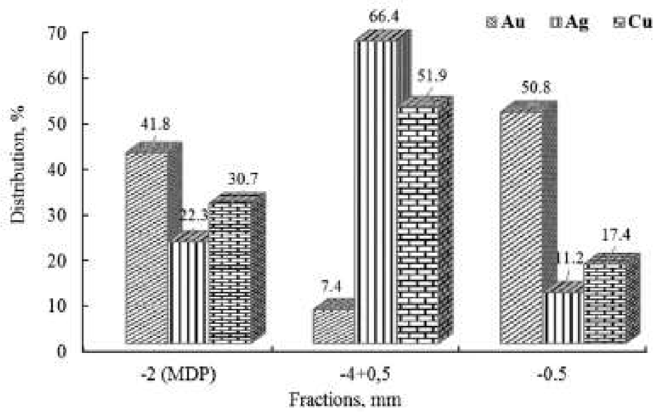



Figure 15: Metal distributions versus size fractions (Tanısalı et al., 2020)

To improve the efficiency of separation, the shaking table separation was implemented on MDP, −4 + 0.5 mm, and −0.5 mm size fractions. The results obtained for each fraction were heavy (concentrate) and light products (tailings).

Table 9: The result of shaking table separation at different fractions (Tanısalı et al., 2020)

| | | | Au | | Ag | | Cu | |
|---|---|---|---|---|---|---|---|---|
| Groups | Products | Amount, % | C, g/t | D, % | C, g/t | D, % | C, % | D, % |
| **MDP** | Concentrate | 18.1 | 259 | 33.5 | 677 | 20.0 | 59.9 | 28.8 |
| | Tailing | 5.2 | 231 | 8.6 | 276 | 2.3 | 14.9 | 2.1 |
| | **Total** | **23.3** | **253** | **42.1** | **587** | **22.3** | **49.8** | **30.9** |
| **−4 + 0.5 mm** | Concentrate | 33.7 | 28 | 6.9 | 1198 | 65.7 | 56.1 | 50.2 |
| | Tailing | 8.9 | 2 | 0.1 | 14 | 0.2 | 5.6 | 1.3 |
| | **Total** | **42.6** | **23** | **7.0** | **949** | **65.9** | **45.5** | **51.5** |
| **−0.5 mm** | Concentrate | 10.2 | 657 | 47.8 | 522 | 8.7 | 61.4 | 16.7 |
| | Tailing | 23.9 | 18 | 3.1 | 79 | 3.1 | 1.5 | 0.9 |
| | **Total** | **34.1** | **209** | **50.9** | **212** | **11.8** | **19.3** | **17.6** |
| **Feed** | | **100.0** | **140** | **100.0** | **613** | **100.0** | **37.6** | **100.0** |

*C: Content, D: Distribution*

The authors concluded that gravity separation was not suitable for the MDP since there was no significant improvement. It was verified that 67.2% wt. of the feed was obtained as a final concentrate with 202 g/t Au, 883 g/t Ag and 54.7% Cu, while a final tailing was discarded with average metal contents of 14 g/t Au, 61 g/t Ag and 2.61% Cu. The light fraction product was subjected to leaching using H2SO4 and HNO3 at 80°C for two h resulting in an extraction about 92% of copper, 59% of Au and 98% of Ag. Direct leaching tests from crushing process were also using optimized conditions were also applied and 45% of Au, 87.6% of Ag, and 70.8% of Cu were extracted.

Over the past decades, different technologies and processes have been adapted / developed for the recovery of PCB residues, especially in the recovery of metals embedded in the polymers of these residues.

Metallurgical and physical-mechanical methods have existing and proven technologies for the material in question. In both technologies there is a need of a comminution of the residues, as it enables the liberation of metals, consequently allows a more effective application of different technologies and beneficiation processes.

The use of physical-mechanical processes as the main technology or combined with another process, aims to obtain a product with high metals concentration, significantly decreases the environmental impacts, as well as a reduction in the costs associated with obtaining these same metals.

Thinking about that, the present work is based on the application of physical-mechanical processing, by magnetic, gravity and electrostatic beneficiation for the recovery of metals from PCB waste.

# CHAPTER 5

## 5. MATERIALS AND METHODS

### 5.1. Materials

The printed circuit board used in this work, containing all components, were kindly supplied by OSAI spa. It has an area with about 1840 $cm^2$ and a thickness about 2.6mm. Its total weight is 1868.2 grams and represent PCB of a server. Figure 16 shows the original PCB and some identified components.

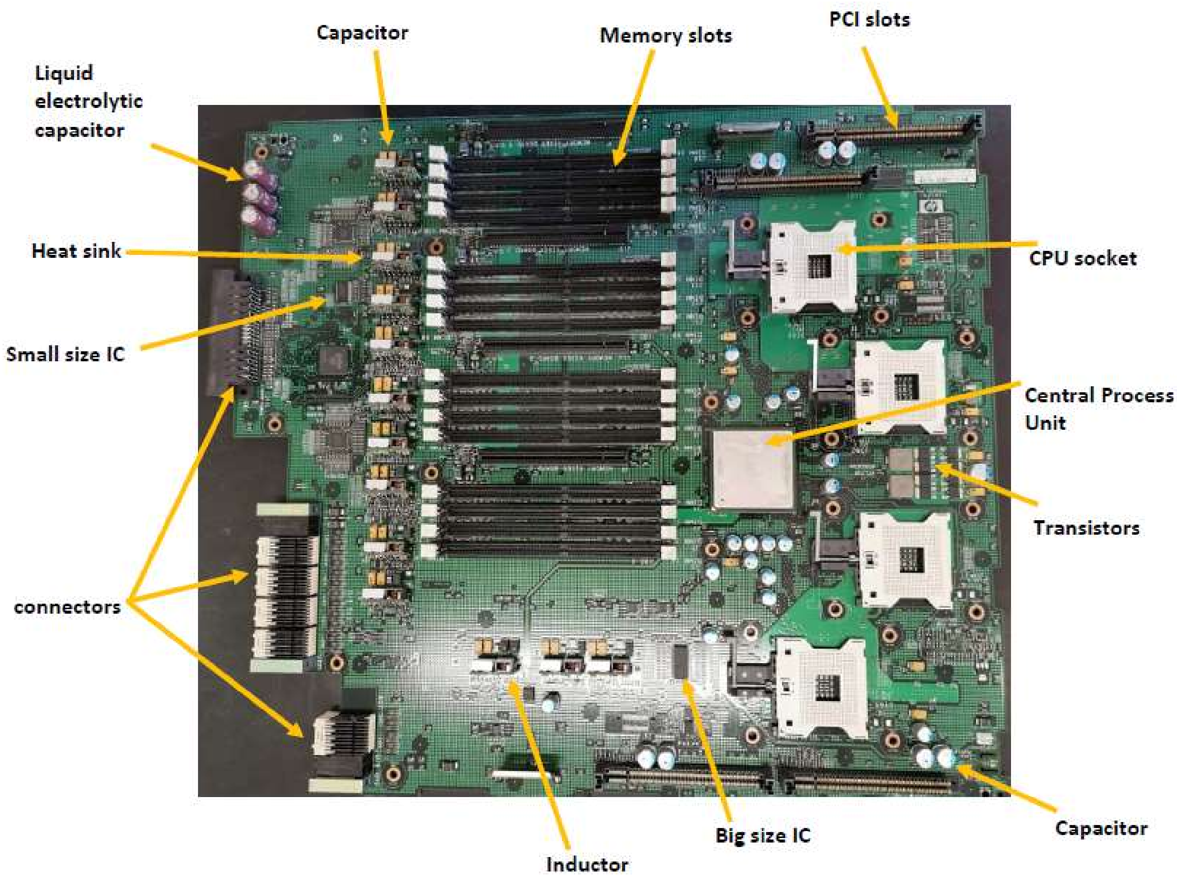


Figure 16: PCB with indication of the some of its components.

### 5.2. Methods

The methodology applied involves the identification of the PCB constituent composition, followed by their physical processing, which started with the dismantling of the board, after a comminution and granulometric classification; subsequently the classified material was subjected to magnetic separation, electrostatic separation, and gravity separation. The process flowsheet done in this work is represent by the Figure 17.

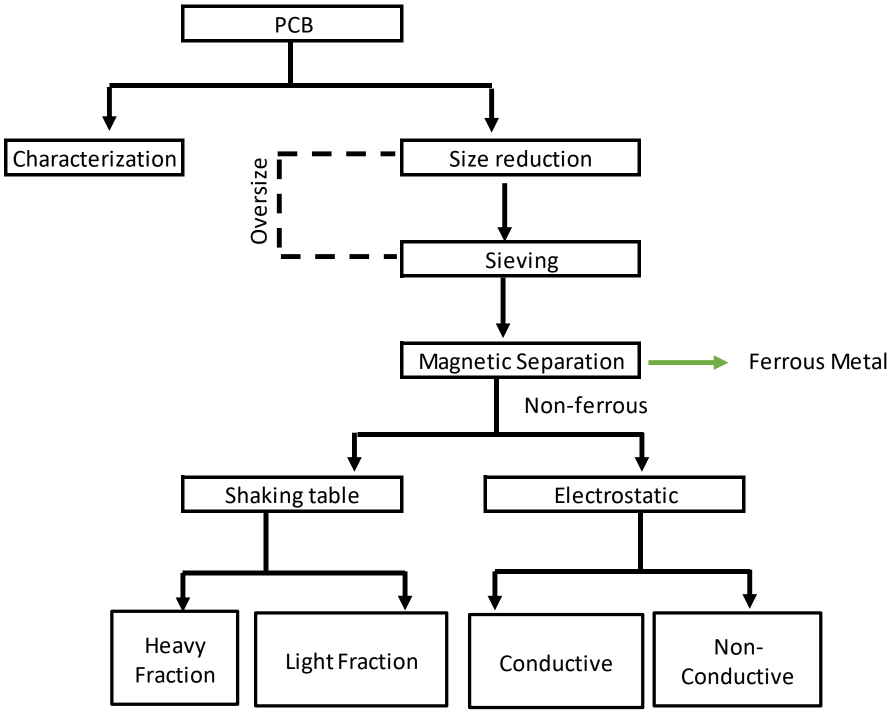



Figure 17: Process flowsheet applied in this study

After the grain size separation, gravity and electrostatic separation, a qualitative (macroscope) analysis was carried out, to assess their content in each of the classes and thus verifying the potential of the method in the recovery of metals present in printed circuit boards.

#### 5.1.1. Dismantling

The removal of the largest volume components was performed. The portion made up of the elements removed from the PCB was called "removed" and not going forward to the subsequent steps and the rest by "board". The board was finally cut in pieces of 2.5x4.0 cm, in order to provide adequate feed for the equipment used in the next stage. Figure 18 shows show the removed part and the cut pieces.

In the Dismantling stage, three capacitors were removed manually and the central processing unit was separated as it can be seen in the Figure 18.

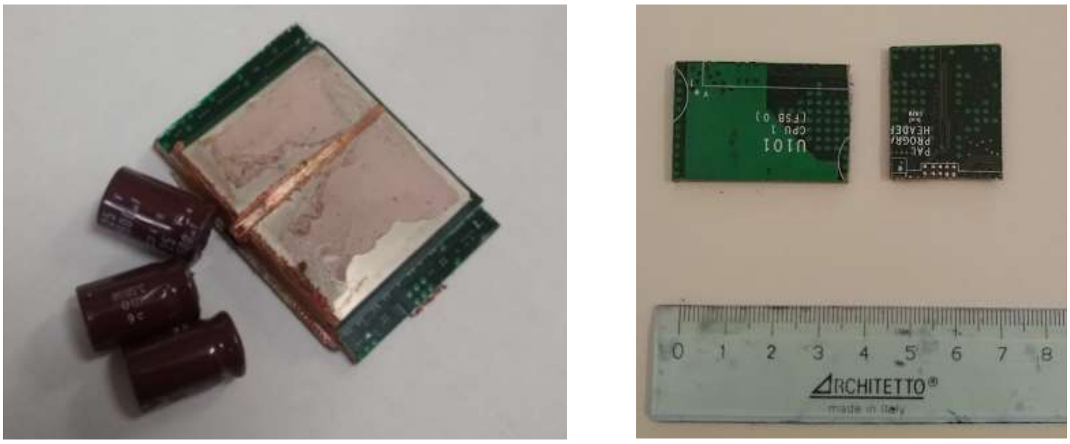



Figure 18: Removed parts from the PCB (left) and PCB pieces after cutting (right)

### 5.1.2. Size Reduction

The equipment used in the comminution of the PCB was: a cutting mill RETSCH SM100 (Figure 19).

Figure 19: Laboratory cutting mill

The cutting mill has a rotor made up of three non-aligned blades, whose action fragments the introduced material. The screen existing at the exit of the fragmentation fixes the particle size of the fragmented material. In the study in question, the grind width was 1.5 mm and 1.0mm, giving output particles smaller than 1.5 mm.

### 5.1.3. Grain size separation

This step had the purpose of separating the fragmented material according to its range in different granulometric classes, allowing later to study the degree of release of the metal in each one.

The fragmented material was sieved using a OMM FTL0200 sieve shaker and a sieve series: 1.18 mm; 0.6 mm, 0.3 mm. After the fourth screen, a collection container was placed. Figure 20 shows this scheme)

The granulometric classification was accomplished by passing a known weight of sample through vibrating screens and weighing the amount collected on each sieve.

Thus, a fraction that passed through. the 1.18mm sieve and was retained in the 0.6 mm sieve was identified as -1.18 + 0.6; if the material passed through the 0.6mm sieve and was retained in the 0.3mm sieve then the identification was -0.6+ 0.3. This nomenclature was adopted for all the material the particle size.


Figure 20: Sieve shaker and the sieves used for this study

### 5.1.4. Magnetic Separation

This step allowed to divide the material flow into two samples, a magnetic and a non-magnetic one. The magnetic separation was performed manually in all classes fraction, it is shown in the Figure 21:

Figure 21: Manual magnetic separation

### 5.1.5. Gravity separation

The non-ferromagnetic fraction, obtained in the previous step, was conducted to a gravity separation on a shaking table WEDAG 1933 (Figure 22), in order to separate the heavier elements from the others.

The following particle size classes were subjected to successive passages in the shaking table: -1.18+0.6mm and -0.6+0.3mm.

Figure 22: Laboratory shaking table

The table consists of a tray partially covered by riffles and based on a frame attached to a vibrating device. The water is distributed over the tray through a perforated tube directly connected to tap.

In the concentrate collection and sterile discharge areas, an L-shaped gutter was placed, with a partition separating these same areas, to collect the products resulting from the separation (concentrated, mix and tailing). After the passage, the products collected in the different fractions were placed to dry in an oven, at 40 ° C.

In order to ascertain the content of gold and copper existing in the classified fractions and after the physical enrichment process studied, samples were collected for and qualitative (visual) analysis using a macroscope.

### 5.1.6. Electrostatic separation

The non-ferromagnetic fraction, obtained in the previous step, was conducted to the electrostatic separation in a roll-type corona electrostatic separator Dings Coronatron (Figure 23). Good conductive material separated from the drum quickly falling into the conductive tank, while poor conductive materials hardly discharge and remain attached to the drum's surface until rubber scrapers peel it off to the non-metallic collecting tank.


Figure 23: Laboratory electrostatic separator

In order to use this equipment in the most efficient way possible, an evaluation of the main operating parameters was carried out, and then its adjustment to the best conditions found. After the best operating conditions were found, the tests were performed to all the classes size.

Two passages were performed. The first one with all the nonmagnetic material and the second one passing just the mix material resulted from the first passage. The following parameters were applied:

Table 10: Parameters of electrostatic separation

| Parameter | Value |
|---|---|
| **Voltage** | 20 kV |
| **Rotation speed** | 30 Hz |

### 5.1.7. Chemical characterization and evaluation

*SEM*

The scanning electron microscopy (SEM) is a widely popular technique used for the material characterization, due to its simple interpretation of the micrographs produced. It is a device efficient to produce images with high magnification and resolution. From its image, it is possible to extract information on material structure and texture and morphological features of the exposed surfaces, such as shape, size, etc.

The laboratory SEM FEI QUANTA INSPECT 200 LV is equipped with Energy Dispersive X-ray detector (EDX or EDS) EDAX GENESIS, an essential accessory in the study of microscopic material characterization. The electron-matter interactions generate X-rays used as a signal to produce characteristic and chemical information of the elements present in the sample.

In the Figure 24 it can be seen the digital images of the analyses done for a Tantalum capacitor presented in the PCB studied.

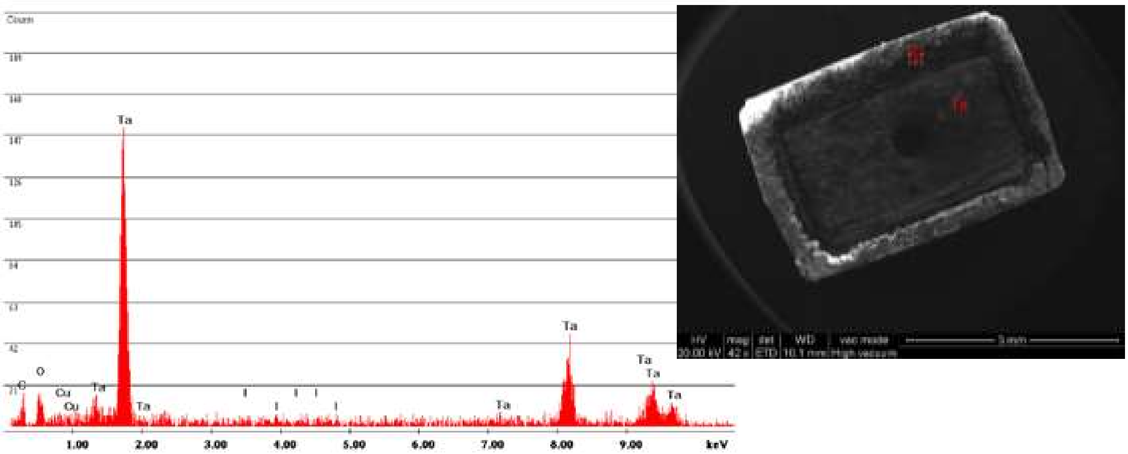



Figure 24:(a) EDS diagram of the capacitor, (b) SEM micrographs of Ta Capacitor

*Macroscope*

The visual analysis was performed using an optical macroscope WILD , in order to characterize the samples morphologically.

All the granulometric fractions were conducted to the visual analysis. With the macroscope, images were done for each product obtained during the physical-mechanical separations. The visual evaluation is done by classifying the grains in different groups : copper, metallic excluding copper, fiber glasses, green plastics and black plastics.

Each colour point represents a group of material obtained; for example, the point yellow represents the copper grains, fiber glass is represented by the blue, and so on. In the end the percentage of each product is calculated in the total

An example of the product evaluation is shown in the Figure 25.


Figure 25: A product macroscope observation with coloured points to evaluate the quality the separation

# CHAPTER 6

## 6. PRESENTATION AND DISCUSSION OF THE RESULTS

### 6.1. PCB characterization

The PBC is divided into two parts:

- Printed circuit board without components connected, also known as Printed Wiring Board (PWB),
- The electronic components.

The PWB of this study is composed of two thicker outer layers and eight thinner inner layers, interspersed with glass reinforced plastic (GRP). as shown in the Figure 26. It also shows a composition of nine copper foils, in which the two externals are thicker than the middle ones.

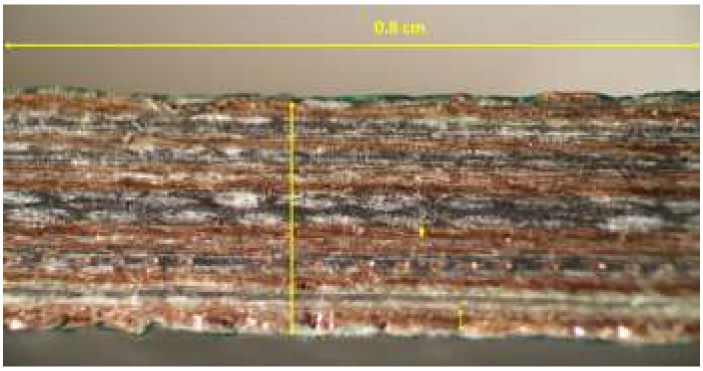



Figure 26: Macroscope cross section image of PWB

Considering this data, it was possible to estimate the weight of the metallic content (copper) containing in the in the PWB (Table 11):

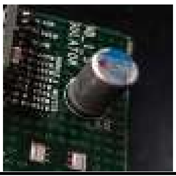
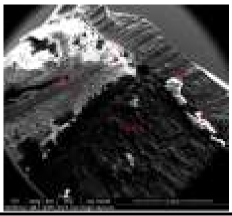
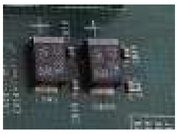
Table 11: PWB composition and weight

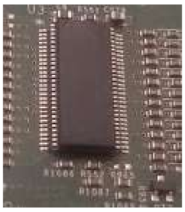
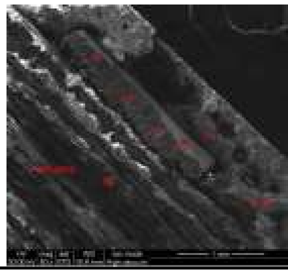
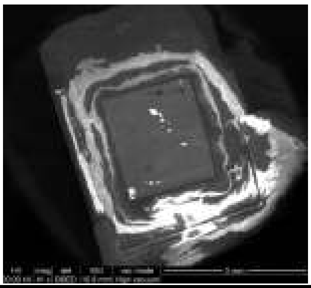
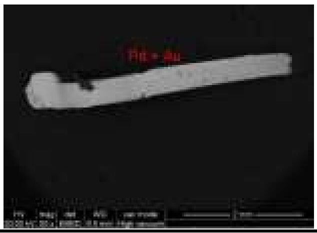
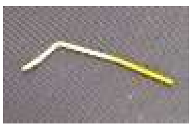
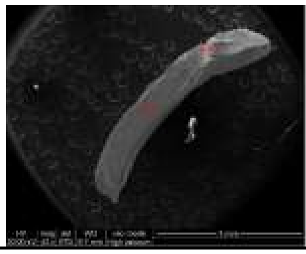
| Material | t [cm] | A [cm2] | ρ [g/cm3] | Mass |
|---|---|---|---|---|
| Copper | 0.019 ± 0.002 | 1840 | 8.96 | 280 – 345 g |
| GRP | 0.24 ± 0.002 | 1840 | 1.9* | 770 – 910 g |
| | | | Total PWB weight = | 1050 – 1255 g |

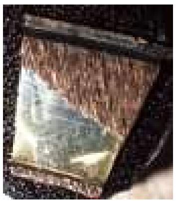
*GRP average density of 1.9 g/cm³ (Goosey et all.).

The components composition analyse was conducted by the SEM with EDS, a technique that allows to identify the elements present. Each electronic component of the board was analysed. The presence of a significant number of metallic elements has been detected. The results are shown in the Table 12.

Table 12: PCB Electronic components and their respective composition

| Component | Character | Image | SEM image | Elements |
|---|---|---|---|---|
| Capacitor | a |  |  | Al, Fe, Si, S |
| | b |  |  | Ag, Al, Cu, Si |
| | c |  |  | Mn, Si, Ta |
| | d |  |  | Si, Ta |
| | f |   |  | Ba, Sn, Cu |
| Inductor | |  |  | Cu, Fe |

| Component | Character | Image | SEM image | Elements |
|---|---|---|---|---|
| Integrated System | |  |  | Si |
| Transistor | |  |  | Si, Sn, Pb |
| Connectors | a (PCB slots) |  |  | Au, Ni |
| | b |  |  | Au, Cu, Ni, Pd, Sn |
| | c (Memory slots) |  |  | Au, Ni |
| | d |  |  | Au, Cu, Sn |

| Component | Character | Image | SEM image | Elements |
|---|---|---|---|---|
| | e |  |  | Au, Cu, Ni, Pd |

It was observed (b, d and e) that the components of the connectors are made of a coat Au-Ni-Pd while inside there is Cu. The small presence of lead (Pb) and tin (Sn) found in the transistor is due to the solder.

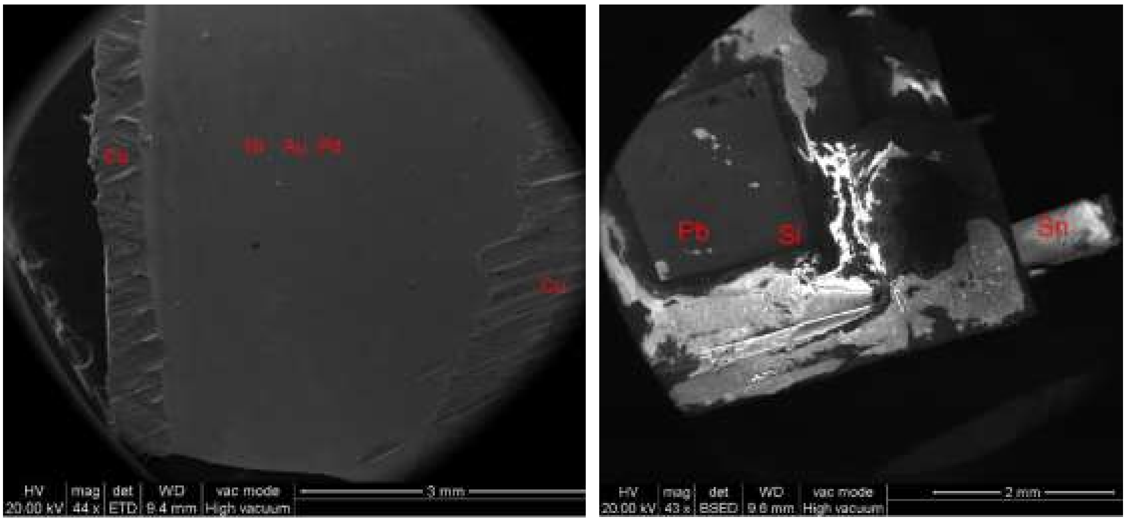



Figure 27: Connector 'e' (left) and transistor (right) analysed with SEM

After this analysis, it can be noticed that the elements composition are in accordance with the Table 4 shown in the chapter 3. Based on this table, in which an average of 34% of total PCB weight is considered metallic substances, the mass of metals in components and the weight of non-metallic fraction were estimated. Then, the final PCB composition characterization is shown in the Table 13:

Table 13:Characterization of the PCB metallic and non-metallic fraction

| **Printed Circuit Board** | | | |
|---|---|---|---|
| Metals non-Cu (e-components) | 356 – 291 | g | **34%*** |
| Cu (PWB) | 280 – 345 | g | |
| GRP (board) | 770 – 910 | g | 66% |
| Other non-metallic parts | 464 – 324 | g | |
| **Total weight** | **1870 g** | | **100%** |

* Percentual based on Table 4 in the chapter 3

## 6.2. Dismantling, size reduction, grain size separation

The initial stages carried out in this work were common to those used in conventional technologies for the recovery of PCB waste described in Chapter 4. In the Dismantling step, three capacitors and the central processing unit were separated to "Removed" fraction, totalizing 65.95 grams.

The size reduction performed in the mill made possible the releasing or exposing the metals in the epoxy matrix, resulting a product consisted of particles of different sizes. A significant release of fine particles was observed.

The grain size separation step provided the separation of the previously fragmented material in different classes.

Table 14: Weight in percentage for each class size after crushing (not considering losses)

| Size | Weight% |
|---|---|
| **+1.18 mm** | 15.8% |
| **-1.18 +0.6 mm** | 49.9% |
| **-0.6 +0.3 mm** | 13.2% |
| **- 0.3 mm** | 21.1% |
| **Total =** | 100% |

It can be observed that 15.8% of the material mass was obtained in particles size over 1.18 mm. An amount of 49.9% of material with particles between 1.18 mm and 0.6 mm, 13.2% of material with particles between 0.6 mm and 0.3 mm and 21.1% of material with particles less than 0.3 mm.

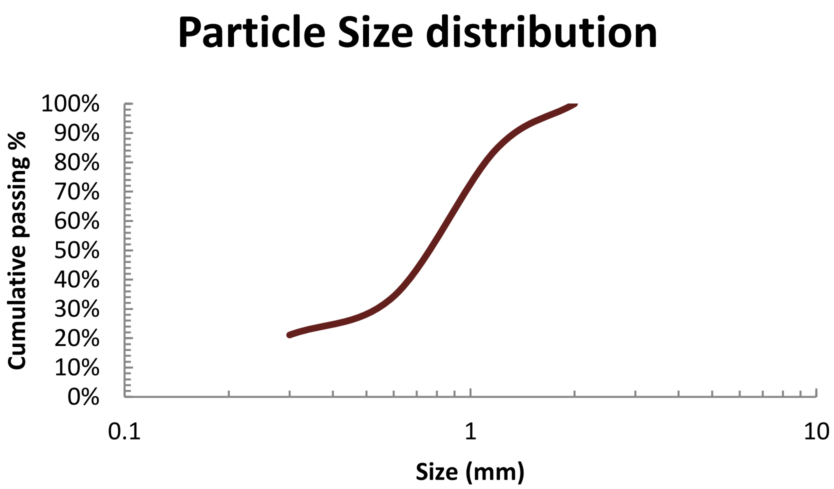



Figure 28: Particle size distributions of the PCB after size reduction

## 6.3. Evaluation of the Physical Processes in the Metal Recovery

### 6.2.1. Magnetic separation

The execution of this step allowed the separation of ferromagnetic metals; the results for each class size fraction is shown in the graph below (Figure 29):

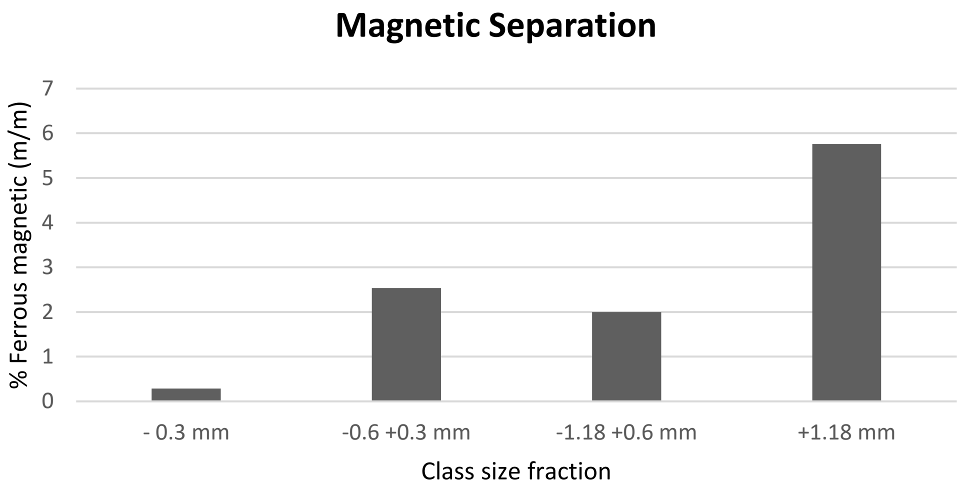



Figure 29: Quantity of ferromagnetic metals separated by the different class size

The class with the smallest size -0.3 mm was the one that presented the lowest value of separated ferromagnetic elements, 0.3% (m/m), this may be associated with its low presence.

In the class size -0.6+0.3 mm and -1.18+0.6 mm, the values obtained were, respectively, 2.5% (m/m) and 3.0% (m/m), for both granulometric classes, represented only the separate ferromagnetic elements.

The greater amount of ferromagnetic material is observed in the + 1.8mm fraction, this may be due to the element being used in larger components, such as supports, and remains in the larger fractions due to its mechanical properties, making it more difficult to grind than polymeric materials or ceramic, which have brittle properties.

Although the amount of magnetic material present in printed circuit boards is small, it is interesting to separate it before performing electrostatic separation, since the magnetic force influences the particles, resulting in a poor separation of copper.

*Product evaluation*

The Figure 30 shows the macroscope observation of the magnetic material for each fraction size.

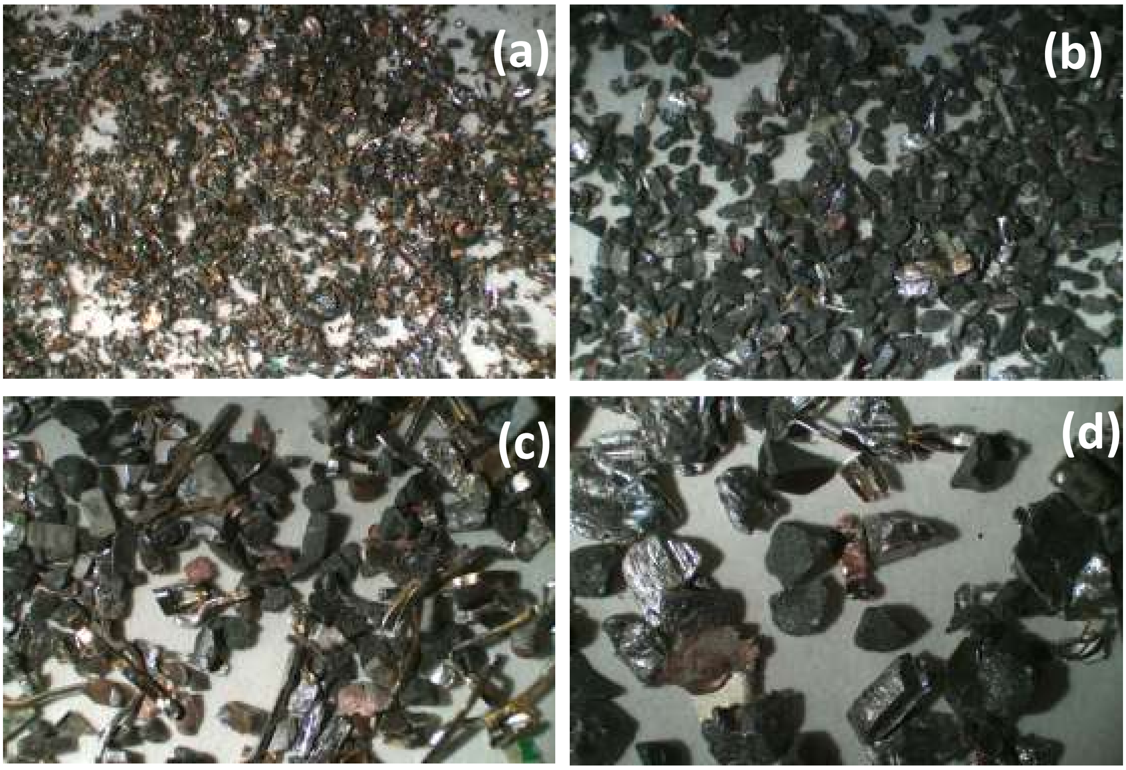



Figure 30: Observation of Magnetic Separation results for the particle size class: a) -0.3mm; b) +0.6-0.3mm; c) +1.18-0.6mm; d) +1.18mm

It can be observed some metals such as copper are also found in the magnetic fraction, as it is a metal with a high amount in PCBs, it ends up being dragged along with the iron and nickel particles. And it is also the result of the agglomeration of particles, attracting non-magnetic elements by the magnetic fraction.

All the ferrous metal product obtained from magnetic separation is considered recovered.

### 6.2.1. Gravity separation

The two size fractions -1.18+0.6 and -0.6+0.3 mm of non-ferrous material were conducted successfully to the wet shaking table separation. The grain size class -0.3 mm, despite being within the operating size, was not subjected to this treatment due to the difficult collection of products after separation. Regarding the + 1.18mm class size, despite a possible efficient separation, it was not subjected because the volume of material was too low to perform the process.

During the experimental work, it was observed, for the particle size class -0.6+0.3 mm, the fluctuation of some particles - in flakes and filaments - above the riffles, contrary to what is expected. This fact was possibly due to at least one of the following phenomena: inability of the metallic particles to break the surface tension of the water, to the shape, high angle of inclination of the table, transporting of the metallic particles by the non-metallic ones.

Table 15: Weight l of the products from shaking table as percentage

| Class size | Products | %Wt |
|---|---|---|
| 1.18+0.6 mm | Concentrate | 59% |
| | Middling | 33% |
| | Tailing | 6% |
| | Loss | 5% |
| | Total | 100% |
| -0.6+0.3 mm | Concentrate | 32% |
| | Middling | 55% |
| | Tailing | 9% |
| | Loss | 4% |
| | Total | 100% |

The sample conducted to the gravity separation were equal to 170.7 g for the class size -0.6+0.3 mm and 652.75 g for the class size 1.18+0.6 mm. The products obtained were weighed and the data are shown in Table 15: In both cases, the separations were satisfactory, obtaining a concentrate product rich in metallic elements and a tailing product poor, as it was desirable.

*Product Evaluation*

After the gravity separation by the shaking table, the different products obtained were observed with the macroscope to qualitatively assess the metallic content. Figure 31 and Figure 32 show the observations of the granulometric class -0.6+0.3 mm and 1.18+0.6 mm, respectively.

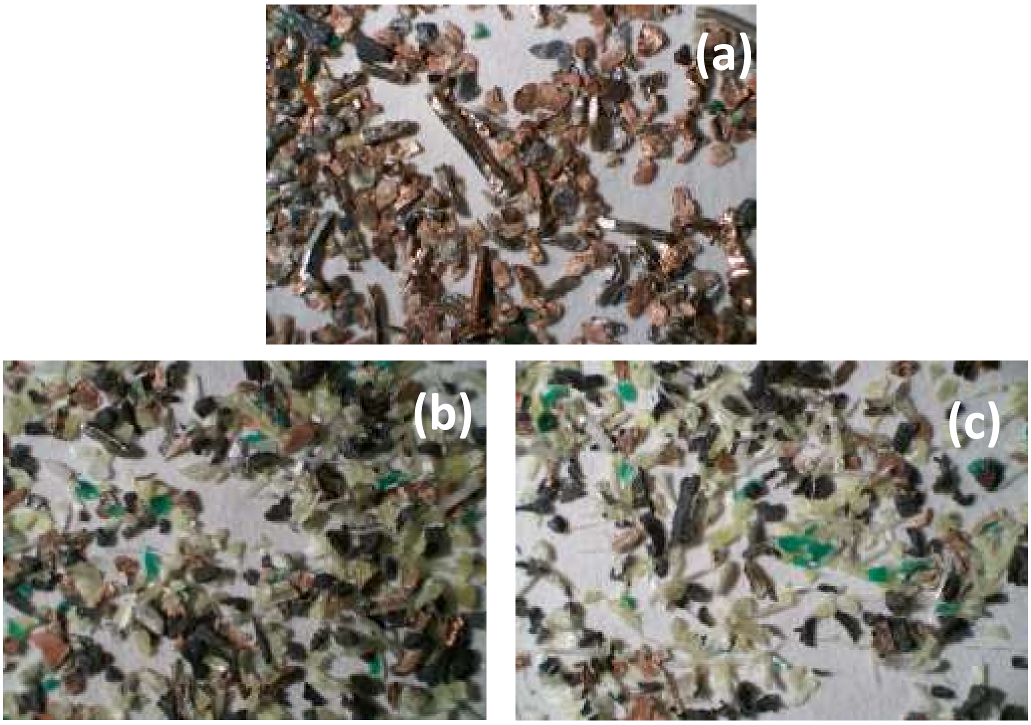



Figure 31: Observation of the result of Gravity Separation for the particle size class -0.6+0.3mm: a) concentrate; b) middling; c) tailing

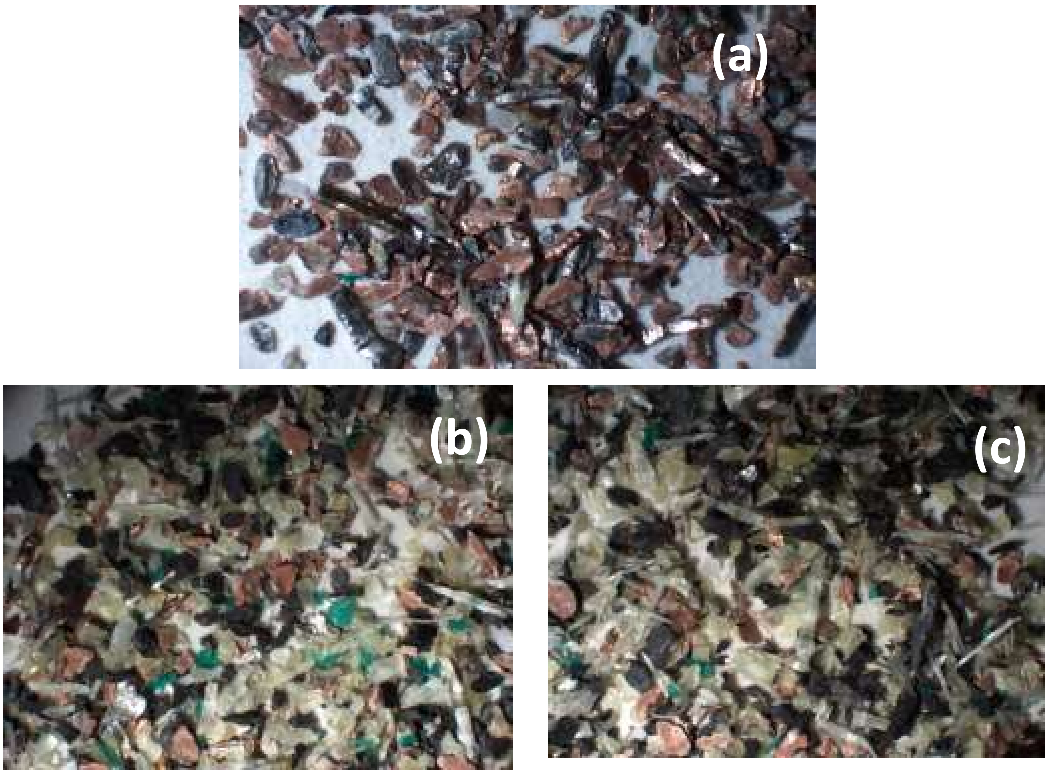



Figure 32: Observation of the result of Gravity Separation for the particle size class -1.18+0.6mm: a) concentrate; b) middling; c) tailing

The concentrate, middling and tailing resulted were conducted to a visual evaluation and three photos from different parts of the sample were taken. The products are composed of particles with many different colours. The grains were classified into five different groups, copper colour, metals excluding copper (Me), black (plastic) colour, fiber glass and green plastic. The grains for each type were counted (as shown in the Figure 25) and the percentage in the total composition of the three photos was identified. The results are shown in Table 16 and Table 17:

Table 16: Results of visual evaluation for the class size -0.6+0.3 mm from the gravity separation (Me : metals excluding copper)

| Gravity Separation – Class size -0.6+0.3 mm | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Colour type** | | **Concentrate** | | **Middling** | | **Tailing** | |
| *Metals* | Copper | 40% | 64% | 11% | 12% | 6% | 7% |
| | Me | 24% | | 1% | | 1% | |
| *Non-metals* | Black plastic | 5% | 36% | 19% | 88% | 27% | 85% |
| | Fiber glass | 28% | | 59% | | 61% | |
| | Green plastic | 3% | | 10% | | 5% | |

Table 17: Results of visual evaluation for the class size -1.18+0.6mm from the gravity separation (Me : metals excluding copper)

| Gravity Separation – Class size -1.18+0.6mm | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Colour type** | | **Concentrate** | | **Middling** | | **Tailing** | |
| *Metals* | Copper | 43% | 67% | 10% | 16% | 5% | 9% |
| | Me | 24% | | 6% | | 4% | |
| *Non-metals* | Black | 10% | 33% | 21% | 84% | 29% | 91% |
| | Fiber glass | 18% | | 52% | | 58% | |
| | Green plastic | 5% | | 10% | | 4% | |

The recovery of metals is considered only for the concentrate product. The metallic part found in the middling and tailing products are considered as a loss.

### 6.2.2. Electrostatic separation

In this step, an equipment that is traditionally applied to the recovery of PCB metals, the electrostatic separator was used. The first step was to determine the operating conditions appropriate to the type of material that was intended to separate. The selection of the parameters to be used was as mentioned in Section 5.1.6. The products obtained are given in the table below:

Table 18: Weight percentual of the products obtained from electrostatic separation

| Electrostatic Separation | | |
|---|---|---|
| **Class size** | **Products** | **% Wt** |
| **+1.18mm** | Conductive | 53% |
| | Mix | 11% |
| | Non-conductive | 35% |
| **-0.3 mm** | Conductive | 15% |
| | Mix | 1% |
| | Non-conductive | 84% |

Comparing the results, it is possible to observe a reduction in the metallic material for the granulometric class -0.3mm, this is due to the fact that it consists mainly of fibrous material resulting from the fragility of the laminate and its subjection to shear forces at the time of comminution.

*Product evaluation*

After the electrostatic separation, the different products obtained were observed with the macroscope to qualitatively assess the metallic content. Figure 33 and Figure 34 show the observations of the granulometric class -0.3mm and +1.18mm, respectively.

Observing the Figure 33, the conductive product is composed in its mostly metallic elements in copper colour and some in silver colour. The mix product despite having a predominance of metallic elements with a copper colour, it also has polymeric elements. The non-conductive product has an appearance with a predominance of polymeric fragments in greenish colour.

As predicted, in the Figure 34, fibbers and resins are attached to the metal elements. The conductive product is made of metallic elements - flakes and filaments - the first being more abundant. It was also observed that they have copper, gold and silver colours. The mix product is composed of metallic and no metallic elements. And the non-conductive product has an appearance with a predominance of polymeric fragments in black colour and fibber glass.

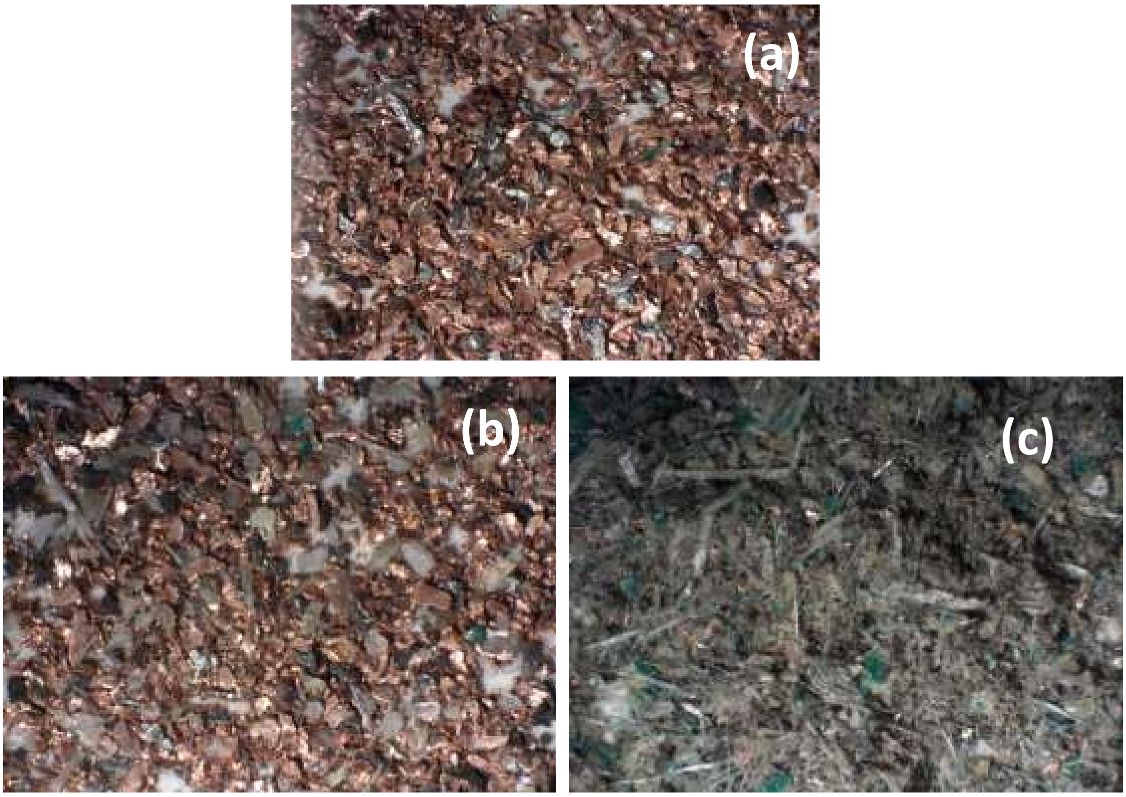



Figure 33: Observation of the result of Electrostatic Separation for the particle size class -0.3mm: a) conductive; b) mix; c) non-conductive

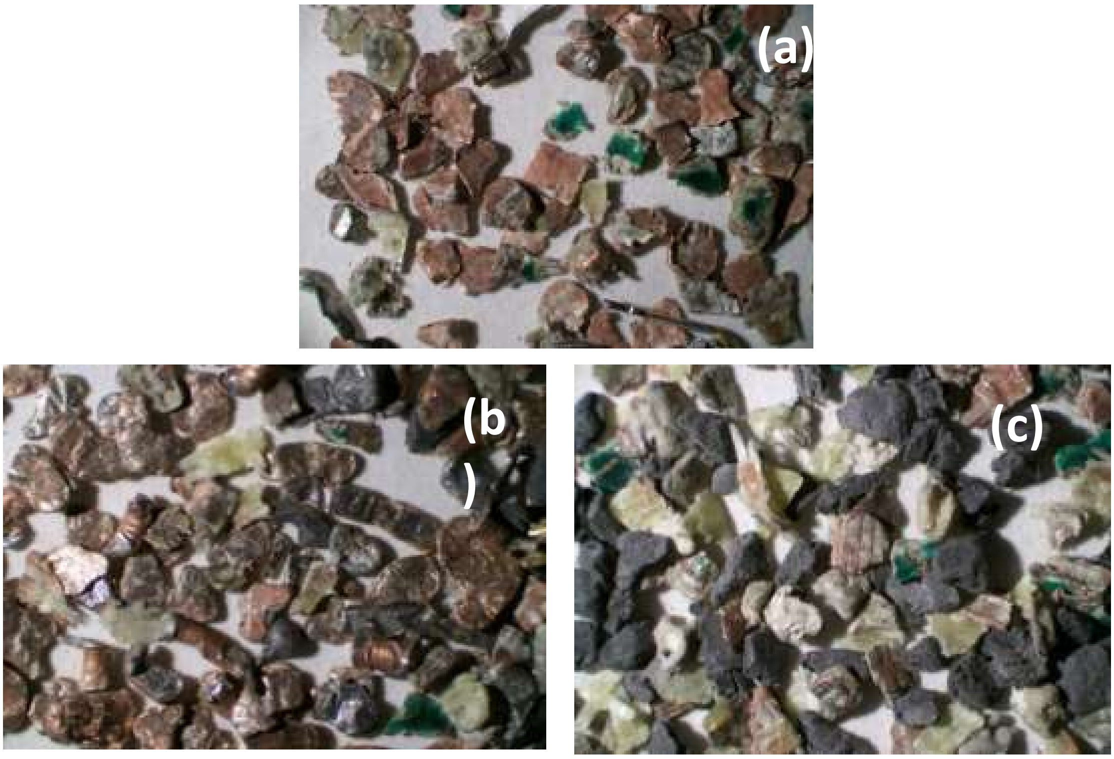



Figure 34: Observation of the result of Electrostatic Separation for the particle size class +1.18mm: a) conductive; b) mix; c) non-conductive.

The conductive, mix and the non-conductive obtained from electrostatic separation were conducted to a visual evaluation. The grains colours classified in the same way as it has been done in the gravity separation products evaluation. In the class size product with the grains -0.3 mm, an estimative of the quantity of particles for each colour type has been obtained through a visual observation of the image area. In this way, it was possible to identify the percentage composition of the metallic material in each product. For the class size product with the grains +1.18mm, the grains for each type were counted and the percentage composition was identified. Table 19 and Table 20 show the results.

The recovery of metals is considered for the products conductive and mix. The metallic part found in the non-conductive product is considered as a loss.

Table 19: Results of visual evaluation for the class size -0.3mm from the electrostatic separation (Me : metals excluding copper)

| Electrostatic Separation – Class size -0.3mm | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | **Colour type** | **Conductive** | | | **Mix** | | | **Non-conductive** | |
| Metals | Copper | 81% | 91% | | 65% | 75% | | 2% | 3% |
| | Me | 9% | | | 10% | | | 1% | |
| Non-metals | Black | 3% | 9% | | 5% | 25% | | 12% | 97% |
| | Fiber glass | 5% | | | 18% | | | 62% | |
| | Green plastic | 1% | | | 2% | | | 23% | |

Table 20: Results of visual evaluation for the class size +1.18mm from the electrostatic separation (Me : metals excluding copper)

| Electrostatic Separation – Class size +1.18mm | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | **Colour type** | **Conductive** | | | **Mix** | | | **Non-conductive** | |
| Metals | Copper | 55% | 61% | | 58% | 71% | | 5% | 6% |
| | Me | 6% | | | 14% | | | 1% | |
| Non-metals | Black (plastic) | 0% | 39% | | 5% | 29% | | 49% | 94% |
| | Fiber glass | 34% | | | 21% | | | 41% | |
| | Green plastic | 5% | | | 2% | | | 4% | |

One sample of the conductive product for the size -0.3mm was conducted to SEM analysis (Figure 35).

As expected (Table 21), copper was the element found in the greatest amount. This is the main metal used in the manufacture of PCBs and its presence is mainly associated with the conductive trace in the substrate board and also due to its presence in some electronic components.


Figure 35: Conductive material of the fraction size -0.3mm: Stub photo (left) and SEM image (right)

Table 21: Percentage of the elements found in the conductive product after electrostatic separation using SEM

| Element | Sample |
|---|---|
| Cu | 54% |
| Al | 4% |
| Zn | 7% |
| Sn | 4% |
| Ni | 8% |
| Au | 0% |
| Ba | 3% |
| Fe | 5% |
| Mn | 4% |
| Ta | 1% |
| Pd | 0.2% |
| Mg | 0% |
| S | 0.3% |
| Si | 10% |
| Ca | 6% |
| Pb | 0% |

Iron is used in some magnetic components and in PCB connections. Zinc is found mainly in resistors and also in Sn-Zn welds. Nickel is applied to metal alloys of electronic components, such as wires and resistive conductive films. Gold, despite having only an indication of its presence in the PCBs studied (<1%), due to its good electrical conductivity, as well as its malleable and ductile nature, is used in the microchip connection pin coatings (Jianzhi et al., 2004; Tanısalı 2020).

About the critical raw material, the technique indicated the presence of Tantalum (Ta) in concentrations also around 1%. Rare elements are used in the manufacture of electronic devices for PCBs because they have the characteristic that, when added to a semiconductor, change their electrical properties (Jianzhi et al., 2004).

## 6.4. Metal Recovery Balance

For the evaluation of the metal recovery of the separation process it was decided to assess the efficiency as a function of the percentage of the copper; since this it is a precious metal and highly present in the PCB, making it the main target of separation.

The copper particles and the other materials were evaluated by the image fields captured and the particles belonging to the same particles group were counted. The percentage distribution, on numerical terms, of the for the different fractions and obtained products was established.

The Table 22 shows the recorded of the different particles group, copper (Cu), metals excluding copper (Me) and non-metals (NM) materials, for each experiment performed.

All the ferrous product obtained from the magnetic separation is considered recovered. In the gravity separation, the recovery of metals is measured by the concentrate product. In contrast, the metallic fraction recovery considered for the electrostatic separation is the products conductive and mix. The other metallic fractions in the products are considered as a loss.

It can be observed that a good recovery is obtained using the magnetic separation for iron and its alloys, only in the finer fractions a small percentage of non-ferrous materials are dragged and remain attached to the iron grains.

The recovery showed good and similar percentages in the two granulometric classes conducted by gravity separation, 64% for fraction + 0.6-0.3mm and 67% for the fraction of + 1.18-0.6 mm, which shows an efficient technique for this range particle size. A metal loss of 11% and 15% occurs for these fractions, respectively.

For the finer particle size class, electrostatic separation is considered ideal not only because of the difficulty to apply the shaking table, but also due to the fact that the metallic percentage (heavy product) is low. In the granulometric class + 1.18mm, even though the electrostatic separation showing relatively good to the presence of copper, there is a high existence of plastics and glass fiber embedded to copper grains, making a product poor in concentration.

Regarding the recovery, it is also possible conclude that 88% of copper and 78% of metals in terms of the numerical presence in the products, not in terms of grade.

Although physical-mechanical processes have the benefit of low capital and operating costs, it is also important to highlight the high loss of materials throughout the processes carried out. When compared to the initial feed, we notice a total loss of 22%. Tuncuk et al., (2012) affirms that during physical separation processes, losses can reach amounts of 10–35%.

Table 22: Weights related to the different experiments (including losses) and the percentage of the materials (Cu: Copper, Me: metals excluding Copper, NM: non-metallics) found in their products

| Class size [mm] | Weight [g] | Technique | Product | Product Weight [g] | Percentage of material | | |
|---|---|---|---|---|---|---|---|
| | | | | | Cu | Me | NM |
| +1.18 | 245.2 | Electrostatic | Conductive | 122.14 | 55% | 6% | 39% |
| | | | Mix | 26.56 | 58% | 14% | 29% |
| | | | Non-conductive | 82.25 | 5% | 1% | 94% |
| | | Magnetic | Ferrous | 13.36 | 1% | 99% | 0% |
| | | Loss | | 1 | - | | |
| +1.18-0.6 | 744.4 | Shaking table | Concentrate | 383.23 | 43% | 24% | 33% |
| | | | Middling | 201.89 | 10% | 6% | 84% |
| | | | Tailing | 35.39 | 5% | 4% | 91% |
| | | Magnetic | Ferrous | 14.61 | 2% | 98% | 1% |
| | | Loss | | 109.27 | - | | |
| +0.6-0.3 | 193.02 | Shaking table | Concentrate | 54.31 | 40% | 24% | 36% |
| | | | Middling | 93.12 | 11% | 1% | 88% |
| | | | Tailing | 16.16 | 6% | 1% | 93% |
| | | Magnetic | Ferrous | 4.9 | 2% | 95% | 1% |
| | | Loss | | 17.42 | - | | |
| -0.3 | 309.78 | Electrostatic | Conductive | 42.6 | 81% | 9% | 9% |
| | | | Mix | 1.96 | 65% | 10% | 25% |
| | | | Non-conductive | 231.5 | 2% | 1% | 97% |
| | | Magnetic | Ferrous | 0.89 | 28% | 70% | 2% |
| | | Loss | | 32.83 | - | | |
| Other losses | | | | 215 | | | |

Analysing the results, it was also identified the relative composition of the materials for each particle size, reported in Table 23. It can be noticed; the average percentage composition of the sample differs from that previously hypothesized in paragraph 3.2 which reported an average composition of the PCB about 34% metals and 66% non-metallic. This is due to the fact that, the visual result shows this higher presence, the element content in each product is not pure. For example, in the coarser grains, there is a copper percentage of 33%, but surely the copper content of this product is not 100%. In contrast, for the finer fraction, the percentage of copper in the product, even being 15%, the purity is relatively higher due to the release of grains.

Table 23: Material percentage compositions by the size fraction. The weight is not included the losses. (Cu: Copper, Me: metals excluding Copper, NM: non-metallics)

| Class size [mm] | Weight [g] | Percentage of material | | |
|---|---|---|---|---|
| | | Cu | Me | NM |
| + 1.18 | 244.31 | 33% | 10% | 57% |
| 0.6-1.18 | 635.12 | 29% | 19% | 52% |
| 0.3-0.6 | 168.49 | 20% | 11% | 69% |
| 0 - 0.3 | 276.95 | 15% | 3% | 83% |

# CHAPTER 7

## 7. CONCLUSION

The recycling of PCBs is currently done through various techniques (mechanical-physical, chemical). It is important prior to perform the characterization of the material to be recycled in to choose the best procedure, in order to guarantee higher performance in the recovery of materials present in electronic waste. The diversity of metals present and the complexity of metal and non-metal associations implies difficulties for the development of treatment processes of WEEE.

According to the characterization performed, it can be confirmed that that scrap of printed circuit boards is an interesting secondary source of raw materials. It contains metals that may justify its use from an economic point of view, especially copper, since it can be recovered. In addition, the PCBs contain precious metals such as gold and silver, which despite being present in small concentrations can also be recovered. And due to the characteristics of electronic scraps, they have also a high potential environmental contamination.

Also, it is relevant to remark that PCB are rich in CRMs making them interesting resources for urban mining, and for some of them do not have specific treatments and larger research should be made in order to improve their recovery.

As an initial step, it is advantageous to perform a pre-processing of the boards, removing some components, reducing undesirable materials, to minimize wear on the comminution equipment. The physical-mechanical processing implies conventional processes: dismantling, fragmentation, and separation of the material in different granulometric classes.

The comminution step enabled the liberation of the metals embedded in board. The different mechanical behaviour, presented in the distinct elements, provided to the particles resulting from fragmentation, characteristics necessary for their subsequent separation.

Although the characterization of the products was carried out by a qualitative technique, the products in terms of the presence of metallic elements corresponded to efficient results.

The application of magnetic separation proved to be efficient, as it enabled the accumulation of iron in the magnetic fractions (85-99%) and it is possible to conclude that the largest amounts of iron are found in the large particle size fraction of the PCB.

In the separation by gravity, finest and coarsest classes fraction were excluded due to operational reasons and volumetric availability, respectively. The results show a good metal recovery, about 64% d for class + 0.6-0.3m and 67% for class + 1.18-0.6 mm.

The difference in electrical conductivity between metals and non-metals present in the PCB is an important condition to separate. The portion of conductive material (Cu) was 55% for the coarsest particle size fraction and 81% for the finest. This indicates the efficiency of the electrostatic separation, mainly concentrating this element, as well as the reduction size providing the liberation of this metal. For the purpose of obtaining pure copper in the coarsest fraction, it would be necessary to adopt complementary refining techniques, such as hydrometallurgy techniques.

Concerning about the influence of granulometry on the concentration of materials in the PCB, copper is concentrated in the larger granulometries. The lowest concentration (15%) was in the smallest particle size. For the other metallic materials, the highest concentrations are found in the intermediate fractions.

Non-metallic fractions (which contain polymers and ceramics) must be assessed separately to be properly disposed of or sent to the polymer and ceramic recycling processes.

This study enabled the acquisition of knowledge related to the physical-mechanical process treatment, as well as its application in the recovery of metals in PCBs, demonstrating that the processes used help the characterization of the material, and also increases the exposure of the metal, facilitating its refinement and further processing.

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