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Dismantling and copper recovery from Waste Printed Circuit Boards (WPCBs) using an integrated hydro-electrometallurgical approach

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“Science knows no country, because knowledge belongs to humanity,

and is the torch which illuminates the world”

-Louis Pasteur, chemist and microbiologist

Summary

The well-being of modern society greatly depends on knowledge and technology. The technology’s irrepressible march in parallel to the urbanization and industrialization of many developing countries are leading to growing diffusion of electrical and electronic equipment and consequently, of technological wastes.

Printed Circuit Boards (PCBs) are essential components in almost every electrical and electronic equipment. Usually, it contains hazardous substances as well as valuable materials; therefore, the development of recycling strategies is of paramount importance in order to convert PCBs waste from pollution source to valuable resource of secondary raw materials. PCB is a predominantly copper-rich material (up to 29% by weight), which makes the recovery of this metal a priority for recycling processes.

The first part of the PhD thesis provides an extensive literature review on Waste Printed Circuit Boards (WPCBs) recycling in order to highlight the main issues related to the existing technologies. The current processes to recover and recycle metals from WPCBs are either pyrometallurgical or hydrometallurgical with the consequent release of toxic gasses or high volumes of acid wastewaters. Besides, the heterogeneous materials present in PCBs lead to very complex recycling processes constituted by several unit operations. Therefore, the development of simple and environmentally acceptable recycling processes is of primary importance in a future perspective of sustainable developing.

In this PhD research, a novel method for copper recovering from WPCBs was investigated. Emphasis was given to electrochemical methods which have shown vast potential in terms of low energy consumption, low environmental impact, high output and simple flowsheet. In particular, an integrated hydro-electrometallurgical approach was used for recovering as much copper as possible from WPCBs.

The PhD work can be divided in two parts. The first one was devoted to dismantling of WPCBs by a hydrometallurgical route. An H_2SO_4-$CuSO_4$-NaCl solution of well-defined composition was used in the presence of blowing air for dissolving all solders and contacts that maintain electrical and electronic components connected to the board. An efficient components' detachment was achieved at low temperature without releasing toxic gases and damaging components, which can be easily recycled or sent to further treatment. The feasibility of electrochemical recovery of copper from the resulting solution was verified through a preliminary cyclic voltammetry study aimed at finding the optimum process parameters. After this, an electrochemical cell directly fed with the solution coming from WPCBs dismantling was employed for investigating the simultaneous copper deposition and leaching solution restoration. The results were highly encouraging because indicate the possibility to obtain pure copper operating in both galvanostatic and potentiostatic mode after the removal of the surface impurities by dipping in slightly acidified NaCl solution.

The second part of the research activity focuses on recovering copper from disassembled PCBs waste. According to the most recent innovations in the field of WPCBs recycling, the attention was directed towards the development of an entirely electrometallurgical method. In order to simplify the overall process, pieces of PCB were used instead of pulverized samples. The same PCB pieces resulting from the dismantling/leaching stage in H_2SO_4-$CuSO_4$-NaCl solution could be used in order to recover copper from both the PCB structure and oxidation of electronic components' contacts. The PCB pieces were directly used for a simultaneous electroleaching-electrodeposition process after the solder mask removal. The dissolution of solder mask by NaOH is fundamental to expose metallic copper to the electrolytic solution. Two different configurations of the electrochemical cell were investigated, both operating in galvanostatic mode.

Nomenclature

Acronyms and abbreviations

ATA	Advanced Technology Attachment
BFR	Brominated Flame Retardant
CFC	Chlorofluorocarbon
CMB	Computer motherboard
CPU	Central Processing Unit
CRT	Cathode Ray Tube
CV	Cyclic Voltammetry
D-sub	D-subminiature
ECs	Electronic Components
EDS	Energy Disperse Spectroscopy
EEE	Electric and Electronic Equipment
ENIG	Electroless Nickel Immersion Gold
EPA	Environmental Protection Agency
e-waste	Electronic waste
HASL	Hot Air Solder Leveling

IC	Integrated Circuit
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometer
LCA	Life Cycle Assessment
MW	Molecular Weight
NEMA	National Electrical Manufacturers Association
NHE	Normal Hydrogen Electrode
NOP	Nucleation overpotential
ORP	Oxidation-Reduction Potential
OSP	Organic Solderability Preservative
PAH	Polycyclic Aromatic Hydrocarbons
PBDDs	Polybrominated Dibenzodioxins
PBDE	Polybrominated Diphenyl Ether
PBDFs	Polybrominated Dibenzofurans
PCB	Printed Circuit Board
PCI	Peripheral Component Interconnect
PLC	Programmable Logic Controller
RAM	Random Access Memory

REE	Rare-Earth Element
RJD	Rivet Joint Devise
RoHS	Restriction of Hazardous Substances
SCE	Saturated Calomel Electrode
SEM	Scanning Electron Microscope
SJD	Screw Joint Devise
SMD	Surface Mounted Devise
SPD	Socket Pedestal Device
SWV	Square Wave Voltammetry
TBBA	Tetrabromobisphenol A
TBE	Tetrabromoethane
THD	Through-Hole Device
WEEE	Waste Electric and Electronic Equipment
WPCBs	Waste Printed Circuit Board
XRD	X-Ray Diffraction

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Chapter 1

Waste Printed Circuit Boards (WPCBs): from pollution to resource

Introduction

The fast and continuous growth of the electronic market has led to an improvement of the people’s lifestyle with the production of new goods that are always more accessible to everyone, but have shorter lifetime. This, in parallel to the urbanization and industrialization of many developing countries, is causing an increase of both technological waste volume and global demand of raw materials for their construction. This is a key problem in the light of the progressive natural resource depletion. According to the most reliable estimates, about 20-50 million tons of electronic wastes are produced globally every year, with consequent negative impact on both environment and humans, if are sent to landfill without proper recycling. The new challenge for the future is to shift the paradigm of e-waste from toxic pollution source to valuable resource in the context of circular economy and sustainable development.

The first section of the chapter intends to provide a definition and classification of e-waste, reporting also the global situation in matter of hi-tech wastes. The second section focuses on wastes of PCBs, which constitutes about 3-5% of the total e-waste generated. WPCBs will be presented, providing information about their composition determining the economic and environmental attractiveness which justifies the continuous research for their efficient management.

1.1 What is e-waste?

1.1.1 Definition, classification and legislation

There is not a standard definition for e-waste (electronic waste) or WEEE (Waste Electric and Electronic Equipment), generally, various types of EEE are included by the term. The European WEEE Directive 2012/19/EU provides the following definition: “*Electrical or electronic equipment which the holder discards or intends or is required to discard including all components, sub-assemblies and consumables, which are part of the product at the time of discarding*” **[1]**. The current e-waste comprises a particularly complex waste flow in terms of the variety of products. According to Directive 2012/19/EU, from 15 August 2018, e-waste is divided into the following six categories:

1. Temperature exchange equipment (e.g. refrigerators, freezers, air conditioners, heat pumps);
2. Screens, monitors, and equipment containing screens having a surface greater than 100 cm^2 (e.g. televisions, monitors, laptops, notebooks);
3. Lamps (e.g. fluorescent lamps, LED lamps);
4. Large equipment (any external dimension more than 50 cm) such as washing machines, clothes dryers, dish-washing machines, large printing machines and photovoltaic panels;
5. Small equipment (no external dimension more than 50 cm) such as ventilation equipment, microwaves, toasters, electric shavers, calculators, radio sets, video cameras, electrical and electronic toys, small electrical and electronic tools, small medical devices, small monitoring and control instruments;

6. Small IT and telecommunication equipment (no external dimension more than 50 cm) such as mobile phones, GPS, pocket calculators, routers, personal computers, printers, telephones.

The European Directive 2012/19/EU, which replaced the previous 2002/96/EU and 2003/108/EU **[2, 3]**, represents the only notable example of specific and clear legislation on WEEE recycling around the world. Except for Europe, the others countries seem to be slow in initiating and adopting WEEE regulations. Currently, only 66% of the world population is covered by national e-waste management laws that, however, represents an increase compared to 44% estimated in 2014 (Figure 1.1.1.1). This considerable increase was mainly due to India, where legislation was adopted in 2016. It is important to note that many countries with national WEEE legislation do not always enforce the law or do not have measurable collection and recycling targets that are essential for effective policies **[4]**. This is a serious problem because e-waste contains toxic substances as well as valuable materials so that its management is relevant both in terms of wastefulness of resources and environmental impact.

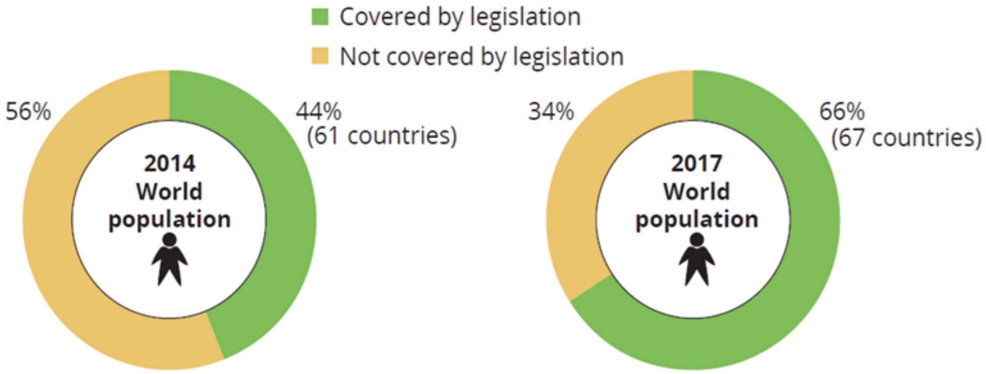


Figure 1.1.1.1 World population (and number of countries) covered by e-waste legislation in 2014 and 2017 [4]

In this regard, European WEEE Directive aims primarily to prevent the generation of WEEE and secondly, to promote reuse, recycling and other forms of recovery of WEEE in order to reduce the disposal of wastes and to contribute to the efficient use of the resources and recovery of valuable secondary raw materials. This principle is often identified as that of the “3 Rs”, referring to Reduce, Reuse and Recycle. The directive also seeks to promote the design and production of EEE in the perspective of reducing the use of hazardous substances and facilitating re-use, dismantling and recovery of WEEE. Indeed, it is strictly connected with RoHS (*Restriction of Hazardous Substances*) regulation, also known as Directive 2002/95/EU **[5]**, which restricts the use of six hazardous materials in the production of electrical and electronic equipment, including lead, mercury, cadmium, hexavalent chromium, polybrominated diphenyl ethers and polybrominated biphenyls **[6-7]**.

In addition to take action upstream of the problem, the directive imposes also some minimum collection rates. In particular, starting from 2019, each Member State of UE will have to ensure the achievement of a minimum annual collection rate equal to 65% of the average weight of EEE placed on the market in the three preceding years in the Member State concerned, or alternatively 85% of WEEE generated on the territory of that Member State. Several countries around the world have followed the good example of Europe but certainly not with the same effort.

1.1.2 Composition

In terms of composition, e-waste can be defined as a mixture of various metals with various types of plastics and ceramics. The composition depends strongly on several factors such as the type of electronic device, the model, manufacturer, date of manufacture, and the age of the scrap **[7-9].** For instance, scraps from IT (Information Technology) and telecommunication systems contain a higher amount of precious metals than scraps from household appliances **[7, 10].** Besides, old WEEEs have more value because concentration of nonferrous metals and precious metals has gradually decreased over the years in EEE.

Metals in e-waste can be grouped into *precious metals* such as Au and Ag; *platinum group metals* such as Pd and Pt; *base metals* such as Cu, Fe, Zn, Al and

Ni; *metals of concern* such as Hg, Be, Pb, Cd and As; and *scarce metals* such as Te, Ga, Se, Ta and Ge **[11]**. The percentage of plastic contained in WEEE is around 10-30 % and may include more than 15 different polymers, mainly polystyrene, acrylonitrile-butadiene-styrene, polycarbonate blends, high-impact polystyrene and polypropylene **[12]**. In the case of the small WEEE, may be present 21 different types of polymers. Figure 1.1.2.1 shows the typical fraction of materials generally found in a WEEE.

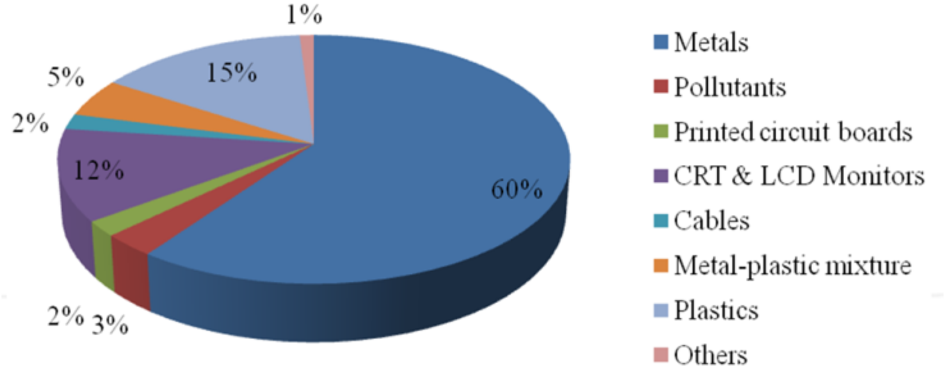
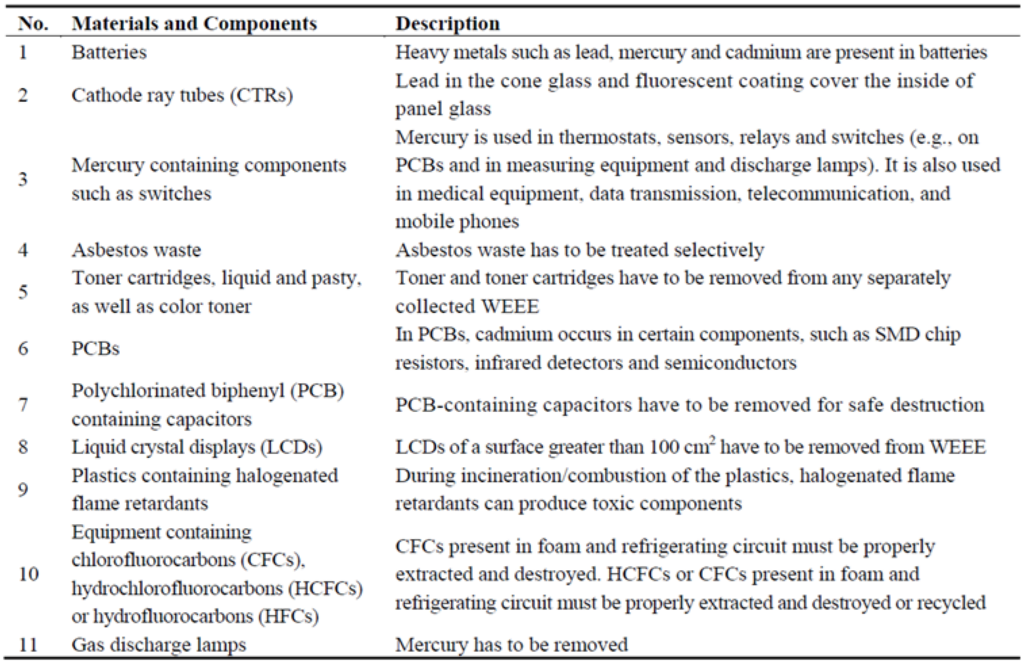


Figure 1.1.2.1 Material fraction in a WEEE [4]

This large variety of composition makes WEEE a possible source of secondary raw materials. A mobile phone can contain more than 40 different elements. The main recovery attractiveness comes from precious and base metals. It is important to note that some materials such as gold and copper can be mined more effectively from e-waste compared to mining from ore. Copper and gold content in WEEE is 13-26 and 35-50 times more concentrated than in their ores, respectively **[7]**.

By contrast, e-waste contains various hazardous material such as heavy metals and brominated flame retardants (BFRs) including polybrominated diphenyl ethers (PBDEs) and tetrabromobisphenol A (TBBA) **[6, 12-13]**. Soil, water and air around e-waste processing sites are 100 times more contaminated by PBDEs, heavy metals and polycyclic aromatic hydrocarbons (PAHs) than other places **[14]**. Thanks to the new emerging regulations on e-waste subject, future electronic wastes are expected to contain significantly lower amount of hazardous materials. However, to date the market has not still detected a reliable replacement for halogenated flame retardants. In Table 1.1.2.1, some of the major hazardous components found in WEEE are shown. Obsolete freezers, air conditioners, refrigerators contain ozone depleting chlorofluorocarbons (CFCs). Circuit boards found in most of the electronic devices may contain arsenic, cadmium, chromium, mercury, lead, and other toxic chemicals. A typical printed circuit board contains approximately 50 g of tin-lead solder per square meter **[15]**. The cathode ray tubes (CRTs) widely used as a video display component of both old televisions and computers contain great amounts of lead **[4, 12]**.



No.	Materials and Components	Description
1	Batteries	Heavy metals such as lead, mercury and cadmium are present in batteries
2	Cathode ray tubes (CTRs)	Lead in the cone glass and fluorescent coating cover the inside of panel glass
3	Mercury containing components such as switches	Mercury is used in thermostats, sensors, relays and switches (e.g., on PCBs and in measuring equipment and discharge lamps). It is also used in medical equipment, data transmission, telecommunication, and mobile phones
4	Asbestos waste	Asbestos waste has to be treated selectively
5	Toner cartridges, liquid and pasty, as well as color toner	Toner and toner cartridges have to be removed from any separately collected WEEE
6	PCBs	In PCBs, cadmium occurs in certain components, such as SMD chip resistors, infrared detectors and semiconductors
7	Polychlorinated biphenyl (PCB) containing capacitors	PCB-containing capacitors have to be removed for safe destruction
8	Liquid crystal displays (LCDs)	LCDs of a surface greater than 100 cm^2 have to be removed from WEEE
9	Plastics containing halogenated flame retardants	During incineration/combustion of the plastics, halogenated flame retardants can produce toxic components
10	Equipment containing chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) or hydrofluorocarbons (HFCs)	CFCs present in foam and refrigerating circuit must be properly extracted and destroyed. HCFCs or CFCs present in foam and refrigerating circuit must be properly extracted and destroyed or recycled
11	Gas discharge lamps	Mercury has to be removed

Table 1.1.2.1 Major hazardous components and materials in WEEE [11]

1.1.3 Global status and trends

The relevance of the WEEE problem is strictly connected to the amount of hi-tech wastes globally generated. In Figure 1.1.3.1 the trend in the production of WEEE is reported. Estimations say that the quantity of e-waste generated in 2016 was around 44.7 million metric tonnes (Mt), or 6.1 kg per inhabitant, which is the equivalent of almost 4.500 Eiffel Towers. The quantity is expected to grow to 52.2 Mt in 2021, with an annual growth rate of 3 to 4%. In 2016, Asia was the first producer of e-waste (18,2 Mt), followed by Europe (12,3 Mt), America (11,3 Mt), Africa (2,2 Mt) and Oceania (0,7 Mt) **[4]**. Europe is the second largest producer; but has the highest collection rate (35%). America collects only 17% that is comparable to the collection rate in Asia (15%). The low collection rate compared to the total amount of e-waste generated is partly due to the absence of official e-waste statistics in many countries. In particular, only the 20% of 44.7 Mt of wastes produced in 2016 is documented to be properly collected and recycled, whereas the majority (76%) is untraced and unreported; the remaining 4% (1.7 Mt) ends up in waste bins from the richest countries without being differentiated.

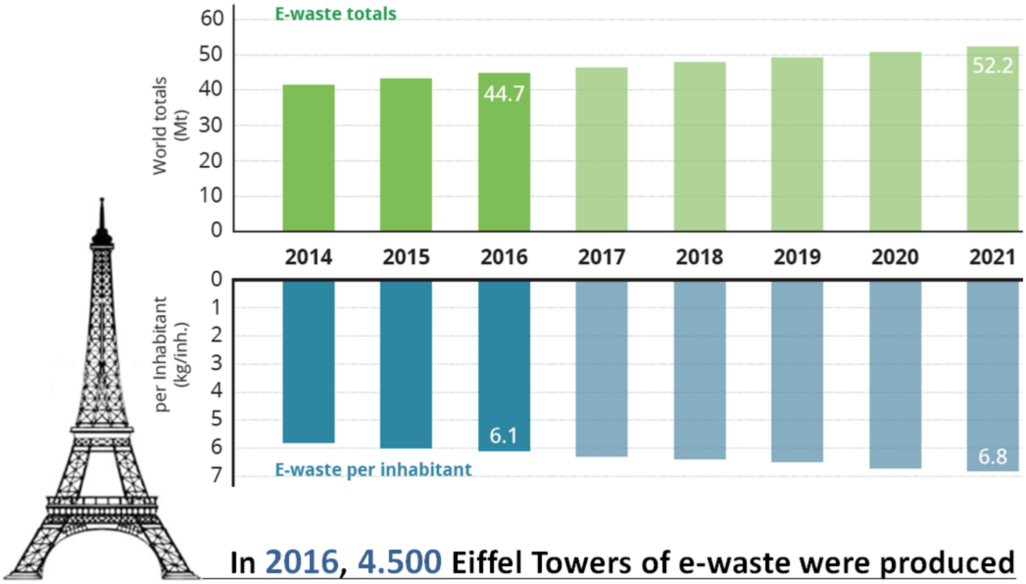


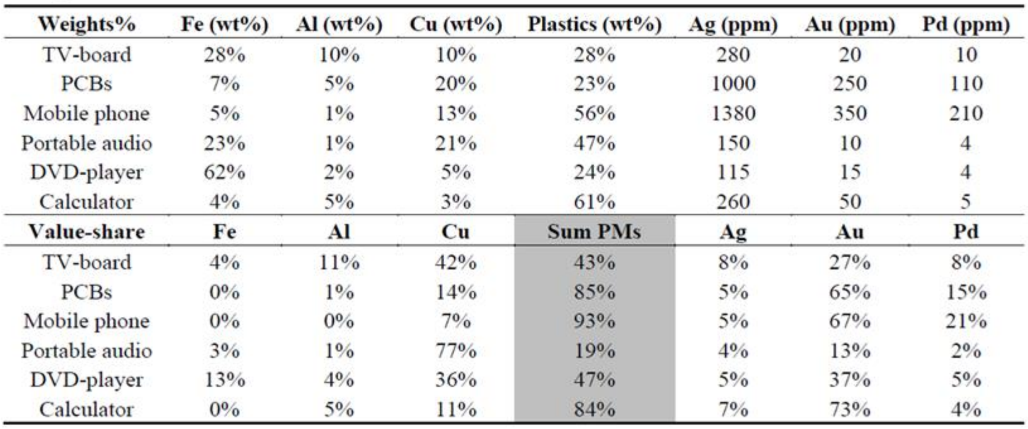
Figure 1.1.3.1 Global e-waste generated (note: 2017-2021 are estimates) [4]

E-waste generated in developed countries is often exported for recycling in developing countries, especially in China, India, and Pakistan, where labor is relatively cheap and the lack of national regulations permits the treatment of e-waste with rudimental methods such as open burning. Incineration of WEEE leads to the release of toxic substances such as polybrominated dibenzo-dioxins (PBBD) and polybrominated dibenzo-furans (PBDF) coming from flame retardants **[15-17]**. Traditionally, e-waste is disposed in landfills or incinerated. It was estimated that emissions from waste incineration produce 36 metric tonnes per year of Hg and 16 metric tonnes per year of Cd in EU **[8]**.

Therefore, a correct e-waste management is of primary importance to protect the environment and human health, also because e-waste recycling has the potential to become an attractive business.

1.1.4 Intrinsic value

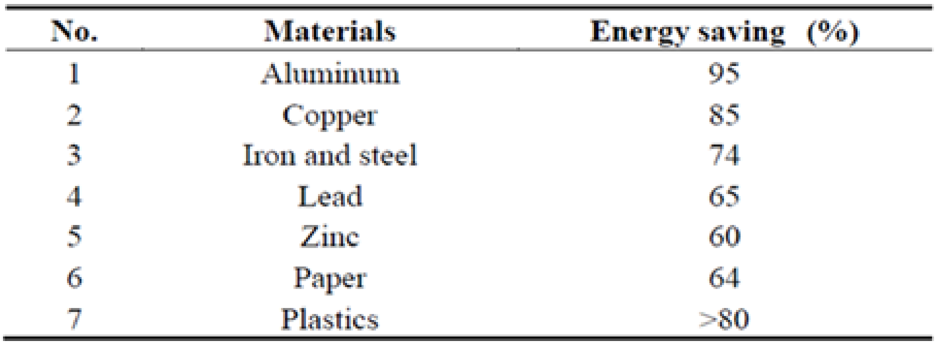
The value of the raw materials present in e-waste globally produced in 2016 was estimated at approximately 55 billion Euros, which is more than the 2016 Gross Domestic Product of most countries in the world **[4]**. The recovery of precious and base metals represents the main economic drive toward recycling of e-waste owing to their associated value. As it can be seen in Table 1.1.4.1, copper is the highest value metal in all types of e-scrap, after precious metals.



Weights%	Fe (wt%)	Al (wt%)	Cu (wt%)	Plastics (wt%)	Ag (ppm)	Au (ppm)	Pd (ppm)
TV-board	28%	10%	10%	28%	280	20	10
PCBs	7%	5%	20%	23%	1000	250	110
Mobile phone	5%	1%	13%	56%	1380	350	210
Portable audio	23%	1%	21%	47%	150	10	4
DVD-player	62%	2%	5%	24%	115	15	4
Calculator	4%	5%	3%	61%	260	50	5
Value-share	**Fe**	**Al**	**Cu**	**Sum PMs**	**Ag**	**Au**	**Pd**
TV-board	4%	11%	42%	43%	8%	27%	8%
PCBs	0%	1%	14%	85%	5%	65%	15%
Mobile phone	0%	0%	7%	93%	5%	67%	21%
Portable audio	3%	1%	77%	19%	4%	13%	2%
DVD-player	13%	4%	36%	47%	5%	37%	5%
Calculator	0%	5%	11%	84%	7%	73%	4%

Table 1.1.4.1 Weight vs value distribution [11] (note: metals prices from which value-share of each metal was calculated are related to 2006)

According to the data supplied by U.S Environmental Protection Agency (EPA), a significant energy saving results from using recycled materials than virgin materials. Energy saving for some of the most common materials is shown in Table 1.1.4.2.



No.	Materials	Energy saving (%)
1	Aluminum	95
2	Copper	85
3	Iron and steel	74
4	Lead	65
5	Zinc	60
6	Paper	64
7	Plastics	>80

Table 1.1.4.2 Recycled materials energy saving over virgin materials [11]

The circular economy concept could offer huge economic and employment opportunities. All countries would have to adopt strategies to sensitize people to the important of e-waste management, for example disclosing data and statistics showing the environmental and economic benefits resulting from a better management of such wastes.

1.1.5 Italian scenario

Legislation in Italy is harmonized with European Directive 2012/19/EU, which increases the responsibility of producers that would have to finance the collection from collection facilities of the waste from their own products at least, and also their treatment, recovery and disposal. 4.107 municipal collection centers for household WEEE were operative in Italy during 2016. Each collection center was member of the WEEE Coordination Centre **[18]**. The total quantity of WEEE collected in 2016 was 283.075 tons, 13,5% higher than in 2015 **[18]**. The highest collection rate was reached in the northern regions. Despite the positive data, the percentage of collection estimated at about 40% is not still enough to attain the

European target of 45% of EEE placed on market in the period 2016-2018 **[19]**. However, the correct management of WEEE has led to many social and environmental benefits. It has been estimated that 110-120 million Euros were saved in 2015 for the purchase of raw materials due to the recovery of materials from WEEE. The emissions of climate-altering gases avoided in the same year were estimated at 1.1 million tons of CO_2 equivalent **[19]**. These values could significantly increase if the targets imposed by WEEE European Directive will be achieved.

It can be concluded that an efficient management of e-waste, in addition to lead economic benefits, can also contribute to i) decrease volume of generated wastes; ii) decrease consume of natural resources; iii) preserve environment and human health.

1.2 WPCBs: a challenge for the future

1.2.1 Global status and trends in WPCBs production

Great relevance in terms of economic and environmental impact have the wastes coming from Printed Circuit Boards (PCBs). Practically, all electronic devices contain printed circuit boards as basic building block.

A PCB mechanically supports and electrically connects through conductive tracks all electrical and electronic components mounted on the board such as integrated circuit, capacitors, resistors, inductors, relays, etc. PCBs represent approximately 3% by weight of the mass of WEEE generated globally **[6, 14, 20]**.

Figure 1.2.1.1 shows the trend of the PCB industries' investments in millions of US$. The continuous growth in PCBs production, which is strictly connected with the growth of electronic market, will lead to enormous generation of waste PCBs.

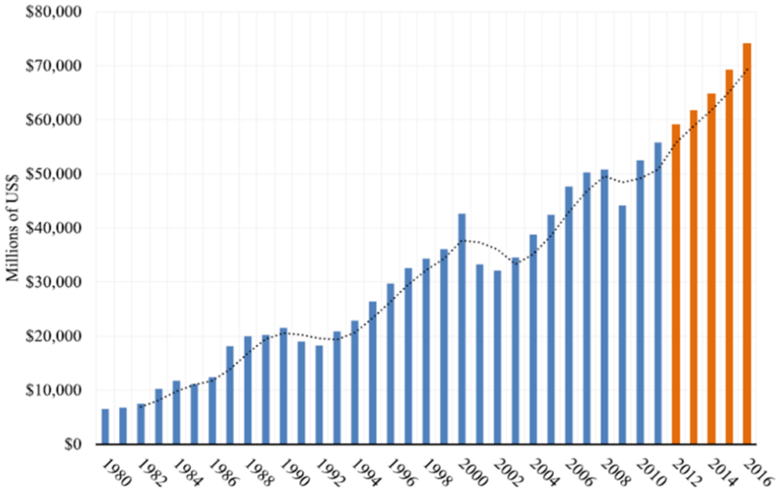


Figure 1.2.1.1 Trends in global PCB production in millions of $US (note: the period 2012-2016 is a forecast) [14]

As it can be seen in Figure 1.2.1.2, China is leader in PCB production reaching almost half of the total PCB market, followed by South Korea and Taiwan **[21]**. These countries, in addition to be the main producers, have also become the final destination for illegal e-waste traffic. About 12,75 millions of personal computers were thrown away in the US in 2012, about 10,2 millions of these were exported to either China or others Asian countries **[22]**. In China, like in other developing countries, many cities have been transformed into open air dumps.

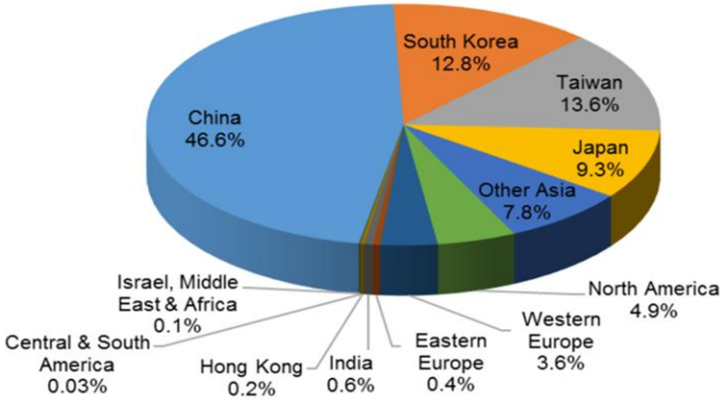


Figure 1.2.1.2 PCB production by major producing countries and regions in 2015 reported by WECC-Member Associations [21]

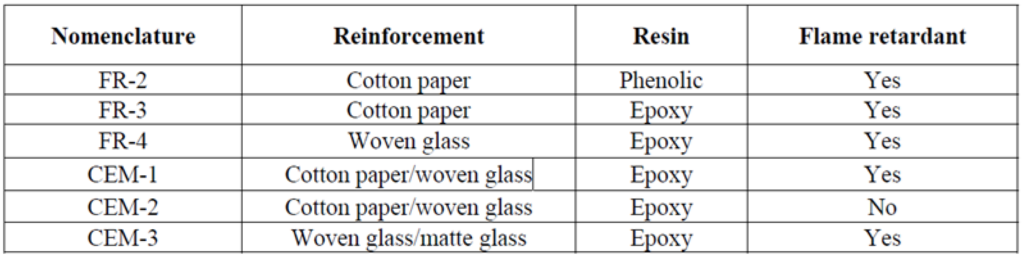
1.2.2 Characterization of WPCBs: structure and composition

All PCBs essentially consist of three parts:

- A non-conducting substrate or laminate;
- Conducting substrate printed on or inside the laminate;
- Components mounted to the substrate.

PCBs have to guarantee excellent mechanical, electrical and thermal properties. The non-conducting substrate provides mechanical properties. FR-4 is the most common substrate used for computers and communication equipment, while FR-2 is predominantly used for home electronic and television **[13]**. FR is the acronym for "Flame Retardants" and indicates some chemicals which are added either to prevent fire onset or to slow its propagation.

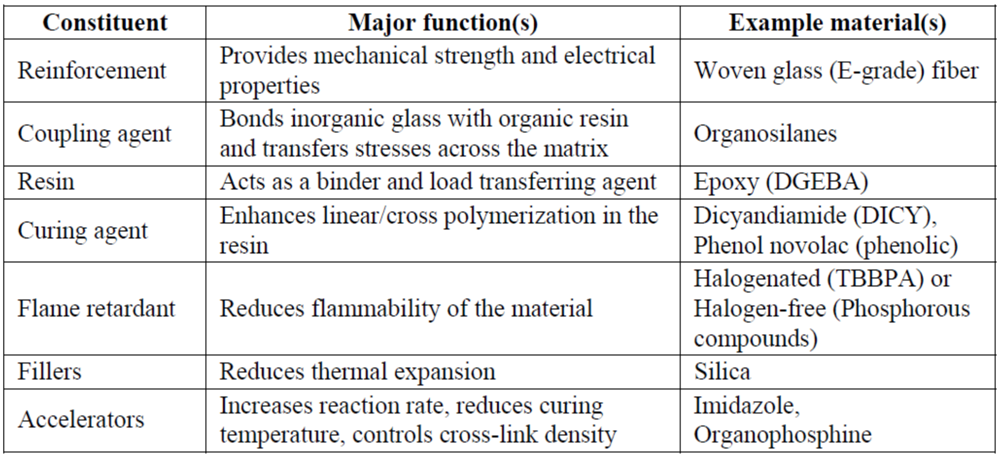
FR-2 is a composite material made of paper impregnated with a plasticized phenol formaldehyde resin, while FR-4 is a composite material composed of woven fiberglass cloth impregnated with an epoxy resin. Some of the common types of substrate are shown in Table 1.2.2.1. The nomenclature for each type of material is given by the National Electrical Manufacturers Association (NEMA), in Virginia, USA **[23]**.



Nomenclature	Reinforcement	Resin	Flame retardant
FR-2	Cotton paper	Phenolic	Yes
FR-3	Cotton paper	Epoxy	Yes
FR-4	Woven glass	Epoxy	Yes
CEM-1	Cotton paper/woven glass	Epoxy	Yes
CEM-2	Cotton paper/woven glass	Epoxy	No
CEM-3	Woven glass/matte glass	Epoxy	Yes

Table 1.2.2.1 Some of the common types of substrate used for PCBs construction [23]

Today, high-value devices contain preferentially FR4 substrate due to the high thermal resistance and negligible water absorption. For higher temperatures resistances, other resins such as polyimides, cyanates, PTFE, epoxy-PPE blends, and even ceramics are often used. Some additives such as curing agents, flame retardants, fillers, and accelerators are added to the resin to improve the performance of laminate. The typical constituents of a FR-4 laminate are reported in Table 1.2.2.2.



Constituent	Major function(s)	Example material(s)
Reinforcement	Provides mechanical strength and electrical properties	Woven glass (E-grade) fiber
Coupling agent	Bonds inorganic glass with organic resin and transfers stresses across the matrix	Organosilanes
Resin	Acts as a binder and load transferring agent	Epoxy (DGEBA)
Curing agent	Enhances linear/cross polymerization in the resin	Dicyandiamide (DICY), Phenol novolac (phenolic)
Flame retardant	Reduces flammability of the material	Halogenated (TBBPA) or Halogen-free (Phosphorous compounds)
Fillers	Reduces thermal expansion	Silica
Accelerators	Increases reaction rate, reduces curing temperature, controls cross-link density	Imidazole, Organophosphine

Table 1.2.2.2 Typical constituents of FR-4 laminate [23]

Bromine-based flame retardants are traditionally used to reduce the flammability of the laminate, which can ignite either during soldering of the components on the platform or as result of electric energy impacts **[13, 24]**. TBBPA is the most commonly used halogenated flame retardant for epoxy resin. Although halogenated FRs are still predominant, halogen-free FRs are gaining importance owing to the new environmental legislations such as RoHS Directive **[6, 13, 25]**. Nitrogen or phosphorous-based compounds (e.g. organophosphate esters) and metal hydroxides (e.g. aluminum hydroxide and magnesium hydroxide) are some of the most used halogen-free flame retardants **[23].**

In addition to the nature of the substrate, PCBs can be classified as single-sided, double-sided and multi-layer in dependence on the numbers of conductive layers.

Single-sided PCBs are the most basic type of PCB. Accordingly, they are cheap and well suited to simple and high volume products. Single-sided PCBs are constituted by only one conductive copper layer placed on one side of the substrate (*core*). Above the copper layer, which provides conducting path for the various components on the board, a solder mask layer is present in order to protect the board against environmental damage and solder shorts (also known as *solder bridges*), which take place when two or more pins become connected through an excessive application of solder, as in Figure 1.2.2.1. Finally, a silkscreen layer lies on the top of solder mask for adding information such as company logos, serial numbers, or helpful instructions in assembling, testing, and servicing the circuit board. Single-sided PCBs are the ideal choice for low density design.

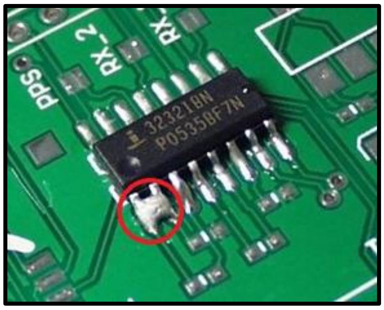


Figure 1.2.2.1 A close up of a solder bridge formed between two of the pins on an integrated circuit

Double-sided PCB, is a type of PCB which has conductive copper layers on both sides of the substrate (*core*). Figure 1.2.2.2 shows a schematization of a double-sided PCB.

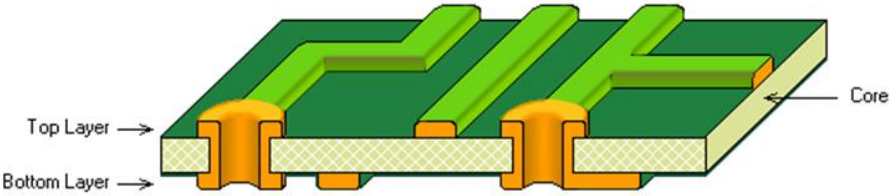


Figure 1.2.2.2 Structure of a double-sided PCB with plated through holes

The layers are electrically connected by holes drilled on the board and made conductive by electroplating. A solder mask lies above the two copper layers and a silkscreen above solder mask on both side of the board. Double-sided PCBs feature moderate level of complexity, allowing higher circuit density than single-sided PCBs and lower costs than multilayer PCBs.

Multi-layer PCBs are developed by incorporating more double-sided PCBs together using an insulating material (*pre-peg*) as a binder. Figure 1.2.2.3 shows the structure of a multilayer PCB. Core and pre-peg layers are made by the same materials but pre-peg is not fully cured, which makes it more malleable and flexible than the core. In order to fabricate a multilayer PCB, alternating layers are stacked and pressed at high temperature to remove any air bubble trapped between the layers. Often two layers work as power supply and ground planes, while the other ones are used for signal wiring between components. Sometimes, more layers than one are used for both power and ground planes, especially if the different components on the PCB require different supply voltages. In a multi-layer PCB, the number of conductive layers is generally between 4 and 8 but some applications can require a greater number. For instance, some smartphones are equipped with 12 layer PCBs.

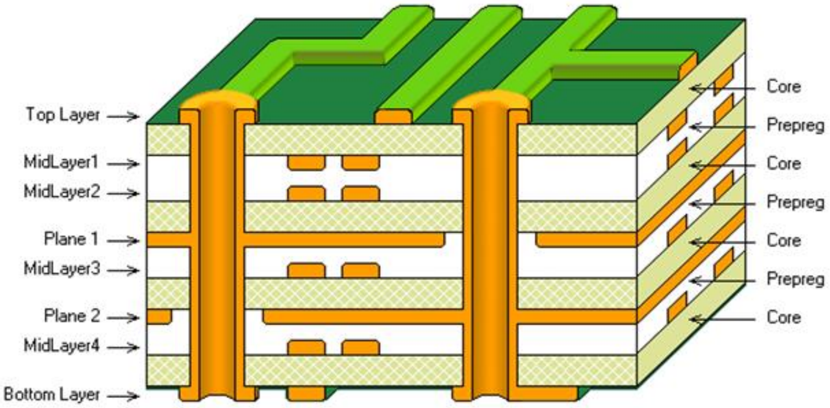


Figure 1.2.2.3 Structure of a multi-layer PCB

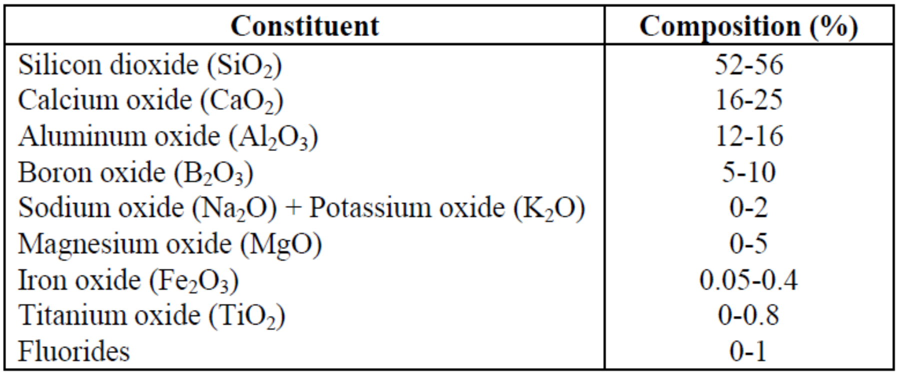
The placing on the market of multi-layer PCBs allowed the miniaturization of the circuits and consequently that of many electronic devices such as smartphones and computers. However, multilayer PCB requires higher manufacturing costs and time than single layer or double layer PCB.

Electronic components are mounted on PCBs through various types of connections. The most common are THD (Through-Hole Device) and SMD (Surface Mounted Device). By *through-hole* technology, component pins are inserted into holes drilled on PCB and are fixed on the opposite side with a molten metal solder, while the components are soldered directly on the outer surface of PCB when *surface-mount* technology is used (see Figure 1.2.2.1). Usually, the soldering paste is a Sn-Pb alloy, but new solder compounds are now used according to the EU Directive RoHS, which restricts the use of lead. Common lead-free solders contain a high proportion of tin (often greater than 90% of the total metal content), while the remaining content is mainly a mixture of silver and/or copper **[23, 26-29]**. Although Sn-Ag-Cu alloy probably offers the best alternative to lead-based solders, other tin-based alloys containing antimony, bismuth and zinc have also been developed and are preferred by different industries **[28]**. Besides, a fully lead-free electronic assembly requires also a lead-free finish, therefore new surface finishes have been introduced in PCB manufacturing including OSP (Organic Solderability Preservative), immersion silver, Lead-free HASL (Hot Air Solder Leveling) and ENIG (Electroless Nickel Immersion Gold) **[27-29]**. One of the main limitations of lead-free solder is certainly its higher melting point (around 220°C) than lead-based solder (around 180°C), which can require more thermal resistant laminates and other precautions **[23]**.

Although composition of PCB depends on the age, type and manufacturer, it can be said that typically PCBs contain 40% of metals, 30% of organics and 30% of ceramics **[11, 14, 20, 30].**

Ceramic fraction, which mainly comes from the reinforcing material used for PCB substrate, is constituted by silica, alumina, alkali and alkaline earth-oxides, and small amounts of other mixed oxides such as barium titanate **[14, 30]**. As an example, in Table 1.2.2.3 is reported a typical composition of woven glass fiber cloth used in FR-4 laminates **[23]**.

Plastic fraction mainly consists of polymers such as polyethylene, polypropylene, polyesters, polycarbonates, phenols, epoxies, formaldehyde, etc., whereas the rest of the plastics are mainly halogenated and nitrogen-containing polymers **[14, 30]**.



Constituent	Composition (%)
Silicon dioxide (SiO_2)	52-56
Calcium oxide (CaO_2)	16-25
Aluminum oxide (Al_2O_3)	12-16
Boron oxide (B_2O_3)	5-10
Sodium oxide (Na_2O) + Potassium oxide (K_2O)	0-2
Magnesium oxide (MgO)	0-5
Iron oxide (Fe_2O_3)	0.05-0.4
Titanium oxide (TiO_2)	0-0.8
Fluorides	0-1

Table 1.2.2.3 Typical constituents of woven glass (E-glass) fiber cloth used in FR-4 laminates [23]

Finally, the metallic fraction in PCB is constituted by many different elements covering great part of the periodic table. It is reported that there are up to 60 kinds of elements contained in WPCBs **[31],** some of which are summarized in Figure 1.2.2.4 and classified as normal, precious, heavy, rare-earth metals and non-metals. As shown in the figure, there are more than 40 kinds of metals in WPCBs.

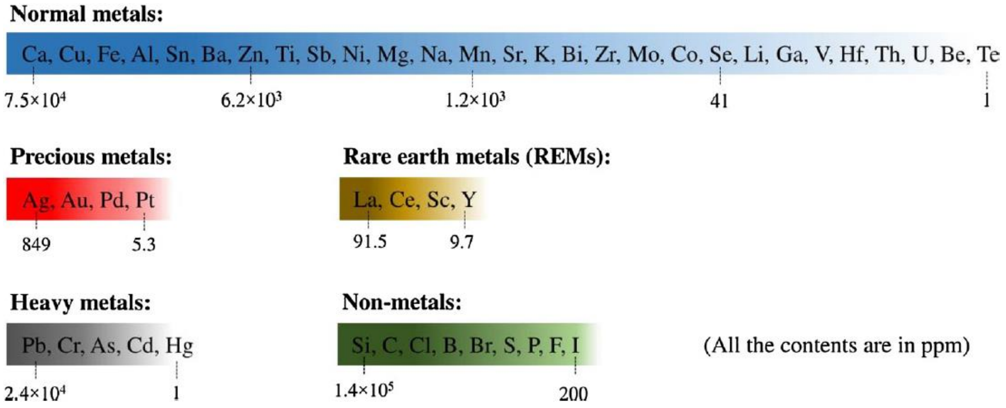
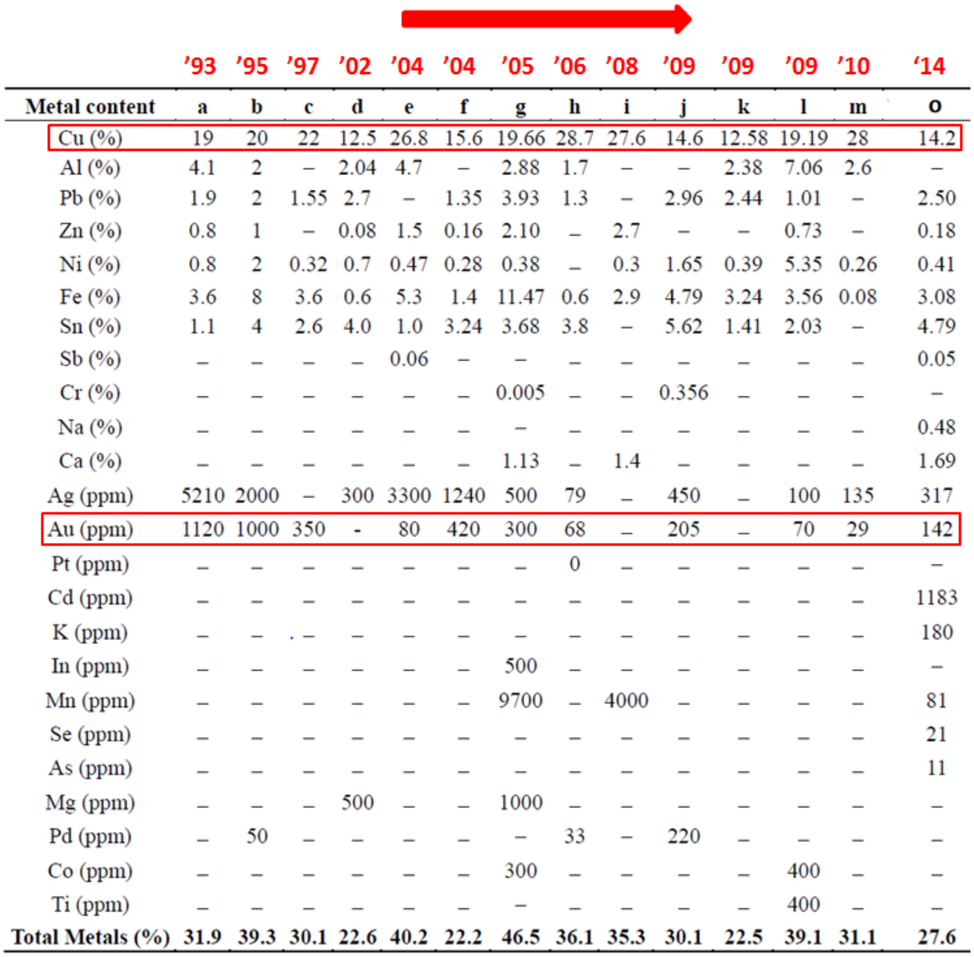


Figure 1.2.2.4 Content of elements in WPCBs [31]

The metallic content of the PCB is different according to different authors because it depends on several factors, such as age, type and manufacturer **[7, 8, 11, 13, 32-47]**. Table 1.2.2.4 shows the PCBs' chemical composition reported by different authors.



	'93	'95	'97	'02	'04	'04	'05	'06	'08	'09	'09	'09	'10	'14
Metal content	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**	**j**	**k**	**l**	**m**	**o**
Cu (%)	19	20	22	12.5	26.8	15.6	19.66	28.7	27.6	14.6	12.58	19.19	28	14.2
Al (%)	4.1	2	–	2.04	4.7	–	2.88	1.7	–	–	2.38	7.06	2.6	–
Pb (%)	1.9	2	1.55	2.7	–	1.35	3.93	1.3	–	2.96	2.44	1.01	–	2.50
Zn (%)	0.8	1	–	0.08	1.5	0.16	2.10	–	2.7	–	–	0.73	–	0.18
Ni (%)	0.8	2	0.32	0.7	0.47	0.28	0.38	–	0.3	1.65	0.39	5.35	0.26	0.41
Fe (%)	3.6	8	3.6	0.6	5.3	1.4	11.47	0.6	2.9	4.79	3.24	3.56	0.08	3.08
Sn (%)	1.1	4	2.6	4.0	1.0	3.24	3.68	3.8	–	5.62	1.41	2.03	–	4.79
Sb (%)	–	–	–	–	0.06	–	–	–	–	–	–	–	–	0.05
Cr (%)	–	–	–	–	–	–	0.005	–	–	0.356	–	–	–	–
Na (%)	–	–	–	–	–	–	–	–	–	–	–	–	–	0.48
Ca (%)	–	–	–	–	–	–	1.13	–	1.4	–	–	–	–	1.69
Ag (ppm)	5210	2000	–	300	3300	1240	500	79	–	450	–	100	135	317
Au (ppm)	1120	1000	350	-	80	420	300	68	–	205	–	70	29	142
Pt (ppm)	–	–	–	–	–	–	–	0	–	–	–	–	–	–
Cd (ppm)	–	–	–	–	–	–	–	–	–	–	–	–	–	1183
K (ppm)	–	–	–	–	–	–	–	–	–	–	–	–	–	180
In (ppm)	–	–	–	–	–	–	500	–	–	–	–	–	–	–
Mn (ppm)	–	–	–	–	–	–	9700	–	4000	–	–	–	–	81
Se (ppm)	–	–	–	–	–	–	–	–	–	–	–	–	–	21
As (ppm)	–	–	–	–	–	–	–	–	–	–	–	–	–	11
Mg (ppm)	–	–	–	500	–	–	1000	–	–	–	–	–	–	–
Pd (ppm)	–	50	–	–	–	–	–	33	–	220	–	–	–	–
Co (ppm)	–	–	–	–	–	–	300	–	–	–	–	400	–	–
Ti (ppm)	–	–	–	–	–	–	–	–	–	–	–	400	–	–
Total Metals (%)	**31.9**	**39.3**	**30.1**	**22.6**	**40.2**	**22.2**	**46.5**	**36.1**	**35.3**	**30.1**	**22.5**	**39.1**	**31.1**	**27.6**

Table 1.2.2.4 Chemical composition of PCBs (components included) reported by different authors: a) Feldam et al. [35], b) Menetti et al. [36], c) Iji et al. [37], d) Veit et al. [38], e) Zhao et al. [39], f) Kim et al. [40], g) Wang et al. [41], h) Creamer et al. [42]; i) Marco et al. [43], j) Hino et al. [44], k) Das et al. [45], l) Yoo et al. [46], m) Oliveira et al. [47], o) Bizzo et al. [32]

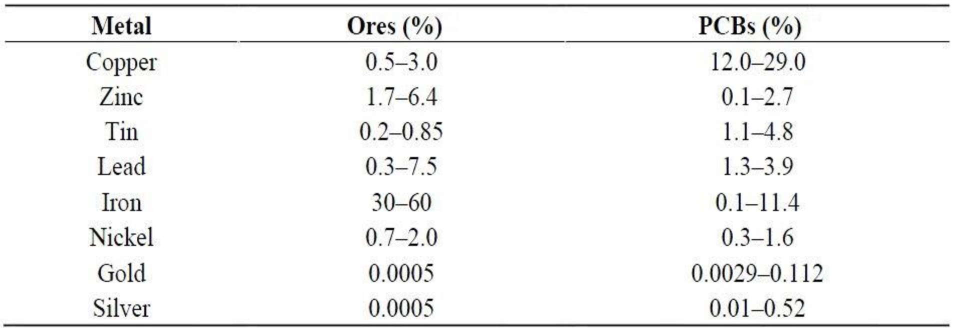
It can be observed that copper is the metal present at higher concentration, because it forms the conductive layer for electrical connection between the components. Abundant amounts of other base metals such as Fe, Al, Pb and Sn are also present. In particular, great attention must be turned to lead that belongs to the category of hazardous compounds and it is present in almost all data reported by the different authors without evident reduction of its concentration over time. However, elsewhere **[48]** it is reported that Pb concentration in WPCBs was two orders of magnitude higher before 2005 than in the period 2005–2009. Other toxic metals such as Cd, As, Cr and Sb are present in PCBs. Antimony trioxide, which may be present with polymers as a flame retardant, is suspected to be carcinogenic **[14]**. Cadmium is toxic at very low exposure levels and has acute and chronic effects on health and environment. Once Cd enters into the body causes multi-system and multi-organ injury **[14]**. Elevated levels of Cr in umbilical cord blood in infants owing to mother's exposure to e-waste recycling are correlated with DNA damage **[14, 49]**.

Precious metals are also present, mainly gold and silver. However, it is important to note that their content has fallen in recent years (see Table 1.2.2.4). Gold concentration is decreased of two orders of magnitude from 1993 to 2010. Gold is mainly used as a finish material for electric contacts. Cui et al. **[20]** reported that contact layer thickness in the ’80 was in the region of 1-1.25 µm interval, while in modern appliances it is between 300 and 600 nm. Contrarily, copper content remained constant over the years between 12% and 29% by weight because to date, it does not exist a metal having the same electrical properties at the same price of copper.

Platinum group metals, rare and rare-earth metals are prevalently contained in electronic components mounted on PCBs. The platinum group metals are present in relays, switches or in sensors; tantalum in capacitors; indium and gallium in transistors; cobalt in batteries and steel alloys; etc. Besides, small amounts of rare-earth elements (REEs) such as La, Eu, Nd and Ce can be contained in capacitors, integrated circuits, resistors, transistors, LEDs, switches etc. **[50]**. However, the extraction of REEs from WPCBs was generally considered to be economically unviable due to their low content in the PCBs.

1.2.3 Intrinsic value of WPCBs

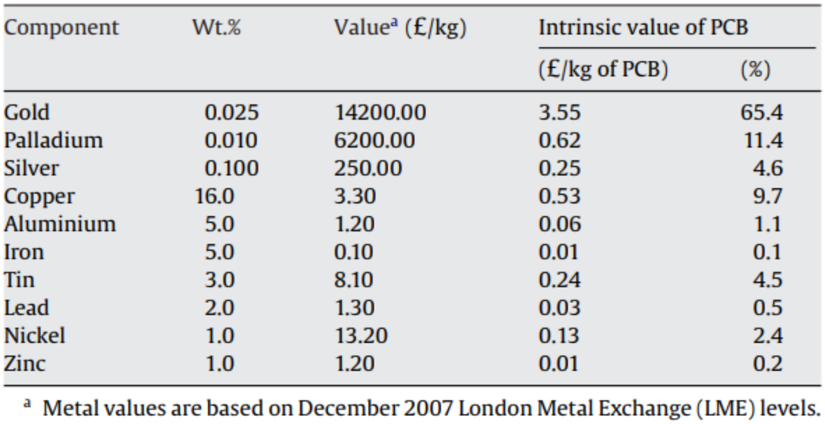
The intrinsic value of PCBs certainly increases considering that some metals are found in discarded PCBs in concentrations higher or equal to those found in natural deposits. Indeed, WPCBs have been defined as "urban mine". Table 1.2.3.1 shows the amounts of various metals found in nature as mineral deposits and the content of the same metals in PCBs **[30]**. The content of some valuable metals such as copper, tin, gold and silver is much higher in PCBs than in their respective ores/concentrates. This comparison justifies the growing importance of WPCBs as a possible source of secondary raw materials and the economic incentive to develop processes aimed to recover metals from discarded PCBs.



Metal	Ores (%)	PCBs (%)
Copper	0.5–3.0	12.0–29.0
Zinc	1.7–6.4	0.1–2.7
Tin	0.2–0.85	1.1–4.8
Lead	0.3–7.5	1.3–3.9
Iron	30–60	0.1–11.4
Nickel	0.7–2.0	0.3–1.6
Gold	0.0005	0.0029–0.112
Silver	0.0005	0.01–0.52

Table 1.2.3.1 Metal content of ores and PCBs [32]

The intrinsic value of PCBs is mainly due to precious metals and copper according to Table 1.2.3.2. However, it is important to note that owing to the progressive reduction of the precious metals content in PCBs, copper could gain a greater share of value in the future. This could lead to prefer the developing of processes based on base metals recovery, mainly copper, rather than precious metals. Indeed, a recovery process becomes more complicated and unprofitable when the elements are available in small concentration and gold concentration is expected to further decrease in the future.



Component	Wt.%	Value[a] (£/kg)	Intrinsic value of PCB	
			(£/kg of PCB)	(%)
Gold	0.025	14200.00	3.55	65.4
Palladium	0.010	6200.00	0.62	11.4
Silver	0.100	250.00	0.25	4.6
Copper	16.0	3.30	0.53	9.7
Aluminium	5.0	1.20	0.06	1.1
Iron	5.0	0.10	0.01	0.1
Tin	3.0	8.10	0.24	4.5
Lead	2.0	1.30	0.03	0.5
Nickel	1.0	13.20	0.13	2.4
Zinc	1.0	1.20	0.01	0.2

[a] Metal values are based on December 2007 London Metal Exchange (LME) levels.

Table 1.2.3.2 Compositions and the intrinsic values of PCB metals [34]

1 ton of WPCBs with all components is worth about 1.000-5.000 Euros in Europe **[51]**. However, the mix of plastics, ceramics and metals, which makes difficult the separation of each fraction, has hindered the diffusion of industrial process based on the recovery of metals from WPCBs. Besides, the few examples of industrial processes for recovering metals from WPCBs are complex and not environment-friendly. For all these reasons, WPCBs represent a challenge in the field of the circular economy and sustainable development. The challenge mainly concerns the development of both cleaner and simpler recycling processes, which should also be more flexible than the current ones because WPCBs composition is continuously changing.

In the following chapter the typical approach adopted for PCB recycling will be presented and each stage discussed in more detail.

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Chapter 2

Recycling of WPCBs

Introduction

For several years, waste PCBs have been poorly managed and their handling has been carried out mainly through disposing in landfill or incineration along with other municipal wastes. However, the new legislations on e-waste have encouraged the development of recycling processes. Currently, recycling processes result very complex due to the heterogeneous composition of WPCBs. A typical recycling process consists of pre-treatment, metal extraction by metallurgical route and purification. Dismantling, liberation of metals from non-metals and separation/recovery of non-metallic fraction through physical or chemical processes constitute the pre-treatment of WPCBs and allow to increase the concentration of metals in the residue in order to facilitate their subsequent recovery. The metallic fraction of WPCBs can be further processed by pyrometallurgical, hydrometallurgical or biometallurgical processes. Currently, e-waste recycling is dominated by pyrometallurgical route mainly due to its ability to accept any forms of scrap. However, it suffers from important limits, such as high environmental impact and partial separation of metals resulting in a limited metal grade. Consequently, hydrometallurgical and biometallurgical routes have been much investigated in the last years. The purpose of the present chapter is to provide a comprehensive description of each step of the recycling chain of WPCBs, reporting also some examples of industrial recycling processes.

2.1 Disassembly

Disassembly/dismantling is the first step in recycling chain of waste PCBs and consists of the removal of components from the board in order to simplify the subsequent recovery of materials. Such operation allows to selectively separate reusable components as well as hazardous components, such as batteries and capacitors, which have to be treated differently in a dedicated facility or disposed in appropriate way **[1-5]**. Electronic components are mounted on PCB by various types of connections. These connections are typical of following type: through-hole device (THD), surface mounted device (SMD), socket pedestal device (SPD), screw joint devise (SJD) and rivet joint devise (RJD) **[6]**. The last two act only as a mechanical connection, while THD, SMD, and socket pedestal act as mechanical and electrical connections. THD and SMD components are soldered to the board, while socket pedestal is a solder-free connection. There are several methods by which these connections can be removed. For instance, socket pedestal connection can be broken by applying a small and nondestructive force; but, the methods used for dismantling components with SMD and THD connections are always destructive and involve the melting or leaching of the solder. This can be achieved by either a chemical treatment using a liquid reagent or thermal treatment using direct heating, high-temperature gas, and liquid heating medium **[7]**. In the literature are reported different examples of using infrared rays, hot air, special liquids (such as methylphenyl silicone oil and some ionic liquids) as heating medium and also as leaching agent (e.g. fluoroboric acid containing H_2O_2) to remove solder from the PCB assemblies **[8-10]**. It is important to note that the current disassembling methods require the use of potentially polluting liquids or the heating of the board with the possible release of toxic gases due to thermal degradation of plastics. Besides, the addition of external forces (e.g. impact, vibration, scraping etc.) for the separation of unsoldered components can lead to damage of reusable components **[11]**. Several research projects are in progress for developing less energetic and more environmentally friendly dismantling processes which allow to preserve the components and the board.

The disassembly process may be manual, automatic or semiautomatic. Currently, manual disassembly is the most common technique adopted in most of the recycling plants. However, the current manual disassembly is totally insufficient and unprofitable in the light of the expected mass of WPCBs which will have to be recycled in the future **[12-13]**. Besides, it requires direct human contact with waste **[14].** Two methods can be used for automatic disassembly: selective or simultaneous disassembly. In selective disassembly, some specific components are identified and removed individually. This principle is named “look and pick”. In simultaneous disassembly, the whole flat board is heated and all components are “wiped off” simultaneously and then identified and sorted on the basis of geometry, density, or using magnetic effect. This method is also named “evacuate and sort” and leads to higher efficiency, but also higher risks of damaging the components. An image-processing and database are used to identify the components and then, different PLC (*Programmable Logic Controller*) modules can be adopted in designing further route for dismantling. Modern identification systems use optical measures such as 1-D, 2-D or 3-D pictures, radiograph, or infrared pictures for recognition of the components. For simultaneous disassembly, the 1-D signals are suitable to obtain good results, while selective disassembly needs 3-D signals.

Feldmann et al. **[12-13]** developed an automatic disassembly unit module in 1994, which consisted of a preliminary selective dismantling unit with a 3-D picturing process to remove reusable and hazardous components followed by a simultaneous dismantling unit using an infrared radiator to remove all the remaining components that were transferred to an identification unit. However, automatic disassemblers still remain expensive and therefore recommended for high-metal content waste.

2.2 Liberation of metallic fraction

After dismantling of WPCBs and removal of the hazardous components, different unit operations such as shredding, crushing and grinding can be applied to liberate metals from plastics and ceramics **[2]**. Various types of hammer, rotary, disc crushers, cutters, and shredders equipped with a bottom sieve are used for liberation **[15]**. Generally, WPCBs are first cut into roughly fragments with shredders or granulators and then further reduced into fine particles with various types of mills such as cutting, ball, disc, hammer mills, etc. **[4, 15-16]**. The liberation degree of metals from non-metals is mainly affected by particles size. Zhang and Forssberg **[17]** found that metallic particles below 2 mm achieve an almost complete liberation. According to their results, ferromagnetic and copper below 6 mm sized particles were completely liberated, whereas aluminum was found to be liberated in much coarser fraction (> 6.7 mm). Generally, metal liberation degree increases with decreasing particle size; however, for superfine particles (-0.074 mm), the subsequent operation of separating metals from non-metals through physical methods becomes more difficult **[18]**. For example, in electrostatic separation of metallic particles from non-metallic ones, the particles are easily repelled, attracted or agglomerated together with the decrease in size **[18]**. Besides, fine grinding can lead to an excessive generation of dangerous fine dust. Indeed, one of the major problems related to the mechanical pre-treatment of WPCBs is the generation of fine dust during crushing and grinding containing plastics, metals, ceramic and silica. Furthermore, the local temperature of WPCBs can increase during crushing, leading to localized pyrolysis with possible release of toxic substances. Another important drawback of mechanical processing concerns the loss of metals during shredding and grinding, which can cause a negative effect on the economy of the whole recycling process.

2.3 Separation/recovery of non-metallic fraction

After liberation, the metallic fraction can be separated from the non-metallic one by physical or chemical methods. The main purpose of chemical processes is to convert polymers contained in PCBs into chemical feedstocks or fuels. At variance, in physical processes, plastics and ceramics contained in PCBs are separated and sent to landfill, incineration or reused as very low cost fillers in the construction industry **[19]**. The separation/recovery of non-metals from more valuable metallic fraction is of primary importance in the hydrometallurgical route, but it is not always required in the pyrometallurgical one. Indeed, integrated metal smelters use organic fraction of WPCBs directly in smelting process to partially replace coke as a fuel **[20]**.

Physical recycling process is generally preferred to the chemical one because more environmentally friendly. Besides, since chemical process involves reactions at high temperature, it results more convenient from an industrial point of view to treat WPCBs directly by the pyrometallurgical route. For this reason, many projects are in progress to find alternative uses for non-metallic fraction

2.3.1 Physical processes

Physical processes include magnetic separation, density based separation, electrostatic separation, shape based separation, flotation or a combination of these techniques.

Magnetic separation can be used to separate magnetic particles such as Fe, Ni and steel from non-magnetic particles such as plastics, glass, Al and Cu. Low-intensity drum magnetic separators are generally used to recover ferrous materials. Over the past decade, there have been many advancements in the design and operation of high-intensity magnetic separators, mainly as a result of the introduction of rare earth alloy-based permanent magnets capable of providing very high field strengths and gradients **[14]**. However, magnetic separators are not very useful for crushed PCBs due to agglomeration of the particles during the process that leads non-ferrous materials to escape together with ferrous ones. Veit et al. **[21]** employed a magnetic field of 6.000–6.500 Gauss to separate the ferromagnetic elements. The concentration of Fe and Ni in the magnetic fraction was, on average, 43% and 15.2%, respectively. However, there was a considerable amount of Cu impurity in the magnetic fraction as well. Generally, magnetic separation is applied before electrostatic separation.

Gravity is widely used to separate lighter fraction from the heavier one according to their density difference. WPCBs consists essentially of plastic having a density less than 2.0 g/cm^3; light metals, primarily Al, and glass having a density of about 2.7 g/cm^3; and heavy metals, essentially Cu and ferromagnetics, having a density greater than 7 g/cm^3 **[15]**. Zheng et al. **[22]** used an air classification method in which separation is based on the settling velocity of the particles in air and reported a maximum copper content in non-metallic fraction of only 1.6%. Also water or heavy liquids (e.g. tetrabromoethane) can be used as viscous media for separating metals from plastics and ceramics. One of the major disadvantages of this methodology is that efficiency of separation strongly depends on size and shape of the particles, therefore, a close size control of feed to gravity separation equipment is required to minimize size effects **[23]**.

Electrostatic separation can be used to separate materials of different electrical conductivity (or resistivity). The two main techniques are: corona electrostatic separation and eddy current separation. The first one separates metals (conductive) from non-metals (non-conductive), while the eddy current method separates ferrous metals from non-metals. In corona electrostatic separation Figure 2.3.1.1a, small particles are passed along a vibratory feeder to a rotating roll to which is applied a high voltage electrostatic field using a corona and an electrostatic electrode. The non-metallic particles become charged and remain attached to the drum eventually falling off into storage bins; whereas the metallic particles discharge rapidly in the direction of an earthed electrode **[23]**. Li et al. **[24]** found that the best particle size range is between 0.6 and 1.2 mm and that productivity decreases for finer particles. The method has the advantage of being environmentally friendly, producing no wastewater and no gaseous emissions. Eddy current separators operates using a rotating drum with rare-earth permanent magnets which induce eddy current in non-ferrous metallic particles with a resultant repulsive force between particles and drum magnet that moves particles away from the drum Figure 2.3.1.1b. The typical particle size range is between 3 and 150 mm **[23]**.

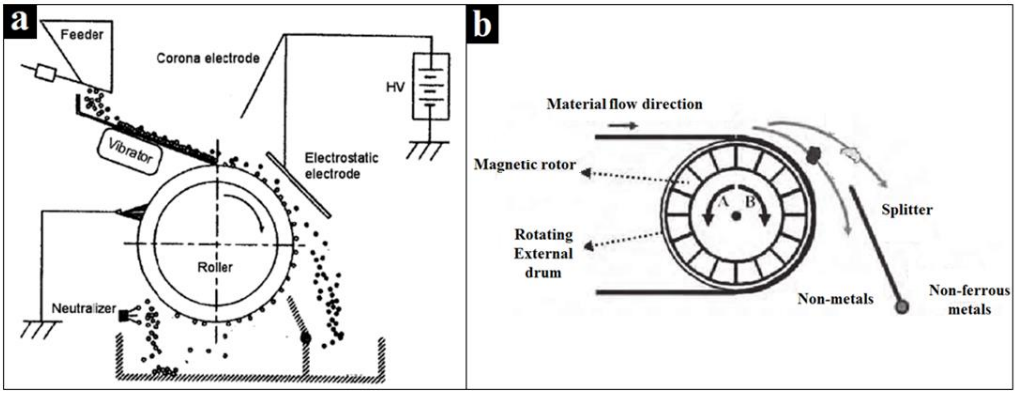


Figure 2.3.1.1 a) Corona electrostatic separator [25]; b) Eddy current separator [26]

In shape based separation, metallic particles can be separated from the non-metallic ones because they assume a spherical shape during grinding due to their malleability and ductility while ceramics and plastics remain non-spherical due to their brittle fracture. Flottation has also been investigated to separate plastics, which are naturally hydrophobic, from metals in the case of fine particles because the other separation methods cannot be effective when the particles are too fine.

Physical processes are relatively simple, convenient, and environmentally friendly. However, a consistent loss of metals occurs during mechanical processing and physical liberation is estimated at about 10-35% of the total metal content.

Usually, more techniques of physical separation are coupled in recycling process of WPCBs to maximize the recovery of materials. For example, magnetic separation can be followed by eddy current and density-based separation in order to sequentially separate ferrous metals, then non-ferrous metals, and finally separate plastics from ceramics for density difference.

In recent years, many papers have been published on potential uses of non-metallic fraction resulting from physical processes **[27-29]**. Non-metallic fraction can be used as an either reinforcing filler in both polyester and polypropylene composites, or in high density polyethylene. The glass fibers and resins powder contained in the non-metallic fraction can also be used to strengthen the asphalt or as sound and thermal insulation materials. Hadi et al. **[28]** tested the use of non-metallic fraction as an adsorbent material for heavy metals after chemical activation with potassium hydroxide. Ke et al. **[29]** produced porous carbon from non-metallic fraction of FR-3 type of waste PCBs via physical and chemical activation techniques. The recovery/recycle of non-metals has gained much attention because they constitute the major fraction of material present in WPCBs and their reuse greatly increases the feasibility of hydrometallurgical route for WPCBs recycling.

2.3.2 Chemical processes

In chemical processes, WPCBs are depolymerized into smaller useful molecules by several techniques such as pyrolysis, gasification and depolymerization using supercritical fluids. Unlike physical processes where the organic fraction is simply separated, in chemical processes, it is converted into chemical feedstocks and fuels.

Pyrolysis is carried out in the absence of oxygen or in the presence of some inert gases at a temperature between 400 and 700°C. During pyrolysis, the polymers are decomposed to low molecular weight products and finally converted into gas, oil and char. According to the study of Hall et al. **[30]**, pyrolysis of waste computer PCBs leads to approximately 22.7% oil, 4.7% gas and 70% copper-rich residue. The pyro-gases have high heating value resulting valuable for combustion, the oils can be recycled as raw materials for chemical /petrochemical industries, and the solid residue can be sent to metallurgical processes for metals recovery. Compared with incineration, the quantity of greenhouse gases produced during pyrolysis and released in environment is notably reduced **[31-32]**. Nevertheless, the presence of dioxins and furans precursors in the pyrolysis oil represents a serious problem. The quantity of halogenated compounds in the oil decreases with increasing temperature and time of reaction. Also the particles size influences the quality of pyrolysis oil; large particles (4 cm^2) lead to contamination of oil that will have to be purged for further utilization **[4]**. A size of 1.5–2 cm^2 is typically used, which require a simpler mechanical pre-treatment than that employed in physical processes **[33]**. Some of the recent studies suggest that the addition of $CaCO_3$ and Fe_2O_3 during pyrolysis can control the release of brominated compounds and other organic compounds like benzene.

Gasification converts organic materials into carbon monoxide and hydrogen (syngas) by reactions at high temperature with a controlled amount of oxygen and/or steam. The gasification can be described as a partial oxidation of hydrocarbons and the temperature might up to 1600 °C at a pressure of up to 150 bar **[31]**. CO_2, H_2O, CH_4 and soot might be the byproducts. In gasification, a small amount of bromine is present in the char, but the major part ends up into syngas, which has to be cleaned before using for energy recovery or chemical synthesis. However, it was found that after high temperature treatment (1150°C) and shock cooling of gas at about 50°C, the emission of PBDFs (polybrominated dibenzofurans) and PBDDs (polybrominated dibenzodioxins) is minimized **[31]**. This indicates that gasification could be an eco-efficient technology to dispose the WEEE plastics if proper control of the gas emission is designed.

In recent years, supercritical fluids have been used as an effective medium to oxidize organic materials to CO_2 and H_2O. Supercritical water and methanol have been used for depolymerization of thermoset resins in WPCBs **[34-36]**. The lower critical temperature and pressure of methanol (Tc=240°C, Pc=8.09 MPa) compared to those of water (Tc=374°C, Pc=22.1 MPa) allow milder operative conditions. During the process, alkali cations are used to capture bromine and make the process more environmentally friendly. In the study by Chien et al. **[36]**, the resin conversion in supercritical water at 520°C for 10 min was 0.90 and the solid residue was mainly constituted by copper in the form of Cu_2O, CuO and $Cu(OH)_2$. The resin conversion is defined as the ratio between carbon content in the residue and carbon content originally present in waste PCB. The authors also found that NaOH enhanced the PCBs oxidation and Br retention in the liquid phase. Xiu et al. **[35]** studied the use of supercritical methanol to separate polymers and metals from comminuted PCBs (<1 mm). The highest conversion was obtained at 380°C for 120 min. The oil did not contain brominated compounds due to the complete decomposition and the content of copper in the solid residue was approximately three time of that in the original material.

Supercritical fluids and gasification technology have a potentially smaller environmental impact than pyrolysis process due to the high debromination efficiency, but the energy consumption is higher.

2.4 Metal recovery

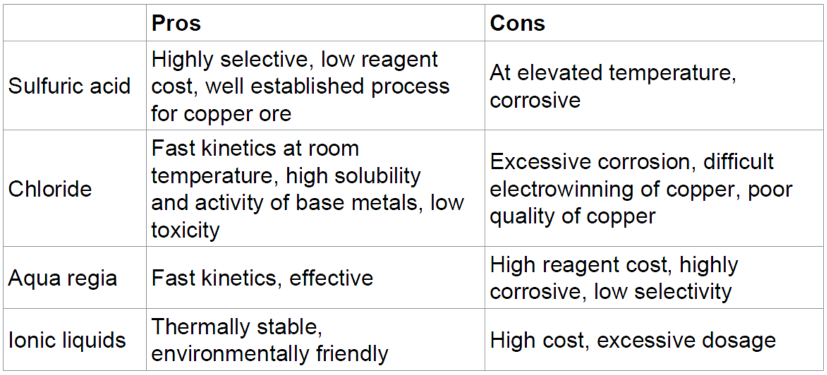
The metallic fraction separated from WPCBs during preprocessing can be further treated using three different techniques: hydrometallurgical, pyrometallurgical and biometallurgical. Each methodology will be discussed in more detail in the following.

2.4.1 Hydrometallurgical route

Hydrometallurgical route involves metals leaching by means of a solvent from the residue resulting from WPCBs pre-treatment. The leach solution is then subjected to separation and purification procedures such as adsorption, solvent extraction, precipitation and ion-exchange to isolate and concentrate the metal of interest. This route is based on traditional hydrometallurgical technology of metals extraction from their primary ores. The main goal of the process consists in recovering precious metals, which have the highest value in waste PCBs.

Generally, base metals are firstly leached to enrich the solid residue of precious metals and therefore enhance their subsequent recovery. Besides, base metals recovery has a substantial impact on the economics of the process due to their high content in WPCBs. Among base metals, copper is the metal of greatest interest.

The leaching of base metals is usually conducted using different acids such as H_2SO_4, HNO_3, aqua regia ($HCl:HNO_3=3:1$, v/v) and HClO with various oxidants including H_2O_2, O_2, Fe^{3+} and Cl_2 **[19, 37-42]**. Recently, a lot of alternatives to the use of such corrosive acids have been tested including ionic liquids. For instance, copper can also be effectively extracted through ammoniacal leaching **[43-45]**. The solution from the leaching of the base metals mainly contains copper. After a solid-liquid separation, it can be further treated by purification or directly sent to the electrochemical copper recovery. Comparison between the most used reagents for the leaching of the base metals is shown in Table 2.4.1.1.



	Pros	**Cons**
Sulfuric acid	Highly selective, low reagent cost, well established process for copper ore	At elevated temperature, corrosive
Chloride	Fast kinetics at room temperature, high solubility and activity of base metals, low toxicity	Excessive corrosion, difficult electrowinning of copper, poor quality of copper
Aqua regia	Fast kinetics, effective	High reagent cost, highly corrosive, low selectivity
Ionic liquids	Thermally stable, environmentally friendly	High cost, excessive dosage

Table 2.4.1.1 Comparison of potential leaching reagents for base metals [19]

Precious metals, mainly Au, Ag and Pd, are chemically stable and in WPCBs, they are also combined with other materials so that their extraction is very challenging. Therefore, leaching solution with high oxidizing power must be used. Sheng and Etsell **[46]** tested the recovery of gold from WPCBs by leaching of base metals in HNO_3 followed by leaching of Au in aqua regia and finally, precipitation of Au with ferrous sulphate. The reactions involved during leaching in aqua regia are

$2HNO_3 + 6HCl \rightarrow 2NO + 4H_2O + 3Cl_2$ (2.4.1.1)

$2Au + 9HCl + 3HNO_3 \rightarrow 2AuCl_3 + 3NOCl + 6H_2O$ (2.4.1.2)

$3HCl + HNO_3 \rightarrow Cl_2 + NOCl + 2H_2O$ (2.4.1.3)

However, the construction of a leaching reactor suitable for highly corrosive HNO_3 and aqua regia, limits its industrial feasibility. Senanayake **[47]** studied the kinetics of gold oxidation using different extracting systems, and also reported the following stability order of Au(I)-complexes with different ligands: $CN^- > HS^- > S_2O_3^{2-} > SC(NH_2)_2 > OH^- > I^- > SCN^- > SO_3^{2-} > NH_3 > Br^- > Cl^- >$ CH3CN. In the case of Au(III)-complexes, the stability order was $CN^- > OH^- > SCN^- > Br^- > Cl^-$. From the study, it emerges that cyanide is certainly the best extracting reagent for gold, in fact, it has been used in the mining industry for more than one century. The overall gold cyanidation reaction is

$4Au + 8CN^- + O_2 + 2H_2O \rightarrow 4Au(CN)_2^- + 4OH^-$ (2.4.1.4)

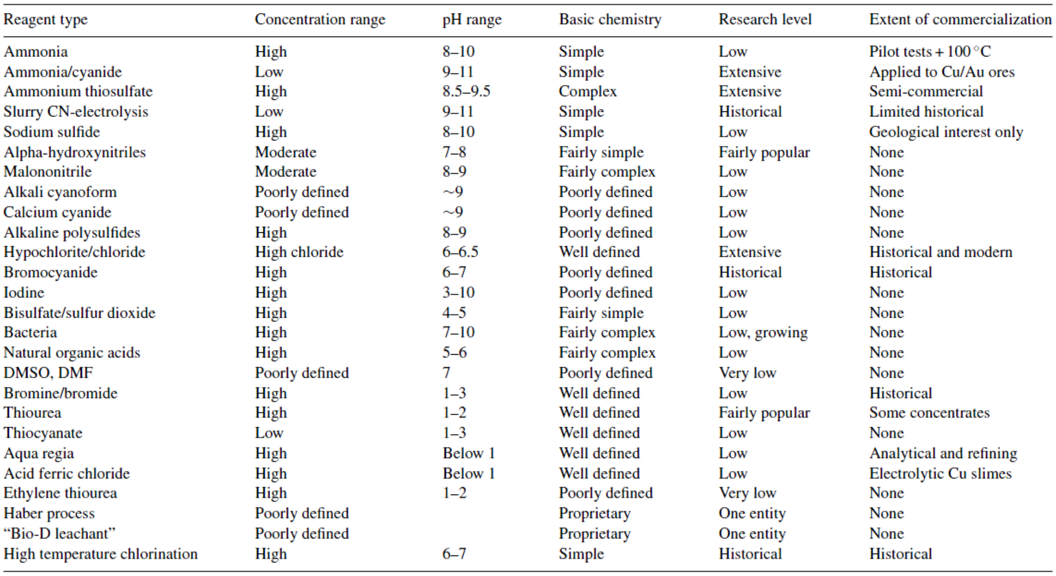
The maximum dissolution of gold, silver, palladium, and platinum in cyanide solution can be obtained at pH 10-10.5 and the order of activity for metals is Au > Ag > Pd > Pt **[48]**. Nevertheless, the rising environmental issues regarding the use of cyanide has led to find new gold leaching agents. Table 2.4.1.2 summarizes the alternatives to cyanide, but some of them have been scarcely investigated. The most realistic alternatives to cyanide are thiourea and thiosulfate.

Unlike cyanide, thiourea ($SC(NH_2)_2$) forms a cationic complex with gold in acidic solution of H_2SO_4 as described by the following reaction

$Au + 2SC(NH_2)_2 \rightarrow Au(SC(NH_2)_2)_2^+ + e-$ (2.4.1.5)

It was found that the addition of ferric ion, usually in the form of $Fe_2(SO_4)_3$, into leaching system is advantageous for gold and silver recovery **[49]**. Using this leaching system, Lee et al. **[50]** obtained complete gold and silver extraction in 24 h at 20°C after roasting, size reduction (0.84 mm) and magnetic separation.

Nevertheless, the high cost and rapid consumption of thiourea have hindered its extensive use. Indeed, in the presence of ferric sulphate, thiourea rapidly disappears in form of $(FeSO_4{\cdot}CS(NH_2)_2)^+$. Besides, thiourea has low selectivity which involves the need to remove base metals before leaching of the precious ones. Ficeriova et al. **[51-52]** obtained dissolution in single step of Au, Cu, Fe, Pb and Zn equal to 90%, 68%, 45%, 43%, and 28%, respectively at ambient temperature using a leaching solution having 10 g/L of $CS(NH_2)_2$, 10 g/L of H_2SO_4 and 5 g/L of $Fe_2(SO_4)_3{\cdot}9\,H_2O$.



Reagent type	Concentration range	pH range	Basic chemistry	Research level	Extent of commercialization
Ammonia	High	8–10	Simple	Low	Pilot tests + 100 °C
Ammonia/cyanide	Low	9–11	Simple	Extensive	Applied to Cu/Au ores
Ammonium thiosulfate	High	8.5–9.5	Complex	Extensive	Semi-commercial
Slurry CN-electrolysis	Low	9–11	Simple	Historical	Limited historical
Sodium sulfide	High	8–10	Simple	Low	Geological interest only
Alpha-hydroxynitriles	Moderate	7–8	Fairly simple	Fairly popular	None
Malononitrile	Moderate	8–9	Fairly complex	Low	None
Alkali cyanoform	Poorly defined	~9	Poorly defined	Low	None
Calcium cyanide	Poorly defined	~9	Poorly defined	Low	None
Alkaline polysulfides	High	8–9	Poorly defined	Low	None
Hypochlorite/chloride	High chloride	6–6.5	Well defined	Extensive	Historical and modern
Bromocyanide	High	6–7	Poorly defined	Historical	Historical
Iodine	High	3–10	Poorly defined	Low	None
Bisulfate/sulfur dioxide	High	4–5	Fairly simple	Low	None
Bacteria	High	7–10	Fairly complex	Low, growing	None
Natural organic acids	High	5–6	Fairly complex	Low	None
DMSO, DMF	Poorly defined	7	Poorly defined	Very low	None
Bromine/bromide	High	1–3	Well defined	Low	Historical
Thiourea	High	1–2	Well defined	Fairly popular	Some concentrates
Thiocyanate	Low	1–3	Well defined	Low	None
Aqua regia	High	Below 1	Well defined	Low	Analytical and refining
Acid ferric chloride	High	Below 1	Well defined	Low	Electrolytic Cu slimes
Ethylene thiourea	High	1–2	Poorly defined	Very low	None
Haber process	Poorly defined		Proprietary	One entity	None
"Bio-D leachant"	Poorly defined		Proprietary	One entity	None
High temperature chlorination	High	6–7	Simple	Historical	Historical

Table 2.4.1.2 Suggested alternatives for leaching of gold to cyanide [48]

Another non-toxic and non-corrosive reagent along with thiourea is the thiosulfate ($S_2O_3^{2-}$). Gold dissolution in ammoniacal thiosulfate solution is an electrochemical reaction catalyzed by small concentrations of Cu^{2+} that can be described as following

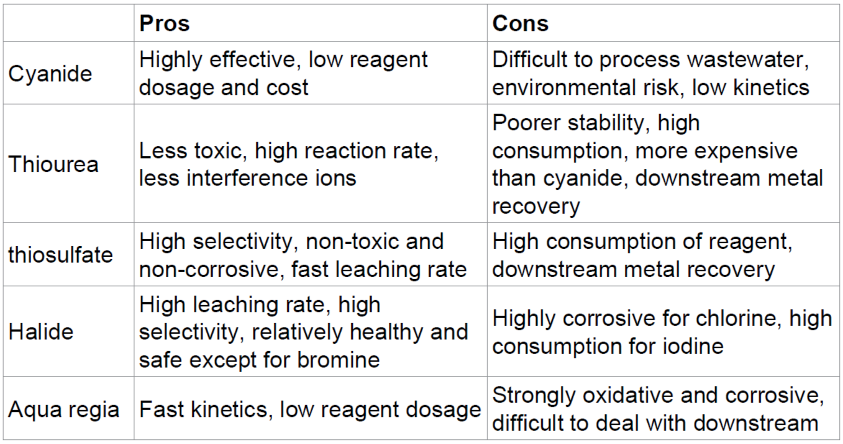
$$Au + 5S_2O_3^{2-} + Cu(NH_3)_4^{2+} \rightarrow Au(S_2O_3)_2^{3-} + 4NH_3 + Cu(S_2O_3)_3^{5-} \qquad (2.4.1.6)$$

$$2Cu(S_2O_3)_3^{5-} + 8NH_3 + \tfrac{1}{2}\,O_2 + H_2O \rightarrow 2Cu(NH_3)_4^{2+} + 2OH^- + 6S_2O_3^{2-} \qquad (2.4.1.7)$$

The above reactions could proceed very slowly without cupric ions. However, too much copper in solution could adversely affect the leaching process because copper as well as other metals can increase the decomposition of thiosulfate. Therefore, a pre-leaching stage aimed to remove copper and other metals from WPCBs is suggested before thiosulfate leaching. At ambient temperature, pH has to be maintained at about 9-10 to avoid degradation of thiosulfate and ensure the stability of Cu(II)-ammonia complex. Oh et al. **[53]** extracted 95% Au within 48 h and 100% Ag within 24 h by leaching in 0.2 M $(NH_4)_2S_2O_3$-0.02 M $CuSO_4$-0.4 M NH_4OH solution at 40°C after physical pre-treatment and removal of the base metals. The main drawback related to thiosulfate leaching is its high consumption which makes the process economically unfavourable, despite the potential environmental benefits.

The use of halides has been widely investigated as an alternative to cyanide leaching. Gold can form both Au(I) and Au(II) complexes with chloride, bromide and iodide. Different authors have found electrogenerated Cl_2 as a promising oxidant for gold leaching from WPCBs **[54-56]**. However, the handling of chlorine gas and the requirement of special reactors hinders the application of chlorine/chloride leaching system. Iodide leaching is considered non-toxic, non-corrosive and very selective towards gold. It was found that addition of an oxidant to iodide leaching enhances the gold recovery and decreases the consumption of reagent. Xu et al. **[57]** achieved 95% of gold recovery after 4 h at ambient temperature using H_2O_2 as an oxidant in I_2/I^- leaching system. Xiu et al. **[58]** obtained good extractions of Au, Ag and Pd by leaching in I_2/KI solution after supercritical water pre-treatment of WPCBs. The main obstacles in iodine/iodide leaching process are the high consumption and cost of reagent. A comparison between the main leaching reagents for gold is shown in Table 2.4.1.3.

Some studies reported the use of non-cyanide lixiviants for the extraction of Ag and Pd, such as acidic solutions containing an oxidant (e.g. HCl/Cu^{2+}, HCl/ClO^-_3, H_2SO_4/Cu^{2+}, H_2SO_4/Fe^{3+}). All have been developed at laboratory scale and have low selectivity **[59-63].** At present, thiourea and thiosulfate seem to be the most realistic alternatives.



	Pros	**Cons**
Cyanide	Highly effective, low reagent dosage and cost	Difficult to process wastewater, environmental risk, low kinetics
Thiourea	Less toxic, high reaction rate, less interference ions	Poorer stability, high consumption, more expensive than cyanide, downstream metal recovery
thiosulfate	High selectivity, non-toxic and non-corrosive, fast leaching rate	High consumption of reagent, downstream metal recovery
Halide	High leaching rate, high selectivity, relatively healthy and safe except for bromine	Highly corrosive for chlorine, high consumption for iodine
Aqua regia	Fast kinetics, low reagent dosage	Strongly oxidative and corrosive, difficult to deal with downstream

Table 2.4.1.3 Comparison of potential leaching reagents for gold [19]

2.4.2 Pyrometallurgical route

Pyrometallurgy is the traditional approach for metal recovery from WPCBs. Currently, more than 70% of WPCBs are treated by pyrometallurgical route **[2]**; the remaining part is treated by mechanical and physical processing. The main advantage of pyrometallurgical treatment consists in its flexibility, i.e. the ability to accept any forms of scrap. Hence, e-waste can be simultaneously treated with other types of metal scraps and incorporated into smelting process of copper or lead concentrates. Copper and lead smelters have been successfully used by different companies as installations for the recovery of base and precious metals from electronics waste. Regarding these smelters, waste PCBs are fed directly into a smelting furnace after a minimum pre-processing that includes the removal of hazardous components and coarse crushing. The crushed scraps are burned to remove the organic material, which contribute as a source of energy during smelting, while the refractory oxides form a slag phase together with some metal oxides. This approach does not allow the aluminum and iron recovery because they are transferred into the slag. Besides, individual recovery of metals at high purity can hardly achieved by pyrometallurical route with the consequent need to integrate the technique with hydrometallurgical or electrometallurgical operations, such as the electrorefining. Currently, various industrial processes are used globally for extracting metals from e-waste, including the Noranda process in Quebec, Umicore integrate smelting and refining facility in Belgium, Rönnskär smelters in Sweden, Kosaka’s recycling plant in Japan, the Kayser recycling system in Austria and the Metallo-Chimique N.V plants operating in Belgium and Spain **[20]**.

In the Noranda process, about 100.000 tons of e-waste per year are recycled. A scheme of the process is shown in Figure 2.4.2.1. Copper concentrate and scraps are fed together into a molten metal bath (1250°C) which is churned by oxygen. The combustion of plastics contained in e-scrap, including WPCBs, reduces the energy cost of the process.

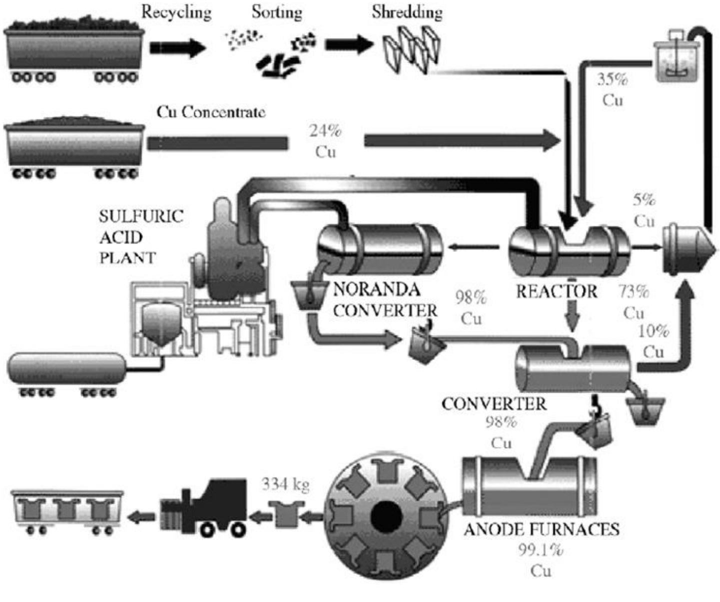


Figure 2.4.2.1 Schematic diagram for the Noranda smelting process [48]

The purpose of the smelting stage is to convert impurities including iron, lead and zinc into oxides which segregate into a silica-based slag, and produce the so-called *copper matte* which mainly consists of copper and iron sulphides with a copper content in the range of 50-75% by weight. The slag is cooled and processed to recover more metals before disposal; instead, the copper matte is transferred to the converters to reach a purity of 98%. The obtained copper, known as a *blister copper*, is put into an anode furnace that refines the blister copper to anode-grade copper (99.1%). The remaining impurities mainly contain precious metals along with other recoverable metals such as selenium, tellurium, and nickel. The subsequent electrorefining of the product coming from fire-refining allows the recovery of these valuable metals.

Another application for pyrometallurgical process to recover metals from e-waste is practiced at the Boliden Ltd. Rönnskär Smelter in Sweden. In Figure 2.4.2.2 is reported a block diagram of the process. Electronic scraps are treated together with both copper and lead concentrates. In particular, high copper containing scraps are fed into the smelting process directly, but low-grade scraps are fed into the Kaldo furnace. This last produces a mixed copper alloy that is sent to the copper converting while the dusts containing Pb, Sb, In and Cd are sent to other operations for lead recovery. The main steps for producing copper and precious metals are roasting, smelting, converting, refining in anode furnaces and electrorefining.

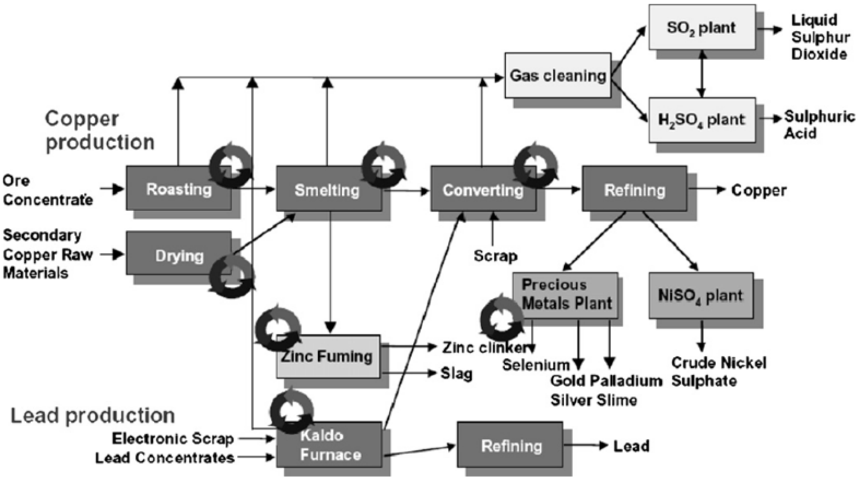


Figure 2.4.2.2 Schematic diagram for the Rönnskär Smelter [48]

In recent years, Umicore developed an integrated process composed of several pyrometallurgical, hydrometallurgical and electrochemical operations for precious and base metals recovery from various industrial wastes as well as consumer recyclables such as car exhaust catalyst and PCBs. On average, 250.000 tons of feed material are treated annually. It is the world's largest recycling facility with an annual production of over 50 tons of platinum group metals, 100 tons of gold and 2.400 tons of silver. Figure 2.4.2.3 shows the process flow diagram.

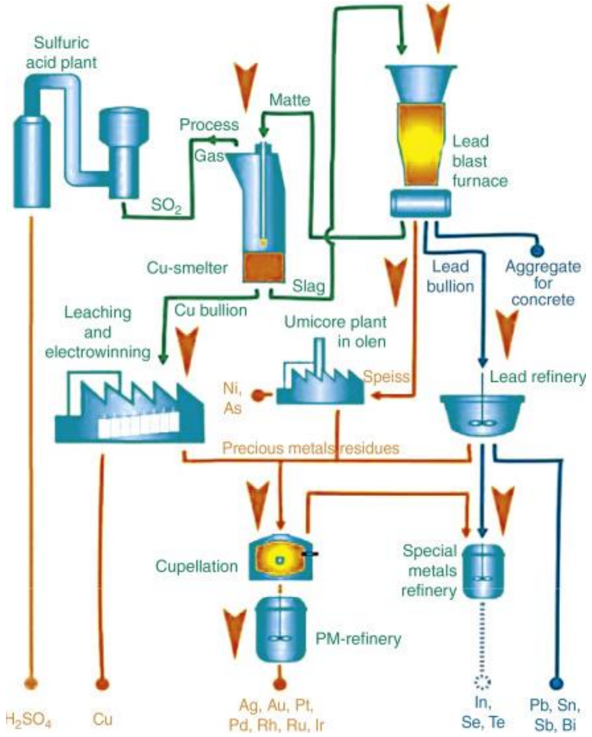


Figura 2.4.2.3 Flow sheet for Umicore's integrated metals smelter and refinery [20]

The heart of the process is the IsaSmelt furnace where plastics partially replace coke as a reducing agent and source of energy for smelting. In the Umicore process, the input material is different from ores/concentrates and usually does not contain sulfur. Therefore, the roasting stage to remove sulfur as SO_2 is no longer required and the smelting operates under reducing conditions to produce crude copper directly, also known as *black copper* or *bullion copper*, rather than copper matte. The copper content in black copper usually varies in the range of 60-85% by weight. In principle, this product could be sent subsequently to the traditional converting and refining stages. On the contrary, in Umicore process, the bullion copper is treated by copper-leaching followed by electrowinning for obtaining pure copper while copper-leached residue is sent to precious metal refinery. The oxidized slag resulting from IsaSmelt furnace is further treated into the lead blast furnace that produces impure lead bullion, nickel speiss, copper matter and depleted slag. The Harris process (lead refinery) is used to refine lead bullion that contains fewer precious metals. Pure lead, sodium antimonite and special metals (indium, selenium and tellurium) are produced during the Harris process. Bismuth and tin are sold to other companies to produce pure metals. Nickel is leached out from nickel speiss as a sulfate. The remaining residue is sent to the precious metals refinery unit. Overall, the Umicore integrated smelter and refinery can recover a total of 17 metals.

The high calorific value of WPCBs makes their incineration feasible. Indeed, incineration is a widespread disposal method of WPCBs. Unlike smelting, formation of melts is avoided during incineration. Typically, rotary furnaces are used in such a process; however, stationary fluidized bed has also been tested for e-waste incineration at laboratory scale. Samples of PCBs were heated for 3 min at 840–850 °C and 6.2 vol% of oxygen. Weight loss of the incinerated material was equal to about 21 wt % and the final product was then pulverized below 0.2 mm and treated by hydrometallurgical route for copper recovery **[64]**. In order to reduce the emission of polluting gases, e-waste is burnt at temperatures above 800°C and then gaseous products are heated above 1100°C. It was found that small amounts of e-waste, especially organic components, can be safely added to municipal waste to generate energy **[65]**. However, the presence of brominated flame retardants in e-waste makes incineration a not wise choice for WPCBs recycling.

Recently, molten salt recycling processes have been investigated to reduce the air pollution problems encountered in traditional pyrometallurgical route. The process can be performed at low temperatures (<500°C) using eutectic salt composition. Molten mixtures of inorganic salts, such as KOH-NaOH and NaOH-$NaNO_3$ have been used to recovery metals from WPCBs obtaining very encouraging results **[66-67]**. Non-metallic part is dissolved in the molten salt and remains trapped there, leaving a copper-rich residue. The main advantage of the technology consists in trapping halogens in the molten salt as alkali metal halides, reducing the environmental impact of the process. In addition, a considerable energy saving occurs due to the lower temperature of the process compared to the traditional pyrometallurgical one. In brief, molten salt process represents a significant advancement in the area of pyrometallurgical processes for metal recovery from WPCBs.

2.4.3 Biometallurgical route

Biometallurgy is one of the most promising technologies in metallurgical processing of WPCBs due to the lower investment cost, environmental impact, energy consumption than conventional pyrometallurgical and hydrometallurgical routes **[2]**. In the mining industry, biometallurgy is well established for recovering metals, especially copper and gold, from very low-grade ores and concentrates. However, most of applications of the biometallurgy for WPCBs recycling are still at laboratory scale. Bioleaching and biosorption are the two main areas of biometallurgical route for metal recovery.

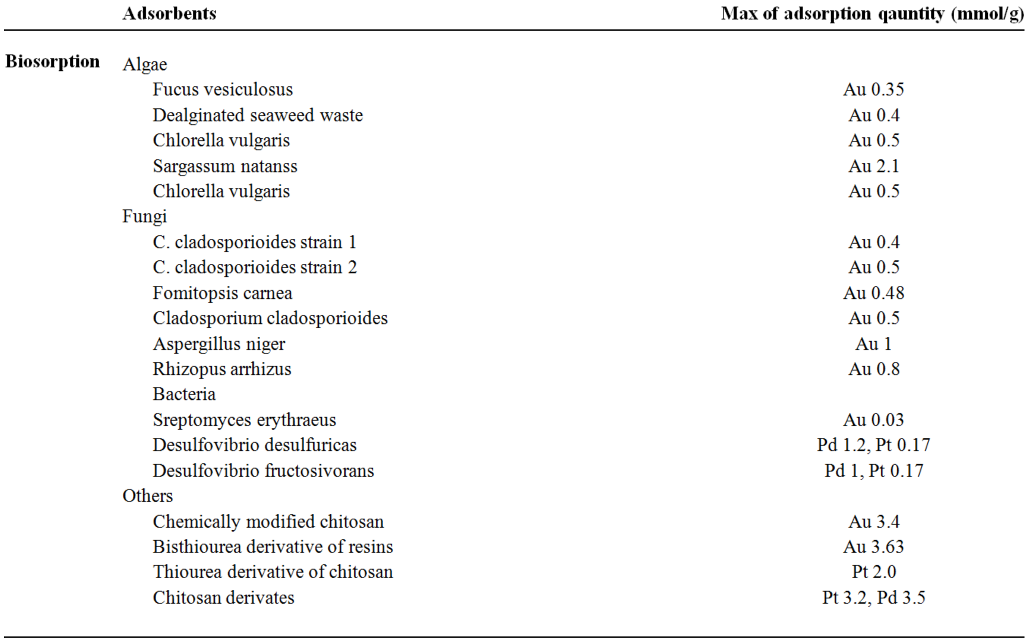
In bioleaching, metals present in the environment are oxidized by bacteria-assisted reactions and brought into solution. Acidophilic group of bacteria such as *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*, *Leptospirillum ferrooxidans*, and *Sulfolobus sp* plays an important role in bioleaching of base metals. Wang et al. **[68]** used A. ferrooxidans and A. thiooxidans as bioleaching bacteria to solubilize Cu, Pb and Zn from printed wire boards. The solubilizing capability for metals increased when a mixed culture of A. ferrooxidans and A. thiooxidans was used, reaching a copper extraction of 99.9% under specific operative conditions. Other studies **[69-70]** showed that the mechanism of copper solubilization can be divided into two phases as described by the following reactions

$$4Fe^{2+} + O_2 + 4H^+ = 4Fe^{3+} + 2H_2O \qquad (2.4.3.1)$$

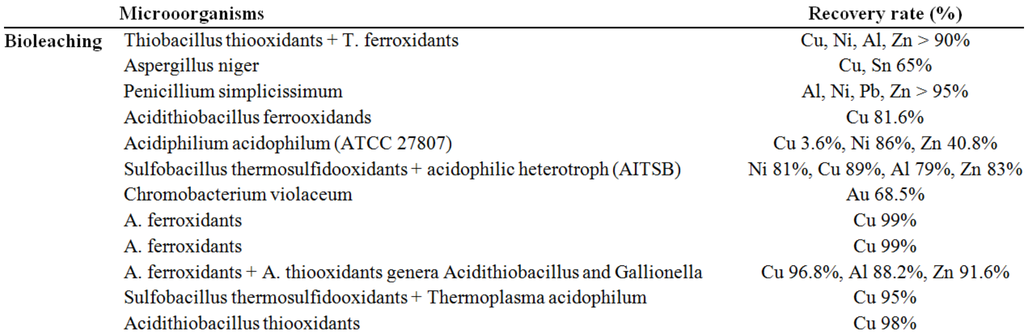
$$Cu + 2Fe^{3+} = Cu^{2+} + 2Fe^{2+} \qquad (2.4.3.2)$$

In the first phase, the ferrous ions are used from bacteria as an energy source and oxidized to ferric ions. In the second phase, copper is dissolved by ferric ions which are reduced regenerating the ferrous ions according to a cyclical mechanism. Besides, the leaching mechanism shows the influence of Fe^{3+} on the leaching rate. In particular, the rate of copper extraction increases with increasing of Fe^{3+} concentration. Faramarzi et al. **[71]** used different cyanogenic bacterial strains (*Chromobacterium violaceum, Pseudomonas fluorescens, Bacillus megaterium*) to recover gold from electronic scrap and found a 14.9% maximum gold dissolution in the form of dicyanoaurate $[Au(CN)^{2\,-}]$. The major drawbacks associated to bioleaching process are the very slow reaction rate and precipitation of metals, mainly copper, which was observed by several researchers during microbial leaching of e-waste. The addition of elevated amounts of scrap facilitates metal precipitation and also leads to an increase in pH due to the alkalinity of e-waste with consequent toxic effects on the microorganisms. However, it was found that the addition of complexing agent like citric acid can increase the solubility of copper and the efficiency of the process **[48]**.

Biosorption is a passive physico-chemical interaction between the charged surface groups of microorganisms (algae, fungi or bacteria) and ions present in a leach solution. Ion-exchange, complexation, coordination and chelation are the main interactions established between metal ions present in the environment and ligands present on the cell surface. Also dead or inactive microbial biomass can bind and concentrate metal ions from solutions. Au(III) was successfully recovered in the form of metallic gold nanoparticles using dead biomass of the brown alga *Fucus vesiculosus*. The greatest gold uptakes were obtained at pH 7. The marine alga *Sargassum natans* and the fungal cells of *Aspergillus niger*, *Mucor rouxii* and *Rhizopus arrihus* were also found to uptake precious metals like gold **[72].** However, recovery of metals from e-waste by biosorption is only just beginning. Cramer et al. **[73]** demonstrated the bioseparation procedure to recover Au and Pd from e-waste leach solution using *Desulfovibrio desulfuricans* biomass. The method allows the recovery of Au and Pd in the presence of an excess of Cu through a 3-steps process. Au(0) and Pd(0) were recovered by bacteria-mediated precipitation during the 1-st and 2-nd step, respectively; while copper was removed from the precious metal-depleted solution as a mixture of hydroxide and sulfate in the 3-rd step by biogas generated through *K. pneumoniae* or *E. coli*. Table 2.4.3.1 summarizes some results on metals extraction by biometallurgy.



	Adsorbents	**Max of adsorption qauntity (mmol/g)**
Biosorption	Algae	
	Fucus vesiculosus	Au 0.35
	Dealginated seaweed waste	Au 0.4
	Chlorella vulgaris	Au 0.5
	Sargassum natanss	Au 2.1
	Chlorella vulgaris	Au 0.5
	Fungi	
	C. cladosporioides strain 1	Au 0.4
	C. cladosporioides strain 2	Au 0.5
	Fomitopsis carnea	Au 0.48
	Cladosporium cladosporioides	Au 0.5
	Aspergillus niger	Au 1
	Rhizopus arrhizus	Au 0.8
	Bacteria	
	Sreptomyces erythraeus	Au 0.03
	Desulfovibrio desulfuricas	Pd 1.2, Pt 0.17
	Desulfovibrio fructosivorans	Pd 1, Pt 0.17
	Others	
	Chemically modified chitosan	Au 3.4
	Bisthiourea derivative of resins	Au 3.63
	Thiourea derivative of chitosan	Pt 2.0
	Chitosan derivates	Pt 3.2, Pd 3.5



	Microorganisms	Recovery rate (%)
Bioleaching	Thiobacillus thiooxidants + T. ferroxidants	Cu, Ni, Al, Zn > 90%
	Aspergillus niger	Cu, Sn 65%
	Penicillium simplicissimum	Al, Ni, Pb, Zn > 95%
	Acidithiobacillus ferrooxidands	Cu 81.6%
	Acidiphilium acidophilum (ATCC 27807)	Cu 3.6%, Ni 86%, Zn 40.8%
	Sulfobacillus thermosulfidooxidants + acidophilic heterotroph (AITSB)	Ni 81%, Cu 89%, Al 79%, Zn 83%
	Chromobacterium violaceum	Au 68.5%
	A. ferroxidants	Cu 99%
	A. ferroxidants	Cu 99%
	A. ferroxidants + A. thiooxidants genera Acidithiobacillus and Gallionella	Cu 96.8%, Al 88.2%, Zn 91.6%
	Sulfobacillus thermosulfidooxidants + Thermoplasma acidophilum	Cu 95%
	Acidithiobacillus thiooxidants	Cu 98%

Table 2.4.3.1 Adsorbents and microorganisms used for metal recovery by biometallurgical route [72]

2.5 Purification and recovery of metals

Purification is the last step in the recycling chain of WPCBs. It involves all useful unit operations to obtain target metals at the desired degree of purity. The solution resulting from the leaching treatment of WPCBs contains several metals solubilized that have to be selectively separated. The product leaving the anode furnace in a typical pyrometallurgical treatment of WPCBs contains several metals to separate, mainly copper together with small amounts of precious metals and base metals residues.

Various methods and options can be used for selective recovery of the target metals from the leach solution, such as precipitation, solvent extraction, cementation, ion exchange, adsorption, electrowinning, etc. These methods can also be used in integrated pyrometallurgical processes (e.g. Umicore process). In turn, electrorefining is the usual technique employed for purifying the product leaving the anode furnace in the traditional pyrometallurgical treatment. In this case, the fire-refined copper acts as an anode in an electrochemical cell where an ultrapure copper sheet is used as a cathode. Copper ions from the anode are deposited on the cathode. The less noble impurities than copper are dissolved and remain in solution, while nobler ones precipitate on the bottom of the cell where they are collected and sent to the precious metals refinery unit.

Cementation of precious metals, such as Au, Ag and Pd from H_2SO_4 or chloride leach solutions using Cu/Zn/Al powders is a well-known and widespread process.

Since the 1890, zinc cementation has been used to recover gold from cyanide solutions at commercial scale **[48]**. The major reactions involved during cementation are the cathodic deposition of gold and anodic corrosion of zinc that occurs at the surface of zinc particles.

$$2Au(CN)_2^- + 2e^- \rightarrow 2Au + 4CN^- \quad (2.5.1)$$

$$Zn + 4CN^- \rightarrow Zn(CN)_4^{2-} + 2e^- \quad (2.5.2)$$

Cementation can also be employed for copper extraction by adding metallic iron in leach solutions **[19]**. A widely experienced problem during displacement reaction is the passivation of the reductant metal surface by forming a layer of metal oxide or hydroxide, which inhibits the further advancement of redox reaction **[74]**. Others significant drawbacks are the large consumption of cementing metal and the H_2 generation in acidic environment.

One of the most common method to purify a solution from metals consists in precipitating metal-ions by addition of NaOH, lime, etc. In the study by Yang et al. **[75]**, about 99% of Sn, Fe, Cu and Zn were precipitated at pH values of 1.5 for Sn, 3 for Fe, 6 for Cu and 8 for Zn, respectively**.** Besides, precipitation of $PbSO_4$ occurred by adjusting the SO_4^{2-}/Pb^{2+} molar ratio at 1.4. Gold recovery by precipitation from thiourea, thiosulfate and thiocyanate solutions is generally conducted using sodium borohydride ($NaBH_4$) as a reducing agent **[76-77]**. Several reducing agents has been tested for gold precipitation from aqua regia leach solution, such as ferrous sulfate ($FeSO_4$), oxalic acid ($H_2C_2O_4$), hydrazine (N_2H_4), stannous chloride ($SnCl_2$), sulfur dioxide (SO_2), sodium sulfite (Na_2SO_3) and sodium nitrite ($NaNO_2$) **[46, 78-80]**. The reductants $FeSO_4$, $H_2C_2O_4$, and N_2H_4 were compared in the study by Saadatjoo et al. **[79]**. The authors concluded that ferrous sulfate reduces gold ions to metallic gold rapidly with high purity, but for higher purities, oxalic acid could be a better choice. Guo et al. **[67]** reported the purification of an alkaline leach solution using glucose for Cu precipitation, lime for Sn, and finally, Na_2S for Pb and Zn. Copper precipitation in the form of

$CuSO_4 \cdot 5H_2O$ starting from a sulphate leach solution can also be induced by an evaporative crystallization rather than electrochemically **[81-82]**.

Solvent extraction is a technique widely used both for base and precious metals extraction from leach solutions. Compared to the other techniques, solvent extraction has the advantage to be high selective towards specific metals. In the mining sector, several systems have been investigated for gold extraction from cyanide solutions, including organophosphorus derivatives, guanidine derivations, and mixture of amines-organophosphorus derivatives **[48]**. Similar extractants have also been investigated in the field of WPCBs recycling. LIX-79 diluted in cumene and Cyanex 921 diluted in xylene are commercial extractants of gold from cyanide solutions. The subsequent stripping of gold from the resulting solution can be performed using NaOH or NaCN for LIX-79 and water or KCN for Cyanex 921. Park and Fray **[83]** used toluene for gold extraction from aqua regia solutions coming from leaching of WPCBs and then, dodecanethiol and sodium borohydride solutions were used for gold nanoparticle formation. Chmielewski et al. **[84]** selected diethyl malonate ($C_7H_{12}O_4$) as the best extractant of gold from aqua regia solutions with a saturation capacity of 140 g/l. As regards copper, extractants based on oximes are widely used for its extraction from acidic sulfate-based leach solutions in mining. In particular, modified aldoximes and aldoxime-ketoxime mixtures are the most widely used copper extracting systems **[85]**. Generally, in order to obtain high purity copper, solvent extraction is followed by stripping with sulfuric acid and electrowinning, which is an electrolytic process for recovering dissolved copper using an applied potential. Some specific oximes such as LIX 54 and LIX 64N were also used for extracting copper from ammonia-based leach solutions. The same approach was tested in the field of WPCBs management. Yang et al. **[86]** have recovered 99.6% of copper from ammonia-based leach solutions using LIX 84 diluted in kerosene and copper was then stripped by sulfuric acid. Finally, the authors obtained ultrafine copper particles with approximately 1.5 μm diameter from the stripped solution using oleic acid as a surfactant and sodium hypophosphite as a reductant. LIX 984 diluted in kerosene was successfully used for copper extraction from acidic leach solution of HNO_3 and the subsequent stripping was carried out with either HNO_3 or H_2SO_4 **[87-88]**. LIX 26 in decanol was used to remove impurities such as Co, Ni, Zn, Al, Mn and Pb from ammoniacal solution containing large amount of monovalent copper. Copper was then recovered from the purified solution by electrowinning, while base metals were stripped from the organic phase by sulfuric acid and recovered as their respective sulfate **[89]**.

Activated carbon has been used for gold adsorption from cynide solutions since 1946 in mining. Altansukh et al. **[90]** have extended the use of activated carbon to the treatment of WPCBs. In particular, 98% of gold was adsorbed onto the activated carbon from a pregnant solution resulting from a iodine/iodide leaching of WPCBs under the following conditions: particle size of carbon, < 75 µm; carbon dose, 1 g/L; pH of pregnant solution, 3.2; shaking speed, 140 rpm; temperature, 20°C; and time, 30 min. In the study, base metals were leached before precious ones. Indeed, a previous step of base metal removing is often required because activated carbon can also partially adsorb base metal ions **[74]**. Overall, adsorption is still poorly applied in the field of WPCBs recycling.

In comparison with activated carbon, ion exchange allows to obtain higher adsorption and Au recovery rates **[74]**. Commercial IEX resins have been successful used in recovering gold from thiosulfate leach solution in mining. Gel type resins with a polystyrene divinylbenzene matrix and quaternary ammonium functional groups (e.g. Dowex G51, Dowex 21 K and amberlite IRA-410) have also been investigated. Kim et al. **[91]** used Amberlite XAD-7HP to adsorb Au from chlorine solution coming from leaching of WPCBs and reported that small amount of copper was also co-loaded. To achieve higher selectivity of ion exchange, many researchers are testing new resins, especially modified by functional groups.

A few studies exist on the use of electrochemical techniques for gold recovery from WPCBs. Lekka et al. **[92]** investigated direct electrodeposition of gold from aqua regia leach solution in the presence of copper as possible interferent. They obtained a compact deposit of pure gold by electrodeposition at 0.55 V vs $Ag/AgCl/KCl_{3M}$, but with low efficiency owing to the competitive reduction of Cu^{2+} to $CuCl_2^-$. Kasper et al. **[93]** reported that 99% Au could be selectively deposited over Cu from ammoniacal thiosulfate leach solution by controlling potential in a range between -400 and -500 mV vs Ag/AgCl. Contrarily, electrochemical methods, i.e. electrowinning and electrorefining, are the most used techniques for obtaining pure copper from WPCBs, as seen above. From the environmental point of view, electrochemical methods are superior in comparison to the other purification techniques because the main reagent is electron that is clean. However, the drawback of these methods is the selectivity.

2.6 Concluding remarks

Pryrometallurgical process is currently the most used method for WPCBs recycling. The main driving force which has led some companies to invest in pyrometallurgical processes is the possibility to treat e-waste directly in smelting process together with other types of waste or with copper and lead concentrates. However, the traditional smelting technologies give rise to the following limits:

1. Recovery of Fe and Al is not possible because they end up in the slag phase;
2. Recovery of plastic is not possible because it is burned and utilized as a source of energy or as a reducing agent;
3. Ceramic component of e-waste can increase the volume of slag in the blast furnaces increasing the risk of losing metals;
4. Only partial separation of metals can be achieved using pyrometallurgy. Other complementary either hydrometallurgical or electrometallurgical steps are subsequently necessary to obtain high-grade metals;

5. Great investments are required to maximize the recovery of valuable metals and to control gas emission to protect the environment;
6. There is generation of hazardous gasses containing chlorinated and brominated dioxins and furans. Besides, the flue dust can contain some fraction of Zn, Pb, Sn, Cd and Hg due to the high processing temperatures.

Although pyrometallurgy has been improved in the last years, for example adding a mechanical-physical pretreatment of e-waste, some pollution problems are still inevitable. Biometallurgy could be a promising alternative; however, it suffers from low reaction rate and low recovery efficiency. Certain microorganisms treat only specific metals and the metal content that can be treated is also limited. Besides, the reaction mechanisms at the base of bioleaching and biosorption processes are still discussed. Therefore, the more realistic alternative to the traditional pyrometallurgical approach is hydrometallurgy. It is more selective towards metal recovery, easier to be controlled and creates less environmental hazards than pyrometallurgical route. The process does not generate gas emission, dust or slag to further treat. The investment and operating costs are lower than the traditional pyrometallurgical process. However, some limits still have to be overcome such as the consistent loss of metals during mechanical and physical pretreatment of WPCBs, the toxicity of cyanide-based leaching solutions and the high consumption of reagent in the leaching not cyanide-based solutions. Besides, the removal of base metals before leaching of precious ones involves the use of different solvents resulting in large volumes of effluents to be disposed. The research efforts are mainly focused on finding new less-polluting and low cost leaching agents and reducing metal losses during operations. Probably, different technologies should be integrated to meet the requirements of environmental protection and industrial feasibility of WPCBs recycling.

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Chapter 3

Copper recovery from the urban mine of WPCBs

Introduction

Electronic waste, in particular discarded PCBs, is a promising secondary source of metals. Cu is the predominant metal by weight along with substantial amounts of other base and precious metals. Copper content in WPCBs ranges between 12% and 29% by weight while that in ore deposits between 0.5% and 3%, therefore WPCBs can be considered as a modern urban mine of copper.

In the last few years, the demand of copper has increased dramatically. Copper is widely used in a multitude of different applications due to its unique and exceptional properties. In order to meet the future demand of copper and preserve the natural resources, a key role could be played by WPCBs recycling.

The first section of the chapter deals with the importance of copper for human life, reporting updated data on copper production, consumption and long-term availability. The second section of the chapter is dedicated to the description of the methods currently used in the mining industry for copper extraction from the natural deposits. This part is relevant because most of the techniques used in the primary copper production subsequently have been extended to the treatment of WPCBs. The third section provides a comprehensive review of all methodologies used for the recovery of copper from WPCBs, reporting the main innovations in the field of pyrometallurgy, hydrometallurgy and biometallurgy. Besides, the new entirely electrometallurgical processes will be presented.

3.1 About copper

Copper is one of the few metals that can be found in nature in a directly usable metallic form (native metal). This led to very early human use in several regions. It is estimated that copper has been in use by civilization for over 10.000 years. A copper pendant discovered in what is now northern Iraq has been dated to about 8,700 B.C. Copper was the first metal to be smelted from sulfide ores, c. 5000 B.C., the first metal to be cast into a shape in a mold, c. 4000 B.C. and the first metal to be purposefully alloyed with another metal, tin, to create bronze, c. 3500 B.C. Currently, over 400 copper alloys are in use, each with a unique combination of properties to suit many applications, manufacturing processes and environments. The Egyptians had many uses of copper and in their culture, copper represented eternal life. In the Roman era, copper was principally mined on Cyprus, indeed, the name of the metal comes from the Latin word cuprum, meaning “from the island of Cyprus.”

Copper is vital to the health of humans, animals and plants and is an essential part of the human diet. Copper-rich foods include dried beans, almonds, broccoli, chocolate, garlic, soybeans, peas, whole wheat products and seafood. Virtually, every cell in the body utilizes copper and, together with iron and zinc, copper makes up the trio of minerals essential to our well-being. The adult body contains between 1.4 and 2.1 mg of copper per kilogram of body weight **[1]**.

Copper boasts of a combination of properties that make it versatile, unique and irreplaceable in many applications. Copper is the best conductor of electricity except for silver. Its electrical and thermal conductivity, along with properties of high ductility and malleability make it one of the most demanded metals by industry, eclipsed only by iron and aluminum. From common household electrical wiring to boat propellers and from photovoltaic cells to saxophones, copper and its alloys are employed in a multitude of end-uses. Copper is also corrosion resistant, antimicrobial and infinitely recyclable without any loss of performance. It is estimated that 80 percent of all mined copper during the past 10,000 years is still in use somewhere today **[2]**. About 33% of the current world annual copper demand is supplied by recycled copper.

The Copper Development Association (CDA) **[1, 3]** classified the applications of copper in four end-use sectors: electrical, construction, transport, and other. The percentage of global copper production consumed by each sector is estimated by the CDA to be:

- 65% Electrical, copper is used in electronic connectors, printed circuit boards, semi-conductors, micro-chips, circuitry wiring and contacts, etc.;
- 25% Construction, copper is used in the tubes for drinking water, in seawater feed lines, in the tubes for heat exchangers in chemical plants, etc.;
- 7% Transport, copper is used in motors and wiring, springs, steering systems, avionics, etc.;
- 3% Other, copper is used in musical instruments, coinage, art, architecture, etc.

As it can be seen, copper application areas cover a wide variety of different disciplines. For example, the total weight of copper in a vehicle ranges from 15 Kg for a small car to 28 kg for a luxury car; high-speed trains use 10 tonnes of copper per km of track; 2% of an airliner's weight can be attributed to copper **[2]**.

In nature, copper occurs in a variety of minerals, including native copper, copper sulfides such as chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), digenite (Cu_9S_5), covellite (CuS), and chalcocite (Cu_2S), copper carbonates such as azurite ($Cu_3(CO_3)_2(OH)_2$), and malachite ($Cu_2CO_3(OH)_2$), and copper oxides such as cuprite (Cu_2O) and tenorite (CuO). The most abundant minerals are chalcopyrite and bornite, which cover 80% of currently known deposits. Ore grade and mineral composition vary depending on the type of mineralization. Most mines operate with copper concentrations between 0.2 and 0.8%, some of the richest ore bodies, located in central to South Africa, can contain 5-6% of copper. A broad classification of copper deposits is on the ways of deposits formation. According to this classification, there are two important types of copper deposits: porphyry copper and sediment-hosted copper. Porphyry copper deposits, which are associated with igneous intrusions, yield about two-thirds of the world's copper and are therefore the most important types of copper deposit **[4]**. Sediment-hosted copper deposits, which are contained in sedimentary rocks, account for approximately one-fourth of the world's identified copper resources. In Figure 3.1.1 a global copper map is reported showing the distribution of porphyry copper and sediment-hosted copper deposits around the world. As it can be seen, large porphyry copper deposits are found in mountainous regions of western North America and in the Andes Mountains of South America.

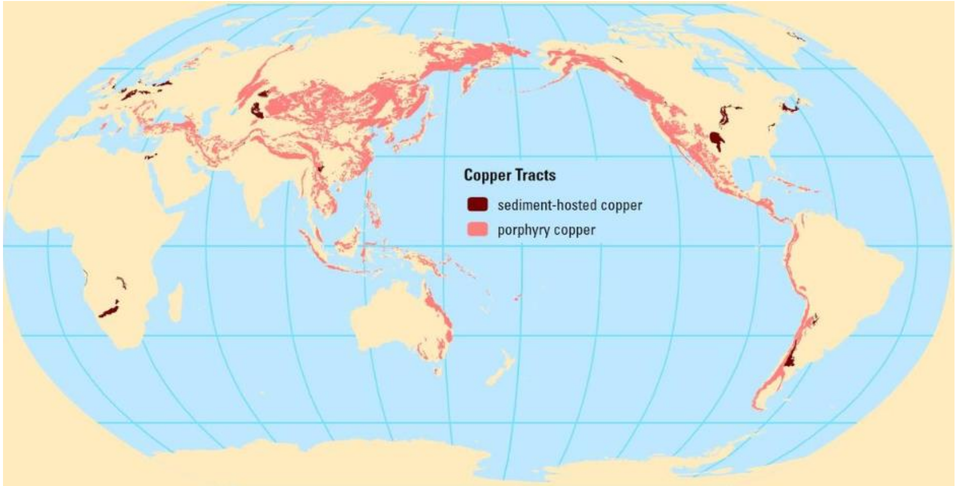


Figure 3.1.1 Distribution of known porphyry copper deposits and sediment-hosted copper deposits around the world. Released by USGS in July 2016 [5]

United States were the largest producers of copper until 2000 then the primacy passed to Chile. As it can be seen from Figure 3.1.2, North America copper production declined from 36% in 1960 to 13% in 2017. In contrast, Latin America exhibited a significant growth during the same period. In 2017, about 42% of the total copper mine production was attributed to Andes Mountains.

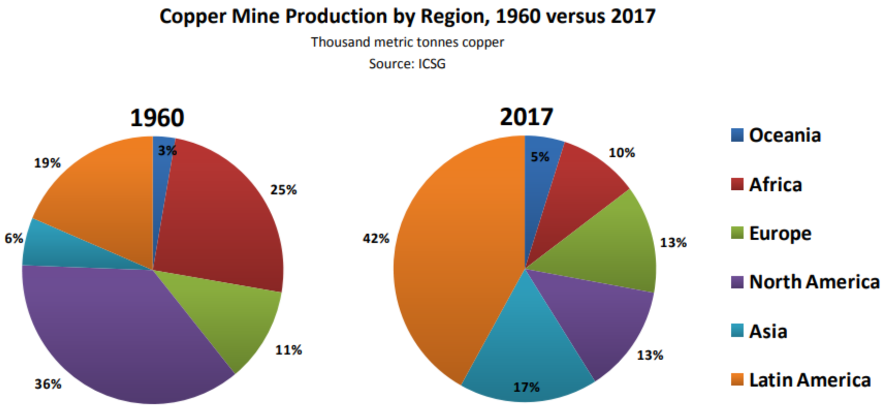


Figure 3.1.2 Copper mine production by region, 1960 vs 2017 [6]

The world's production (supply) and consumption (demand) of copper have increased dramatically in the past 25 years. Because of the entry of developing countries in the global market, the demand for mineral commodities, including copper, has greatly increased. In Figure 3.1.3 the worldwide production of copper in the period 1960-2017 is shown.

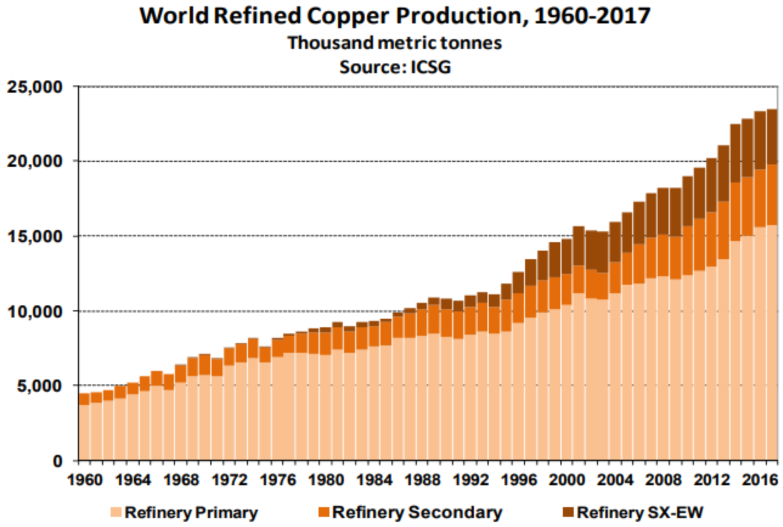


Figure 3.1.3 World refined copper production in the period 1960-2017 [6]

Over the last 25 years, copper production has doubled from about 11 million tonnes in 1992 to about 23 million tonnes in 2017. Due to the introduction of solvent extraction-electrowinning technology, refined copper worldwide production from leaching ores has increased from less than 1% in the late 1960's to 16% in 2017. Besides, secondary copper refined production reached 17% of the total copper refined production in 2017. About copper consumption by region, interesting results are reported by the United States Geological Survey (USGS) for the period 1980-2012 **[5]**. Copper consumption in emerging economies, such as China and India, increased considerably from 1980 to 2012 (Figure 1.3.4). Until 2002, the United States were the leading copper consumer and annually used about 16% of total world refined copper, but have been overtaken by China from 2002. The booming economy in China contributed to quadrupling its annual refined copper consumption during the 12 years from 2000 to 2012.

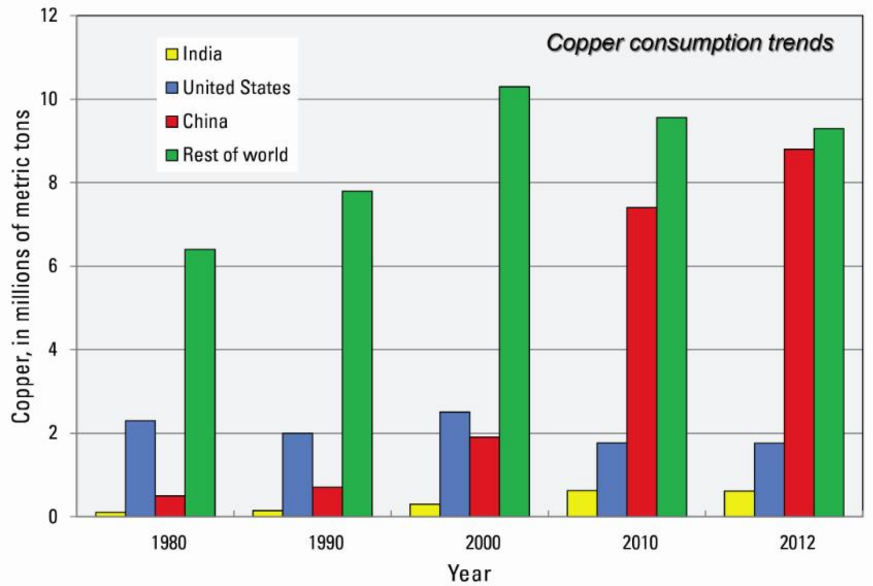


Figure 3.1.4 Global copper consumption [5]

The future availability of minerals is based on the distinction between reserves and resources. Reserves are deposits that have been discovered, evaluated and assessed to be economically profitable. Resources are far greater and include reserves, discovered deposits which are potentially profitable and undiscovered deposits that are predicted, based on preliminary geological surveys **[2]**.

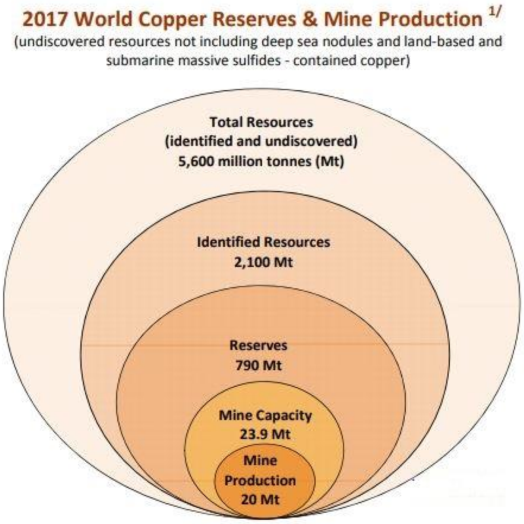


Figure 3.1.5 2017 World copper reserves and mine production

According to the USGS data **[5]**, copper reserves currently amount to around 790 million tonnes while identified and undiscovered copper resources are estimated to be around 2,100 Mt and 3,500 Mt, respectively (Figure 3.1.5). The latter does not consider the vast amounts of copper found in deep sea nodules and land-based and submarine massive sulfides. On average, 40 years of copper reserves and over 200 years of resources left have always been estimated since 1950 **[5]**. It is important to note that current and future exploration will increase both reserves and resources. Besides, a significant contribute will also be supplied from the amount of copper that is already in use today thanks to recycling of end of life products. Indeed, to ensure that a sufficient quantity of copper will be available to meet the future demand, it is necessary to increase the level of recycling. In this context, copper-rich wastes, such as PCBs wastes, will become ever more important in the future.

3.2 Copper mining

Copper ore is extracted using three different techniques depending on the characteristic and geographic location of the ore body. Open-pit mining is the most common technique and consists in extracting rock or minerals from the earth by their removal from an open pit. This technique is appropriate for near-surface (<100m) ore **[7]**. Underground mining methods are used to extract minerals from deep in the earth, sinking a vertical shaft into the earth to reach the copper ore and driving horizontal tunnels into the earth. The third method consists in pumping a weak sulfuric acid leaching solution through boreholes drilled into a deposit to dissolve copper. The solution containing the dissolved ore is then pumped up to the surface and processed.

After extraction, the ore is crushed, ground into powder and concentrated up to 25-35% copper content. The ore is enriched using a process called froth flotation where the undesired material (named gangue) sinks to the bottom and is removed. Once the copper has been concentrated, it can be converted into pure metal by

- Pyrometallurgical processes, including smelting and electrolytic refining;
- Hydrometallurgical processes, including leaching, solvent extraction and electrowinning.

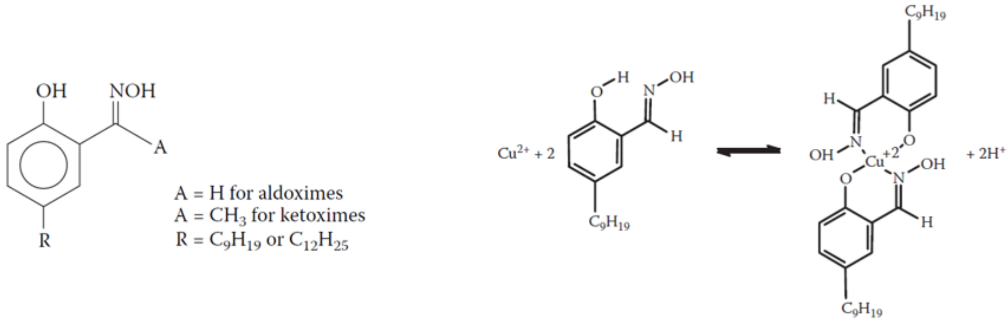
Currently, hydrometallurgy is primarily used only for oxide ores. However, some studies on extraction of copper from primary sulfides by hydrometallurgy are ongoing. Hydrometallurgical processes have many advantages over pyrometallurgical ones, including: i) the possibility of processing lower grade ore, ii) the possibility of operating at low temperatures obtaining higher energy efficiencies, iii) a lower environmental impact because no waste gases are given off, iv) low capital and operational costs which make hydrometallurgy more economical for smaller scale operations.

The following stages are involved in pyrometallurgical process: roasting, smelting, converting and fire refining. Matte copper (35-68 wt.% Cu) is firstly produced by smelting. It consists mainly of copper and iron sulphides, then blister copper (97-99 wt.% Cu) is produced by converting and finally anode copper (99.5 wt.% Cu) by fire refining. The anode copper can be further purified to 99.95-99.96% by electrolytic refining. The roasting process is generally conducted in reverberatory furnaces. In the roaster, the copper concentrates are heated to about 650°C and partially oxidized to remove most of the sulfur as SO_2 gas, which can be captured and converted in sulfuric acid. This operation is no longer used and direct smelting is now preferred. Smelting is carried out at 1000-1500°C in the presence of air or oxygen-enriched air in a variety of furnaces such as reverberatory furnaces, flash furnaces, IsaSmelt furnaces etc. The purpose of such operation is that to eliminate as much of the undesired iron, sulfur and gangue minerals (such as silica, magnesia, alumina and limestone) as possible. This is achieved by adding silica, which traps iron oxide formed during oxidation of iron sulfides in a separate slag. The slag forming reaction is

$$FeO + SiO_2 \rightarrow FeO \cdot SiO_2 \qquad (3.2.1)$$

Slag is less dense than matte, so it can be easily removed and discarded because it forms a layer that floats on top of the matte. The so obtained matte copper contains mainly copper and iron sulfides which are converted to oxides by blowing air through the molten matte in the converter. This produces so much SO_2 that can be captured to make sulfuric acid. A silica and lime flux is added to separate iron with the slag leaving blister copper. The blister copper is put into an anode furnace where it is converted to anode-grade copper in two stages by removing most of the remaining sulfur and iron, and then removing oxygen introduced during the first stage. The second stage is carried out by blowing natural gas, or some other reducing agent, through the molten copper oxide. The anodes cast during the fire refining are immersed in an aqueous solution of copper sulfate and sulfuric acid and refined by electrolysis. At the anode, copper and less noble metals dissolve. Nobler metals such as silver, gold, selenium, and tellurium settle to the bottom of the cell as an anode slime. Copper(II) ions move through the electrolyte to the cathode where they are deposited on a pure copper foil. Less noble metals than copper remain dissolved in solution without interfering at cathode.

The production of high-purity copper by a combination of leaching, solvent extraction and electrowinning for the primary processing of copper has enjoyed spectacular growth over the past 35 years. Approximately 20% of all copper currently produced worldwide is obtained by leaching mainly of oxide ores. The operating cost of this process is typically 30% less per kg of cathodic copper than conventional pyrometallurgical production **[8]**. Generally, weak sulfuric acid is used as a leaching agent for copper dissolution from its minerals. The resulting solution, known as *pregnant leach solution*, is recovered and then contacted with an organic solvent, referred to as the *extractant* in the solvent extraction stage. Here, the copper is extracted away from the leach solution leaving behind most of the impurities. The most used extractantans of copper from sulphate liquors are known as oximes. The basic structures of the oximes are shown in Figure 3.2.1, where A = H is for *aldoximes* and A = CH_3 for *ketoximes*. The R-chain is usually C_9H_{19} and occasionally $C_{12}H_{25}$. The complexation of copper by these extractants is shown in Figure 3.2.1.

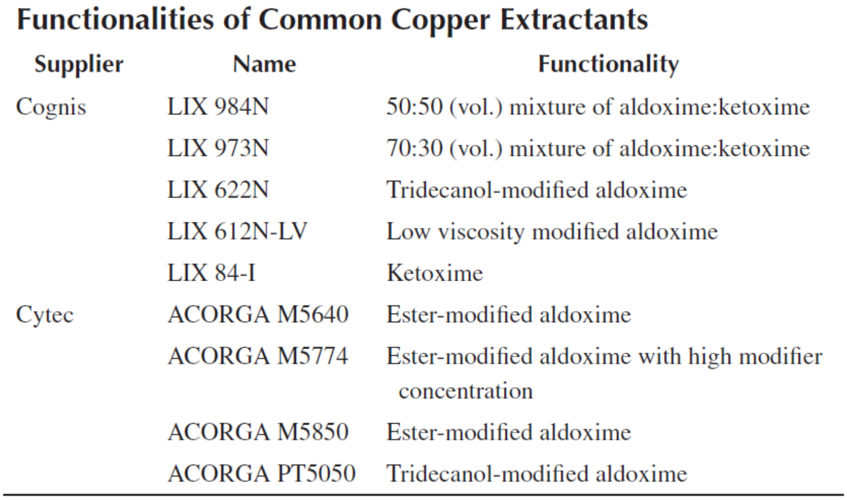


Extraction: $Cu^{2+} + 2\,RH \rightarrow CuR_2 + 2\,H^+$

Stripping: $CuR_2 + 2\,H^+ \rightarrow Cu^{2+} + 2\,RH$

Figure 3.2.1 Copper oxime extractants and mechanism of copper complexation by oxime extractants [8]

Since the complexation is an un-complete reaction, copper can be stripped from the organic phase by the contact with a strongly acidified aqueous solution according to Le Chatelier's principle. The resulting purified solution can be transferred to the final electrowinning stage for obtaining pure copper deposits at the cathode of the electrolytic cell. The first commercial extractants were all based on ketoximes (e.g. LIX 63, LIX 65, LIX 65N etc.), but they were replaced by the second generation of extractants based on aldoximes. Aldoximes exhibit very fast extraction kinetics, high selectivity towards copper and high loading capacity. Copper selectivity over iron is about 2000:1, while that of ketoximes is about 300:1. However, they extract at pH values below 1 making the stripping of copper difficult. Aldoximes are therefore combined with polar organic compounds, known as *modifiers*, so that copper can be stripped at the typical acid strength of spent electrolyte coming from electrowinning (~180 g/l H_2SO_4) **[8]**. A third class of extractants is represented by mixtures of aldoximes and ketoximes. Today, modified aldoximes and aldoxime–ketoxime mixtures are the most widely used copper extractants. The most common copper extractants in commercial use today are shown in Table 3.2.1.



Functionalities of Common Copper Extractants

Supplier	Name	Functionality
Cognis	LIX 984N	50:50 (vol.) mixture of aldoxime:ketoxime
	LIX 973N	70:30 (vol.) mixture of aldoxime:ketoxime
	LIX 622N	Tridecanol-modified aldoxime
	LIX 612N-LV	Low viscosity modified aldoxime
	LIX 84-I	Ketoxime
Cytec	ACORGA M5640	Ester-modified aldoxime
	ACORGA M5774	Ester-modified aldoxime with high modifier concentration
	ACORGA M5850	Ester-modified aldoxime
	ACORGA PT5050	Tridecanol-modified aldoxime

Table 3.2.1 Main copper extractants in commercial use today [8]

Leaching of copper has also been performed by either ammoniacal solutions or particular strains of bacteria. The Arbiter plant in Anaconda, Montana, used an ammoniacal leaching solution to dissolve copper from sulfide concentrates and LIX 64N asan extractant of copper from the leach solution **[8]**. More recently, BHP

Minerals (now BHPBilliton) developed the Escondida process in which copper concentrates are leached with ammonia and ammonium sulfate, and then purified by solvent extraction with LIX 54, which is a β-diketone having an higher copper loading capacity (~30 g/l) than ketoximes. Bioleaching is used in synergy with solvent extraction/electrowinning process for low-grade sulfide copper minerals. Modern commercial application of bacterial leaching began in the 1950s at Kennecott's Bingham mine near Salt Lake City, Utah **[1]**. Following early development work and application in the United States, Chile has become a major developer of bioleaching on an industrial scale. Generally, the capital cost of a bioleaching operation is considerably less, by about 50%, than that of a conventional pyrometallurgical process. Sulphide minerals are insoluble in water or acid solutions unless they are first oxidized. The kinetics of the oxidation process can be considerably improved by the introduction of *Thiobacillus ferrooxan* and *Thiobacillus thiooxan* bacteria into the system. The former catalyzes the oxidation of iron whereas the latter catalyzes the oxidation of sulphur. There are two dominant views on the mechanisms involved in bioleaching. According to the first one, the overall leaching process occurs by microbial oxidation of ferrous ions to ferric followed by the chemical oxidation of the sulphide mineral by the ferric ions. The microorganisms play also the role of regenerating Fe^{3+} from Fe^{2+}. This is known as the *indirect mechanism* and can be described by the following equations **[9]**

$$MS + 2Fe^{3+} \rightarrow M^{2+} + 2Fe^{2+} + S^0 \qquad (3.2.2)$$

$$2Fe^{2+} + 0.5O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O \qquad (3.2.3)$$

According to the second view, microorganisms directly oxidize minerals and solubilize metals. The reactions are **[9]**

$$MS + H_2SO_4 + 0.5O_2 \rightarrow MSO_4 + S^0 + H_2O \qquad (3.2.4)$$

$$S^0 + 1.5O_2 + H_2O \rightarrow H_2SO_4 \qquad (3.2.5)$$

In practice, metals can be dissolved from minerals directly by the metabolism of the cell or indirectly by the metabolic products. However, the model of direct and indirect leaching is still under discussion. Several researches reported that some fungal strains such as *Aspergillus niger* and *Penicillium simplicissimum* can be used for bioleaching of copper from primary resources. Fungi-assisted leaching does not rely on microbial oxidation of metal but rather uses microbial metabolism as a source of acids that directly dissolve the metal.

Most of the techniques used to extract copper from the minerals have been extended also for its extraction from wastes, being well-known and consolidated. A comprehensive description of all techniques applied for copper extraction from waste of PCBs will be reported in the following.

3.3 Recycling of copper from WPCBs

WPCBs can contain up to 40 different metallic elements **[10]**. Among these, copper is the most abundant. Copper concentration in WPCBs ranges between 12% and 29% by weight. Considering that copper concentration in ores ranges between 0.5% and 3% **[11]**, WPCBs can be considered as an urban copper mine. Due to its high content in WPCBs, copper recovery could play a key role in economic balance of recycling plants, although it has lower added value than precious metals. From industrial point of view, the typical approach adopted for WPCBs recycling consists in pyrometallurgical processes. However, the relevant problems associated to this approach, discussed in the second chapter, have encouraged the research to develop new processes based on hydrometallurgical, biometallurgical and electrometallurgical techniques or on a combination of these. From the literature, it can be found a typical approach adopted for copper recovery from WPCBs that generally includes the phases reported in the scheme of Figure 3.3.1. It is important to point out that several variations to the flowsheet of Figure 3.3.1 can be found in the literature, such as the processes based on biometallurgy. However, the most used technique consists in dissolving copper by means of a leaching agent and then recovering copper from the leach liquor directly by electrowinning or after a purification step.

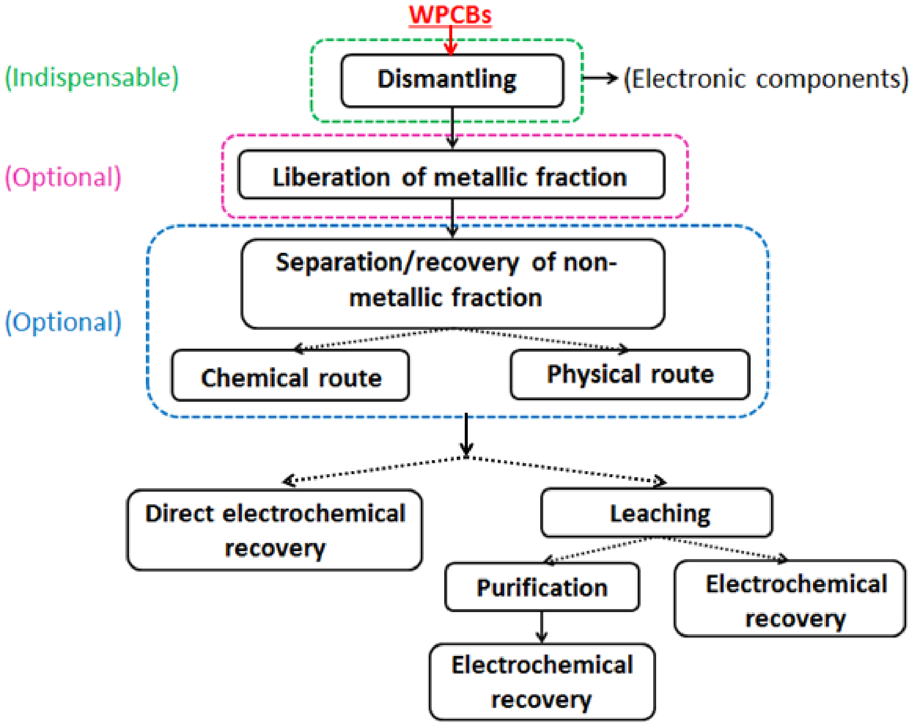


Figure 3.3.1 Possible paths of a typical copper recovery process from WPCBs

According to the literature **[12-14]**, electrolysis is an ideal process to recover copper due to its simple flowsheet, low energy consumption, high output and low environmental pollution. For this reason, new and entirely electrometallurgical processes have been developed in the last few years in order to minimizing the number of unit operations involved in WPCBs recycling, the use of solvents and therefore, the environmental impact and energy consumption. Besides, Figure 3.3.1 shows that both mechanical processing of WPCBs and separation/recovery of the non-metallic fraction through either physical or chemical methods can be avoided. Indeed, in order to simplify the recovery process and to avoid the loss of metals during the pre-treatment of WPCBs, some authors reported the use of large pieces of WPCBs having a surface ranging from 10 to 25 cm^2 **[15-19]**, which can be directly processed either by leaching **[16, 17]** or electrochemically **[15]** after the solder mask removal by means of NaOH or H_2SO_4 concentrated solutions. In other cases, the large pieces of WPCBs are pre-treated by pyrolysis before leaching **[18]** or bioleached directly **[19]**.

The current technologies on copper recovery from WPCBs will be better discussed in the following with particular attention towards the hydrometallurgical and earlier electrometallurgical routes.

3.3.1 Pyrometallurgical route

The classical approach industrially adopted for copper recovery from WPCBs consists in combining pyrometallurgical stage with electrochemical refining unit. The recycling plants introduce WPCBs into the smelting stage of copper or lead concentrates after a minimum pre-treatment. Contrarily, the new smelting plants use an integrated approach in which pyrometallurgical, hydrometallurgical and electrometallurgical techniques are combined together **[9, 20-21]**. The Umicore process represents an example of integrated pyrometallurgical approach. In the new plants, the e-waste is thermally treated together with other metallic scrap and not with copper or lead concentrates. The smelting stage is carried out under reducing conditions and the product is impure copper named *black copper*, containing approximately 60-85% by weight of copper. A schematic representation of a pyrometallurgical process for e-waste recycling is shown in Figure 3.3.1.1. After smelting, the stages of the process are equivalent to those of primary copper production and include refining of the black copper by oxidation in a converter, fire-refining to produce anode-grade copper and electrolytic refining to reach a copper purity of more than 99.9%. The anodic slime leaving the electrorefining unit is further treated for the recovery of precious metals. In Umicore process, the black copper is treated by leaching followed by electrowinning.

In the last few years, pyrometallurgical technology has been significantly updated mainly in improving treatment of waste gas in smelting and refining stages and addition of the mechanical-physical pre-treatment of e-waste.

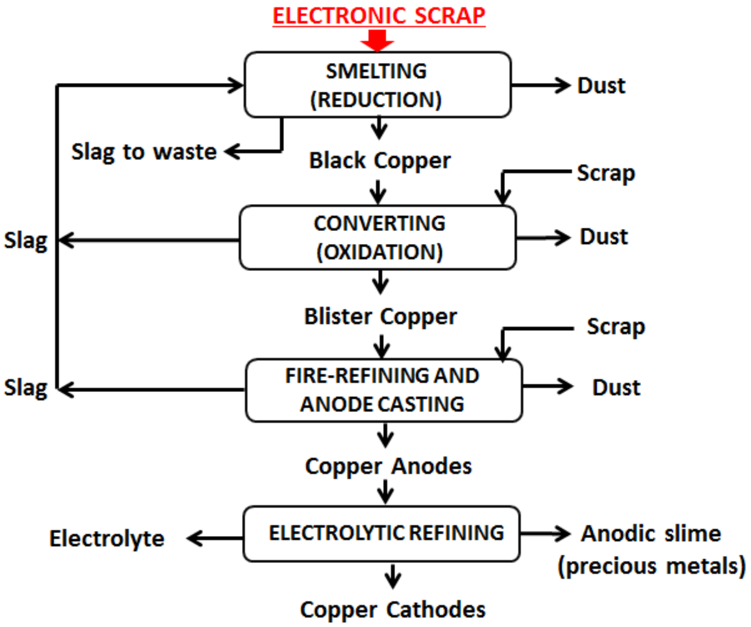


Figure 3.3.1.1 A schematic flow sheet of a typical pyrometallurgical process for WPCBs recycling

However, although pyrometallurgy has been further improved, some pollution problems are still inevitable. This has been the driving force for the development of the new molten salts technology. Molten salts allow to operate at lower temperatures (T<500°C) using eutectic salt compositions. Molten salts process reduces the energy cost, corrosion of the installation and harmful gas emission. Flandinet et al. **[22]** reported a process in which molten KOH-NaOH eutectic bath ($T_{melting}$=170°C) was used to dissolve non-metallic fraction from crashed PCBs samples at 300°C, leaving a copper-rich residue. The carbon dioxide produced during the molten salt oxidation of resin and plastics was trapped in the melt by forming molten carbonates and silicates. In addition, halogens were converted to alkali metal halides, which remained in the molten salt. Finally, operating without oxygen, the flue gas contained almost 30% of hydrogen and therefore, it was potentially usable as a fuel gas or synthesis gas. Guo et al. **[23]** proposed an alkali fusion-leaching-separation process for metals recovery from WPCBs using a low-cost oxidizing flux of NaOH–$NaNO_3$ as a reaction medium at a temperature of 500°C. In the alkali fusion–leaching process, amphoteric metals such as Sn, Pb, Zn and Al were converted into sodium salts and dissolved in solution, thus they were separated from Cu and precious metals which remained in the residue. Subsequently, metals in solution were further extracted via precipitation processes, and metals in the residue were recovered using an acid leaching-electrowinning process. Recoveries of metals were 98.66% of Cu, 96.08% of Sn, 91.25% of Zn, and 78.78% of Pb, respectively. Molten salts process represents the most significant progress in the area of pyrometallurgy, but further studies are required because it is still a recent technology in the field of WPCBs recycling.

3.3.2 Hydrometallurgical route

A great number of papers have been published about leaching of copper from waste PCBs. Hydrometallurgical route is the most investigated technique in the field of copper recovery from e-waste. Copper can be effectively leached using either acidic or ammoniacal solutions. Besides, some novel leaching systems have been proposed in recent years, such as ionic liquids and chelating agents.

3.3.2.1 Acidic leaching

Traditional leaching methods employ mineral acids, such as H_2SO_4, HNO_3 and HCl as lixiviants. Base metals such as Zn, Sn, Fe, Ni, Pb and Al are successfully dissolved in such acids, however, Cu needs of oxidizing acids (e.g. HNO_3) or non-oxidizing acids (e.g. H_2SO_4, HCl) in the presence of an oxidant such as air/O_2, H_2O_2, Cl_2, Cu^{2+} and Fe^{3+} **[24]**.

The use of nitric acid as a leaching agent for copper extraction from WPCBs has been investigated by different authors **[25-30]**. The reaction of copper with aqueous nitric acid solution can be expressed as follows

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2H_2O + 2NO_2 \qquad (3.3.2.1.1)$$

Le et al. **[30]** reported that dissolution of copper from pre-treated WPCBs increased with temperature, HNO_3 concentration and with decreasing in pulp density. However, acid concentration cannot be increased excessively to avoid reduction of pH that can hinder further operations such as solvent extraction and electrowinning. A copper dissolution of 99% was achieved in 1 h along with other metals such as Ni, Fe, Zn and Pb with 3.5 mol/L HNO_3 at 323 K and 120 g/L pulp density, while Sn dissolution was found to be negligible even at high concentration of HNO_3 and elevated temperature. Copper was then extracted from the leach solution by solvent extraction with LIX 984N in kerosene, stripped with sulfuric acid and recovered by electrowinning. In the study by Mecucci et al. **[25]**, tin was precipitated in the form H_2SnO_3 during leaching of WPCBs in HNO_3 for acid concentrations higher than 4 M. Copper and lead were directly recovered electrochemically from the leach solution using a simple undivided cell where Cu was deposited at cathode and PbO_2 at the anode without any preliminary purification step. Generally, the current efficiency obtained in copper electrolysis from nitric acid solutions is quite low and decreases with HNO_3 concentration increasing. Mecucci et al. **[25]** explained the low current efficiency with both re-dissolution of deposited copper and competitive hydrogen evolution at cathode. Indeed, a pH correction is suggested before electrolysis. Maguyon et al. **[27]** concluded that leaching of WPCBs with nitric acid shows better Cu recovery than in aqua regia and diluted the leach solution before electrodeposition for pH correction.

HCl is less common for copper extraction from WPCBs. Havlik et al. **[31]** used 2 M HCl solution to extract more than 80% of tin after 120 min. at 80°C from pre-treated WPCBs by mechanical-physical route. However, copper extracted was less than 1% due to the non-oxidizing environment. According to the authors, this was valid for the whole range of temperature 0-100°C, because the values of ΔG^0 in this temperature range were positive.

$Cu + 2HCl_{(aq)} = CuCl_2 + H_{2(g)}$ ΔG^0_{80}=92.58 KJ/mol (3.3.2.1.2)

$2Cu + 2HCl_{(aq)} = 2CuCl + H_{2(g)}$ ΔG^0_{80}=1.68 KJ/mol (3.3.2.1.3)

The small amounts of copper found in solution were probably due to the leaching of copper oxides which naturally cover copper particles. Thermodynamically, this was possible according to the following reactions

$Cu_2O + 2HCl_{(aq)} = 2CuCl + H_2O$ ΔG^0_{80}=-81.306 KJ/mol (3.3.2.1.4)

$CuO + 2HCl_{(aq)} = CuCl_2 + H_2O$ ΔG^0_{80}=-33.73 KJ/mol (3.3.2.1.5)

Similar considerations can be also made for extraction of copper in H_2SO_4 acid solutions. Castro et al. **[32]** tested the following leaching solutions for the extraction of copper and tin from a WPCBs powder: 2.18 N H_2SO_4, 2.18 N H_2SO_4 + 3 N HCl, 3 N HCl, and 3 N HCl + 1 N HNO_3. After 120 min. at 60°C, the 3 N HCl + 1 N HNO_3 leaching solution exhibited the highest extraction power for both tin (98%) and copper (93%), while the lowest values were obtained with 2.18 N H_2SO_4 (2.7% Sn and <0.01% Cu) solution. Copper extraction by 2.18 N H_2SO_4 + 3 N HCl and 3 N HCl leaching solutions was 8.9% and 33.2%, respectively. An improvement of the leaching performances of copper in H_2SO_4 and HCl solutions can be achieved after a thermal pre-treatment of WPCBs **[33-34]** because copper oxide can be more efficiently leached in a non-oxidizing environment than copper metal. Masavetas et al. **[33]** obtained Cu recovery of 97.5%, 65% and 76.5% in HNO_3, HCl and H_2SO_4, respectively after a thermal pre-treatment at 500°C for 1 h in both air and nitrogen atmosphere of WPCBs small pieces (~1x2 cm). More than 98% of copper was then recovered by electrowinning from the three different leaching solutions. An almost complete extraction of copper can also be achieved with only H_2SO_4 operating under pressure (2 MPa) and at high temperature (~120°C) **[24]**.

Although nitric acid and aqua regia are more suitable for copper leaching than sulfuric acid, they are extremely corrosive and lead to the release of harmful gaseous reaction products such as NOx mixtures. Similar problems are also associated with HCl solutions, which have also low copper recovery efficiencies. For all these reasons, sulfuric acid is the most preferred leaching agent for copper dissolution from WPCBs. However, an oxidant has to be added to the sulfuric acid solution to operate in milder conditions of temperature and pressure. H_2O_2 is the most common oxidant coupled with H_2SO_4 for the extraction of copper by the reaction **[35-36]**.

$$Cu^0 + H_2O_2 + H_2SO_4 = Cu^{2+} + SO_4^{2-} + 2H_2O \quad \Delta G^0_{80}=-77.941 \text{ Kcal/mol} \quad (3.3.2.1.6)$$

Oh et al. **[35]** reported an extraction greater than 95% for copper and other base metals (Fe, Zn, Ni and Al) by leaching for 12 h, at 85°C with 2 M H_2SO_4, and 0.2 M H_2O_2. H_2O_2 has been extensively used as an oxidant mainly due to its high reduction potential of 1.77 V vs SHE. However, it suffers from high cost and remarkably high consumption due to its high decomposition rate particularly at high temperatures and in the presence of metal ions **[37]**. Therefore, Fe^{3+} has been investigated as an alternative oxidant due to its low cost, easy regeneration and high reduction potential (+0.771 V vs SHE) **[38-44]**. The reaction of metal leaching can be described as follows

$$Me + nFe^{3+} = Me^{n+} + nFe^{2+} \qquad (3.3.2.1.7)$$

One of the main drawbacks related to the use of ferric ions is the consequent contamination of the leach solution which can reduce the current efficiency of the final electrochemical copper recovery. However, it was found that the downstream can be purified by goethite and jarosite precipitation before electrowinning **[42, 45]**. Fe^{3+} can be used both in HCl and H_2SO_4 solutions. Diaz et al. **[43]** tested two different leaching systems: 0.1 M $Fe_2(SO_4)_3$-1 M H_2SO_4 and 0.2 M $FeCl_3$-0.5 M HCl. Base metals extraction efficiencies for the leaching with sulfate and chloride matrix were 97.5% and 99.6% for Cu, 43% and 100% for Sn, 97.1% and 94.4% for Zn, 6.41% and 100% for Pb, respectively. The low extraction efficiencies for Sn and Pb in sulfate media were due to the precipitation of SnO_2 and PbSO4, respectively. Generally, the regeneration of the oxidant is always included in the leaching processes mediated by Fe^{3+}. Fogarasi et al. **[39-41]** used $FeCl_3$-HCl as a leaching solution in a reactor combined with a divided electrochemical cell in which electrowwining of copper occurred in parallel with the leaching agent restoration. In particular, the solution leaving the leaching reactor was directly fed to the cathodic compartment for copper deposition and then passed to the anodic one for the oxidation of Fe^{2+} to Fe^{3+}, which was recycled into chemical reactor. The laboratory scale leaching plant allowed the recovery of pure copper with a current efficiency of 63.84% and an energy consumption of 1.75 KWh/Kg copper. Deveci et al. **[42]** performed the leaching of Cu, Ni, Ag and Pd from a powder of WPCBs using a H_2SO_4-NaCl-$Fe_2(SO_4)_3$ solution, achieving 99.9% of copper extraction in 120 min. at 80°C and a solid ratio of 1% w/v. The extraction of Ni, Ag and Pd was 88.1%, 16% and 60.4%, respectively, in identical conditions. Besides, the authors found that the introduction of oxygen for the in-situ regeneration of Fe^{3+} led to a significant improvement in the leaching efficiency of metals particularly at high solid ratios.

Recently, the use of Cu^{2+} as an oxidizing agent for extraction of copper from WPCBs has attracted attention because it allows avoiding the contamination from iron and reducing the costs compared to H_2O_2 **[46-50]**. Barbieri et al. **[38]** evaluated in terms of efficiency and kinetics both $FeCl_3$-HCl and $CuCl_2$-HCl leaching solutions for copper dissolution from WPCBs. They concluded that etching time was lower with ferric than cupric chloride; however, in the case of $CuCl_2$, a complete restoration of the leaching solution was achieved by air oxidation. Cu^{2+} can be used both in chloride and sulphate media; however, Deveci et al. **[46-47]**

found that chloride media was more corrosive and determined a more difficult electrowinning of copper than sulphate media.

3.3.2.2 Alkaline leaching

Several studies using alkaline solutions for leaching of base metals from WPCBs have been reported **[51-56]**. Unlike mineral inorganic acids, ammoniacal leaching solutions showed high selectivity towards copper. Sun et al. **[51]** reported that copper dissolution in ammonia-ammonium solution can be described as follows

$2Cu + O_2 = 2CuO$ (3.3.2.2.1)

$CuO + 2NH_3{\cdot}H_2O + 2NH_4^+ = Cu(NH_3)_4^{2+} + 3H_2O$ (3.3.2.2.2)

Copper is firstly oxidized by means of dissolved oxygen (or H_2O_2) and then, CuO is dissolved by ammonia-ammonium solution as a soluble Cu(I)-ammine complex. The mechanism is quite different in the absence of either oxygen or air atmosphere. Koyama et al. **[52]** demonstrated the feasibility of Cu leaching from WPCBs under a nitrogen atmosphere using a leaching solution containing $CuSO_4{\cdot}5H_2O$, Cu_2O, NH_3 and $(NH_4)_2SO_4$. The $Cu(NH_3)_4^{2+}$ species played the role of oxidant rather than oxygen. Indeed, the oxidation-reduction reactions of Cu(II)/Cu(I) and Cu(I)/Cu are expressed as follows

$Cu(NH_3)_4^{2+} + e^- = Cu(NH_3)_2^+ + 2NH_3$ (3.3.2.2.3)

$Cu(NH_3)_2^+ + e^- = Cu + 2NH_3$ (3.3.2.2.4)

Taking into account that oxidation-reduction potential of $Cu(NH_3)_4^{2+}$/ $Cu(NH_3)_2^+$ is nobler than that of $Cu(NH_3)_2^+$/ Cu, $Cu(NH_3)_4^{2+}$ can work as an oxidizing agent for metallic copper in ammoniacal alkaline solution. Besides, the oxidation-reduction potential of $Cu(NH_3)_2^+$/Cu is nobler than that of hydrogen evolution, therefore it is possible to recover copper by electrowinning from the leach solution. The reaction of copper dissolution in ammoniacal media can be described as follows

$$Cu + Cu(NH_3)_4^{2+} = 2Cu(NH_3)_2^{+} \quad (3.3.2.2.5)$$

The authors found that the effect of temperature on leaching rate was negligible while a significant enhancement of the leaching rate with the initial concentration of Cu(II) was found. Besides, according to the authors, the theoretical power consumption for electrowinning was lower compared to the conventional process in acid solution. Bari et al. **[55]** tested the use of different leaching agents for copper extraction from WPCBs including acidic and alkaline solutions. The best results in terms of selectivity and leachability were found with 5 M NH_3-0.5 M $(NH_4)_2S_2O_8$ solution, achieving an almost complete copper extraction (~ 99%). The extraction of Zn, Ni and Fe was 60%, 9%, and 0%, respectively, which is lower than that obtained with acidic solutions. Despite the higher selectivity for copper recovery by ammoniacal leaching solutions, generally a purification of the leach solution is performed before any further treatment. Alam et al. **[54]** proposed a method to remove impurities from ammoniacal leach solution (pH 9-11) containing large amount of copper. Silver was removed by cementation with copper powder followed by the removal of other base metals (e.g. Co, Ni, Zn, Al, Mn, Pb, etc.) by solvent extraction with LIX 26 which was not able to extract copper. The loaded organic was regenerated by stripping the metals using sulfuric acid. Copper remained in the leach solution in the form of monovalent copper, and it was recovered by electrowinning. An original procedure to recover copper from WPCBs was developed by Liu et al. **[53]**, who used a NH_3/NH_5CO_3 solution in the presence of oxygen to dissolve copper according to the reaction

$$Cu + 3NH_3 + NH_5CO_3 + 0.5O_2 = Cu(NH_3)_4CO_3 + H_2O \quad (3.3.2.2.6)$$

The leach solution was then heated in order to evaporate NH_3 and precipitate $CuCO_3$ according to the equation

$$Cu(NH_3)_4CO_3 = CuCO_3 + 4\ NH_3 \quad (3.3.2.2.7)$$

Ammonia was recovered and recycled while $CuCO_3$ was calcinated at 550°C to recover copper in the form of copper oxide

$$CuCO_3 = CuO + CO_2 \qquad (3.3.2.2.8)$$

The solid residue after filtration of the leach solution was treated with 6 N HCl to dissolve tin and lead. The final residue was used as a filler in the PVC plastics. Except for this process in which ammonia is recovered by distillation, generally, one of the major problems related to the alkaline leaching concerns the risks for human and environment due to the high volatility of the ammonia.

3.3.2.3 Novel leaching methods

Some novel leaching methods for WPCBs recycling have been proposed in the last few years, such as chelating, ionic liquid and sub-/supercritical leaching. Chelating leaching involves the use of a lixiviant with multi-dentate ligands that form complexes with metals or metal ions **[24]**. Chelation technology is well known in the field of the extraction of heavy metals from contaminated soils and industrial waste. Jadhao et al. **[57]** used EDTA as a leaching agent for copper extraction from WPCBs powders and reported a copper dissolution degree of about 84% in 3 h with 0.5 M EDTA at 100°C and pH 7. According to the authors, more than 96% of EDTA can be recovered by precipitation adding sulfuric acid to the chelating solution. However, it is important to point out that a significant consumption of alkali and acid occurs since chelating leaching requires alkaline environment (pH 8-9), while de-chelation requires acidic environment (pH 2-3). This area of research is completely new, and several studies are in progress to find new chelating agents, preferentially biodegradable.

Another field of interest concerns the use of ionic liquids for copper extraction from WPCBs due to their negligible volatility and high conductivity. Huang et al. **[58]** used $[bmim]H_2SO_4$ along with H_2O_2 for Cu extraction from WPCBs. Almost 100% extraction was obtained at 70°C within 2 retention hours by 25 mL of 80%

(v/v) ionic liquid, 10 mL of 30% H_2O_2, and a solid/liquid ratio of 1/25. Similar performances were obtained by Chen et al. **[59]** with five different ionic liquids including [BSO_4HPy]H_2SO_4, [MIm]H_2SO_4, [BSO_3HMIm]OTf, [BSO_3HMIm]OTf and [BSO_3HPy]OTf. The use of ionic liquids for leaching was also tested for dismantling WPCBs **[60-61].** [$EMIM^+$][BF_4^-] is suitable to completely separate electronic components and solders from WPCBs at 240°C; while [BMIm]BF_4 is suitable to remove 90% of components at 250°C and 45 rpm in 12 h. However, the use of ionic liquids in the field of PCB recycling needs further investigations concerning mainly the interference of the other metals and the separation of metals from the leach solution.

3.3.3 Electometallurgical route

One of the major advancement on copper recovery from WPCBs is the development of entirely electrometallurgical processes. Currently, electrochemical techniques are integrated in pyrometallurgical and hydrometallurgical processes as a final step for the recovery of pure copper. However, some papers have been published on copper recovery from WPCBs by simultaneous electroleaching-electrodeposition processes **[15, 62-65]**. There are many advantages related to this technology such as the reduction of unit operations required for metal recovery because copper extraction and its deposition occur simultaneously in the same equipment. Besides, the technology allows the minimization of the use of solvents, gas emissions and energy consumptions.

Kim et al. **[62]** used two different configurations of the electrochemical reactor to investigate the dissolution of Cu along with other base metals such as Pb, Sn, and Zn from WPCBs. In particular, they employed a combined electrochemical reactor (Figure 3.3.3.1a) in which metals leaching occurred simultaneously with Cl_2 generation at the anode; and a separate leaching reactor (Figure 3.3.3.1b) connected to the anode of an electrochemical cell where Cl_2 was anodically produced. Waste PCBs was firstly pre-treated by crushing and magnetic separation. The non-magnetic fraction containing 18-20% by weight of copper was used for the tests. The sample of waste PCBs was directly fed either into the anodic compartment of the combined reactor or into the leaching reactor of the separate reactor.

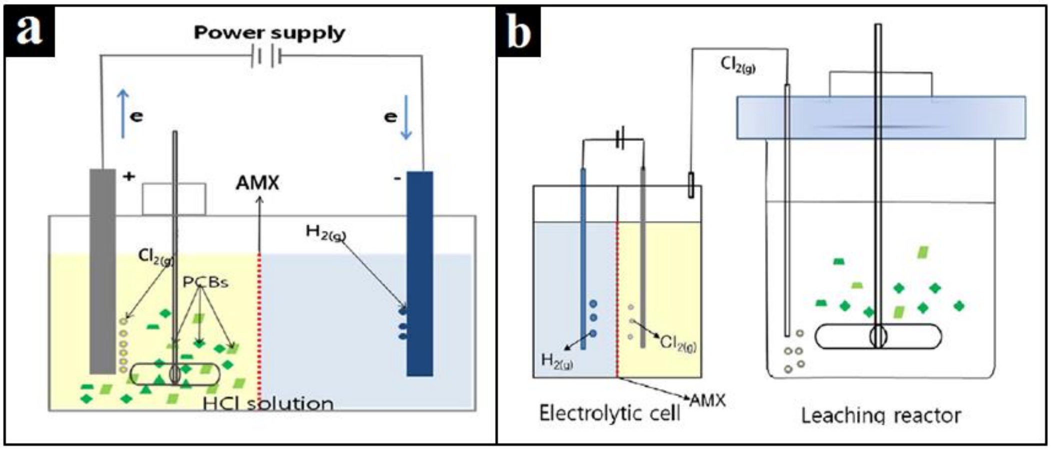


Figure 3.3.3.1 Schematic diagram of the apparatus used by Kim et al. [52]: (a) combined reactor and (b) separate reactor

The anodic reaction was the generation of Cl_2 (E^0= 1.35V vs SHE). However, oxidation from Cu^+ to Cu^{2+} also occurred in the combined reactor due to the presence of Cu^+ in solution produced by leaching of copper mediated by Cu^{2+} ions

$$Cu^{2+} + Cu \rightarrow 2Cu^{+} \qquad (3.3.2.1)$$

When the concentration of Cu^+ available in solution was high enough to consume the applied current, the main anodic reaction changed from Cl_2 generation to the only cuprous oxidation due to the lower oxidation potential of cuprous ions than that of chloride ions. For this reason, leaching efficiency of copper was found to be lower in the combined reactor than in the separate reactor. Leaching rate increased with current and temperature in both reactors. The extraction of Cu, Zn, Sn and Pb in the separate reactor was 71%, 98%, 96% and 96%, respectively in 240 min. using 2.0 mol/L HCl solution at a current density of 714 A/m^2, 323 K temperature and 400 rpm. Copper extraction was limited owing to the passivation of copper particles by a layer of CuCl that occurred when copper dissolution was around 20-

25% in the combined and separate reactor, respectively. Indeed, higher rates of copper leaching were obtained with 3.0 mol/L HCl, which dissolved CuCl more rapidly.

Chu et al. **[63]** produced micro-copper powders by direct electrolysis from concentrated metal scrap coming from the pre-treatment of WPCBs. In particular, concentrated metal scraps were pressed in a steel die of rectangular section by a hydraulic press at 20 MPa and the obtained plates were directly used as an anode for electrolysis. The electrolyte was a mixture of copper sulphate, sodium chloride and sulfuric acid. The authors investigated the effect of $CuSO_4 \cdot 5H_2O$, NaCl and H_2SO_4 concentration, current density and time on current efficiency and copper powder size. They found that current efficiency increased with $CuSO_4 \cdot 5H_2O$ and H_2SO_4 concentration, and current density, while copper powder became finer with the increase of current density and NaCl concentration. The optimum found condition was: 50g/L $CuSO_4 \cdot 5H_2O$, 40g/L NaCl, 118g/L H_2SO_4, 80mA/cm^2 and 3 h. Under these conditions, a current efficiency of 98.12% was found and a particle size of 9.35 μm.

Guimarães et al. **[64]** and Fogarasi et al. **[15]** employed a similar apparatus for direct copper electrolysis from WPCBs, which consisted of an undivided electrochemical cell where a pre-treated sample of WPCBs was directly used as an anode. In particular, Guimarães et al. used a powder of WPCBs supported by an AISI 304 stainless steel basket as an anode; while Fogarasi et al. used large pieces of WPCBs (20-25 cm^2) supported by a perforated Pb cage as an anode. The cathode was a stainless steel plate in both studies, whereas the electrolyte was a $CuSO_4$-H_2SO_4 solution and an H_2SO_4 solution in the study of Guimarães et al. and Fogarasi et al., respectively. At the end of the process, Guimarães et al. achieved a copper recovery of 96% while Fogarasi et al. of 77%. However, the process developed by Fogarasi et al. was less energy consuming since WPCBs was pre-treated only through cutting and dissolution of the solder mask with concentrated H_2SO_4 instead of being ground into powder.

3.3.4 Biometallurgical route

Biological processes are a promising eco-friendly and economically feasible approach for WPCBs recycling. Among the biological technologies, microbial leaching is the most common method for extracting the metallic portion from e-waste, because it is suitable to convert the compounds into a soluble form. Mainly three microbial groups are involved in this process: autotrophic bacteria, heterotrophic bacteria, and heterotrophic fungi **[66]**. Bacteria such as *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*, *Leptospirillum ferrooxidans*, and *Sulfolobus sp*., are well known consortia for the bioleaching activity while fungi such as *Penicillium simplicissimum* and *Aspergillus niger* also take part in metal leaching process. Cu bioleaching efficiencies from e-waste vary widely from 50% to 100% for times typically exceeding 5 days and pulp densities of 1-3% (w/v) **[67]**. The main influencing parameters are pH, redox potential, microbial activity, and pulp density. Several studies have demonstrated that metal leaching efficiency can be improved through addition of acid and iron, because the whole process is controlled by the initial pH, Fe^{2+} concentration and the rate of ferric ions generation **[66]**. This confirms the occurrence of an indirect leaching mechanism by means of biogenic sulfuric acid and ferric iron, similar to that of sulphide minerals.

$$4Fe^{2+} + O_2 + 4H^+ = 4Fe^{3+} + 2H_2O \tag{3.3.4.1}$$

$$Cu + 2Fe^{3+} = Cu^{2+} + 2Fe^{2+} \tag{3.3.4.2}$$

Fe^{2+} in the solution plays a role as an electron donor and is oxidized to Fe^{3+} by iron-oxidizing bacteria. Fe^{3+} then acts as an oxidizing agent catalyzing the leaching of metals. However, the mechanism of metal dissolution from electronic waste material has been long debated and recently the occurrence of both direct and indirect mechanisms was proposed **[68]**. Metal removal efficiencies are reported to decrease significantly with increasing pulp density. This can be due to the alkaline nature of the waste material, which creates a high pH environment where the microorganisms do not thrive. Besides, metal precipitation was found to occur at high pulp density and a toxic effect on bacteria was revealed owing to the non-metallic fraction of WPCBs (i.e. epoxy-coated substrate and organic fraction). Choi et al. **[69]** added citric acid to increase the solubility of copper and improve the efficiency of the bioleaching process. The results showed that in the absence of citric acid only about 37 wt% of the total leached copper remained dissolved; however, it increased more than 80 wt% in the presence of citric acid that acts as a ligand.

Several researchers reported that fungi have an impressive ability to produce different types of amino acids, organic acids (e.g. citric and oxalic acid) and other metabolites in the process of metals dissolution from e-waste, and the organic acids play an important role as proton generators and ligands. Brandl et al. **[70]** used bacteria (*Thiobacillus thiooxidans*, *T. ferrooxidans*) and fungi (*Aspergillus niger*, *Penicillium simplicissimum*) to leach metals from e-scrap. According to the authors, the formation of inorganic and organic acids caused the mobilization of metals. The leaching results showed that both fungal strains were able to mobilize Cu and Sn by 65%, and Al, Ni, Pb, and Zn by more than 95%. At scrap concentrations of 5–10 g/L, Thiobacilli were able to leach more than 90% of Cu, Zn, Ni, and Al. Pb precipitated in the form of $PbSO_4$ while Sn precipitated probably in the form of SnO. For a more efficient metal mobilization, the authors proposed a two-step leaching process where biomass growth was separated from metal leaching.

Other than addition of iron and acid or the development of multi-stage processes, different procedures have been experienced to increase the efficiency of bioleaching, such as the use of ligands (e.g. EDTA) in combining with microbes (e.g. A. ferrooxidants) for copper extraction. It was found that addition of sulphur can enhance the extraction of copper owing to the increase of sulfuric acid production by bacteria. Ilyas et al. **[71]** reported 90% of copper extraction in 12 days with the addition of $FeS + S^0$.

Recent developments in biotechnology have also concerned the acclimatization of microbes to extreme bioleaching conditions, the understanding of the metal mobilization mechanism, and toxicity characteristics. However, one of the most promising solution seems to be the use of an hybrid (integrated) technique, for instance, combining both chemical and biological methods. Harikrushnan et al. **[72]** recovered copper, nickel and zinc from WPCBs using a combined approach of biometallurgical (biological) and hydrometallurgical (chemical) techniques. The hybrid method was compared against the individual chemical and biological methods and proved to be a better method than the other two, being rapid, efficient, economical and eco-friendly. The optimum found combination was 4 days of *Acidithiobacillus ferrooxidans* leaching, followed by 30 minutes of nitric acid leaching. The microorganisms provide sulfuric acid for a proton attack and oxidise ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}) for an oxidative attack of the metals

$$2\ FeSO_4 + H_2SO_4 + 0.5\ O_2 + \text{bacteria} = Fe_2(SO_4)_3 + H_2O \qquad (2.3.4.1)$$

$$M + Fe_2(SO_4)_3 = M^{2+} + 2\ Fe^{2+} + 3\ SO_4^{2-} \qquad (2.3.4.2)$$

The integrated method removed nearly 100% of Cu, Ni and Zn for 10 g/L of e-waste and approximately 85% of Cu and 98% of Ni and Zn at 50 g/L. The integrated method was the most efficient for the recovery of Cu, Ni and Zn, followed by the chemical and biological methods, respectively at 50 g/L. Adversely, the three methods were found to be almost equally efficient for 10 g/L concentration of e-waste

It can be concluded that biological methods have a great potential in the treatment of waste for metal recovery, particularly if integrated with chemical methods. Certainly, it will play a significant role in WPCBs recycling in the future.

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Chapter 4

Dismantling and electrochemical copper recovery from WPCBs in H_2SO_4–$CuSO_4$–NaCl solutions

Introduction

Dismantling is the first and most delicate step in recycling chain of WPCBs. The current technologies for electronic components (ECs) detachment involve either the use of potential polluting liquids or the heating of the solders above the melting point with the possible release of toxic gases, consumption of energy and damage of some reusable components.

In this work, the use of a few aggressive and cheap leaching solution for WPCBs dismantling was investigated. In particular, a H_2SO_4-$CuSO_4$-NaCl solution of well-defined composition was used to leach out all exposed metals from not pre-treated WPCBs to disassemble ECs without damaging. In the acidic solution, Cu^{2+} behaves as an oxidant while Cl^- as a ligand to stabilize Cu^+ by chloro-complexes formation. The feasibility of electrochemical recovering of copper from the resulting solution was verified through a preliminary cyclic voltammetry study aimed at investigating the electrochemistry of copper deposition in sulfate-chloride solutions in the presence of other metal ions. Then, a divided electrochemical cell was employed to investigate simultaneous copper recovery and oxidant restoration.

Part of the work of this chapter has been conducted in the Lab of the Faculty of Chemistry and Chemical Engineering at Babeş-Bolyai University, Cluj-Napoca, under the supervision of Professors P. Ilea, S.-A. Dorneanu and G.L Turdean.

4.1 H_2SO_4–$CuSO_4$–NaCl leaching solution: state of the art

In recent years, a large number of papers have been published dealing with the leaching of copper from WPCBs due to its relevant abundance. Copper can be effectively leached using either acidic or ammoniacal solutions. The last ones have demonstrated high selectivity towards copper **[1-3]**. However, traditional leaching method employs mineral acids, mainly H_2SO_4 for its easy regeneration and low cost, but also aqua regia, HCl, and HNO_3 **[4-6].** Generally, an oxidizing agent, such as Cl_2, O_2, H_2O_2, Fe^{3+}, is added to the leaching solution to enhance extraction efficiency **[7-12]**. Hydrogen peroxide is extensively used for its high redox potential (1.78 V) despite the high cost and consumption particularly at high temperatures **[11]**. Ferric ion represents a cheap alternative and it can be easily regenerated **[13]**. The use of Fe^{3+} was investigated by different authors achieving high dissolution rate for metals. The principal drawback is the contamination of the leach solution, which can, however, be purified by goethite and jarosite precipitation before electrodeposition **[13]**.

Recently, the use of Cu^{2+} as an oxidizing agent for the extraction of copper from WPCBs was tested to avoid the contamination from iron and reduce the costs compared to H_2O_2 **[14-16]**. The leaching of copper mediated by Fe^{3+} or Cu^{2+} ions in chloride solutions was also investigated for the treatment of copper concentrates in the mining industry. HydroCopper® process (at pilot scale) is a recent technology developed to leach copper from chalcopyrite concentrates with the use of HCl–$CuCl_2$–NaCl solutions **[15]**.

In the field of waste management, Deveci et al. investigated both HCl-$CuCl_2$-NaCl and H_2SO_4-$CuSO_4$-NaCl solutions for highly effective leaching of Cu, Fe, Ni and Ag **[14, 15]** from pulverized samples of WPCBs. However, the HCl-$CuCl_2$-NaCl solution was found to be extremely corrosive and determining a difficult electrowinning of copper. The presence of chloride in H_2SO_4/$CuSO_4$ solutions is crucial because Cl^- acts as a ligand stabilizing the Cu^+ ions in the form of copper-chloro complexes and hence, activates the Cu^{2+}/Cu^+ redox couple. The mechanism of copper dissolution is

$$Cu^0 + Cu^{2+} \rightarrow 2Cu^+ \qquad (4.1.1)$$

$$Cu^+ + nCl^- \rightarrow CuCl_n^{1-n} \qquad (1 \leq n \leq 4) \qquad (4.1.2)$$

Depending on chloride concentration, cupric copper (Cu^{2+}) may also present as $CuCl_n^{2-n}$ complexes. From equation (4.1.2), it is evident that a sufficient level of chloride should be maintained in the leaching solution to prevent the precipitation of Cu^+ in the form of CuCl (for n=1).

According to the authors **[14],** Cu^{2+} is electrochemically faster than Fe^{3+} and can become more powerful than Fe^{3+} as an oxidant at high chloride concentrations (e.g. $\geq \sim 4.2$ M). Indeed, although the standard reduction potential of the Cu^{2+}/Cu^+ couple is relatively low (0.16 V/NHE), an increase of the chloride concentration can elevate the value. This is due to the increase of the Cu^+-Cl complexes stability compared to Cu^{2+}-Cl with the increase of chloride concentration, particularly at $[Cl^-] > 0.1$ M. On the contrary, Fe^{3+}-Cl complexes become more stable than Fe^{2+}-Cl with $[Cl^-]$ increase, reducing the potential of Fe^{3+}/Fe^{2+} redox couple.

Interesting results have been reported by Herreros et al. **[17]**, who studied the dissolution kinetics of metallic copper with NaCl-$CuSO_4$ in HCl rather than H_2SO_4, determining the influence of stirring, temperature, and total copper and chloride concentrations. Dissolution kinetics of copper was positively influenced by an increase in temperature while it was insensitive to stirring for velocities above 350 rpm, suggesting a chemical reaction control. The reaction rate was found to increase in proportion to the total copper concentration. On the contrary, a decrease of the reaction rate was observed increasing the concentration of Cl^- owing to the lower availability of free Cu^{2+} ions in solution, which were identified as the main active species. Based on the experimental results, the authors suggested that copper dissolution occurs in the following steps

$$Cu_{(s)} + Cu^{2+}{}_{(aq)} \rightarrow 2Cu^{+}{}_{(ads)} \tag{4.1.3}$$

$$Cu^{+}{}_{(ads)} + 2Cl^{-}{}_{(aq)} \rightarrow CuCl_2^{-} \tag{4.1.4}$$

When the ratio of the total chloride concentration and that of copper (C_{cl}/C_{Cu}) is high, reaction (4.1.3) is the overall controlling step. On the contrary, when the ratio is low, reaction (4.14) is limited and CuCl precipitation occurs on the copper surface hindering the leaching process, in accordance with the following reaction

$$Cu^{+}{}_{(ads)} + Cl^{-}{}_{(aq)} \rightarrow CuCl_{(s)} \tag{4.1.5}$$

The authors recommend a C_{cl}/C_{Cu} ratio not less than 8 and not higher than 16.5 to avoid the decrease of free Cu^{2+} ions availability.

In the study by Deveci et al. **[14],** the extraction of metals from WPCBs with H_2SO_4-$CuSO_4$-NaCl was investigated changing temperature (20-80°C), solid ratio (1-15% w/v), initial concentration of both cupric (0.5-7.5 g/L Cu^{2+}) and chloride (4.7-46.6 g/L Cl^{-}) ion. PCBs wastes were initially subjected to a manual separation of the components and then to a two-stage crushing until a dimension of 250 µm. The leaching tests were performed in a glass reactor equipped with a four-blade mechanical stirrer, setting time and speed to 120 minutes and 675 rpm, respectively. H_2SO_4 concentration was maintained constant at 0.5 M. The results showed that temperature and initial concentration of Cu^{2+} are the most influential factors and their increase improves the extraction of copper. Similarly to the study of Herreros et al. **[17]**, the authors found a strong interaction between the concentration of copper and chloride. In particular, the Cl^{-}/Cu^{2+} ratio must be maintained sufficiently high to achieve high metal extractions but not too much to avoid a decrease in Cu^{2+} availability. The best experimental conditions found were a temperature of 80°C, a solid ratio of 1% w/v and a Cl^{-}/Cu^{2+} ratio of 21 (46.6 g/L of Cl^{-} and 4 g/L of Cu^{2+}). Under these conditions, a complete extraction of copper from WPCBs was achieved, and higher to 90% for Fe, Ni, Ag and 58% for Pd.

The increase of the solid ratio adversely influenced the leaching of metals with no copper extraction for values higher than 10% w/v. However, the introduction of either air or oxygen led to a significant improvement due to the in-situ regeneration of the Cu^{2+} oxidant through the following reactions

$$4CuCl^-_2 + O_{2(aq)} + 4H^+ \rightarrow 4Cu^{2+} + 8Cl^- + 2H_2O \qquad (4.1.6)$$

$$4CuCl^-_2 + O_{2(aq)} + 4H^+ \rightarrow 4CuCl^+ + 4Cl^- + 2H_2O \qquad (4.1.7)$$

$$4CuCl^-_2 + O_{2(aq)} + 4H^+ \rightarrow 4CuCl_2 + 2H_2O \qquad (4.1.8)$$

Besides, oxygen can contribute to the oxidation of metals, particularly that of palladium, both directly and indirectly by activation of the Fe^{3+}/Fe^{2+} redox couple. The presence of iron in solution was determined by its dissolution from WPCBs.

Ping et al. **[16]** carried out a leaching of copper from WPCBs at room temperature using a dilute solution of sulfuric acid in which Cl^- acted as a complexing agent while Cu^{2+} and O_2 as oxidants. WPCBs were pretreated by a mechanical process to obtain a metal powder with high copper content. A lot of tests were carried out to study the influence of some parameters on the leaching rate. The optimum conditions were: 40 g/L NaCl, 30 g/L $CuSO_4 \cdot 5H_2O$, 1.12 M H_2SO_4, 1/15 (g/mL) solid–liquid ratio and 5.5 h. The reaction mechanism in the presence of blowing air is

$$Cu^{2+} + Cu \rightarrow 2Cu^+ \qquad (4.1.9)$$

$$Cu^+ + Cl^- \rightarrow CuCl \qquad CuCl + Cl^- \rightarrow CuCl_2^- \qquad (4.1.10)$$

$$4CuCl_2^- + O_2 + 2H_2O \rightarrow 2[Cu(OH)_2 \cdot CuCl_2] + 4Cl^- \qquad (4.1.11)$$

$$4CuCl_2^- + O_2 + 2H_2O \rightarrow 2[Cu(OH)_2 \cdot CuCl_2] \qquad (4.1.12)$$

$$2[Cu(OH)_2 \cdot CuCl_2] + H_2SO_4 \rightarrow CuSO_4 + CuCl_2 + 2H_2O \qquad (4.1.13)$$

$$CuSO_4 + 5H_2O \rightarrow CuSO_4 \cdot 5H_2O \qquad (4.1.14)$$

Therefore, copper is recovered in the form of pure $CuSO_4 \cdot 5H_2O$ by an evaporative crystallization of the leach solution. Besides, Cl^- behaves as a catalyst in leaching copper process because it is consumed and then regenerated from equation (4.1.11). The authors claim that the leaching time can be reduced of 2 h performing an electro-extraction of copper in a divided electrochemical cell where a graphite anode and a stainless steel cathode were used. The powder of mechanically pretreated waste PCBs was directly put into the anodic compartment and oxygen was generated in-situ as a product of anodic reactions. In this case, the improvement in leaching performances was determined by the anodic oxidation of Cl^- to Cl_2, which was dissolved in water to form the strong oxidant HClO.

These studies suggest that H_2SO_4-$CuSO_4$-NaCl leaching solution can represent a few aggressive and cheaper alternative for the efficient extraction of copper and other metals from WPCBs. In this work, H_2SO_4-$CuSO_4$-NaCl solution was tested to disassemble ECs by leaching all exposed metals from not pre-treated WPCBs. Then, the recovery of copper from the resulting solution was also investigated after a preliminary electrochemical characterization of the leach solution by cyclic voltammetry (CV). The treatment of WPCBs investigated in the present work consists in only two stages: i) ECs detachment by metals leaching; ii) electrochemical recovery of copper from the leach solution.

4.2 Electronic components detachment from WPCBs by metals leaching in H_2SO_4–$CuSO_4$–NaCl solution

The first step of the study was aimed at finding the exact composition of the leaching solution for the complete dissolution of all exposed metallic parts from not pre-treated WPCBs and simultaneous detachment of all ECs. Experimental procedure and results will be reported in the following.

4.2.1 Material and methods

In order to find the best composition for H_2SO_4-$CuSO_4$-NaCl leaching solution, some experiments were conducted at different concentration of H_2SO_4,

$CuSO_4 \cdot 5H_2O$, and NaCl. The experiments layout is shown in Table (4.2.1.1). All the chemical reagents were of analytical grade. Each experiment of Table (4.2.1.1) was repeated 3 times at least.

Experiment number	Leaching Solution number	NaCl (mol/L)	$CuSO_4 \cdot 5H_2O$ (mol/L)	H_2SO_4 (mol/L)	C_{cl}/C_{cu} ratio
1	1	2	0.2	0.5	10
	2	2	0.2	1	10
	3	2	0.2	2	10
2	1	2	0.05	0.5	40
	2	2	0.1	0.5	20
	3	2	0.4	0.5	5
3	1	1	0.4	0.5	2.5
	2	3	0.4	0.5	7.5
	3	4	0.4	0.5	10

Table 4.2.1.1 Leaching experiments layout

During each experiment, three reactors containing three leaching solution of different composition simultaneously worked for better observing the effects on WPCBs induced by variation in the concentrations of H_2SO_4 (experiment 1), $CuSO_4 \cdot 5H_2O$ (experiment 2) and NaCl (experiment 3), respectively. A scheme of the experimental setup is shown in Figure 4.2.1.1. Each reactor was a cylindrical glass vessel filled with 500 mL of leaching solution. Air was blown into the reactors through an air pump equipped with a polyethylene diffuser with a flux of 4 L/min. The time of each test was of 12 h.

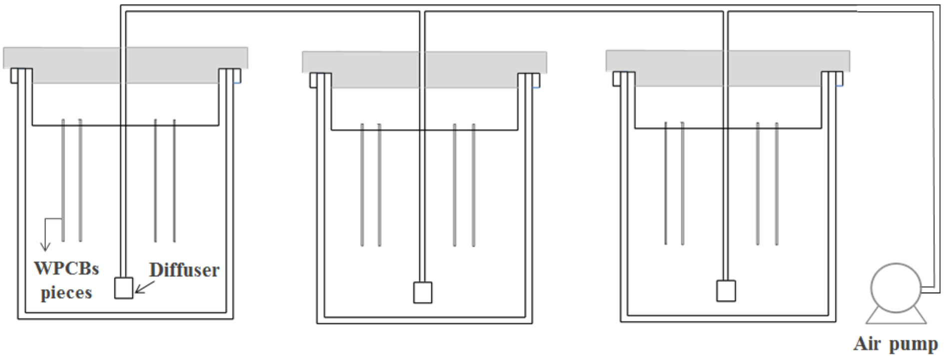


Figure 4.2.1.1 Experimental leaching setup

Motherboards of old and obsolete computers were used as source of WPCBs. In order to fit the computer motherboards into the leaching reactors, they were cut into large pieces of 7-30 cm^2. The cut was performed in order to select areas containing some characteristic ECs connected to the board through different type of metals. For the study, motherboard pieces containing the following ECs were selected

1. PCI (*Peripheral Component Interconnect*) slots;
2. ATA (*Advanced Technology Attachment*) connectors;
3. D-sub connectors;
4. Surface mounted integrated circuit.

The motherboard pieces containing these components were mounted into each reactor in a vertical position and were separated each other to avoid contact between metallic parts (Figure 4.2.1.1). The picture of a typical sample selected for the leaching tests is shown in Figure 4.2.1.2.

The selected ECs are representative of the metal composition generally found in computer motherboards. They are constituted by a thermoplastic housing and electrically connected to the board by pins in brass or bronze with a final finishing in gold or tin over nickel or copper. The external terminals (leads) of the integrated circuit (IC) typically are constituted of a Ni-Fe alloy base material, such as either Kovar (54Fe/29Ni/17Co) or Alloy 42 (58Fe/42Ni) **[18]**. D-sub connectors have an external metallic shell in tin plated steel. The Ni-based screws were initially removed from these last components to avoid an increase in leaching time due to their high thickness. Besides, the ECs were positioned on the board through a Pb-Sn soldering paste having usually a composition of 62 wt.% Sn and 38 wt.% Pb **[19].**

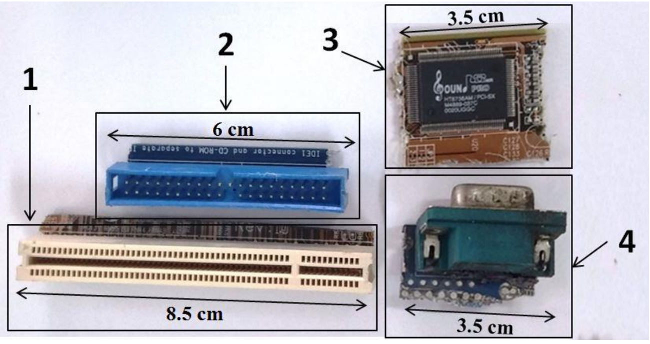


Figure 4.2.1.2 Picture of the motherboard pieces selected for the leaching tests containing the following ECs: (1) PCI slot, (2) ATA connector, (3) SMT integrated circuit, (4) D-sub connector

Therefore, Pb, Sn, Fe, Zn, Cu, and Ni were the main base metals that it was expected to find in the solution resulting from dismantling/leaching of WPCBs **[20]**. The average initial weight of the selected motherboard pieces was about 43.3 g with a solid to liquid ratio (S/L) of 0.0866 g/mL, which corresponds to 11.55 mL of solution per g of solid.

4.2.2 Results and discussion

H_2SO_4-$CuSO_4$-NaCl solution was already used for the successful leaching of metals from disassembled and pulverized WPCBs, while never it was used before to disassemble ECs directly from not pre-treated boards. The reactions involved in metal leaching are

$$nCu^{2+} + Me = nCu^{+} + Me^{n+} \qquad (4.2.2.1)$$

$$Cu^{+} + nCl^{-} \rightarrow CuCl_n^{1-n} \qquad (1 \leq n \leq 4) \qquad (4.2.2.2)$$

Reaction 4.2.2.1 shows that the leaching process occurs by a displacement reaction driven by Cu^{2+} ions in solution; while reaction 4.2.2.2 evidences the key role of Cl^-

in stabilizing Cu^+. In addition, the availability of Cu^{2+} ions is of fundamental importance, therefore, it needs to restore those consumed in 4.2.2.1. A possible way consists in blowing air into the solution **[14-16]**, according to

$$4Cu^+ + O_2 + 4H^+ = 4Cu^{2+} + 2H_2O \qquad (4.2.2.3)$$

The key role of oxygen was immediately evident from a preliminary leaching test conducted without air blowing. Indeed, being the components placed in vertical position into the reactor, the metallic parts dissolved easier were those near to the air/solution interface, where the concentration of oxygen was higher. As shown in Figure 4.2.2.1, the pins of PCI slot are completely dissolved in the upper region (on the right in the picture) and just corroded in the lower region (on the left in the picture).

Figure 4.2.2.1 Photo of a PCI slot after leaching without air blowing in H_2SO_4-$CuSO_4$-NaCl solution

The first leaching experiment was carried out setting the concentration of NaCl and $CuSO_4 \cdot 5H_2O$ at 2 M and 0.2 M respectively, with a C_{cl}/C_{cu} ratio of 10 according with other studies **[14, 17]**. H_2SO_4 concentrations of 0.5 M, 1 M, and 2 M were used for the three leaching solutions inside the three different reactors of Figure 4.2.1.1. It was found that higher acid concentrations were reducing the dissolving action of the solution, likely due to passivation effect on steel and solder parts. Accordingly, Figure 4.2.2.2 a-b shows that connector and inserted pins remained on WPCB after treatment in 1 M H_2SO_4, whereas complete detachment of the connector and dissolution of the pins occurred in 0.5 M. Besides, damages to the plastic housing of ECs were observed at acid concentrations higher than 0.5 M hindering their future recycling.

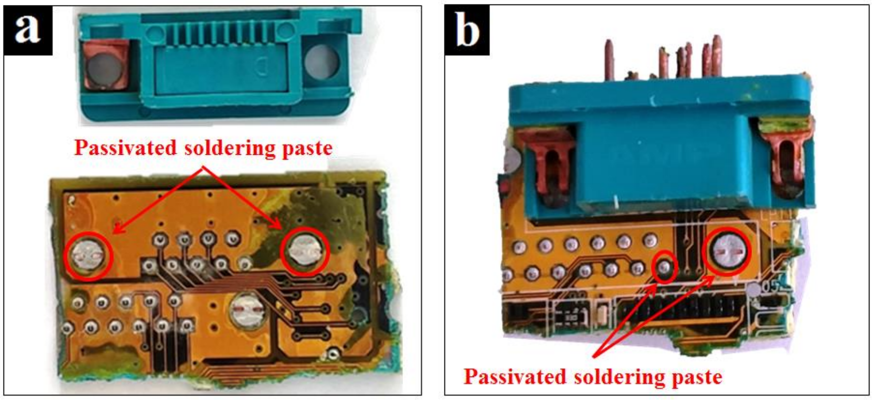


Figure 4.2.2.2 D-sub connectors after leaching in 0.1 M $CuSO_4$-2 M NaCl solution containing different concentrations of H_2SO_4: a) 0.5 M and b) 1 M, respectively

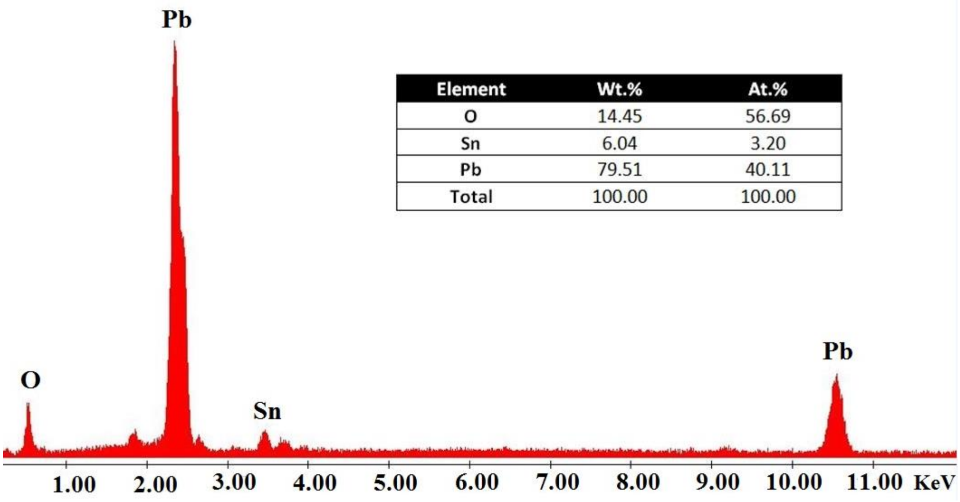
In Figure 4.2.2.2, the soldering alloy surface appears of white color probably due to its partial passivation by precipitation of lead sulfate, according to

$$\text{Pb-Sn} + 4\text{Cu}^{2+} = \text{Sn}^{2+} + \text{Pb}^{2+} + 4\text{Cu}^{+} \qquad (4.2.2.4)$$

$$\text{SO}_4^{2-} + \text{Pb}^{2+} = \text{PbSO}_4 \downarrow \qquad (4.2.2.5)$$

Reaction 4.2.2.4 schematises the oxidation of both Sn and Pb that in the presence of sulfate precipitates in the form of $PbSO_4$ owing to a solubility in cold water of only 4.56 mg per 0.1 L of water, while $SnSO_4$ is largely more soluble with 33 g per 0.1 L **[21].** Passivation occurrence of the soldering alloy due to $PbSO_4$ precipitation is supported by the EDS analysis performed in these white areas. Figure 4.2.2.3 confirms the presence there of lead, whereas tin is almost completely dissolved. Indeed, the atomic fraction of lead (Pb/(Pb+Sn)) was of about 0.93 (Figure 4.2.2.3). The thickness of the passive film was lower in the test at 0.5 M H_2SO_4.

Another important experimental evidence emerged from the first set of leaching/dismantling tests was the instantaneous copper cementation on less noble metal surfaces, which can lead to a drastically reduction of Cu concentration in solution.



Element	Wt.%	At.%
O	14.45	56.69
Sn	6.04	3.20
Pb	79.51	40.11
Total	100.00	100.00

Figure 4.2.2.3 EDS spectrum and elemental composition related to the white area of the soldering alloy shown in Figure 4.2.2.2

A second leaching experiment was conducted to deeply investigate the effect of a different initial concentration of copper on the extraction efficiency. Three solutions at 0.05 M, 0.1 M and 0.4 M of $CuSO_4 \cdot 5H_2O$ were used for the test with concentration of NaCl at 2 M and that of H_2SO_4 at the best value found during the first leaching experiment (0.5 M). A picture of the samples after 12 h of leaching is shown in Figure 4.2.2.4.

The results obtained at 0.05 M were similar to those obtained at 0.1 M of $CuSO_4$. On the contrary, significant differences were observed at 0.4 M. In particular, only at this initial concentration of Cu it is possible to disassemble ATA connector and dissolve all metallic part of D-sub connector (Figure 4.2.2.4). This can be due to the large excess of chloride with respect to copper in the tests at 0.05 M $CuSO_4$ with $C_{cl}/C_{cu}=40$ and 0.1 M $CuSO_4$ with $C_{cl}/C_{cu}=20$, which leads to a decrease in the activity of free Cu^{2+} within the medium.

It was found that 0.4 M $CuSO_4$ is adequate to provide enough Cu^{2+} ions in solution to sustain reaction 4.2.2.1, according to Herreros et al. **[17]** who showed that the rate of copper dissolution was increasing with initial Cu^{2+} concentration. Besides, a bigger amount of copper since the beginning of the leaching process can contribute to compensate that lost owing to cementation. Nevertheless, when 0.4 M $CuSO_4$ was used, traces of a white precipitate were found on the reactor bottom. The white compound was probably CuCl generated by the low concentration of chloride in the media. Indeed, at low initial C_{Cl}/C_{Cu} ratios, the formation of chloro-complexes is limited with consequent poor stabilization of Cu^+ ions in solution which leads to the following reaction

$$Cu_{(s)} + Cu^{2+}_{(aq)} + 2Cl^-_{(aq)} \rightleftarrows 2CuCl_{(s)} \qquad (4.2.2.6)$$

where (s) and (aq) indicate solid and aqueous phase, respectively. Therefore, for working with 0.4 M of copper, a higher concentration of Cl^- should be selected to guarantee a C_{Cl}/C_{Cu} ratio higher than 5, thus avoiding CuCl precipitation.

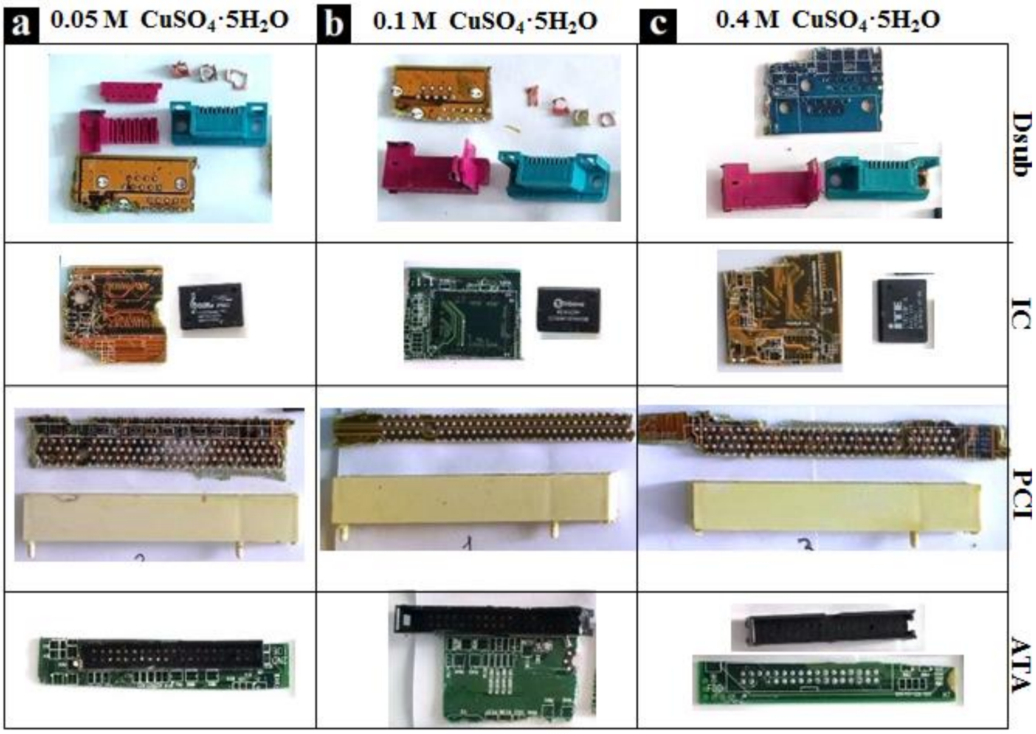


Figure 4.2.2.4 Samples after leaching test in 0.5 M H_2SO4-2 M NaCl solution containing different concentrations of $CuSO_4 \cdot 5H_2O$: a) 0.05 M, b) 0.1 M, and c) 0.4 M

In order to better investigate the strong interaction between total copper and total chloride concentration, a third leaching experiment was performed at different concentrations of NaCl. Three solutions containing 1 M, 3 M and 4 M respectively of NaCl were used for the tests. The concentration of H_2SO_4 was set at 0.5 M and that of $CuSO_4 \cdot 5H_2O$ at 0.4 M. A picture of the samples after 12 h of leaching is shown in Figure 4.2.2.5.

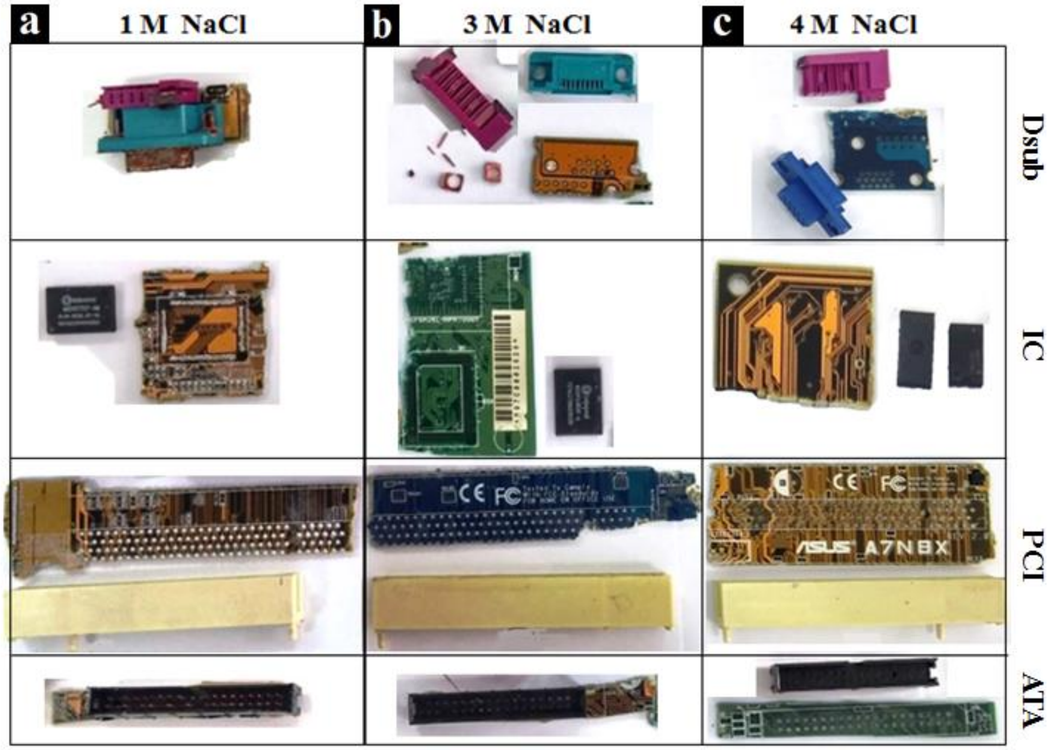


Figure 4.2.2.5 Samples after leaching test in 0.4 M $CuSO_4 \cdot 5H_2O$ -0.5 M H_2SO_4 solution containing different concentrations of NaCl: a) 1 M, b) 3 M, and c) 4 M

When NaCl concentration in the bath was lowered from 4 M to 1 M, an abundant white precipitate of CuCl was formed owing to the low C_{cl}/C_{cu} ratio (~2.5). Therefore, a very low extraction of metals was found in the test with 1 M NaCl. After 12 hours of dismantling/leaching, D-sub connector was still assembled to the board and its metallic shell just corroded; also the ATA connector was still linked to the board and its pins not dissolved (Figure 4.2.2.5a). The best results were obtained with 4 M NaCl leaching solution. Indeed, Figure 4.2.2.5c shows that the components are completely disassembled from the board included also the ATA connector, which is the hardest component to dismantle. Starting from 4 M chloride concentration, also the soldering paste appears to be dissolved better, likely due to the increase in lead solubility at higher chloride concentrations. The measured weight loss of WPCBs after 12 h was of about 9%, 20% and 23% for the leaching solution containing 1 M, 3 M, and 4 M of NaCl, respectively.

Even if the board pieces appeared almost completely free from metals after 12 h in 4 M NaCl-0.5 M H_2SO_4-0.4 M $CuSO_4$ leaching solution, it should be noted that the removal of Pb-Sn solders was not complete. The passivation of Pb-Sn solders can also hinder pins dissolution inside the through holes. However, a complete removal of the soldering alloy was possible by alternating 12 h of leaching with 12 h of dipping in 4 M NaCl solution for two times. It was found that the amount of soldering alloy was decreasing over each washing up to complete dissolution (Figure 4.2.2.6). The action of concentrated NaCl solution in dissolving lead sulphate can be attributed to the formation of chloro-complexes **[22-23]**.

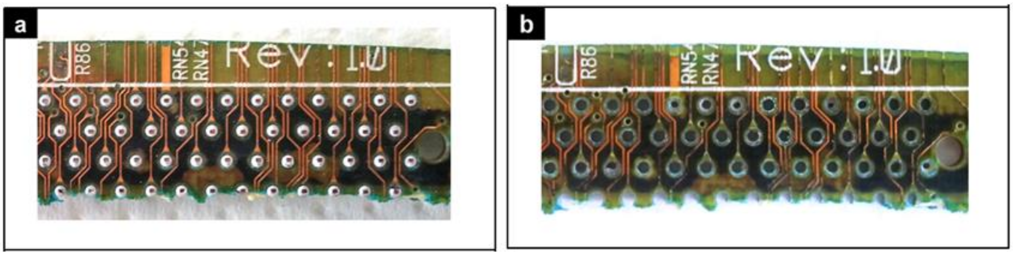


Figure 4.2.2.6 Pictures of WPCBs pieces: a) after 12 h of leaching in 4 M NaCl-0.5 M H_2SO_4-0.4 M $CuSO_4$ solution; b) after a time of 48 h alternating 12 h of leaching to 12 h of dipping in 4 M NaCl for two times

Besides, it should be noted that, although oxygen contributes to maintain oxidizing conditions, its presence determines pH increase. For this reason, the pH was monitored during leaching in 0.5 M H_2SO_4-0.4 M $CuSO_4$-4 M NaCl solution and an increase was found from -0.2 to +0.53 after 12 hours (Table 4.2.2.1). Thus, pH correction is necessary for longer time to avoid that Fe^{3+} generated from the oxidation of Fe^{2+} in the presence of oxygen precipitates when pH raises above 1 **[13, 15]**.

Time	t_0	t_{3h}	t_{6h}	t_{9h}	t_{12h}
pH value	-0.2	-0.02	+0.01	+0.36	+0.53

Table 4.2.2.1 pH values during leaching in 4 M NaCl-0.5 M H_2SO_4-0.4 M $CuSO_4{\cdot}5H_2O$ solution

On the whole, leaching testes indicated that an efficient dismantling/leaching of WPCBs can be conducted at low temperature using a H_2SO_4-$CuSO_4$-NaCl solution in the presence of blowing air for the in-situ regeneration of the oxidant. In particular, the composition which gave the best results was: 4 M NaCl, 0.4 M $CuSO_4{\cdot}5H_2O$ and 0.5M H_2SO_4 with a C_{Cl}/C_{Cu} ratio of 10.

Both disassembled components and remaining board maintain their structural integrity therefore, they can be easily separated and sent to recycle or further treatments. This is a key point because the current technologies use high temperatures and external forces (impact, shearing, vibration, etc.) for dismantling WPCBs with the consequence of i) damaging the components, ii) releasing toxic substances, and iii) consuming energy. Simultaneously to dismantling, leaching of copper and other minor metals occurs. The recovery of copper from the leach solution was investigated by electrolysis. As reported in Chapter 3, electrolysis is an ideal process for copper recovery. This is a key point because the most current WPCBs recycling technologies allow the recovery of the copper contained in PCBs structure, while that present in electronic components' contacts (pins and leads) is usually lost. In the following, it will be shown the results concerning the recovery of copper from the leach solution after a preliminary cyclic voltammetry study.

4.3 Cyclic voltammetry study

A systematic study focused on leach solution electrochemical characterization by cyclic voltammetry (CV) was undertaken to detect the best operative conditions for copper recovery. In particular, the study was aimed at investigating the electrochemistry of copper deposition in sulfate-chloride solutions in the presence of other metal ions such as Ni^{2+}, Fe^{2+}, Zn^{2+}, Pb^{2+}, Sn^{2+} because similar studies were not found in literature. Experimental procedure and results will be reported in the following.

4.3.1 Material and methods

The copper recovering was studied by cyclic voltammetry. Initially, copper deposition and dissolution were studied in 0.5 M H_2SO_4-4 M NaCl synthetic solution adding 0.4 M of Cu that is the same concentration used for dismantling/leaching. The electrochemical behaviour of Fe, Ni, Zn, Sn, and Pb in the same 0.5 M H_2SO_4-4 M NaCl synthetic solution was also investigated. Then, the modification of the copper voltammetric curve was investigated when Zn, Fe, Ni, Pb, and Sn were added to the copper solution, one at a time. At this aim, the solutions reported in Table 4.3.1.1 were exploited.

Solution number	**NaCl (M)**	**H_2SO_4 (M)**	**$CuSO_4\cdot 5H_2O$ (M)**	**$ZnSO_4\cdot 7H_2O$ (M)**	**$FeSO_4\cdot 7H_2O$ (M)**	**$NiSO_4\cdot 7H_2O$ (M)**	**$PbSO_4$ (M)**	**$SnCl_2\cdot 5H_2O$ (M)**
1	4	0.5	0.1	0.1	0	0	0	0
2	4	0.5	0.1	0	0.1	0	0	0
3	4	0.5	0.1	0	0	0.1	0	0
4	4	0.5	0.033	0	0	0	0.033	0
5	4	0.5	0.033	0	0	0	0	0.033
6	4	0.5	0	0	0	0	0.033	0.033
7	4	0.5	0.033	0	0	0	0.033	0.033

Table 4.3.1.1 List of solutions prepared for cyclic voltammetry study of copper in the presence of other metal ions

The possible interference of such metals on the copper voltammogram was studied using an unitary Me^{n+}/Cu^{2+} concentration ratio. In the case of Pb^{2+}, a lower concentration (33 mM) was used due to the scarce solubility of $PbSO_4$ in the electrolyte. A concentration equal to that of lead was used also for tin in order to study the interference between these two elements (solution #6 in Table 4.3.1.1) since their voltammetric peaks are very close.

Finally, CV of a real leach solution was performed, which was interpreted in the light of the CV of the synthetic solutions.

The CV study was conducted in a standard three-electrode cell with a glassy carbon disk (3 mm diameter) as a working electrode, a coiled platinum wire (0.8 mm diameter and 10 cm long) as a counter electrode, and a silver/silver-chloride electrode in saturated KCl solution as a reference (E^0=0.197 V vs. NHE). In the following, all the potentials are referred to it.

The working electrode was mechanically polished with alumina slurry on cloth until a mirror-bright finishing was obtained, and then washed ultrasonically in doubly distilled water with HNO_3 (1:1 v/v), and ethanol (1:1 v/v) **[24]**. Accurate polishing was necessary to obtain good reproducibility.

All experiments were performed in stagnant solution. The electrode potential was linearly swept at 50 mV/s for three consecutive cycles mainly from +1 V to -0.7 V and vice-versa, which is the interval for obtaining a complete and well defined voltammetric curve for copper.

For better understanding the electrochemical behaviour of the different species in solution, a square wave voltammetry (SVW) was also performed. In this case, the potential was mainly swept from +1.1 V to -0.8 V and vice-versa using the following parameters: pulse height 0.050 V, step height 0.002 V, and pulse width 20 ms.

4.3.2 Results and discussion

4.3.2.1 Cyclic voltammetry study of Cu in synthetic H_2SO_4–NaCl solution

Figure 4.3.2.1.1 shows the differences between the electrochemical behavior of copper in a solution containing only sulfate and that in a solution containing both sulfate and chloride. In the absence of chloride (Figure 4.3.2.1.1a), the voltammetric curve of a glassy carbon electrode in 0.5 M H_2SO_4 solution is flat without copper addition, while there are two peaks (Ia and Ic) when 0.4 M $CuSO_4{\cdot}5H_2O$ (MW 249.88 g/mole) was added. Oxidation (Ia) and reduction (Ic) peaks are associated to the following reaction

$$Cu^{2+} + 2e^- \rightleftarrows Cu^0 \qquad (4.3.2.1.1)$$

This reaction proceeds via a single two electron transfer, which is the typical mechanism of copper deposition and dissolution in a sulfuric acid medium **[25]**. At approximately +0.11 V, the cathodic current starts to sharply increase indicating the start of copper deposition and forms Ic peak. The decaying cathodic current past the Ic peak represents the reaction (4.3.2.1.1) in diffusion controlled regime.

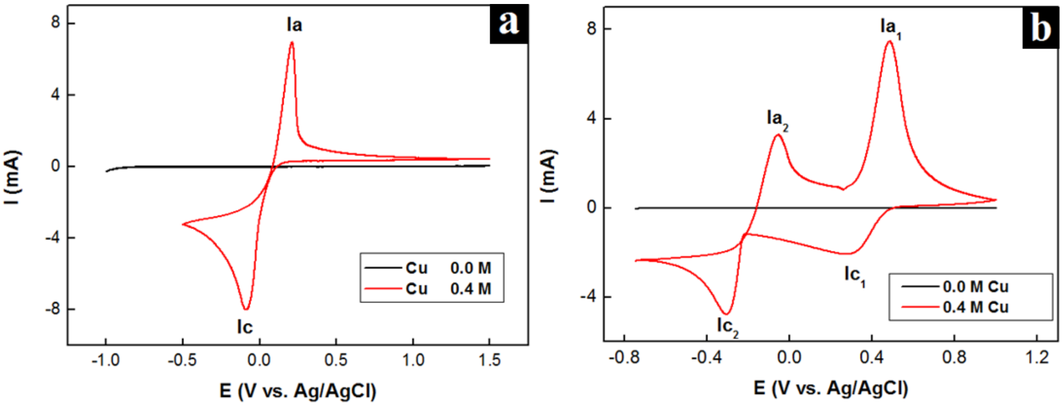


Figure 4.3.2.1.1 CV of a glassy carbon electrode in a) 0.5 M H_2SO_4 and b) 0.5 M H_2SO_4 -4 M NaCl solution without and with addition of 0.4 M $CuSO_4{\cdot}5H_2O$

A different electrochemical behavior of copper is observed in solution containing both 0.5 M H_2SO_4 and 4 M NaCl (Figure 4.3.2.1.1b). In the absence of copper, the voltammetric curve of a glassy carbon electrode in 0.5 M H_2SO_4-4 M NaCl solution is flat, while there are two oxidation and reduction peaks when 0.4 M $CuSO_4{\cdot}5H_2O$ was added. The peaks labelled Ia_1 and Ic_1 are associated to the reaction

$$Cu^{2+} + 2Cl^- + e^- \rightleftarrows CuCl_2^- \qquad (4.3.2.1.2)$$

While Ia_2 and Ic_2 peaks are due to

$$CuCl_2^- + e^- \rightleftarrows Cu^0 + 2Cl^- \qquad (4.3.2.1.3)$$

In practice, a double one-electron transfer occurs owing to the stabilization of Cu^+ in solution as a chloro-complex, because Cu^+ is not stable in solution of only sulfate. Reduction from Cu^+ to Cu^0 starts at about -0.216 V when the cathodic current starts to sharply increase and then forms Ic_2 peak. This value is more negative than that measured for Cu^{2+}/Cu^0 couple in 0.5 M H_2SO_4 (+0.11 V). Such a potential indicates the strong polarization effect of chloride ion on the electrodeposition of copper **[26]**.

Similar behavior was also observed in square wave voltammetry, as shown in Figure 4.3.2.1.2a where the SWV curve of a glassy carbon electrode in 0.5 M H_2SO_4-4 M NaCl solution without and with addition of 0.4 M $CuSO_4 \cdot 5H_2O$ is reported.

The copper voltammetric curves at different concentrations of NaCl are shown in Figure 4.3.2.1.2b. The more negative potential at which copper deposition starts as chloride concentration increases, confirms the polarization effect of chloride ion on copper electrodeposition.

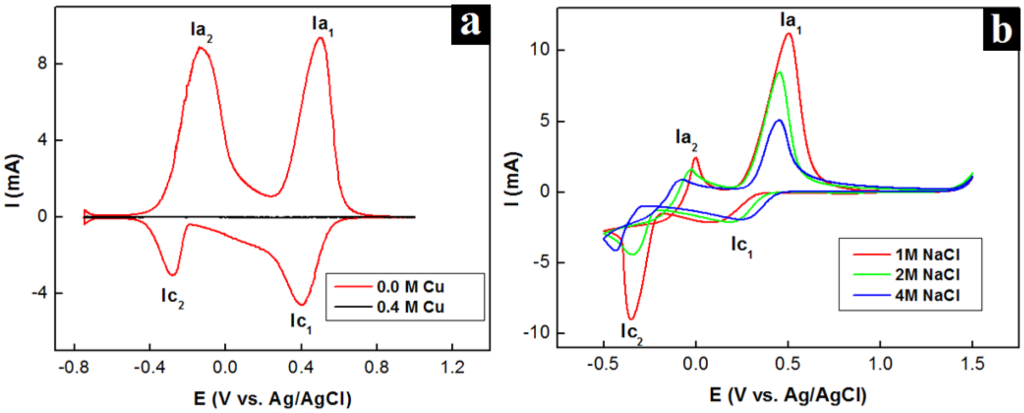


Figure 4.3.2.1.2 a) SWV of a glassy carbon electrode in 0.5 M H_2SO_4 + 4 M NaCl solution without and with addition of 0.4 M $CuSO_4 \cdot 5H_2O$, b) CV of a glassy carbon electrode in 0.5 M H_2SO_4 + 0.4 M $CuSO_4 \cdot 5H_2O$ solution containing different concentrations of NaCl

As it can be seen, an evident increase in Ia_1 and Ic_2 peaks intensity is observed when NaCl concentration decreases from 4 M to 1 M. This was due to the formation of an insoluble CuCl film on the electrode surface during oxidation from Cu^0 to Cu^+ (represented by Ia_2) which occurs through the two following steps **[26-28]**

$$Cu + Cl^- \rightarrow CuCl_{ads} + e^- \qquad (4.3.2.1.4)$$

$$CuCl_{ads} + Cl^- \rightarrow CuCl_2^- \qquad (4.3.2.1.5)$$

Both species undergo a successive oxidation (represented by Ia_1) through these two electrochemical reactions

$$CuCl_2^- \rightarrow Cu^{2+} + Cl^- + e^- \qquad (4.3.2.1.6)$$

$$CuCl_{ads} \rightarrow Cu^{2+} + Cl^- + e^- \qquad (4.3.2.1.7)$$

At higher NaCl concentration (i.e. higher C_{Cl}/C_{Cu} ratio), the adsorbed CuCl film is converted into soluble $CuCl_2^-$ chloro-complex, while oxidation to Cu^{2+} occurs exclusively via reaction 4.3.2.1.6. At lower NaCl concentration (i.e. lower C_{Cl}/C_{Cu} ratio), reaction 4.3.2.1.5 is slower leading to accumulation of CuCl on the electrode so that, oxidation to Cu^{2+} occurs via reactions 4.3.2.1.6 and 4.3.2.1.7 with consequent increase of Ia_1 peak intensity. Similarly, also the intensity of Ic_2 peak increases because the current response includes both reduction from $CuCl_{ads}$ to Cu^0 and from $CuCl_2^-$ to Cu^0. Indeed, although the reduction mechanism is still unclear owing to the effect of a large number of parameters influencing the stability of chloro-complexes that can be formed in the first stage of the reduction, some authors **[27-28]** claim that also Cu^{2+} reduction occurs with intermediate formation of CuCl according to

$$Cu^{2+} + Cl^- + e^- \rightarrow CuCl_{ads} \qquad (4.3.2.1.8)$$

$$CuCl_{ads} + Cl^- \rightarrow CuCl_2^- \qquad (4.3.2.1.9)$$

Then, both CuCl and $CuCl_2^-$ can be further reduced to Cu^0. This is a key point because in a copper recovery process, copper deposit could result contaminated by CuCl in dependence on C_{Cl}/C_{Cu} ratio.

The effect of different Cu concentrations on CV of a glassy carbon electrode in 0.5 M H_2SO_4-4 M NaCl solution is shown in Figure 4.3.2.1.3a-b. An increase in peaks intensity with the increase of copper concentration is revealed, in accordance with Randles-Sevcik's equation **[29]**. Copper deposition starts at about -0.285 V, -0.245 V and -0.216 V for Cu concentrations of 32 mM, 0.12 M and 0.4 M, respectively.

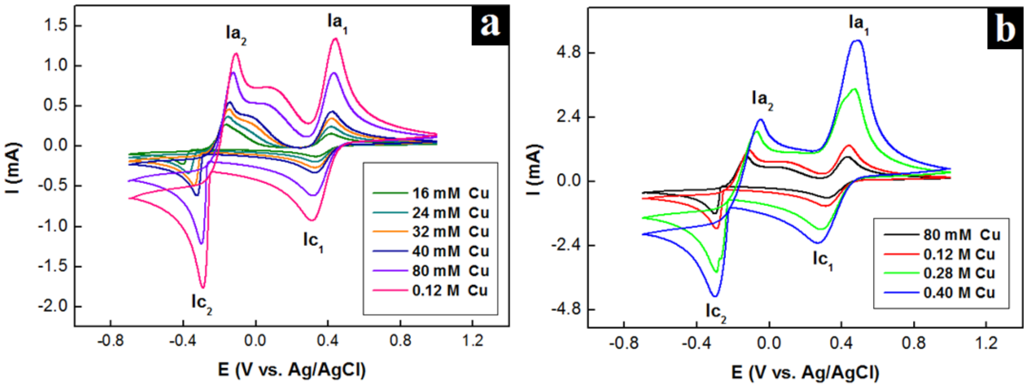


Figure 4.3.2.1.3 (a-b) CV of a glassy carbon electrode in 0.5 M H_2SO_4-4 M NaCl solution at different concentrations of $CuSO_4 \cdot 5H_2O$

The plateau of current next to Ia_2, which becomes clearer as the copper concentration increases (i.e. as the C_{Cl}/C_{Cu} ratio decreases), is probably due to a CuCl layer of increasing thickness in equilibrium with its simultaneous dissolution **[30]**. The significant increase in Ia_1 peak intensity passing from 0.12 M to 0.4 M that partially covers the plateau could be due to an excessive reduction of the C_{Cl}/C_{Cu} ratio with consequent accumulation of CuCl on the electrode surface according to Eq. 4.3.2.1.4. In a process of recovering copper from the solution resulting from WPCBs dismantling, this could result in a lower purity of the deposit because the leaching solution starts from a copper concentration of 0.4 M.

Despite this eventuality, leaching/dismantling tests proved that the initial copper concentration had to be sufficiently high to guarantee the complete dissolution of the metallic fraction from waste PCBs.

4.3.2.2 Cyclic voltammetry study of Pb, Sn, Fe, Zn and Ni in synthetic H_2SO_4–NaCl solution

CV of a glassy carbon electrode scanned from +0 V to -1.25 V and vice-versa in 0.5 M H_2SO_4-4 M NaCl solution with addition of $ZnSO_4 \cdot 7H_2O$ (MW 287.55 g/mol) at different concentrations is reported in Figure 4.3.2.2.1a. The redox process involved during the scan of potential can be described by the following electrochemical reaction

$$Zn^{2+} + 2e^{-} \rightleftarrows Zn^{0} \qquad (4.3.2.2.1)$$

The anodic curve shows a peak (Ia_1) whose intensity increases with zinc concentration, according to Randles-Sevcik's equation **[29]**. The cathodic curve sharply increases at -1.16 V and -1.09 V for a Zn concentration of 35 mM and 0.14 M, respectively, without generating a peak. This can be due to the simultaneous hydrogen evolution reaction which accompanies zinc deposition **[31-35]**.

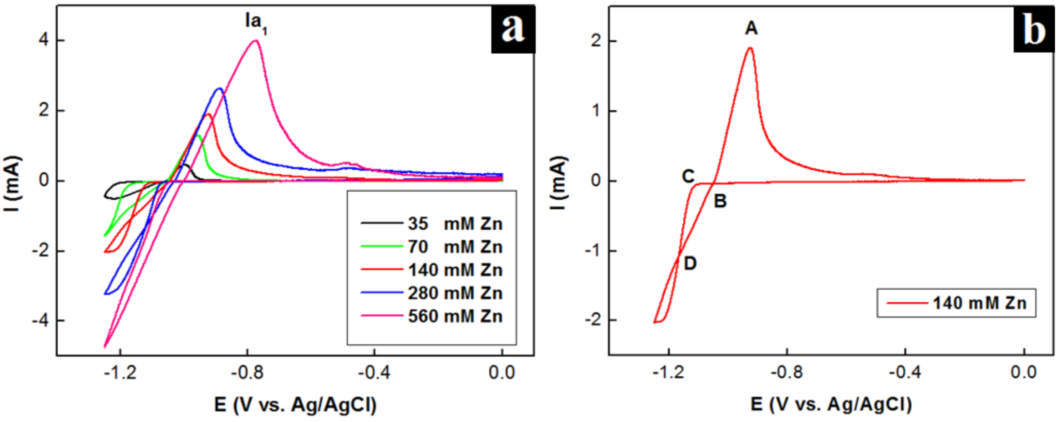


Figure 4.3.2.2.1 CV of a glassy carbon electrode in 0.5 M H_2SO_4-4 M NaCl solution with addition of $ZnSO_4 \cdot 7H_2O$: a) at different concentrations; b) at 140 mM

The voltammetric curve related to a Zn concentration of 0.14 M is shown in Figure 4.3.2.2.1b. The point A corresponds to the dissolution of the cathodically-deposited zinc while point C corresponds to the potential of nucleation starting. The crossover in D is typical of the formation of a new phase involving a nucleation process. Instead, the crossover in B at zero net current represents the equilibrium potential of the couple Zn^{2+}/Zn^0 **[33]**. The potential difference between the reduction potential at point C and the equilibrium potential at point B is a measure of the nucleation overpotential (NOP) for zinc deposition on a foreign substrate in glass carbon **[35]**.

CV of a glassy carbon electrode scanned from +0.8 V to -0.8 V and vice-versa in 4 M NaCl-0.5 M H_2SO_4 solution with addition of $PbSO_4$ (MW 303.26 g/mol) at different concentrations is shown in Figure 4.3.2.2.2a. Despite $PbSO_4$ is poorly soluble in water (44 mg/L), it was found that about 10 g/L of $PbSO_4$ can be dissolved at room temperature in 4 M NaCl-0.5 M H_2SO_4 solution. The value can increase to 12 g/L by means of a bland heating (T=50°C). The increase in solubility can be due to the formation of chloro-complexes according to

$$Pb^{2+} + nCl^{-} = PbCl_n^{2-n} \qquad (n=1,2,3) \qquad (4.3.2.2.2)$$

The highest concentration used for the CV study of lead was 33 mM, which corresponds to the maximum quantity of $PbSO_4$ that can be dissolved in 50 mL of 4 M NaCl+0.5 M H_2SO_4. The peak labelled Ic_1 in Figure 4.3.2.2.2a is associated to the reduction from Pb^{2+} to Pb, which starts at about -0.515 V for the CV curve at 33 mM of Pb. Mehta et al. **[36]** attributed the more negative value than the formal one for the redox couple Pb^{2+}/Pb to the complexation of Pb^{2+} by means of chloride ion. Besides, Figure 4.3.2.2.2a shows an increase in peaks intensity with Pb concentration, according to the theory on CV **[29]**.

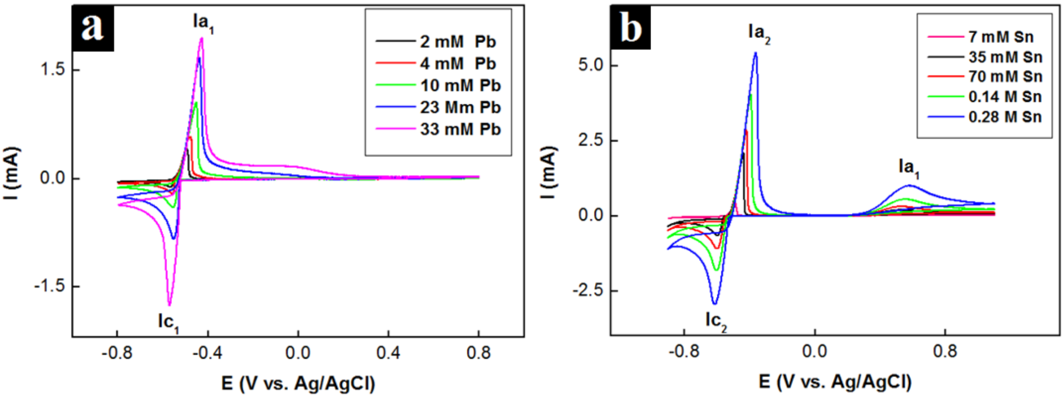


Figure 4.3.2.2.2 CV of a glassy carbon electrode in 0.5 M H_2SO_4-4 M NaCl solution with addition of different concentrations of a) $PbSO_4$ and b) $SnCl_2{\cdot}5H_2O$

Cyclic voltammetry of a glassy carbon electrode in synthetic 0.5 M H_2SO_4-4 M NaCl solution with addition of $SnCl_2{\cdot}5H_2O$ (MW 279.69 g/mol) at different concentrations is shown in Figure 4.3.2.2.2b. The potential was scanned within the interval 1.1 V÷ -0.9 V. The existence of two redox reactions is revealed, which are

$$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+} \qquad (4.3.2.2.3)$$

$$Sn^{2+} + 2e^- \rightleftharpoons Sn^0 \qquad (4.3.2.2.4)$$

The Ia_1 peak is due to reaction 4.3.2.2.3 while the absence of the corresponding reduction peak reveals a strong irreversibility of the process **[37]**. The peaks labelled Ia_2 and Ic_2 are associated to reaction 4.3.2.2.4. For the 35 mM Sn solution, a sharp onset of the cathodic current occurs at about -0.553 V, which is very similar to the value found for the Pb^{2+}/Pb couple at 33 mM of Pb. The presence of a crossover between the cathodic and anodic curve indicates nuclei formation on the electrode surface **[38]**.

Figure 4.3.2.2.3a shows CV curves of a glassy carbon electrode scanned from +1 V to -1.2 V and vice-versa in 0.5 M H_2SO_4-4 M NaCl solution added with different amounts of $FeSO_4{\cdot}7H_2O$ (MW 278 g/mol).

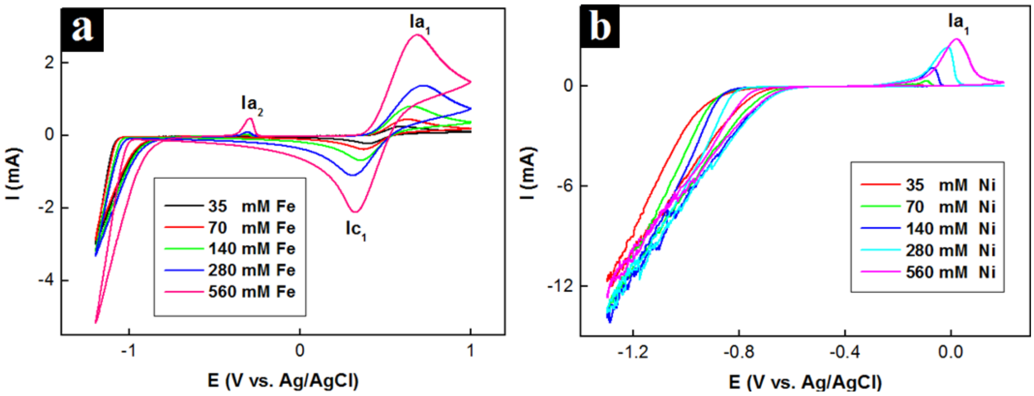


Figure 4.3.2.2.3 CV of a glassy carbon electrode in in 0.5 M H_2SO_4-4 M NaCl solution with addition of a) $FeSO_4 \cdot 7H_2O$ and b) $NiSO_4 \cdot 7H_2O$ at different concentrations

The two redox reactions revealed by the voltammetric curves are

$$Fe^{3+} + e^- \rightleftarrows Fe^{2+} \qquad (4.3.2.2.5)$$

$$Fe^{2+} + 2e^- \rightleftarrows Fe \qquad (4.3.2.2.6)$$

Ia$_1$ and Ic$_1$ peaks of Figure 4.3.2.2.3a are associated to reaction 4.3.2.2.5. The oxidation peak labelled Ia$_2$ is related to reaction 4.3.2.2.6. For all concentrations of Fe, the cathodic current starts to sharply increase at about -1 V without a clear reduction peak coupled to Ia$_2$ likely because iron nucleation starts in parallel with hydrogen evolution **[39]**. The Ia$_2$ peak appears when iron concentration is 0.14 M, at least. Therefore, for lower Fe concentrations, the quantity of iron deposited on the electrode surface is negligible likely because hydrogen gas hinders iron deposition.

Figure 4.3.2.2.3b shows CV curves of a glassy carbon electrode scanned from +0.2 V to -1.3 V and vice-versa in 0.5 M H_2SO_4-4M NaCl solution added with different amounts of $NiSO_4 \cdot 7H_2O$ (MW 280.76 g/mol). The electrochemical behavior is similar to that observed for iron. The Ia$_1$ peak is associated to the reaction

$$Ni^0 \rightarrow Ni^{2+} + 2e^- \qquad (4.3.2.2.7)$$

The corresponding reduction peak does not appear due to reduction of H^+ to H_2 that, according to some authors **[40]**, shields nickel deposition peak. The final cathodic potential was limited until -1.3 V in order to reveal the Ia_1 peak, probably because hydrogen gas hinders nickel deposition **[41]**. The cathodic current starts to sharply increase at -0.95 V and -0.85 V for a Ni concentration of 35 mM and 0.14 M, respectively.

It should be noted that all the voltammograms (Figures 4.3.2.1.3, 4.3.2.2.1-4.3.2.2.3) show an increase of the peak-to-peak separation ($\Delta E\text{p}=E\text{p}^{\text{ox}}$ - $E\text{p}^{\text{red}}$, where $E\text{p}^{\text{ox}}$ and $E\text{p}^{\text{red}}$ are the oxidation and reduction peak potentials, respectively) as the concentration of the electroactive species in solution increases. According to the literature **[42]**, this is due to the fact that the diffusion layer becomes thinner and the concentration gradient steeper with increasing concentration or scan rate.

In 0.5 M H_2SO_4-4 M NaCl, deposition of copper starts enough before than other metal ions, favouring the possibility to obtain a pure copper deposit. For instance, deposition of copper starts at about -0.285 V while that of Pb, Sn, Ni, Fe and Zn at about -0.515 V, -0.553 V, -0.95 V, -1 V and -1.16 V, respectively when Me^{n+} concentration in solution is approximately the same (32-35 mM). To confirm this results, the interference of such metals on the copper voltammogram was investigated.

4.3.2.3 Cyclic voltammetry study of copper with other metal ions in synthetic H_2SO_4–NaCl solution

A list of the solutions prepared to investigate the influence of other metals such as Pb, Sn, Zn, Fe and Ni on CV of copper is shown in Table 4.3.1.1.

It was found that zinc and nickel do not have any influence when the potential is scanned within the range +1 to -0.7 V, which is the best interval to have a complete and well defined copper voltammetric curve.

In Figure 4.3.2.3.1a a square wave voltammetry of a glassy carbon electrode in 0.5 M H_2SO_4-0.1 M $CuSO_4\cdot 5H_2O$-4 M NaCl with addition of $ZnSO_4\cdot 7H_2O$ at different concentrations is reported. In this case, SWV was preferred to CV because the resultant curve does not present any crossover between the anodic and the cathodic curve making easier the comparison of the curves obtained under different conditions.

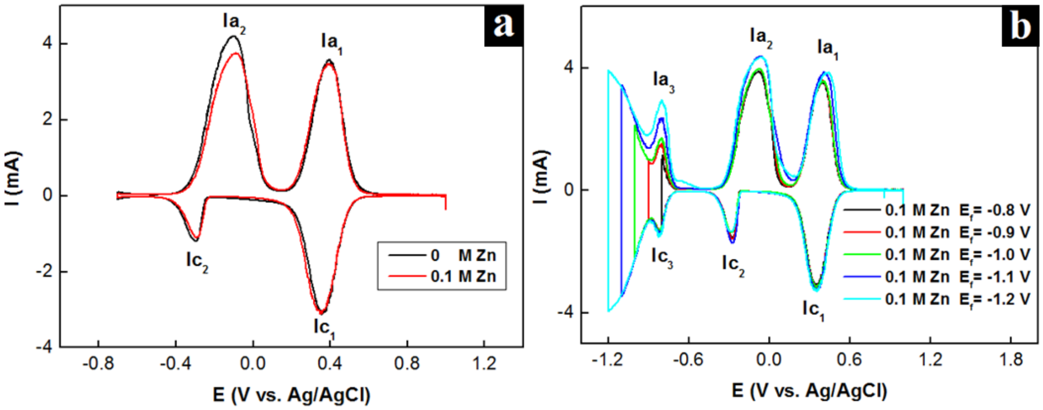


Figure 4.3.2.3.1 SWV of a glassy carbon electrode in 4 M NaCl-0.5 M H2SO4-0.1 M $CuSO_4·5H_2O$ solution with addition of $ZnSO_4·7H_2O$: a) at different concentrations; b) at 0.1 M and different values of the final cathodic potential

As shown, the addition of 0.1 M Zn does not determine any modification on the copper voltammetric curve within the investigated interval of potential. Two specific peaks (Ia_3 and Ic_3) attributable to the Zn^{2+}/Zn couple appear in Figure 4.3.2.3.1b starting from a final cathodic potential (E_f) of -0.9 V. A further reduction of E_f leads to an increase in Ia_3 peak intensity, likely due to the increased amount of zinc deposited on electrode surface because deposition partially continues even after Ic_3 peak together with hydrogen evolution.

Similar results were obtained also for the couple Cu/Ni. Figure 4.3.2.3.2a shows that no modification on square wave copper voltammogram in 0.5 M H_2SO_4-0.1 M $CuSO_4·5H_2O$-4 M NaCl is determined in the interval 1÷ -0.7 V by addition of 0.1 M $NiSO_4·7H_2O$.

In the same interval of potential, the addition of 0.1 M $FeSO_4·7H_2O$ in 0.5 M H_2SO_4-0.1 M $CuSO_4·5H_2O$-4 M NaCl solution determined the appearance of a peak (Ia_3) at +0.549 V related to the Fe^{3+}/Fe^{2+} couple and an increase in Ic_1 peak intensity (Figure 4.3.2.3.2b). Nevertheless, no simultaneous electrodeposition of iron together with copper is revealed in the investigated interval of potential. The plateau of current next to Ia_2 peak is likely due to reduction of copper concentration from 0.4 M to 0.1 M, as shown in Figure 4.3.2.1.3.

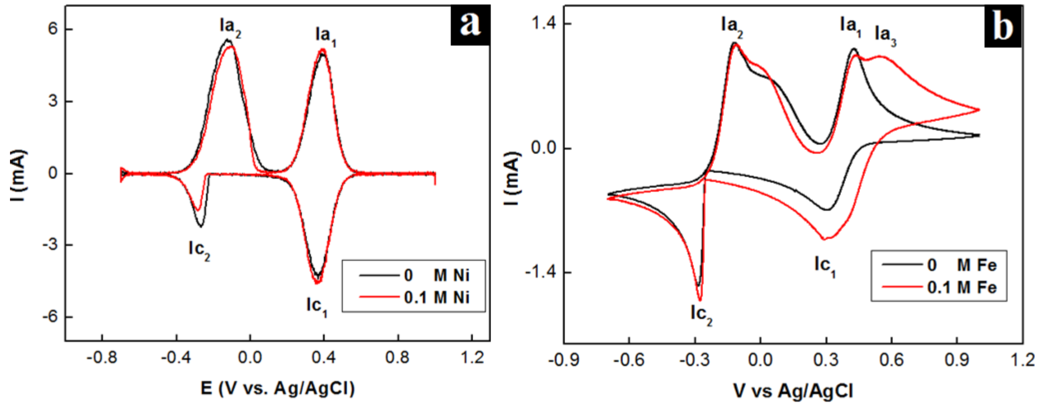


Figure 4.3.2.3.2 a) SWV of a glassy carbon electrode in 4 M NaCl-0.5 M H2SO4-0.1 M $CuSO_4 \cdot 5H_2O$ solution without and with addition of $NiSO_4 \cdot 7H_2O$; b) CV of a glassy carbon electrode in 4 M NaCl-0.5 M H2SO4-0.1 M $CuSO_4 \cdot 5H_2O$ solution without and with addition of $FeSO_4 \cdot 7H_2O$

Figure 4.3.2.3.3 shows the voltammetric curves obtained in 4 M NaCl-0.5 M H_2SO_4-33 mM $CuSO_4 \cdot 5H_2O$ solution with addition of either $PbSO_4$ or $SnCl_2 \cdot 5H_2O$ (see solution number 4 and 5 in Table 4.3.1.1).

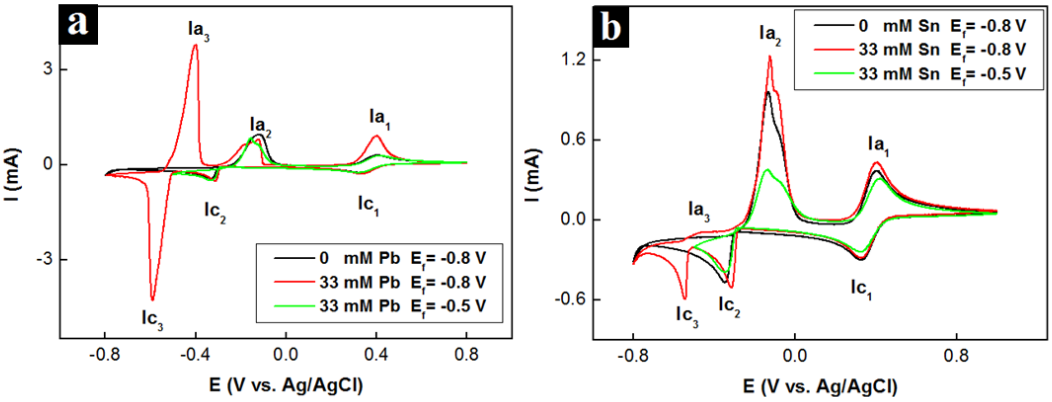


Figure 4.3.2.3.3 CV of a glassy carbon electrode scanned from 1 V to -0.8 V and from 1 V to -0.5 V in 4 M NaCl-0.5 M H_2SO_4-33 mM $CuSO_4 \cdot 5H_2O$ solution without and with addition of a) 33 mM $PbSO_4$; b) 33 mM $SnCl_2 \cdot 5H_2O$

The appearance in Figure 4.3.2.3.3 of a couple of peaks (Ic_3 and Ia_3) attributable to Pb^{2+}/Pb^0 (Figure 4.3.2.3.3a) and Sn^{2+}/Sn^0 (Figure 4.3.2.3.3b) couples indicates the simultaneous electrodeposition of either tin or lead together with copper. However, the same figure evidences that co-deposition of tin or lead can be avoided by reducing the final cathodic potential from -0.8 V to -0.5 V. It should be observed that the current response produced by lead is much more intense than that produced by tin and copper in otherwise identical conditions. Besides, the current response associated to the Sn^{2+}/Sn^{4+} couple was shielded by the Cu^+/Cu^{2+} couple in the same potential interval.

When Pb^{2+} and Sn^{2+} are both present in solution, their detection by CV is rather difficult because there is not a clear separation between the peaks.

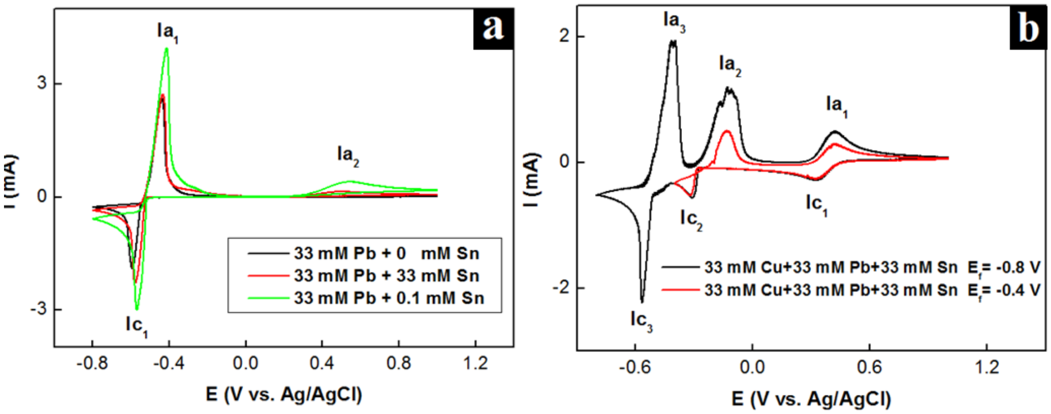


Figure 4.3.2.3.4 CV of a glassy carbon electrode in 4 M NaCl-0.5 M H_2SO_4 solution: a) with addition of 33 mM $PbSO_4$, 33 mM $PbSO_4$ + 33 mM $SnCl_2{\cdot}5H_2O$, and 33 mM $PbSO_4$ + 0.1 M $SnCl_2{\cdot}5H_2O$; b) with addition of 33 mM $CuSO_4{\cdot}5H_2O$ + 33 mM $PbSO_4$ + 33 mM $SnCl_2{\cdot}5H_2O$

Figure 4.3.2.3.4a shows a weak increase of the Ic_1 reduction peak in the CV curve after 33 mM $SnCl_2{\cdot}5H_2O$ addition into a solution containing 0.5 M H_2SO_4+33 mM $PbSO_4$+4 M NaCl. Since the current peak at -0.577 V is due to the reduction reactions of both Pb^{2+} and Sn^{2+} to metallic Pb and Sn, respectively, it can be assumed that the weak increase is due to co-deposition of lead and tin. When tin concentration added to 0.5 M H_2SO_4-33 mM $PbSO_4$-4 M NaCl solution was increased from 33 mM to 0.1 M, the CV curve shows an increase of both Ic_1 and

Ia_1 peaks, and the appearance of a peak at +0.532 V (Ia_2) due to Sn^{2+}/Sn^{4+} irreversible oxidation.

The interaction between Pb, Sn and Cu was also investigated. The CV of a glassy carbon electrode in 0.5 M H_2SO_4-4 M NaCl-33 mM $CuSO_4 \cdot 5H_2O$-33 mM PbSO4-33 mM $SnCl_2 \cdot 5H_2O$ solution is shown in Figure 4.3.2.3.4b. As it can be seen, there is no a clear separation between peaks of Pb and Sn. The couple of Ia_3/Ic_3 peaks can be attributed to both these two elements. However, the figure shows that co-deposition of Pb and Sn together with copper can be avoided reducing the final cathodic potential from -0.8 V to -0.4 V without altering deposition process of copper represented by Ic_2 peak.

Table 4.3.2.3.1 shows the values of potential at which metals deposition starts (E_d) in the CV curves obtained coupling Cu with another metal ion such as Pb, Sn, Ni, Fe and Zn in synthetic 0.5 H_2SO_4-4 M NaCl solution (see solutions 1-5 in Table 4.3.1.1). All the values are extracted assuming as E_d the value of potential at which the cathodic curve starts to abruptly increase.

	Cu/Zn	**Cu/Fe**	**Cu/Ni**	**Cu/Pb**	**Cu/Sn**
$E_{d,Cu}$ (V vs Ag/AgCl)	-0.243	-0.244	-0.263	-0.285	-0.275
$E_{d,Me}$ (V vs Ag/AgCl)	-0.858	-0.740	-0.682	-0.491	-0.510

Table 4.3.2.3.1 Potential values from the CV curves of a glassy carbon electrode in the solutions reported in Table 4.3.1.1

According with Table 4.3.2.3.1, pure copper could be theoretically recovered maintaining a potential just under -0.285 V. In a next step, also lead and tin could be theoretically recovered from the leach solution reducing the potential just under -0.5 V. For the recovery of Ni, Zn and Fe, a further reduction of the potential would be necessary with the risk of hydrogen evolution.

Besides, the electrochemical characterization of the synthetic solutions indicates the possibility of low current efficiency in the copper recovery process from the leach solution due to the consumption of charge at cathode related to the Sn^{2+}/Sn^{4+} and Fe^{2+}/Fe^{3+} redox couples.

4.3.2.4 Cyclic voltammetry study of a real solution resulting from the leaching step

The electrochemical characterization of glassy carbon electrode in synthetic solutions made possible to exhaustively characterize the solution coming from the dismantling/leaching of the WPCB to detect the operative conditions for effective copper recovery **[4, 43]**.

Figure 4.3.2.4.1a shows the CV curve obtained in the leach solution when the potential was scanned in the interval 1÷ -0.7 V. For comparison, the CV curve obtained in 4 M NaCl-0.5 M H_2SO_4-0.4 M $CuSO_4·5H_2O$ synthetic solution (blank solution) is also reported.

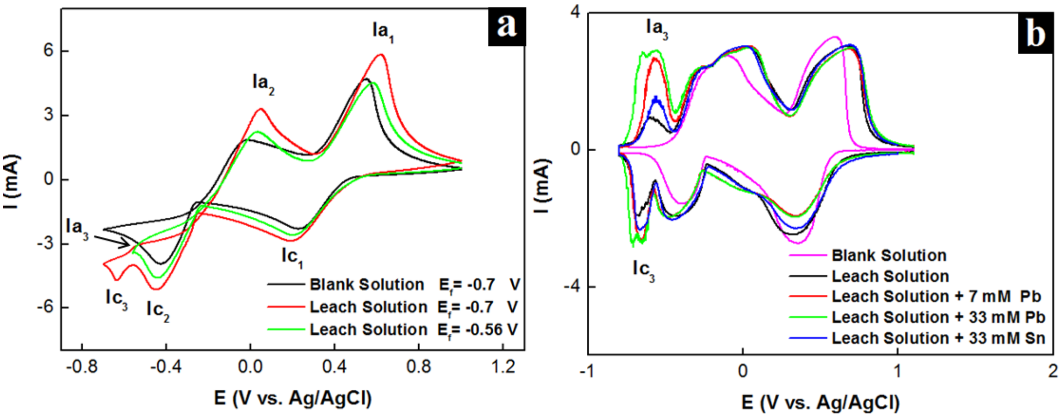


Figure 4.3.2.4.1 a) CV of a glassy carbon electrode in leach solution; b) SWV of a glassy carbon electrode in leach solution with addition of 7 mM Pb, 33 mM Pb and 33 mM Sn

To identify the new appeared couple of peaks, small concentrations of Pb or Sn ions were added to the leach solution for investigating the effect produced on the voltammetric curve. In this case, a square wave voltammetry was preferred since it allows a clearer view of Ia_3 peak. Figure 4.3.2.4.1b shows as the addition of either Pb or Sn to the leach solution increases the intensity of both peaks Ic_3 and Ia_3 without any other modifications. The increase in Ia_3 peak intensity is higher for lead than tin with a possible doubling in otherwise identical conditions. Therefore, the leach solution probably contained both lead and tin, but lead in lower concentrations than tin as also confirmed by the leaching tests that showed a not complete removal of Pb from the soldering paste due to passivation effect.

However, the CV curve marked in green in Figure 4.3.2.4.1a shows that reducing the final cathodic potential from -0.7 V to -0.56 V, it is possible to remove the couple of peaks without influencing the Cu^+/Cu reduction peak (Ic_2) and then, without influencing the copper recovery. Besides, electrochemical characterization of the leach solution suggests to maintain the potential between -0.24 and -0.45 V, i.e. between the potential at which copper deposition starts and that of the cathodic peak for the Cu^+/Cu couple, in order to obtain a pure deposit in the copper recovery process.

4.4 Copper recovery from the leach solution

Copper, in the form of ions, is the most abundant element in the solution from dismantling/leaching of the WPCB. This solution contains several other ions such as Zn^{2+}, Fe^{2+}, Ni^{2+}, Sn^{2+}, Pb^{2+} coming from oxidation of the EC pins and soldering paste. In principle, such ions could interfere with the copper recovery via cathodic deposition, but the electrochemical characterization by CV showed the possibility of selectively recovering metallic copper at high purity. To confirm these findings, specific tests of copper recovering were conducted.

Since in a possible real process the dismantling/leaching of WPCBs could occur simultaneously to the copper recovery, initially, these two steps were coupled for the treatment of an entire computer motherboard. However, due to some difficulties encountered in managing different working parameters for optimization of both leaching and recovery process, it was preferred to study electrochemical deposition of copper separately from leaching. At this purpose, a divided electrochemical cell was assembled with graphite and a pure copper sheet, acting as an anode and a cathode, respectively. The copper recovery tests were conducted in both galvanostatic and potentiostatic mode.

4.4.1 Electrochemical recovery of copper simultaneously with dismantling/leaching of WPCB

A preliminary experiment at large scale was conducted combining a chemical reactor with a divided electrochemical cell for leaching out metals from WPCB and simultaneously recovering copper at cathode and restoring the oxidizing agent at anode. A schematic representation and a photo of the experimental apparatus are reported in Figure 4.4.1.1a and b, respectively.

The chemical reactor was equipped with a perforated rotating drum and filled with a fresh leaching solution having the same composition which gave the best results in the leaching tests, i.e. the following: 0.5 M H_2SO_4, 0.4 M $CuSO_4 \cdot 5H_2O$ and 4 M NaCl. An entire computer motherboard (CMB) was fed into the rotating drum after removal of some ECs and cutting into pieces of 40-100 cm^2. The model of CMB used was “P6BAP-Me-ECS”. ECs manually removed were: the Li-ion battery, aluminum heat sink, Ni-based screws from computer ports and the cylindrical aluminum electrolytic capacitors. A very short mass balance is reported in Figure 4.4.1.2. This minimal mechanical pre-treatment, which took less than 2 min., was fundamental in order to avoid few unwanted problems: risks of explosion due to the extremely reactive inner of Li batteries; risks of leaching solution contamination with extremely toxic polychloride-biphenyls contained in some cylindrical aluminum electrolytic capacitors; the increase of the leaching time due to the high thickness of the mentioned screws; the unjustified consumption of leaching agent for the Al dissolution due to the low commercial value of Al and its difficult recovery from the resulting solution. The final weight of the pre-treated CMB was 472 g.

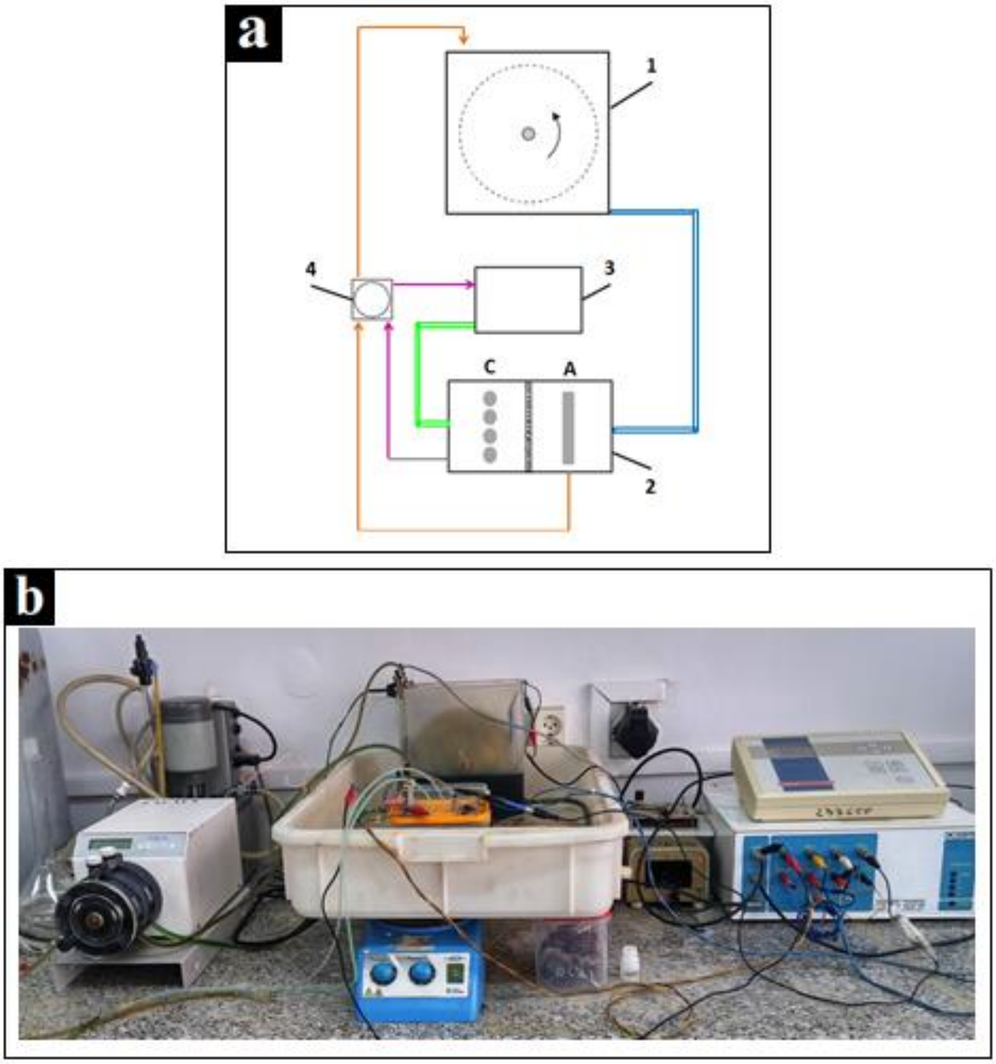


Figure 4.4.1.1 a) Schematic representation and b) photo of the experimental apparatus for dismantling/leaching of WPCB and simultaneous copper recovery. From figure a): 1- Leaching reactor, 2- electrochemical cell for copper recovery, 3- leach solution container, 4- peristaltic pump, A- anode, C- cathode

After the removal of the above mentioned ECs, the remaining board was broken in large pieces in order to full fit the dimension of the rotating drum. It is important to point out that CPU and RAM are not generally found in waste CMBs owing to their high economic value; therefore, they are extracted and improperly treated for gold recovery.

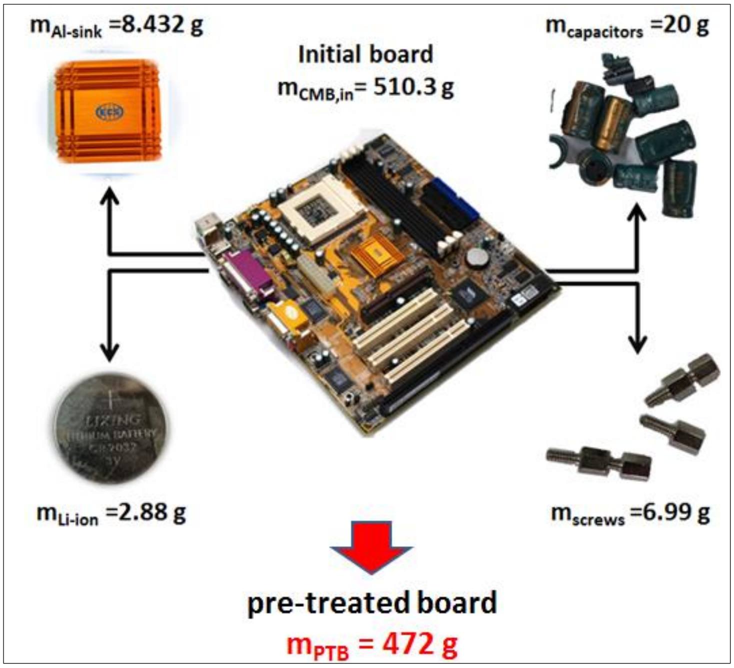
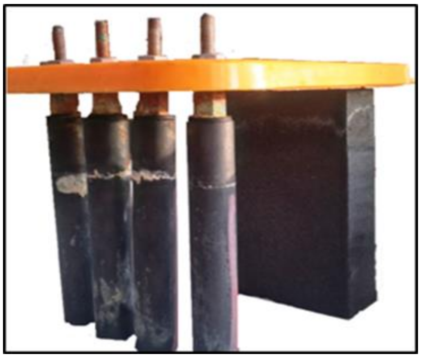


Figure 4.4.1.2 Mass balance of mechanical pre-treatment



The electrochemical reactor consisted of a two compartment cell divided by a ceramic membrane. The anode was a graphite block of dimension 8x7x2 cm, the cathode consisted of four graphite rods each having 1 cm of diameter and 8 cm of length (see the figure on the left).

As shown in Figure 4.4.1.1a, the anodic compartment was in communication with the leaching reactor through a tube (in blue in Figure 4.4.1.1a) and 2.5 L of fresh leaching solution was used to fill them both. The anolyte was pumped from the anodic chamber to the leaching reactor through a peristaltic pump with a flow rate of 300 mL of solution per minute (Qa). In this way, the anode played the same role than oxygen in the leaching tests, which is that of regenerating the oxidizing agent (Cu^{2+}) to guarantee an effective extraction of metals from WPBC. The cathodic compartment was in communication with a collecting vessel for the catholyte through a tube (in green in Figure 4.4.1.1a) and 1.2 L of leach solution coming from the leaching tests in 0.5 M H_2SO_4-0.4 M $CuSO_4 \cdot 5H_2O$-4 M NaCl was used to fill them both. The catholyte was pumped from the cathodic chamber to the collecting vessel with a flow rate of 250 mL of solution per minute (Qc). To improve the mass transport the electrolyte in the cathodic compartment was maintained in agitation through a magnetic needle setting a speed of 400-500 rpm. pH, temperature and redox potential were constantly monitored inside the leaching reactor. The electrode potentials were measured relative to a saturated silver–silver chloride electrode (Ag/AgCl/KClsat.). In the following, all the potentials are referred to it.

On the basis of CV study, a potential of -0.35 V was initially supplied at cathode. However, at this potential value, the resulting current was very close to the lower current limit of the potentiostat (-5A). Besides, the anodic potential exceeded the value of 2 V with a consequent evolution of chlorine. The results were not satisfactory also in the leaching reactor where, owing to an instantaneous cementation, the concentration of copper quickly decreased and therefore, the oxidizing power of the solution. Likely, this was due to the higher S/L ratio (5.3 mL of solution per gram of solid) compared to that used in the leaching tests (11 mL of solution per gram of solid) but, it should be noted that a key parameter for leaching performances was also the flow rate (Qa). In Figure 4.4.1.3 a photo of the CMB after 3 h of leaching is reported. The total loss of weight measured was 50 g, equal to 10.6% of the initial weight of pre-treated CMB. As it can be seen from Figure 4.4.1.3, integrated circuits (IC), CPU socket and PCI slots are completely disassembled from the board preserving their original shape and structure. Integrated circuits can be sent to further treatment, instead, CPU socket and PCI slots can be recycled. However, computer ports (CP in Figure 4.4.1.3), ATA and RAM slots are still assembled to the board; the soldering paste results passivated and not completely dissolved.

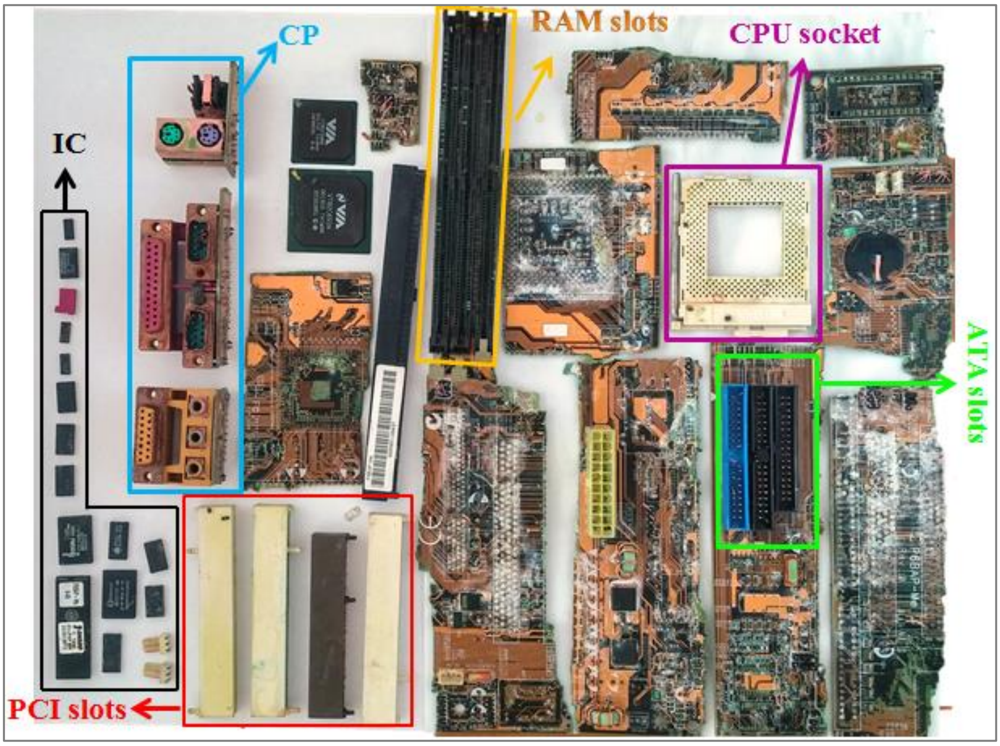


Figure 4.4.1.3 Computer motherboard after 3 h of leaching

Since process optimization required the study of different operating parameters (S/L ratio, Qa, Qc, applied potential etc.), of their interaction and their influence both on the leaching and electrochemical process, it was decided to investigate copper recovery separately from dismantling/leaching.

4.4.2 Electrochemical recovery of copper separately from dismantling/leaching of WPCB

A divided electrochemical cell operating in either galvanostatic or potentiostatic mode was employed to investigate copper recovery. Despite copper recovery was investigated separately from dismantling/leaching, the configuration of the electrochemical reactor was designed to allow copper recovery at cathode and leaching solution restoration at anode in order to simulate a real process in which leaching reactor and electrochemical cell operate in continuous. Experimental procedure and results will be reported in the following.

4.4.2.1 Material and methods

A schematic representation of the electrochemical cell used for copper recovery tests is shown in Figure 4.4.2.1.1. A 99.8% purity copper sheet was used as a cathode, and a graphite block (8x7x2 cm) as an anode. To improve the primary current distribution, one side of the cathode was coated with an insulating resin in order to expose to the electrolyte only the side opposite to the anode.

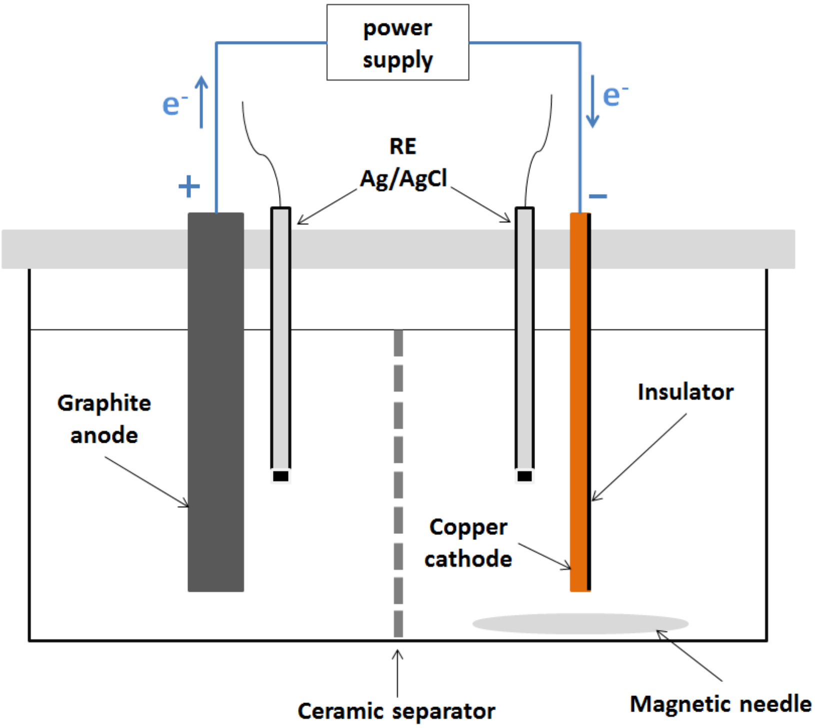


Figure 4.4.2.1.1 Schematic representation of the electrochemical cell used for copper recovery tests

The electrode potentials were referenced to saturated silver–silver chloride electrodes (Ag/AgCl/KClsat.). The anodic and the cathodic compartments were divided by a ceramic membrane, and both filled with the solution resulting from the leaching. The cathodic solution was magnetically stirred at 500 rpm. The electrolyte was the same for both compartments of the cell to simulate a real process in which copper deposition occurs simultaneously to dismantling/leaching.

A possible real process is schematized in Figure 4.4.2.1.2. As it can be seen, the leach solution is directly fed to the cathodic compartment and then passed to the anodic one for the leaching solution restoration. Before use as an electrolyte, Cu^{2+}/Cu^{+} ratio of the leach solution was decreased to avoid excessive electrical charge consume at cathode due to the reduction of Cu^{2+} to Cu^{+}.

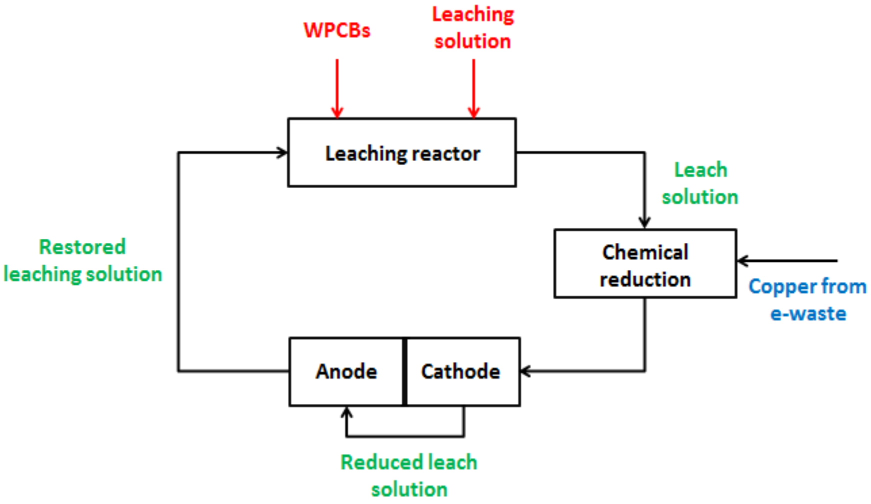
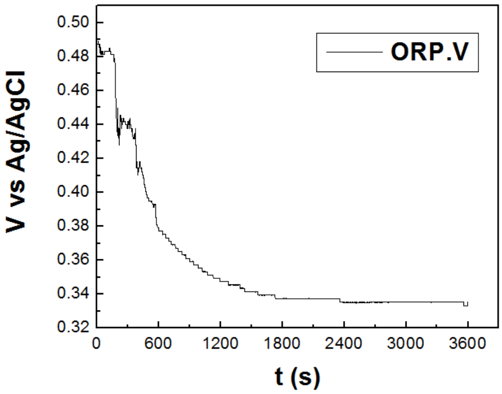


Figure 4.4.2.1.2 Block diagram of a possible real process of WPCBs disassembling and simultaneous copper recovery



At this aim, 50 g of copper from waste electric cables was added to 0.5 L of leach solution. In Figure 4.4.2.1.3 it can be seen as the oxidation-reduction potential (ORP) of the solution decreases from +0.49 V to +0.335 V in 3600 s. During the chemical reduction, the leach solution changed from green to brown.

Figure 4.4.2.1.3 Redox potential profile during chemical reduction of the leach solution

It should be note that, in an industrial perspective, this process could be carried out using the same WPCBs before sending them to the leaching reactor. In this way, the problem of copper cementation in the leaching reactor would be also reduced.

Besides at some point, a purification of the solution leaving the anodic compartment could be required before its recycling in order to avoid the accumulation of metals different from copper, which could compromise copper purity. The removal of such metals could be carried out electrochemically as suggested by CV study, but further studies are required in this regard.

The copper recovery was conducted in both galvanostatic and potentiostatic mode. Generally, electrolysis of copper is carried out in galvanostatic mode. Nevertheless, it was recently shown that it is possible to get high quality deposits through a potential-controlled process, even determining very high current densities **[44]**. In Table (4.4.2.1.1) is reported the experiments setup. A constant current or potential was supplied at cathode. The cathodic surface was modified in each test to investigate an increase in current density without determining a current higher that -1 A that leads to a fast evolution of chlorine at anode where an anodic potential higher than 1.3 V was reached. For the same reason, the time of each test was fixed at 3 hours.

AMPEROSTATIC MODE			
Experimental number	**Electrode Surface (cm^2)**	**Applied current (A)**	**Current density (mA/cm^2)**
1	42	-1	-23.8
2	21	-0.63	-30
3	12	-0.48	-40
4	9	-0.45	-50

POTENTIOSTATIC MODE		
Experimental number	**Electrode Surface (cm^2)**	**Applied Potential (V vs Ag/AgCl)**
5	21	-0.25
6	12	-0.3
7	9	-0.35

Table 4.4.2.1.1 Experiments setup for copper recovery

The cathodic deposits were chemically and morphologically characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The morphology was investigated using a scanning electron microscopy (SEM, FEI mod.: QUANTA 200 FEG) equipped with an X-ray energy dispersive spectrometer. A further characterization was performed by XRD analysis, (Rigaku, D-MAX 25600 HK). All X-ray analyses were conducted in the

2ϑ range from 5° to 100° using the Cu Kα radiation (λ=1.54 Å). Diffraction patterns were analysed by comparison with ICDD database **[45]**.

The current efficiency of copper deposition was determined by the following equation

$$\eta_{Cu}=\frac{W_e}{W_t} \qquad (4.4.2.1.1)$$

where We is the experimental weight of copper deposited on the cathode and W_t is the theoretical weight of deposited copper calculated with Faraday's law

$$W_t=\frac{M_{Cu} I\, t}{z_{Cu} F} \qquad (4.4.2.1.2)$$

where M_{Cu} is the molar mass of copper; I the applied current; t the time of the electrolysis; z_{Cu} the valence of copper; F the Faraday's constant.

4.4.2.2 Results and discussion

In Figure 4.4.2.2.1 a photo of the copper deposits obtained in galvanostatic and potentiostatic modes after 3 h is reported.

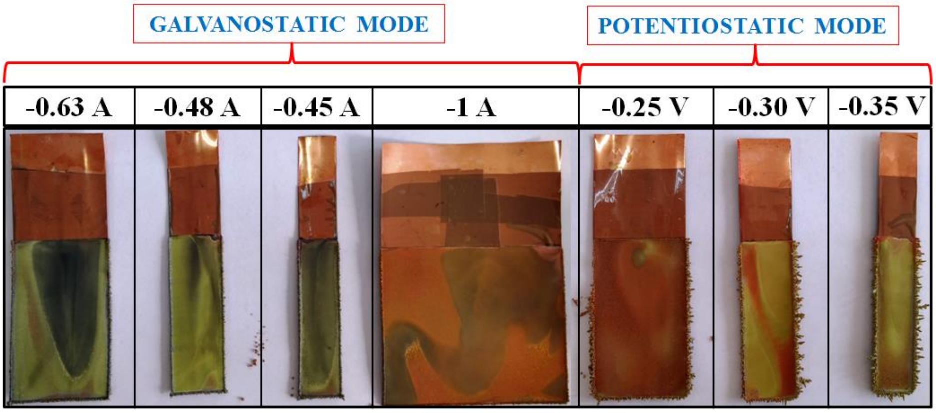


Figure 4.4.2.2.1 Photo of the deposits obtained by copper electrolysis at different operating conditions

Deposits obtained in potentiostatic mode appear dendritic along the edges where the higher local current density favours the dendritic growth **[46-47]**. It's likely that at the edges, copper deposition becomes mass transfer limited or very close to the mass transfer limit. The average cathodic current density was about 60, 80 and 90 mA/cm^2 for cathode polarization at -0.25 V, -0.3 V and -0.35 V, respectively. On the contrary, the current density referred at cathode geometrical area ranged from 23.8 to 50 mA/cm^2 in the galvanostatic mode. Therefore, the current density on the edges was higher in potentiostatic mode than galvanostatic one. The key role of the local current density is further evidenced by the enhancement of the dendritic morphology as the electrode potential was growing from -0.25 V to -0.35 V. The dendritic structure is undesired because the copper deposit must be melted prior to any further working. Of course, this would be a severe disadvantage for technological application.

The deposits of Figure 4.4.2.2.1 appear of a green color especially those obtained at -0.63, -0.48 and -0.45 A. For this reason, an XRD and EDS characterization was conducted. In Table 4.4.2.2.1 the results of the EDS analysis are reported. The as obtained deposits are not pure because contain elements such as Cl and O, in addition to Cu. The atomic composition of the deposits obtained at -0.63, -0.48 and -0.45 A is very similar to that obtained at -0.30 V and -0.35 V. The deposit at higher purity is that obtained at -1 A and, to a lesser extent, the one at -0.25 V.

Element	**POWER SUPPLY**						
	AMPEROSTATIC MODE A				**POTENTIOSTATIC MODE V vs Ag/AgCl**		
	-1	**-0.63**	**-0.48**	**-0.45**	**-0.25V**	**-0.3V**	**-0.35V**
O	15.42%	32.37%	31.05%	31.39%	28.58%	34.75%	40.44%
Cl	16.06%	22.47%	25.92%	25.97%	14.35%	24.12%	21.33%
Cu	68.52%	45.16%	43.02%	42.64%	57.07%	41.13%	38.22%

Table 4.4.2.2.1 Elemental composition (at. %) by EDS analysis of the copper deposits obtained by electrodeposition from the solution resulting from dismantling/leaching of WPCBs

An XRD analysis was performed for identifying the species present in the deposits, the results are shown in Table 4.4.2.2.2. By analogy with EDS results, the deposits obtained at -1 A and -0,25 V contain a fewer number of phases different from copper. The main impurities in all deposits are represented by CuO and CuCl, this last probably determines the greenish color observed in Figure 4.4.2.2.1 in presence of $CuCl_2$. Diffraction patterns were analyzed by comparison with ICDD database **[45]**.

POWER SUPPLY						
AMPEROSTATIC MODE **A**				**POTENTIOSTATIC MODE** **V vs Ag/AgCl**		
-1	**-0.63**	**-0.48**	**-0.45**	**-0.25V**	**-0.3V**	**-0.35V**
Cu CuO CuCl	Cu CuO CuCl Cu_2O $CuCl_2$	Cu CuO CuCl Cu_2O $CuCl_2$ $Cu(OH)_2$	Cu CuO CuCl Cu_2O $CuCl_2$ $Cu(OH)_2$	Cu CuO CuCl Cu_2O	Cu CuO CuCl Cu_2O $CuCl_2$ $Cu(OH)_2$ $Cu_3Cl_4(OH)_2$	Cu CuO CuCl Cu_2O $CuCl_2$ $CuCl_2 \cdot 3Cu(OH)_2$

Table 4.4.2.2.2 Phases detected by XRD analysis on the deposits obtained by copper recovery tests

The presence of CuCl on deposits had already been suggested by CV study, investigating on mechanism of copper deposition in chloride-sulphate solutions (Eq. 4.3.2.1.8 and 4.3.2.1.9). It's likely that, owing to copper dissolution from WPCBs, copper concentration in solution exceeds the initial value of 0.4 M leading to a Cu^{2+} deposition controlled by CuCl formation since Cl^- is not enough to guarantee the conversion in chloro-complexes. As for the presence of CuO, its formation is due to the pH raising at the electrode/electrolyte interface owing to the parasitic reaction of hydrogen evolution, which can accompany copper deposition especially in those points of the electrode surface where high current densities were reached. In fact, in the deposits obtained at -0.3 and -0.35 V, where the average current density is the highest, copper hydroxide and copper-chloride hydroxides appeared.

Tables 4.4.2.2.1 and 4.4.2.2.2 clearly evidence that the purity of the deposit is decaying as the deposition rate is increasing, i.e. when applied current or potential were increasing **[44, 48]**. An exception to this trend is represented by the deposit obtained at -0.25 V, which shows the highest purity together with that obtained at

-1 A, as also confirmed by the less greenish color of deposits obtained under these conditions (Figure 4.4.2.2.1).

In order to obtain pure copper, all deposits were treated to remove the impurities. At this purpose, each sample was held for few minutes (~10 min.) within a concentrated solution of NaCl (4 M) acidified to pH 1 by addition of HCl, washed ultrasonically in doubly distilled water and then cleaned with ethanol. It is important to note that no significant changes of weight were revealed after the cleaning of the samples. In Figure 4.4.2.2.2 is reported a photo of the deposit obtained at -0.45 A before and after the cleaning. As it can be seen, the deposit turns from green to the typical color of electrodeposited copper.

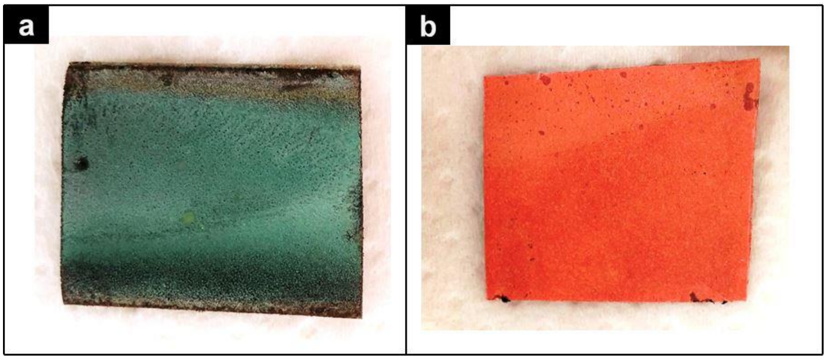


Figure 4.4.2.2.2 Photo of a deposit obtained at -0.45A: a) before and b) after cleaning in 4 M NaCl solution at pH 1

In Figure 4.4.2.2.3 a-b is reported a comparison between EDS spectra before and after the cleaning in NaCl for the deposit obtained at -1 A. The EDS spectrum of Figure 4.4.2.2.3b confirms the disappearance of the peak due to Cl. The same comparison was performed by XRD analysis (Figure 4.4.2.2.3 c-d). Diffraction pattern of Figure 4.4.2.2.3d confirms the absence of CuCl, and the presence of CuO as a unique impurity. When the copper deposits are dipped in 4 M NaCl, CuCl is rapidly converted into soluble chloro-complexes according to the reaction

$$CuCl_{(s)} + (n-1)Cl^{-}_{(aq)} \rightleftarrows CuCl_{n}^{-(n-1)}{}_{(aq)} \qquad (2 \leq n \leq 4) \qquad (4.4.2.2.1)$$

In principle, CuO might be dissolved on dipping the deposit in 4 M NaCl at pH 1. Likely, the acid-base reaction involving a solid phase is not very fast like the formation of the chloro-complexes, therefore, longer dipping time should need, with the risk of copper loss due to

$$CuO_{(S1)}+Cu_{(S2)}+2nCl^{-}_{(aq)}+2H^{+}_{(aq)} \rightleftarrows 2CuCl_{n}^{-(n-1)}{}_{(aq)}+H_{2}O_{(liq)} \quad (2 \leq n \leq 4) \quad (4.4.2.2.2)$$

where (s_1) and (s_2) indicate two distinct solid phases.

Although the deposits weight was not modified by the removal of impurities, starting from a deposit as pure as possible is preferred. In this regard, the better deposits were obtained at -1 A and -0.25 V. This finding suggests the possibility to operate at higher current density through a potential-controlled process making copper deposition faster.

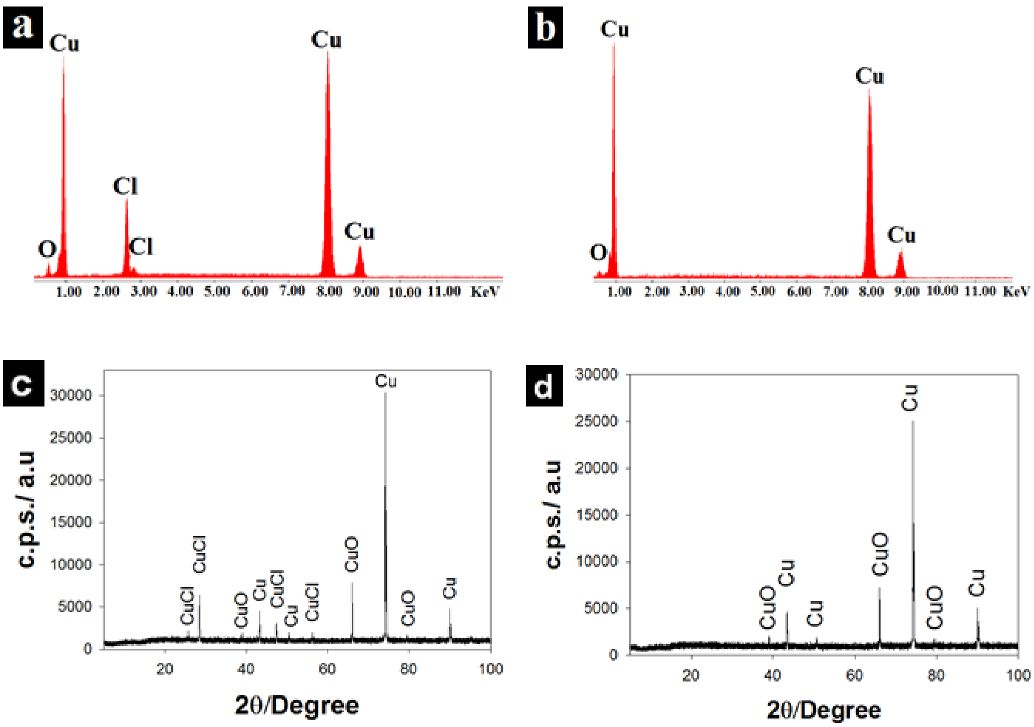


Figure 4.4.2.2.3 EDS spectra (a, b), and diffraction patterns (c, d) of the deposits obtained at -1 A just deposited (a, c); and after dipping in 4 M NaCl at pH 1(b, d)

The morphology of the copper deposit formed at -1 A and -0.25 V is shown in Figure 4.4.2.2.4 a, c, and b, d, respectively, after dipping in 4 M NaCl at pH 1. All deposits showed a planar morphology made of grain conglomerates similar to those found in the literature for electrodeposited copper **[44, 49, 50]**.

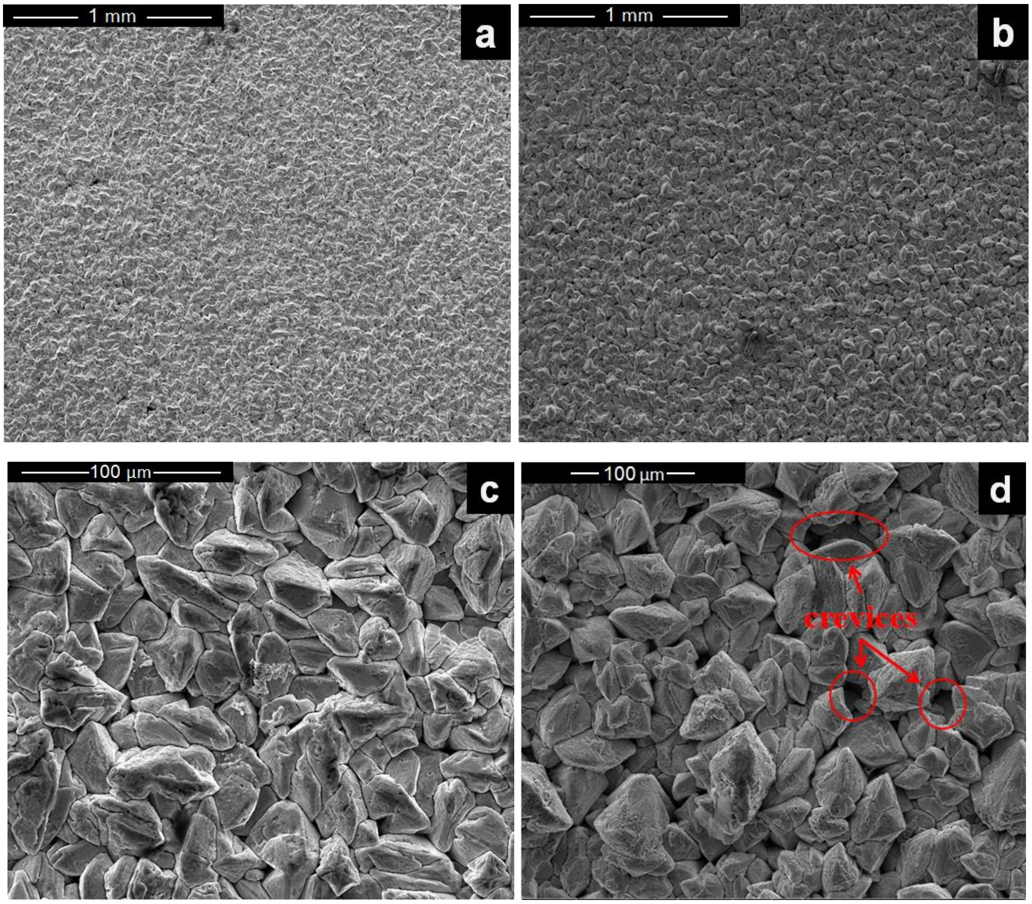


Figure 4.4.2.2.4 SEM micrographs at different magnifications of the copper deposit dipped in 4 M NaCl at pH 1. a), c) galvanostatic deposition at -1 A; b), d) potentiostatic deposition at -0.25 V

In potentiostatic mode (Figure 4.4.2.2.4 b, d), the average size of the grains is larger than that in galvanostatic mode (Figure 4.4.2.2.4 a, c). Normally, grain size decreases with the increase of the current density. However, some authors have reported that the addition of chloride into acidic sulfate solutions increases grain size of the electrodeposited copper **[51]**. It is likely that the concentration of chloride in proximity of the electrode surface increases with the current density leading to larger grains. The deposit obtained at -1 A results more compact than that obtained at -0.25 V where crevices between the particles are observed (circled in red in Figure 4.4.2.2.4d). Likely, this was due to a lower uniformity of the grain size.

The current efficiency of copper deposition was evaluated as ratio of the deposited weight after the cleaning step to the expected one according to Faraday's law (Eq. 4.4.2.1.1 and 4.4.2.1.2). It has been found that the current efficiency was about 45% for deposition at -1 A and 50% at -0.25 V. The low efficiency is mainly due to the competitive reduction from Cu^{2+} to Cu^{+} owing to a non-complete chemical reduction of the leaching solution. It should be note that the redox potential profile of Figure 4.4.2.1.3 reaches a plateau after 3 h, likely due to a passivation of waste copper cables by CuCl determined by the high increase in Cu^{+} concentration at the electrode/solution interface during copper dissolution. Besides, even iron (Fe^{3+}/Fe^{2+}) and tin (Sn^{4+}/Sn^{2+}) couples can contribute to the low current efficiency, according to the CV results.

In Figure 4.4.2.2.5 a-b the counter electrode potential profiles are reported for deposition at -1 A and -0.25 V.

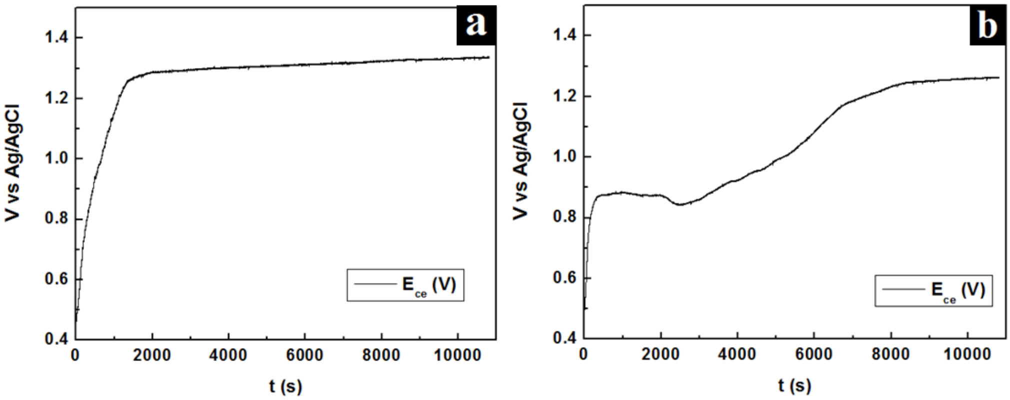


Figure 4.4.2.2.5 Counter electrode potential (E_{ce}) vs time for a) potentiostatic deposition at -0.25 V and for b) galvanostatic deposition at -1 A

As it can be seen, the anodic potential during deposition at -0.25 V remains constant at around 1.3 V, at this value evolution of chlorine at anode occurred. However, during the 3 h, chlorine was consumed as oxidizing agent without being released into the atmosphere leading to a fast regeneration of the Cu^{2+} species. During deposition at -1 A, the anodic potential is lower and reaches the value of 1.2 V after more than 2 h with a consequence slower regeneration of the leaching solution. In fact, at the end of deposition, the anodic solution turned to green for the potentiostatic test and remained brown for the galvanostatic test. Finally, the energy consumption for copper deposition was 2.78 KWh/Kg for the test at -1 A and 3.27 KWh/Kg for the test at -0.25 V. It is important to point out that a typical copper electrowinning consumes 3.45 KWh per Kg of deposited copper **[52]**.

According to these findings, it can be concluded that the better deposit in terms of purity and morphology is obtained in galvanostatic mode at a constant cathodic current of -1 A, even if the current efficiency is lower than 50%. Nevertheless, the potentiostatic mode represents a promising solution from industrial point of view because it allows operating at higher current density and restoring more effectively the leaching solution that could be recycled.

4.4 Conclusions

On the whole, the results indicate that an efficient dismantling/leaching of WPCBs can be conducted using a $NaCl$-H_2SO_4-$CuSO_4$ solution in the presence of blowing air for the in-situ regeneration of the oxidizing agent. In particular, the composition which gave the best results was: 4 M NaCl, 0.4 M $CuSO_4 \cdot 5H_2O$, and 0.5 M H_2SO_4. The disassembled ECs maintain their structural integrity and therefore, they can be easily separated and sent to recycle or further treatments. This is a key point because the current technologies use high temperatures and external actions (impact, shearing, vibration, etc.) for dismantling WPCBs with consequent i) damage of the components, ii) release of toxic substances, and iii) consume of energy. Besides, the dismantling method could be applied to entire WPCBs rather than large pieces containing only some specific components.

Simultaneously to dismantling, leaching of copper and other minor metals occurs. Therefore, copper, which is the most abundant and valuable metal, can be recovered at the cathode of an electrochemical cell fed with the solution coming from dismantling/leaching of WPCBs simultaneously with the oxidant regeneration at the anode. This is a key point because copper contained as a base material in electronic components' contacts is usually lost in most of the recycling technologies.

The current-controlled deposition permits to obtain a deposit of better quality in terms of purity and morphology. On the contrary, the potential-controlled deposition permits to work at higher current density so to shortening the deposition time and leaching solution restoration, but gives worse morphology and slightly lower purity.

In all investigated operating conditions, the copper deposit contained some impurities, mainly of copper(I) chloride, which can be removed by dipping in concentrated NaCl solution slightly acidified with HCl without significant changes in the weight of deposits. Chemical analysis performed on the deposits after the cleaning confirmed that pure copper, with some minor CuO impurity, was obtained from the leach solution.

Further works are currently in progress to improve the deposition current efficiency, recover electrochemically also the other base metals from the leach solution for improving the recycling efficiency of the leaching solution and combine leaching reactor with electrochemical cell for the simultaneous dismantling/leaching and copper recovery.

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Chapter 5

Copper recovery from pieces of disassembled WPCBs by an electrochemical route

Introduction

In the fourth chapter, an innovative method has been presented for WPCBs dismantling by leaching of all exposed metallic parts in H_2SO_4–$CuSO_4$–NaCl solution. The results have shown how electronic components can be effectively removed from WPCBs and copper recovered from the leach solution by an electrochemical route. The remaining fiberglass reinforced epoxy board holds its integrity and can be further treated for metal recovery. In particular, a preliminary chemical and morphological characterization carried out on disassembled WPCBs, guided the work towards the development of copper recovery processes. Indeed, most of copper is still contained in the PCB structure under the solder mask layer.

According to the most recent innovations in the field of WPCBs recycling, an entirely electrometallurgical approach was used for copper recovery. To simplify the overall process, pieces of PCB were used instead of pulverized samples. The PCB pieces were directly used for a simultaneous electroleaching-electrodeposition process after the solder mask removal. Two different configurations of the electrochemical cell were investigated, both operating in constant current mode.

5.1 Copper recovery from PCB pieces: state of the art

In order to develop an effective process for recovering metals from WPCBs, the most investigated methodology is certainly the hydrometallurgical one, which mainly consists of leaching, purification and recovery of metals **[1-3]**. Currently, leaching is conducted on pulverized WPCBs obtained after some pretreatments consisting in dismantling, grinding and separation of non-metallic fraction from the metallic one through either chemical or physical processes. The pre-treated WPCBs can be subjected to either acidic or alkaline leaching in order to dissolve copper, which is finally recovered from the leach solution by electrochemical route either directly or after a purification step consisting of solvent extraction followed by stripping **[4-5]**.

In recent years, many researchers have investigated innovative methods for metals recovery from WPCBs aimed to simplify the recycling processes and reduce their environmental impact. One of these new approaches consists in using pieces of WPCBs rather than pulverized samples **[6-14]**. The use of pieces allows also to avoid both the loss of metals during mechanical processing of WPCBs and the generation of dangerous fine dusts. Adhapure et al. **[6]** used PCB pieces of 4x2.5 cm for a bioleaching process. Before to place PCB pieces in contact with the microorganism, solder mask was removed by dipping PCB overnight in a 10 M NaOH solution. This step is mandatory because the presence of the solder mask makes metals inaccessible to bacteria (or Fe^{3+}). A complete metals removal with the exception of solder traces was achieved after 10 days of incubation. According to the authors, the use of PCB pieces can eliminate the contamination problem of the PCB powder by metal-containing precipitate. All bioleaching processes that use PCB powder for metal recovery encounter problems of precipitate formation. The precipitate, which is composed of Sn, Cu, Pb and Fe, contaminates the powder of PCB, making the overall metal recovery more difficult and complicated. Jadhav et al. **[7-8]** investigated the use of different leaching solutions for metals recovery from PCB pieces after solder mask removal by NaOH. The results showed that 1 M HCl solution was able to dissolve all metals (Cu, Zn, Sn, Ni, Pb, Fe, Al, Ag, Au and Pd) in 22 h from 4x4 cm PCB pieces at room temperature and 150 rpm shaking speed. HNO_3 also solubilized 100% of the metals, but in 96 h. Contrarily, H_2SO_4, $C_2H_4O_2$ (acetic acid) and $C_6H_8O_7$ (citric acid) showed poor metal solubilization with only 8.8%, 9.89% and 19.57% recovery of copper in H_2SO_4 (96 h), $C_2H_4O_2$ (96 h) and $C_6H_8O_7$ (364 h), respectively. In order to reduce the environmental impact of the process, the same authors tested a combination of citric acid (0.5 M) and hydrogen peroxide (1.76 M) to leach metals from 4x4 cm PCB pieces. The mechanism of dissolution proposed was

$$\text{R-COOH} + H_2O_2 \rightarrow \text{R-COOOH} + H_2O \tag{5.1.1}$$

$$\text{R-COOOH} + M + 2H^+ \rightarrow \text{R-COOH} + H_2O + M^{2+} \tag{5.1.2}$$

The organic acid reacts with H_2O_2 generating the peroxy carboxylic acid (5.1.1), which is a powerful oxidants that readily oxidizes metals by reaction 5.1.2. Total metals removal from PCB pieces was achieved after only 4 h through a cheap, simple, and environmentally acceptable procedure. Fogarasi et al. **[9-12]** proposed two original processes for copper recovery from large pieces of WPCBs by an electrometallurgical route. In one of the processes **[9-11]**, copper was recovered from 40-100 cm^2 PCB pieces employing two different types of reactor in series: a leaching reactor using HCl-$FeCl_3$ and a divided electrochemical reactor for simultaneous copper deposition and leaching solution regeneration. The optimal operating conditions for the combined chemical-electrochemical process were ensured at the current density of 4 mA/cm^2 and 0.37 M initial $FeCl_3$ concentration. High purity copper deposit (99.04%) was obtained with a current efficiency of 63.84% and a specific energy consumption of 1.75 KWh/Kg. In a different study **[12]**, the authors investigated the use of 20-25 cm^2 PCB pieces directly as an anode in an undivided electrochemical cell in which deposition of copper occurred on a stainless steel cathode simultaneously to its anodic dissolution. After removal of the solder mask by concentrated H_2SO_4 (~18 M), the PCB pieces were placed into a perforated lead cage together with graphite granules which acted as a current collector. The electrolytic solution was a 2 M H_2SO_4 solution and the electrolysis tests were conducted at a constant current of 20 mA. A total dissolution of metals from PCB pieces was achieved with an energy consumption of 1.06 KWh/Kg and a current efficiency less than 90%. The copper deposit contained some impurities of other metals, mainly tin, and further treatments (e.g. electrorefining) were needed to reach a grade purity. Comparing the two processes, Fogarasi et al. concluded that the mediated dissolution of copper using Fe^{3+}/Fe^{2+} redox couple had a lower environmental impact than the direct one because the regenerated leaching solution could be used for further processing of WPCBs. Besides, concentrated sulfuric acid was extremely dangerous to be handled. Small-size PCBs (1.5-2 cm^2) are widely used in thermal treatments of WPCBs, however, Guo et al. **[13]** tested the use of large-size PCB sample (16-20 cm^2) for a low-temperature (500°C) pyrolysis process carried out in a fixed-bed reactor. The pyrolysis products consisted of 71.60 wt.% of solid residue, 18.23 wt.% of tar and 10.71 wt.% of gas. The solid residue consisted of metals, fiberglass and residual ash from the organic resins. Fiberglass was easily separated via manual operation from the metallic fraction which could be further treated for copper recovery, for example by hydrometallurgical route.

The main obstacle in using large pieces of PCB is the lower surface area exposed to the lixiviant, electrolyte or bacteria. In particular, most of the metals are incorporated inside the structure of PCB and thus, are not easily accessible even after solder mask removal. However, the above studies show how all metals can be effectively removed also from PCB pieces with significant advantages including the simplification of the overall recovery process, and elimination of both the costs and environmental risks related to powder preparation. According to Adhapure et al. **[6]**, the use of PCB pieces can facilitate the reuse of the remaining board (non-metallic part). In the light of these findings, the research activity was focused on using PCB pieces instead of pulverized samples. It is important to note that the same PCB pieces resulting from the dismantling process proposed in Chapter 4 could be used. A preliminary morphological and chemical characterization was carried out on disassembled WPCBs in order to decide towards which metal to focus the research activity.

5.2 Chemical characterization of disassembled WPCBs

The first step of the study was aimed to investigate the structure and composition of the disassembled WPCBs. In particular, the attention was focused on the metallic fraction of WPCBs. The acquisition of detailed information about structure and chemical composition is fundamental for developing new either recycling methodologies or strategies to improve the current ones. As shown in the first chapter, the composition of PCBs is continuously changing, and different authors reported different results. For this reason, an accurate qualitative and quantitative characterization of the feed material was carried out. The experimental procedure and results will be reported in the following.

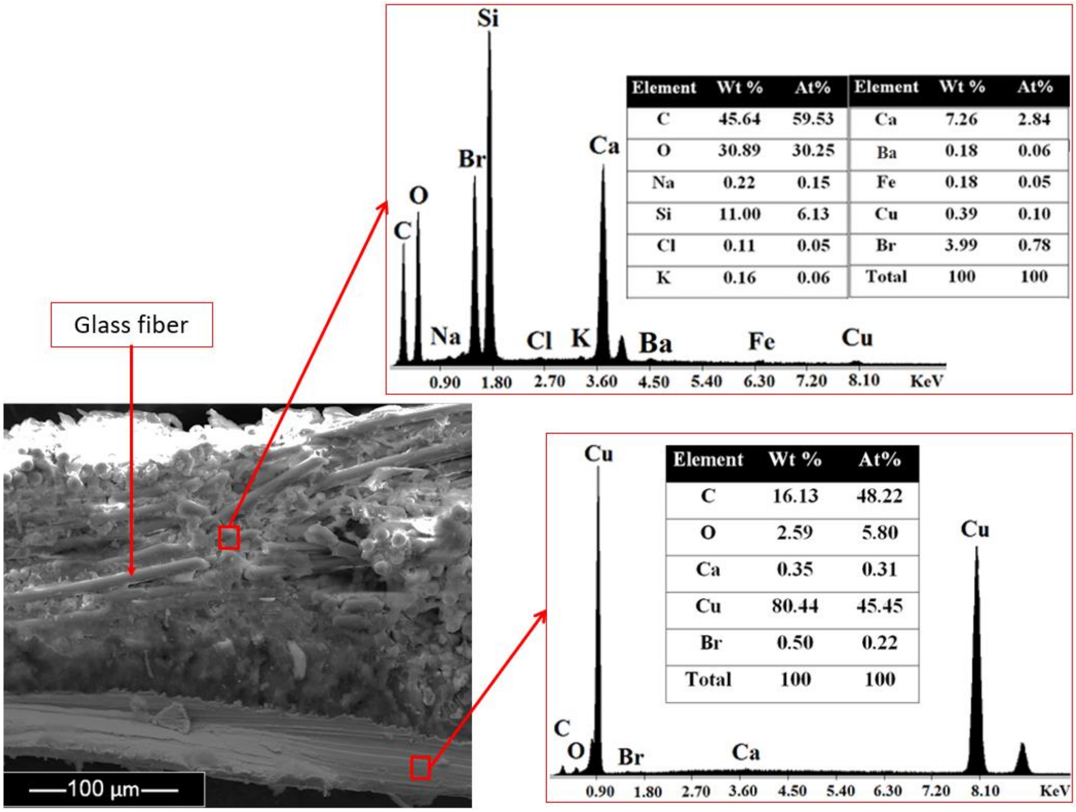
5.2.1 Material and methods

Motherboards of either obsolete or disused computers were used as a source of PCBs. The structure of PCB was investigated using a scanning electron microscopy (SEM, FEI mod.: QUANTA 200 FEG) equipped with an X-ray energy dispersive spectrometer, while the chemical composition was determined by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Perkin Elmer Optima 2100 DV). The ICP-OES analysis was carried out on a sample of pulverized PCBs. To have significant results from a statistical point of view, three PCBs coming from different models of waste computers were dusted to obtain a representative average chemical composition. Before grinding, the electronic components were disassembled from the boards by heating above the melting point of the solder. Then, disassembled PCBs were cut into small pieces (~1x1 cm) and milled using a cutting mill (Pulverisette 15, Fritsch) obtaining an homogeneous powder with particle size of about 1 mm. According to the literature **[8, 14-19]**, an acid digestion was performed dissolving 100 mg of powder in 10 mL of hot aqua regia ($HCl:HNO_3=3:1$, v/v) until the complete dissolution of all metals and subsequently making up to the mark with distilled water in a 100 mL flask. In this way, the concentrations of the analytes were reported in the linearity range of the calibration curve, which was built preparing appropriate multi-standard solutions. These latter were prepared on the basis of a preliminary Energy Dispersive Spectroscopy (EDS) analysis conducted on a pulverized sample of PCBs. The solid residue obtained after acid digestion was also analyzed by EDS to confirm that all metals were dissolved in aqua regia. All the chemical reagents were of analytical grade. The concentrations of Cu, Pb, Sn, Fe, Zi, Ni, Al, Fe, Au, Ba, Ti, and Pd from the leach solution were determined.

5.2.2 Results and discussion

A small piece of PCBs was thermally and mechanically delaminated, then the section was analyzed by SEM, revealing the existence of a multilayer structure constituted by the alternation of compact and fibrous layers. Figure 5.2.2.1 shows a SEM micrograph evidencing a fibrous layer overlying a compact one. EDS analysis revealed that the compact layer is constituted mainly by copper (80.44 wt.%) while the fibrous one is constituted by organic and ceramic materials containing copper traces (0.39 wt.%). EDS analysis of the fibrous layer revealed the presence of Si and Ca along with other elements such as Na, K and Fe which are the typical constituents of the woven glass fiber (see Table 1.2.2.3 in Chapter 1) **[20]**. The glass fibers are also clearly visible in the figure. Likely, the sectioned PCB was a multilayer type and the two layers shown in Figure 5.2.2.1 are the copper foil and the substrate of epoxy resin reinforced with woven glass fibers.

Indeed, according to the literature **[5, 14, 21-23],** the alternation of these layers constitutes the structure of multilayer PCBs.

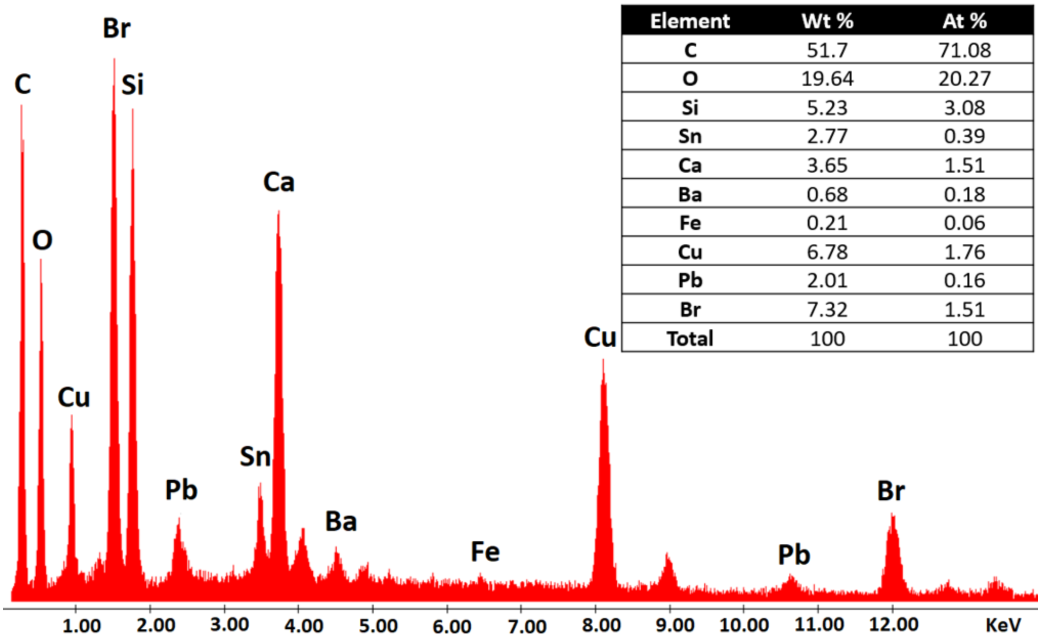


Element	Wt %	At%	Element	Wt %	At%
C	45.64	59.53	Ca	7.26	2.84
O	30.89	30.25	Ba	0.18	0.06
Na	0.22	0.15	Fe	0.18	0.05
Si	11.00	6.13	Cu	0.39	0.10
Cl	0.11	0.05	Br	3.99	0.78
K	0.16	0.06	Total	100	100

Element	Wt %	At%
C	16.13	48.22
O	2.59	5.80
Ca	0.35	0.31
Cu	80.44	45.45
Br	0.50	0.22
Total	100	100

Figure 5.2.2.1 SEM micrograph of the sectioned PCB, showing different composition layers

A preliminary EDS analysis was carried out on the powder resulting from the grinding of three different disassembled computer motherboards. The EDS spectrum of Figure 5.2.2.2 reveals the presence of hazardous elements, such as Br coming from the brominated flame retardants, and Pb coming from the Pb-Sn solders. Copper is the most abundant metal present in the powder of PCBs, other elements were found at higher magnifications in traces including Au, Ni, Zn, K, Na, Ti and S. The first three probably are due to some residues of the electronic components' contacts; while K, Na, and Ti are constituents of the woven glass fiber **[20]**. Sulphur is likely present in the solder mask in combination with barium, which is also revealed from EDS spectrum of Figure 5.2.2.1 and 5.2.2.2, as barium sulfate that is a typical fire retardant **[24]**. Solder mask is an organic material containing also Si, which is used to control the viscosity of the liquid prior to curing. Iron may result from both the substrate and the residue of components' contacts.



Element	Wt %	At %
C	51.7	71.08
O	19.64	20.27
Si	5.23	3.08
Sn	2.77	0.39
Ca	3.65	1.51
Ba	0.68	0.18
Fe	0.21	0.06
Cu	6.78	1.76
Pb	2.01	0.16
Br	7.32	1.51
Total	100	100

Figure 5.2.2.2 Typical EDS spectrum of the PCBs powder

Based on the results obtained by EDS, a more accurate determination of metal concentrations was carried out by ICP-OES. The analytes investigated were the metals revealed by EDS, such as Cu, Pb, Sn, Ni, Fe, Ba, Zn, Au, and Ti along with other metals that are expected in PCBs according to the literature, such as Al and Pd **[17, 25-28]**. The results of the analysis are shown in Table 5.2.2.1. The metal present at higher percentage composition was copper followed by tin and lead. In comparison with the literature **[16-17]**, the found quantity of tin and lead found were greater, likely due to excessive solder residue after disassembly step. As it can be seen, the percentage of precious metals such as gold and palladium is very low, but similar to that reported in other studies **[9, 18, 26, 29]**. Unlike EDS results, small amounts of aluminum were found from acid digestion of PCBs powder.

Elements	Percentage composition (wt.%)
Cu	65.39
Sn	21.48
Pb	12.29
Fe	0.23
Al	0.23
Ba	0.21
Zn	0.1
Ni	0.04
Others	0.03

Table 5.2.2.1 Major metals contained in WPCBs powders

The residue from acid digestion was analyzed by EDS after washing with distilled water. Except for iron, all metals among those investigated by ICP-OES were completely dissolved in aqua regia. Traces of iron remained in the residue, likely coming from the glass fibers which are difficult to dissolve.

The chemical characterization was relevant to understand towards which metal was more profittable to focus the research activity of recovery from disassebled PCBs. In particular, copper was found to be the most abundant metal among those detected by ICP-OES, while precious metals were found only in traces in the powder of WPCBs. According to these results, copper is the most interesting metal and therefore, the study was aimed at developing a copper recovery method which was simple and environmental acceptable. The results related to the recovery of copper from disassembled PCBs will be reported in the following.

5.3 Electrochemical recovery of copper from disassembled WPCBs

In order to simplify the overall copper recovery process, pieces of disassembled PCBs were used rather than pulverized samples. The large pieces could be those resulted from the dismantling process proposed in the previous chapter. In the light of the most recent innovations in the field of WPCBs recycling, it was decided to adopt an entirely electrochemical method for the recovery of copper due to its low environmental impact, low energy consumption, simple flowsheet and high output **[5, 10, 30-31]**. Currently, copper electrolysis is the final step in the recycling chain of WPCBs both in the pyrometallurgical and hydrometallurgical processes. However, in this work, an entirely electrometallurgical process was investigated using an electrochemical cell in which electroleaching of copper from PCB pieces occurs simultaneously to its electrodeposition **[12, 16, 32-34]**. Experimental procedure and results will be reported in the following.

5.3.1 Material and methods

For the tests, motherboards of waste computers were used. Before undergoing the electrochemical process, all electronic components were disassembled from the board by heating above the melting point of the solder. Then, PCB was cut into pieces of about 10x10 cm and every piece was chemically treated to remove the solder mask, which covers the external surface of PCB hindering the contact between copper and the electrolyte. The coating was removed using sodium hydroxide as a chemical reagent **[6-8]**. In particular, PCB pieces were dipped in 10 M NaOH for 24 hours, washed with distilled water to remove any trace of NaOH, and then mounted as an anode for the electrolysis process. A piece of PCB without solder mask was pulverized and analyzed by ICP-OES for determining metal content after NaOH treatment. The alkaline solution used for solder mask removal can be recycled several times before to be disposed.

After pre-treatment, large pieces of PCB were directly mounted as an anode for copper electrolysis using the apparatus schematized in Figure 5.3.1.1. Each PCB piece was sandwiched between two plexiglass slabs with a rubber gasket in the middle to ensure the seal. Ensuring a good seal was important to protect the current collector from the acidic electrolytic solution. Two current collectors were used, one for each side of PCB piece, and were cut perimeter to the board for ensuring the contact with the maximum number of copper tracks. The sandwich structure was tightened through stainless steel bolts covered with an insulating resin to avoid their corrosion during the process.

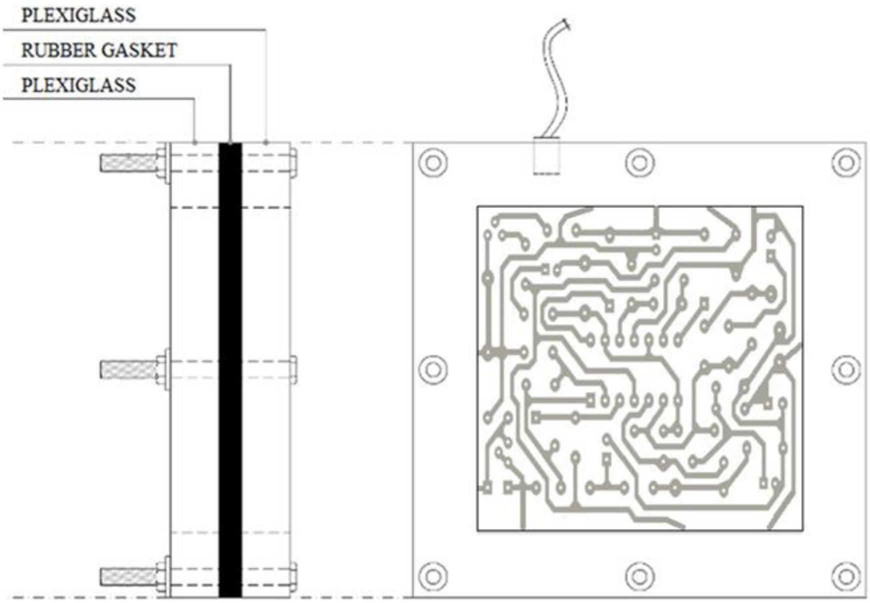


Figure 5.3.1.1 Lateral view and front view of a PCB piece used as an anode

The bench scale experimental setup used for the electrolysis experiments is sketched in Figure 5.3.1.2. A parallel-plate electrode design similar to that used in industrial electrolytic refining of copper was employed **[35-36]**. Each side of PCB was opposite and parallel to a high purity copper cathode (99.8%) having the same dimension of the PCB piece (i.e. 10x10 cm). Both cathode plates were coated on one side with an insulating resin in order to expose to the electrolyte only the side opposite to the anode. The surface of the cathodes was polished before electrolysis using a cloth soaked in slightly acidified water and then washed with water and ethanol in order to remove copper oxides and other impurities which could lead to irregular and imperfect deposits. The electrodes were assembled in the cell at a distance of 3 cm.

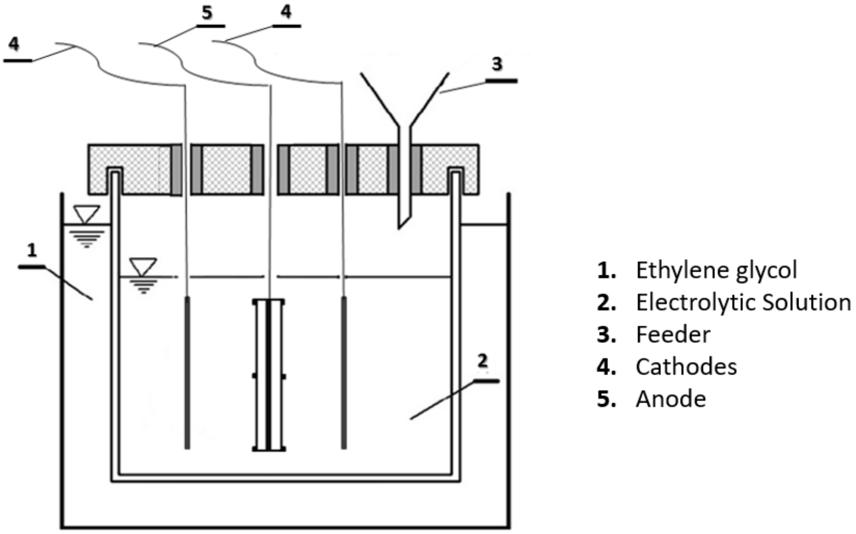


Figure 5.3.1.2 Scheme of the electrochemical cell for copper recovery from large pieces of WPCBs

The cell was a cylindrical glass vessel filled with 3 L of solution. The electrolyte was a mixture of copper sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$) and sulfuric acid (H_2SO_4) with concentrations of 0.7 M and 2 M, respectively. Unlike the industrial copper electrorefining, no other chemicals or additives were added to the electrolyte **[35]**. All the chemical reagents were of analytical grade. Electrolyte temperature was monitored and maintained at 60°C with an external bath of ethylene glycol that was used as a heating fluid. A constant cathodic current of -900 mA was supplied using a PAR Potentiostat/Galvanostat (mod. PARSTAT 2273). The resulting current density was -4.5 mA/cm^2, which was selected for obtaining high quality deposits in terms of purity and structure **[37]**. The cathodic potential was measured relative to a saturated calomel electrode ($Hg/Hg_2Cl_2/KCl$sat.) acting as a reference.

Owing to some problems encountered during electrolysis of large pieces of PCBs, a second configuration of cell was also investigated, and a schematic representation is shown in Figure 5.3.1.3. All the operating conditions were left unchanged, such as composition of the electrolyte, temperature, applied current and total anodic and cathodic surface area. However, in the new configuration, the 10x10 cm PCB piece was cut into smaller pieces of about 2-4 cm^2, which were put inside a stainless steel basket acting as a support and current collector. Besides, the cut pieces of PCB were mixed with an equal weight of graphite granules to reduce the resistivity of the PCB pieces. A 99.8% purity copper sheet was used as a cathode and was placed coaxial to the anodic support. One side of the copper sheet was covered with an insulating material.

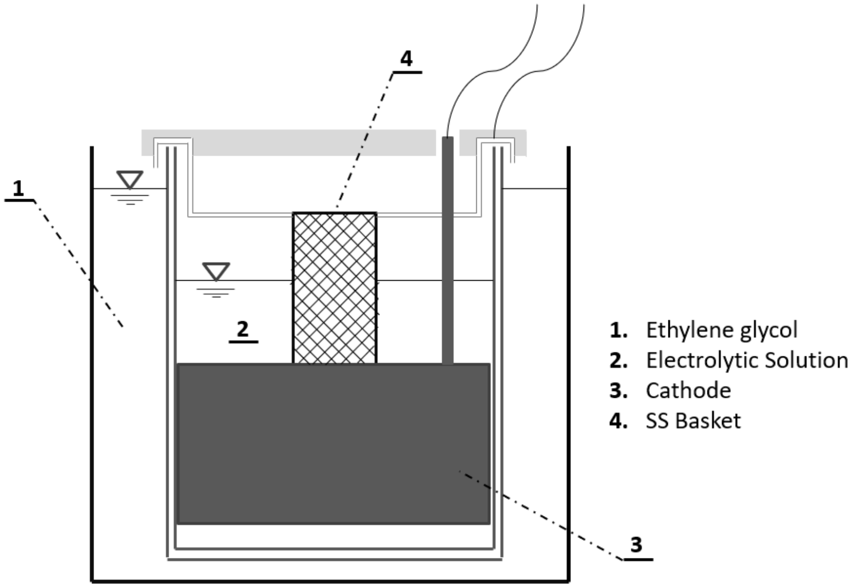


Figure 5.3.1.3 Scheme of the electrochemical cell for copper recovery from small pieces of WPCBs

The current efficiency of copper deposition was evaluated as a ratio of the deposited weight to the expected one according to Faraday's law (see Eq.s 4.4.2.1.1-4.4.2.1.2 in Chapter 4). The copper deposit was chemically and morphologically characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The morphology was investigated using a scanning electron microscopy (SEM, FEI mod.: QUANTA 200 FEG) equipped with an X-ray energy dispersive spectrometer. A further characterization was performed by XRD analysis, (Rigaku, D-MAX 25600 HK). All X-ray analyses were conducted in the 2ϑ range from 5° to 100° using the Cu Kα radiation (λ=1.54 Å). Diffraction patterns were analyzed by comparison with ICDD database (ICDD, 2007) **[38]**. Copper dissolution degree from the PCB pieces was determined by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Perkin Elmer Optima 2100 DV) analysis dissolving in aqua regia all the metals contained in the PCB pieces before and after experiments.

5.3.2 Results and discussion

The electroleaching of copper from motherboards of waste computers was carried out using directly large pieces of PCBs. For this purpose, the motherboard was thermally dismantled, cut into 10x10 cm pieces and chemically treated for solder mask removal by means of 10 M NaOH solution. A flow diagram of the proposed method for copper recovery is shown in Figure 5.3.2.1.

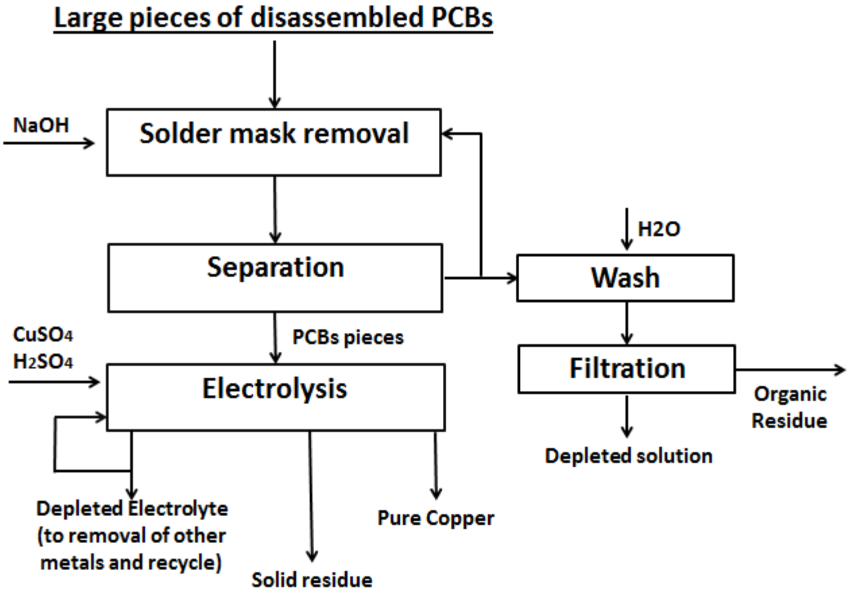


Figure 5.3.2.1 Flow diagram of the copper recovery process

After a solid/liquid separation, the alkaline solution can be reused several times before to be diluted with water and disposed after removal of the epoxy residue by filtration. Figure 5.3.2.2 shows a PCB piece before and after NaOH treatment.

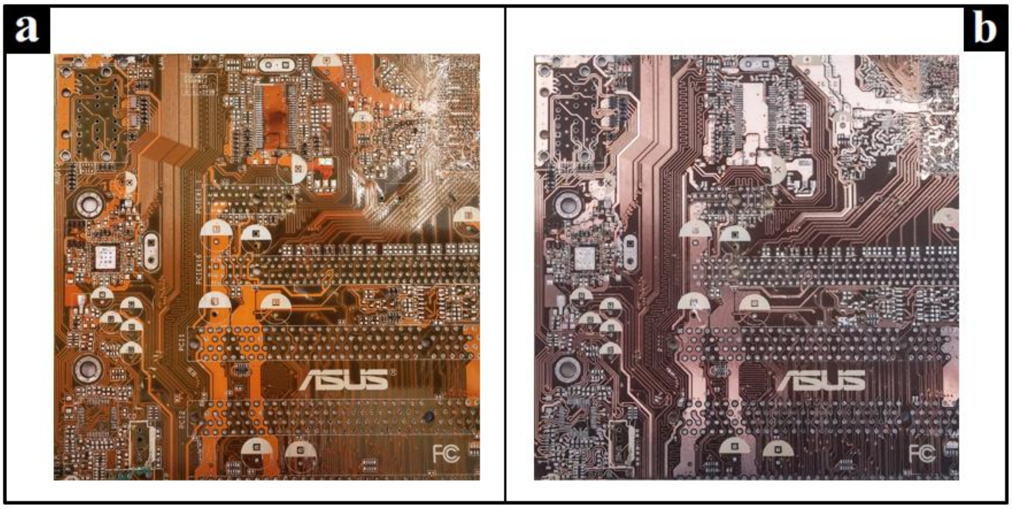


Figure 5.3.2.2 Photo of PCB piece a) before and b) after removal of solder mask

The solder mask was completely removed from the PCB. This step is of primary importance because the coating does not allow the electrolyte to penetrate through the board for extraction of the metals **[6-8]**. The PCB piece was analyzed for determination of the metal content after NaOH treatment. As for the most abundant metals present in PCBs, ICP-OES analysis showed that during NaOH treatment the dissolution of Cu, Pb and Sn was about 6%, 38.7% and 43%, respectively. A dissolution degree similar to that of Pb and Sn was also measured for Ba (42.5%), which is mainly present in the solder mask. The amount of copper leached was very small compared to the average metal content in PCB. A slight swelling of the PCB piece was observed after dipping in the alkaline solution. This could make easier the access of the electrolyte through the board also thanks to the presence of many holes drilled on the PCB for the assembly of electronic components (see Figures 1.2.2.2-1.2.2.3 in Chapter 1).

After solder mask removal, each PCB piece was directly used as an anode for the electrolysis process. A constant cathodic current of -900 mA was supplied at the cathode. The performance of the process was evaluated by means of copper dissolution degree from the PCB piece, quality of the copper deposit, current efficiency, and energy consumption.

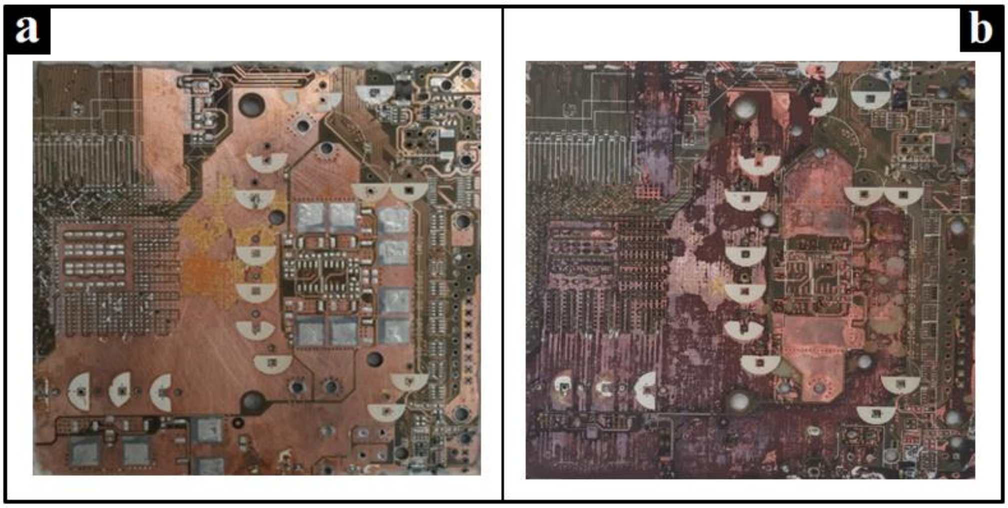


Figure 5.3.2.3 Photo of PCB piece a) before and b) after electrolysis process

Figure 5.3.2.3 shows one side of a PCB piece before (Figure 5.3.2.3a) and after (Figure 5.3.2.3b) the anodic dissolution. As it can be seen, copper was not totally removed from the board. After electrolysis, each PCB piece was reduced into powder and metals dissolved in aqua regia for ICP-OES analysis. The dissolution degree of copper from the PCB pieces ranged between 46% and 50%. The limited copper dissolution was mainly determined by the increase of the copper dissolution overvoltage. Indeed, the insulating nature of the PCB substrate led to a rapid increase of the cell voltage. Generally, after a time of 8 h the cell voltage became unstable with sudden increases up to -8 V. The overvoltage was significant since the beginning of the process. Indeed, the cell voltage remained at about 1.8-2 V except for the first hour in which it did not exceed 0.15-0.2 V. The average value was significantly higher than the cell voltage of a copper electrorefining process

(0.23-0.27 V) **[35]**. Indeed, in an electrorefining process, the cathode reaction is the reverse of that one at the anode; therefore, the cell voltage is exclusively due to voltage drops. In this case, the ohmic drop was more relevant and increased with time up to unacceptable values. The loss of the electrical contact between some copper tracks and current collector was another problem occurring during copper dissolution. However, the experiments revealed that dissolution of some tracks occurred even without being in contact with the current collector, likely because copper was partially converted into copper oxides during NaOH treatment, which can be chemically dissolved by the acidic electrolyte.

After electrolysis, the cathode plates were washed, dried, and then weighed to measure the overall increase of weight and estimate the current efficiency of copper deposition. The current efficiency was about 84%. This value is consistent with other studies reported in the literature concerning the electrolysis of copper from sulfuric acid solution resulting from the treatment of WPCBs **[12, 39-41]**. Likely, some eddy reactions consumed charge for processes different from copper deposition. To have a better idea of what happened at the cathode, a chemical characterization was made on the deposits. The purity of the deposit was determined by EDS and XRD analysis. Figure 5.3.2.4a shows the EDS spectrum of the deposit revealing the presence of only copper without any metallic impurities.

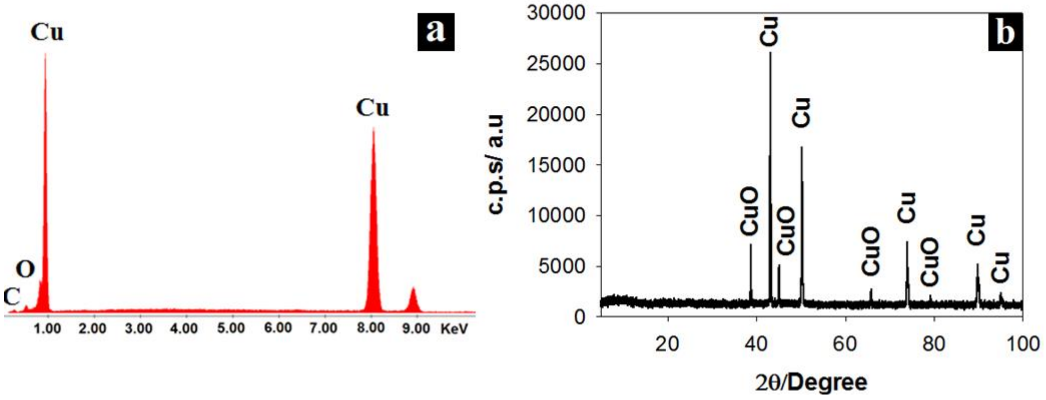


Figura 5.3.2.4 EDS spectrum (a) and diffraction pattern (b) of the copper deposit

The diffraction pattern of the deposit (Figure 5.3.2.4b) evidences that copper is the only phase present even if some diffraction peaks of CuO are also identified. It's well know that copper is easily oxidized in proper conditions, but some undesired reactions could play an important role in copper oxide generation. In particular, hydrogen evolution and oxygen reduction reactions could increase the pH at the cathode/solution interface determining the formation of copper hydroxide, which, however, is dehydrated to generate the more stable copper oxide **[42]**. This was in accordance with both low efficiency and the absence of metallic impurity at the cathode. The cathodic reactions likely occurring at cathode are

$$4H^+ + O_2 + 4e^- \rightarrow 2H_2O \qquad (E°=1.23\ V/NHE) \qquad (5.3.2.1)$$

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad (E°=0.34\ V/NHE) \qquad (5.3.2.2)$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad (E°=0\ V/NHE) \qquad (5.3.2.3)$$

Oxygen reduction is the most favoured reaction, but the absence of solution stirring limited the oxygen transport to cathode. Therefore, the low efficiency was mainly determined by hydrogen evolution reaction. During the electrolysis, the cathodic potential assumed values just upper 0 V/NHE that likely was sufficient to activate hydrogen evolution reaction.

The morphology of the deposits was investigated by SEM. Figure 5.3.2.5a shows a SEM micrograph of the copper deposit with a compact morphology similar to that found in the literature for electrodeposited copper from sulphate solutions **[9, 33, 43]**. Figures 5.3.2.5 b-c show the cross section of the copper deposit. The thickness of the Cu layer is uniform along the entire section analysed at a value of about 32.35 μm. Although the top view shows a very compact deposit, several cavities are present through the thickness of the deposit (Figure 5.3.2.5c) likely due to hydrogen evolution.

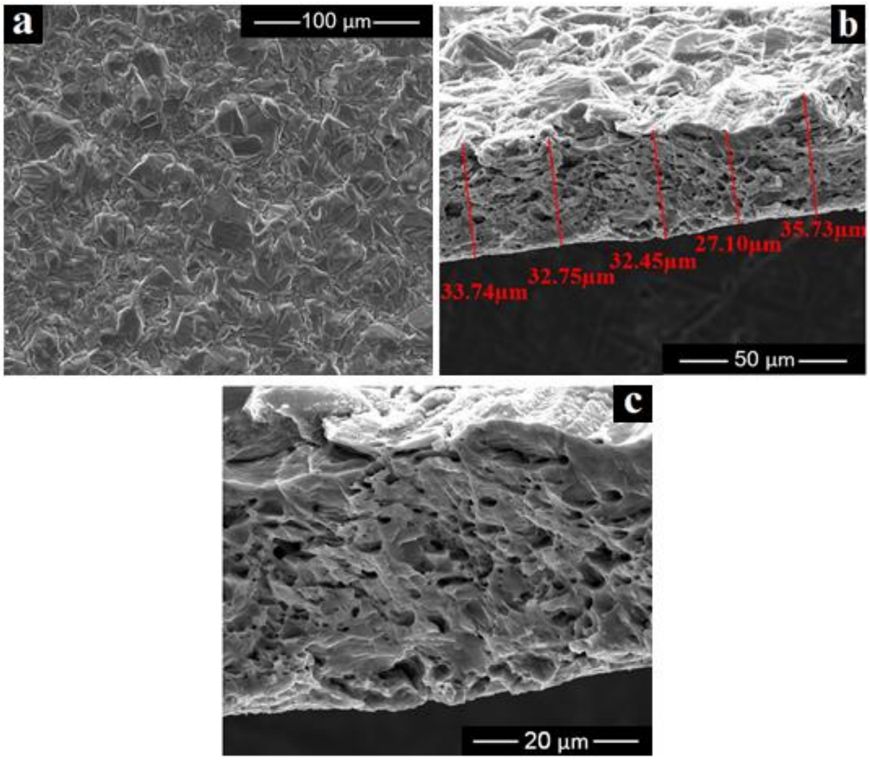


Figure 5.3.2.5 SEM micrographs at different magnifications of the copper deposit: (a) top view, (b, c) cross section

In addition to the high purity of the copper deposit, another relevant advantage of the process consists in the easy removal of the deposit from the support. Figure 5.3.2.6 shows that the copper deposit was in the form of a compact foil easily peeled from the support without damaging it therefore, the support can be easily reused. In the industrial process of copper electrorefining, the easy removal of the cathodic deposit is achieved by smearing the support with mineral oils which can lead to irregularities in the formation of the deposits **[44]**. Besides, additives (e.g. thiourea, gelatin, organosulfonates, chloride etc.) are added to the electrolyte in the industrial process to control the chemical and physical properties of deposits **[37, 45]**. Figure 5.3.2.6 shows that no dendritic structure was formed.

The energy consumption for the process was about 1.7 KWh/Kg. This value is higher than that for the current electrorefining of copper, which consumes 0.25

KWh/Kg, but is significantly lower than that for the copper electrowinning, which currently consumes 3.4 KWh/Kg **[46]**.

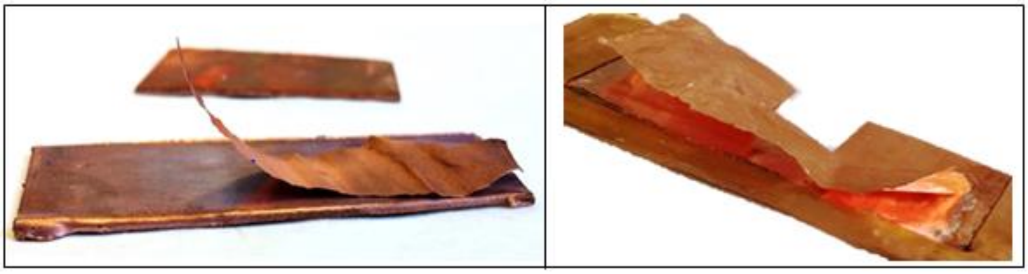


Figure 5.3.2.6 Pictures of the copper deposit

A chemical analysis was carried out both on the electrolytic solution and the solid residue precipitated on the tank bottom (Figure 5.3.2.7a). EDS spectrum of the solid residue (Figure 5.3.2.7b) shows the presence of only lead and tin, with tin traces compared to lead. The atomic fraction of lead (Pb/(Pb+Sn)) was equal to 0.89. Contrarily, the ICP-OES analysis showed that the fraction of lead and tin in the electrolytic solution was 1.66% and 98.34%, respectively. Therefore, tin remained dissolved in $CuSO_4$-H_2SO_4 solution while lead formed the solid residue on the tank bottom. This result suggests the possibility of an easy separation of lead that could be partially recovered in addition to copper. Besides, the recovery of tin from the electrolytic solution by an electrochemical route could be also investigated for improving the recycling efficiency of the electrolyte. Alternatively, the same procedure followed in the industrial copper electrorefining could be used for electrolyte purification. After removal of copper by electrolysis using PbO_2 as an anode and Cu as a cathode, the solution is fed into an evaporative stage where the precipitation of metallic impurities occurs, mainly in the form of sulphides. Then, the purified solution is recycled to the process **[35]**. In the light of these findings, the PCB pieces resulting from the dismantling process described in the fourth chapter could be directly used for the electrolysis rather than being treated with NaCl solution for the complete dissolution of the Pb-Sn solders.

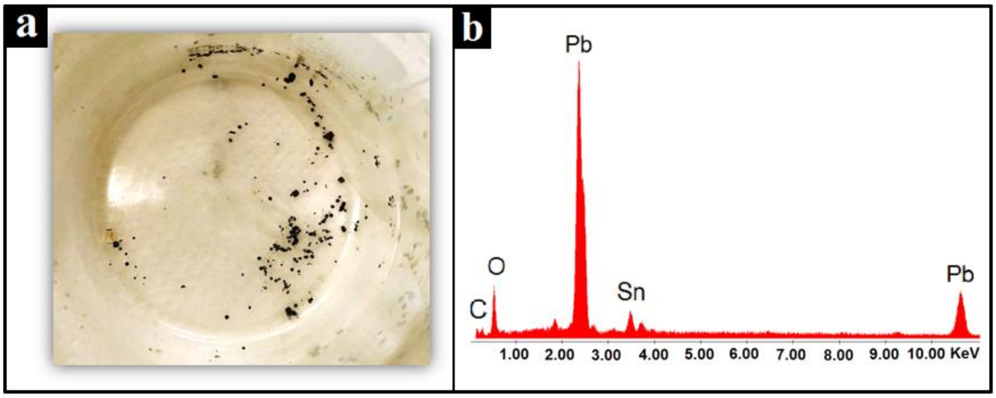


Figure 5.3.2.7 (a) Picture of the solid residue recovered at the end of the electrolysis process; (b) EDS spectrum

High purity copper easily removable from the support was obtained in one-step process after PCB disassembly and solder mask removal. The removal of copper from PCB was limited to about 46-50%. However, the resulting PCB could be a good feed material for a biological treatment where the contents of metal that can be processed are limited **[7, 47-48]**. In particular, copper was found to be the main inhibitor of microorganisms' metabolism followed by nickel and cobalt **[47-48]**. Xiang et al. **[47]** reported that high concentrations of copper extracted from PCBs could inhibit both the rate and degree of the oxidation of ferrous ions by bacterial consortium.

In order to increase copper dissolution degree, a second configuration of the electrochemical cell was investigated. In particular, the 10x10 cm PCB piece was cut into smaller pieces of about 2-4 cm^2 and mixed with an equal weight of graphite granules in order to reduce the resistivity of the PCB material. To directly use small pieces of PCB as an anode for the electroleaching process, a cylindrical stainless-steel basket was used as a support for the PCB pieces and also as a current collector. The cathode was a copper sheet placed coaxial to the cylindrical basket. A scheme of the experimental apparatus is shown in Figure 5.3.1.3. The addition of conductive granules to small PCB pieces allowed to enhance the electrical contact between copper tracks and current collector and reduce the overvoltage related to the insulating nature of the PCB substrate. After 8 h of electrolysis, the copper removal from the board was about 51%, which is similar to the value obtained in the tests with large pieces of PCB. However, after this time, the cell voltage did not increase sudden but remained constant to the initial value. Therefore, it was possible to increase the electrolysis time to 16 h, achieving a total copper removal of 73%. Cell voltage remained constant at about 1.08 V with an energy consumption of about 1.6 KWh/Kg. After 16 h, the cell voltage increased to about 1.8-2 V and the main anodic reaction became oxygen evolution, while copper dissolution stopped. This was due to the very low content of copper remained in PCB pieces. Besides, graphite is a good electrode for oxygen evolution. Pictures of the small PCB pieces before and after electrolysis are shown in Figure 5.3.2.8. Copper appears completely removed from the PCB pieces.

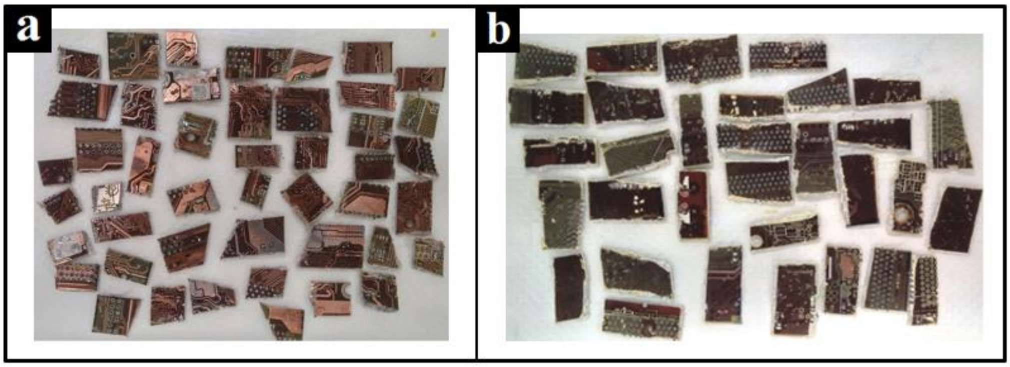


Figure 5.3.2.8 Pictures of the small PCB pieces before (a), and after (b) the electrolysis process

The current efficiency determined by Faraday's law was about 60%. The lower value obtained compared to the electrolysis from large PCB pieces was mainly due to the dissolution of the steel basket which led to the activation of the Fe^{3+}/Fe^{2+} redox couple, which is a troublesome acceptor/donor of electrons. Therefore, in addition to the reactions described by equations 5.3.2.1, 5.3.2.2 and 5.3.2.3, the parasitic side reaction of reduction of Fe^{3+} to Fe^{2+} was also responsible for the loss of faradaic efficiency. The reduction of ferric ions (E^0= +0.77 V/NHE) is more favoured than that of cupric ions (E^0= +0.34 V/NHE). ICP-OES analysis showed a concentration of iron in the electrolyte two orders of magnitude higher than the value of 48 mg/L measured in the tests with large PCB pieces. EDS and XRD analysis performed on the electrodeposited copper gave the same results obtained in the tests with large pieces of PCB.

In order to avoid both the cut into small pieces and corrosion of the support, carbon foam could be used as a current collector in the first configuration of the electrochemical cell investigated. Carbon foam is an innovative material having the advantage to be permeable and inert to the electrolytic solution and therefore, it could be directly placed in contact with the large PCB piece covering its entire surface on both sides. In this way, all copper tracks would be in contact with the current collector enhancing copper dissolution from the board and simplifying the apparatus used as an anode, which no longer requires the use of plexiglass slabs, gaskets and bolts. A set of experiments has already been planned for investigating the use of carbon foam in the cell design.

5.4 Conclusions

In this work, PCB pieces like those that could result from the dismantling step proposed in Chapter 4 were directly used for copper recovery instead of pulverized samples. In particular, the PCB pieces were directly mounted as an anode in an undivided electrochemical cell in which copper electroleaching occurred simultaneously to its cathodic deposition. This is a key point because the current technologies require several operations before recovering copper. Besides, the use of PCB pieces allows also to eliminate both the costs and environmental risks related to powder preparation.

Before undergoing the electrochemical process, the solder mask has to be removed from PCB pieces by chemical treatment in order to expose copper to the electrolytic solution. Two different configurations of the cell were investigated. The first one allows to use large pieces of PCB but, in principle, can be extended to the use of an entire PCB minimizing the number of steps needed for copper recovery. However, the copper dissolution degree from the PCB pieces was limited to 46-50% and thus, the remaining pieces required further treatments. For instance, they could be a good feed material for bioleaching in the perspective to minimize the environmental impact of the global recovery process. The copper removal was increased to 75% with a second configuration of the cell, which however required the cutting of PCB into small pieces. In the future it is planned to investigate the use of carbon foam as a current collector in the first configuration of the electrochemical cell for improving copper dissolution efficiency from large PCB pieces.

Both configurations allow to obtain in a single step high purity copper easily removable from its support. This is a relevant advantage because copper purity is the main issue in WPCBs recycling where the presence of many different metals reduce the selectivity of the recovery. Another benefit from both configurations is the low energy consumption required for the recovery process.

Encouraging findings were obtained from the chemical analysis of both electrolytic solution and solid residue found on the tank bottom showing the possibility of an easy recovery of lead by filtration. Further works are currently in progress regarding the electrochemical recovery of tin from the electrolytic solution in order to maximize the recovery of material from WPCBs and improve the efficiency of the electrolyte recycling. Based on these results, the PCB pieces resulting from the dismantling/leaching step showed in Chapter 4 could be directly used for the electrolysis rather than being treated with NaCl solution for the complete dissolution of the Pb-Sn solders.

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Conclusions

In this PhD work, it has been successfully investigated both dismantling of WPCBs and recovering of copper, which is the predominant metal present in discarded PCBs, using a novel integrated hydro-electrometallurgical approach. The electronic components detachment was achieved via hydrometallurgy dissolving all exposed metallic parts by means of a H_2SO_4-$CuSO_4$-NaCl solution in the presence of blowing air for in-situ regeneration of the oxidizing agent. In addition to the dissolution of Pb-Sn solders, all copper-based contacts (pins and leads) were also effectively leached. In this way, a copper-rich solution suitable for electrolysis process was obtained. The electrochemical recovery of copper from the leach solution was investigated after a preliminary cyclic voltammetry study aimed at finding the optimum operating conditions for electrolysis. A divided electrochemical cell was employed for the cathodic copper deposition simultaneous to the anodic regeneration of the oxidant for the leaching solution recycling. The results show that ECs can be removed without any damaging at low temperature using a less polluting solution, which can be anodically restored and recycled to the process. ECs along with the remaining board maintain their integrity and therefore, they can be easily separated and sent to recycle or further treatments. Besides, high copper purity can be obtained electrochemically from the leach solution with the possibility to operate both in galvanostatic and potentiostatic mode. This is a key point because the most current recycling technologies allow the recovery of the copper contained in the PCB structure, while that present as a base material in all electronic components' contacts is lost.

The second part of the PhD work was aimed at finding a destination for the remaining fiberglass reinforced epoxy board after removal of the ECs. A preliminary chemical characterization suggested as the selective recovery of copper had to be prioritized because copper is both the main and most valuable material in disassembled PCBs. In order to guarantee a simple flowsheet, low energy consumption, and low environmental impact, it was decided to employ an entirely electrometallurgical method using directly large pieces of disassembled WPCBs. The process involved the use of an undivided electrochemical cell operating in galvanostatic mode in which electroextraction of copper from PCB pieces occurred simultaneously to its cathodic deposition. Prior to using PCB pieces as an anode, the solder mask was removed by chemical treatment in NaOH to expose metallic copper to the electrolytic solution. Several challenges have been faced in order to maximize the recovery of copper from the board because the insulating nature of the PCB substrate did not allow extending the electrolysis time until complete copper dissolution. However, the benefit to obtain in a single step copper of commercial grade could be interesting from an economic point of view. Besides, the remaining PCB pieces could be a good feed material for a biological treatment in the perspective to reduce the environmental impact.

The two methods developed for dismantling and treating of disassembled WPCBs use pieces of PCB, but in principle they could use entire PCBs. In perspective of a large scale application, the entire WPCBs could be directly dipped in H_2SO_4-$CuSO_4$-NaCl solution for ECs removal then dipped in NaOH for solder mask removal and finally transferred to the electrochemical cell. In this way, the number of operations needed for copper recovery is minimized.

The PhD work was aimed at giving not only an original contribute on WPCBs recycling but also an answer to the emerging requirements of new cleaner and simpler recovery processes. On the whole, the proposed method satisfy the criteria of simple flowsheet and acceptable pollution, but it is still in an early stage and further investigations are required to evaluate the techno-economic feasibility and environmental sustainability, particularly for large scale applications.

List of publications, conferences and internships

Papers

- **C. Cocchiara**, R. Inguanta, S. Piazza and C. Sunseri, 2016, Nanostructured anode material for Li-ion battery obtained by galvanic process, Chemical Engineering Transactions, 47, 73-78

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- L. Genovese, **C. Cocchiara**, S. Piazza, C. Sunseri and R. Inguanta, 2017, Electrochemical deposition of Ag_2Se Nanostructures, Materials Research Bullettin, 86, 10-18

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- **C. Cocchiara**, B. Patella, F. Ganci, M.G. Insinga, S. Piazza, C. Sunseri, R. Inguanta, 2019, Nanostructured materials obtained by electrochemical methods: from fabrication to application in sensing, energy conversion and storage. In: K.D. Sattler (Ed.), 21st Century Nanoscience- A Handbook, Taylor & Francis Books, Inc.

- **C. Cocchiara**, S.-A. Dorneanu, R. Inguanta, C. Sunseri, P. Ilea, Dismantling and copper recovery from Waste Printed Circuit Boards (WPCBs) in H_2SO_4–$CuSO_4$–NaCl solutions, *Under submission*

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Patents

- **C. Cocchiara**, R. Inguanta, C. Sunseri, Apparato e metodo per il recupero di rame a partire da scarti di dispositivi elettrici ed elettronici, Italian patent 102017000110569 del 03/10/2017

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- **C. Cocchiara**, R. Inguanta, M. Insinga, C. Sunseri, Metodo e kit per il recupero di piombo metallico da componenti di un accumulatore esausto al Piombo-acido, Italian patent 102017000141056 del 06/12/2017

Conferences

- INSTM CONFERENCE, Favignana (TP) 28th June- 1st July 2015 “Nanostructured materials for Sensing, energy conversion and storage” R. Inguanta, **C. Cocchiara**, F. Ganci, A. Moncada, B. Patella, S. Piazza, C. Sunseri S. Lombardo

- International conference on nanotechnology based innovative application for the environment (NINE) 20-23 March, Rome, Italy. “Nanostructured electrochemical devices for sensing, energy conversion and storage” C. Sunseri, **C. Cocchiara**, F. Ganci, A. Moncada, R.L. Oliveri, B. Patella, S. Piazza and R. Inguanta

- International conference on nanotechnology based innovative application for the environment (NINE) 20-23 March, Rome, Italy. “Nanostructured anode material for Li-ion battery obtained by galvanic process” **C. Cocchiara**, R. Inguanta, C.Sunseri and S. Piazza

- ICheaP13- 13th International conference on chemical and process engineering, 28-31 May 2017, Milan, Italy. “Study of a novel electrochemical method for copper recovery from waste printed circuit boards”, **C. Cocchiara**, S. Piazza, C. Sunseri and R. Inguanta

Internships

- Babeş-Bolyai University, Faculty of Chemistry and Chemical Engineering, Cluj-Napoca, Romania, from 1-10-2017 to 1-02-2018, under supervision of Professors Petru Ilea, Sorin-Aurel Dorneanu and Graziella Liana Turdean
- ESI S.p.A Ecological Scrap Industry, Pace del Mela (ME), Italy, from 20-3-2017 to 20-5-2017, under supervision of engineer Mariateresa Amodeo