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FERREIRA DIAS

STUDY OF THE LEACHING PROCESS OF PRECIOUS METALS FROM WASTE ELECTRICAL AND ELECTRONIC EQUIPMENT.

Dissertation for the Master's degree in Biological and Chemical Engineering

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December 2023

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JURY

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December 2023

To my parents, Carlos and Bina, whose support was fundamental. Your love and sacrifices have been my constant companions throughout the highs and lows of my education.

What is important is not to see what no one has ever seen, but to think what no one has ever thought about something that everyone sees...

-Arthur Schopenhauer.

ABSTRACT

The development of modern society is anchored in the advancement of technology, and as a collateral consequence, waste from electrical and electronic equipment (WEEE) is increasing rapidly. This alarming trend poses a serious concern for the depletion of our planet's resources, as the extraction of elements such as metals from the Earth's crust intensifies, pollution and stress on ecosystems increases.

Nevertheless, WEEE still hold significant potential, particularly in recycling valuable elements like precious metals and base metals. Recycling these materials can offer substantial economic and environmental benefits, making it a crucial aspect in the circular economy.

Common processes for metal recovery from WEEE often rely on classic establish techniques such as pyrometallurgy, which raises concerns about energy consumption and pollution, or classic hydrometallurgy, using aggressive solvents harmful to humans and the environment leading stakeholders to seek alternatives, more eco-friendly lixiviants to ensure sustainable and responsible metal recovery.

The work intended to shed some light in the leaching ability of more sustainable agents on printed circuit boards (PCB) and compare their efficiency in the leaching process with classical approaches. Silver recovery from Printed Circuit Boards (PCBs) using thiourea, thiosulfate and sulfuric acid as leaching agents, was studied to compare the effectiveness of alternative leaching agents and validate the methodology. Quantification was performed by Inductively Coupled Plasma-Atomic Emission Spectroscopy and AAS atomic absorption spectroscopy.

Sulfuric acid as predicted was the most effective lixiviant (99,7% yield) followed by Ammonium thiosulfate (72,5% yield) on silver powder samples. In PCBs and complex samples, the use of thiosulfate and thiourea solutions for silver extraction, under the tested conditions, did not show promising results, requiring more studies.

KEYWORDS: WEEE, Hydrometallurgy, Recycling, leaching, silver

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LIST OF SYMBOLS AND ABBREVIATIONS

AAS - atomic absorption spectroscopy

CERENA - Centro de Recursos Naturais e Ambiente

EC’s – Electronic components

EEE - Electrical and Electronic Equipment

ESTBarreiro - Technology School of Barreiro

E-waste - Electronic waste

ICP-AES - Inductively Coupled Plasma-Atomic Emission Spectroscopy

IPS - Polytechnic Institute of Setúbal

IST - Instituto Superior Técnico.

PCBs – Printed Circuit Boards

PLS- Pregnant leach solution

PM - Precious metals

SDGs- United Nations Sustainable Development Goals

UN - United Nations

WEEE - Waste Electrical and Electronic Equipment

WPCBs - Waste Printed Circuit Boards

WSIL - Water-soluble ionic liquid.

1. INTRODUCTION

1.1. FRAMEWORK OF THE PRESENT DISSERTATION

This Dissertation was performed as the conclusion of the Master course in Biological and Chemical Engineering, hosted by the Barreiro School of Technology (ESTBarreiro), Polytechnique University of Setúbal (IPS), Portugal.

The main motivation for this dissertation was to contribute to a more sustainable use of resources, with a specific focus on Waste from Electrical and Electronic Equipment (WEEE) by providing insights and ideas to enhance its recycling technologies.

Embracing Sustainable Development Goals (SDGs),defined by United Nations (UN) especially *Goal n.º 12 - Responsible Consumption and Production, for promoting better consumption and production patterns*, knowing that the unsustainable patterns of consumption and production are in the root causes of the triple planetary crises of climate change, biodiversity loss and pollution [1]. the present work focused on the fastest growing waste stream globally: WEEE, in particular Printed Circuit Boards (PCBs) from mobile phones [2].

In 2012, Wang and Gaustad confirmed that WEEE holds a great potential, especially in recycling their constituent elements, where gold has the highest recovery priority, followed by copper, palladium, aluminum, tin, lead, platinum, nickel, zinc, and silver, with substantial economic and environmental benefits [3].

On the other hand, there are also concerns about the current recycling technologies for the recovery of metals in WEEE. These classic approaches but also alternative methods were investigated in the work.

Previous research has been conducted in the host institution, ESTBarreiro, regarding this subject, namely the project BeGold that was initially undertaken by bachelor course students in the context of their participation in Poliempreende in 2018, aiming the recovery of precious metals using a more sustainable approach.

1.2. OBJECTIVES

The objectives defined for the present dissertation were:

1. State-of-the-art review of current leaching processes for the recovery of precious metals from electronic and electrical materials. Comparison of these processes, highlighting their advantages and disadvantages.

2. Leach metals in PCB from mobile phones and silver particles (2-3.5 μm) with thiosulfate and thiourea: understand their organometallic chemistry and consider their environmental impact, stability, and efficiency. Comparison with classical approaches.

3. Develop alternative methodology to quantifying leached precious metals.

1.3. DEVELOPED ACTIVITIES

This work involved an extensive review of previously published academic papers and other relevant documents that addressed the subject under consideration, complemented by laboratory work. developed in the laboratories of the host institution (Chemical and Biological Engineering Laboratories). The laboratory work included sample analysis by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), courtesy of Dr. Carlos A. Nogueira from Laboratório Nacional de Energia e Geologia, I. P. (LNEG), and Atomic Absorption Spectroscopy (AAS), courtesy of Dr Rosinda Ismael, Dr.Teresa Reis and Professor Lurdes Gameiro from CERENA-Centro de Recursos Naturais e Ambiente, Instituto Superior Técnico (IST).

The work followed the activities represented in the Figure 1.

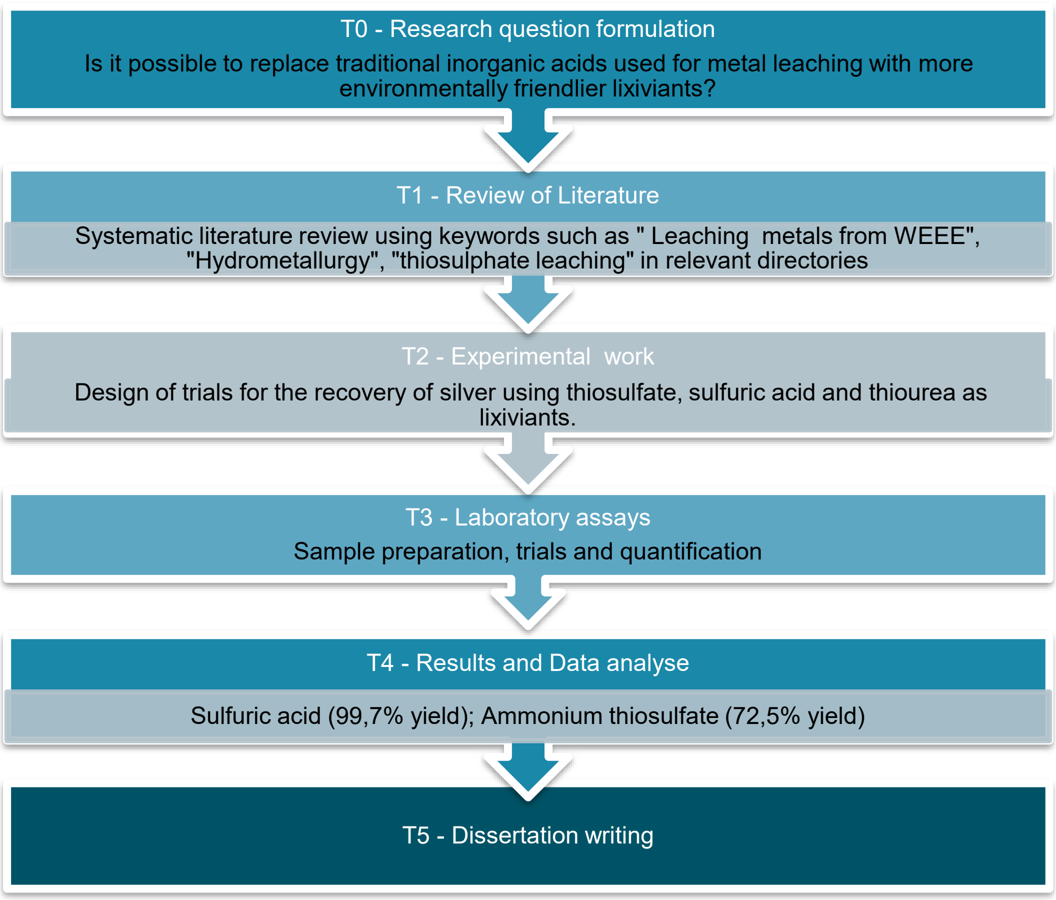
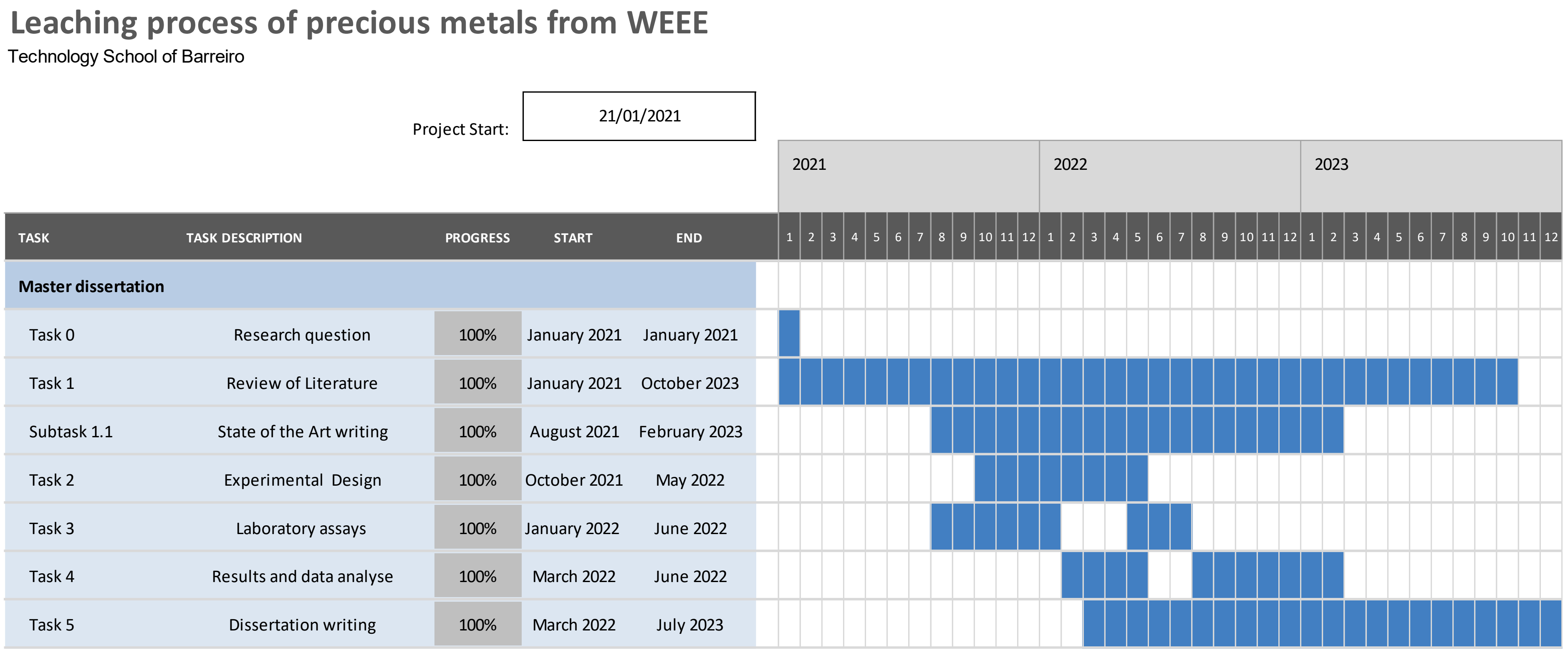


Figure 1 - Research process adopted, representing the tasks from T0 to T5.

1.4. TIMELINE OF THE ACTIVITIES

The activities were carried out accordingly to the schedule shown in Table 1. The project began on January 21st and ended on December 2023.

Table 1 – Gant chart illustrating the timeline for the developed activities from T0 to T5



Leaching process of precious metals from WEEE

Technology School of Barreiro

Project Start: 21/01/2021

					2021												2022												2023											
TASK	TASK DESCRIPTION	PROGRESS	START	END	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12
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2. STATE OF THE ART

In the past decades, a significant amount of research has been conducted on the use of alternative and eco-friendly lixiviants for recovering metals found in electronic waste. Despite this, it remains unclear why these methods have not gained traction and been more implemented on an industrial scale.

2.1. ELECTRONIC AND ELECTRIC EQUIPMENT WASTE (WEEE)

WEEE includes a wide range of products, such as televisions, computers, mobile phones, refrigerators, washing machines, and other household and industrial electronic and electrical equipment corresponding to highly heterogeneous mix of materials.

Printed circuit board (PCB) is a flat board made of non-conductive material, usually fiberglass or a composite epoxy, with conductive pathways "printed" on its surface. These conductive pathways, serve as the electrical connections between various electronic components. It constitute only approximately 6% of the total weight of WEEE [4] but holds a significant portion of the value contained as Xue Wang and colleagues verified in their work in 2012 [2]. Their work identifying PCB as the **top priority** for recovering valuable metals. The metal content in PCBs is approximately 30% and the data collect from several studies (**Table 2**) indicates that copper (Cu), nickel (Ni), lead (Pb) and chromium (Cr) are the most common metals. Other elements such as silver (Ag) and gold(Au) are present in much less quantities, but represents a significative revenue value and have the **highest recovery priority** [3]. Usually, these metals are found in the form of copper layers (10–20%) and applied on its surface, in terminal pins and holes. Metals like gold and silver are used as contact materials due to their high electrical conductivity and chemical stability (oxidation resistance) [5][6].

*Table 2 - Metal concentration (in ppm) of PCBs from mobile phones. n.a. = not analyzed. *Average from* [7]

Elements/Study	Ernst et al. (2003)	Hall and Williams (2007)	Yamane et al. (2011)	Holgersson et al 2017	Smartphones, Holgersson et al 2017	Average in ppm*
Ag	4000	5081	2100	2640	2773	4200
Au	800	19	<10	1051	1083	990
Cd	<1	<5	n.a	<0,2	<0,2	23
Cr	700	801	n.a	865	1219	2100
Cu	200000	272402	344900	342667	395000	257000
Hg	n.a	8	n.a	0,6	0,3	
Ni	20000	8434	26300	11600	15433	23000
Pb	9000	1618	18700	3747	260	12000
Pd	300	<5	n.a	119	55,4	550
Pt	n.a	n.a	n.a	4.3	0,8	
Sb	500	22	n.a	n.a	n.a	1100

Although scarce and finite, non-renewable resources such as coal, oil, metals and minerals are sometimes treated as infinites, driving to a rapid increase in resource consumption that can lead to supply constraints and increased price, as revealed in the work of Choudhury and Mahdi in 2020 [8] which in turn are likely to have significant impacts on society, non-mentioning the amount of potential resources going to landfills as waste.

In this context it seems natural to look to secondary sources for these components, and according to several authors, [9] [10] [11], WEEE have a special role in the recovery of metals. For instance, the work of Holgersson in 2018 [7] determined that WEEE contained significant amounts of precious or semi-precious metals that can be a sustainable alternative source to high-grade ores.

The United Nations (UNs) estimate that the global WEEE was 14 million metric (Mt) tons in 1992, 24 million tons in 2002, 49 million tons in 2012 [12], 53.6 million tons in 2019, and is projected to grow up to 74.7 Mt by 2030 [13] as illustrated in Figure 2.

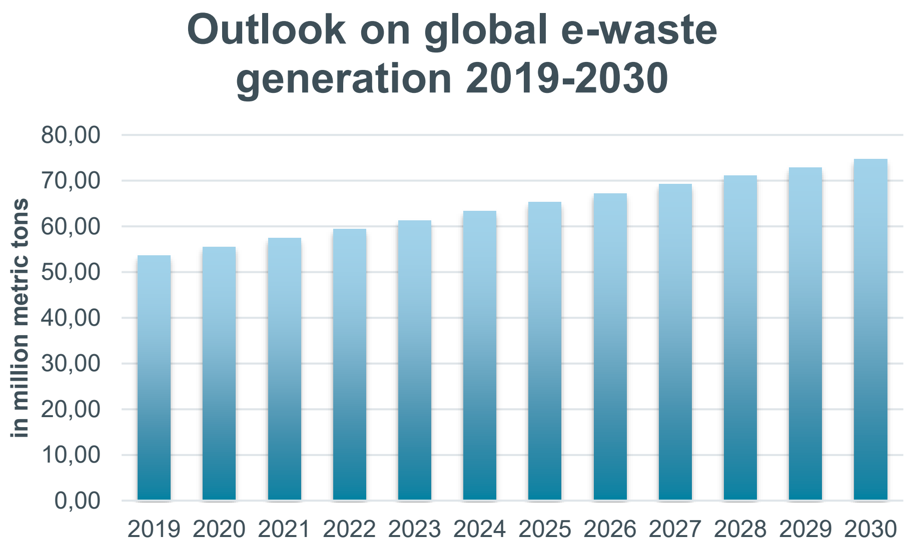


Figure 2 - Projected electronic waste generation worldwide from 2019 to 2030 Source: [13]

The rapid evolution of the technology and the consumer habits has led (and will lead to even higher) to the fast disposal of several electric and electronic devices. This is why WEEE is considered the emerging and fastest growing waste [14], and this why we consider pertinent to embrace alternatives to retrieve metals and to perform a sustainable recycling process.

In the words of UN Environment Program (UNEP) there is a “tsunami of e-waste rolling out over the world”.

The problem of WEEE is aggravated by low recycle rates and big differences between developed and developing countries. For instance, in 2019 Europe collect and recycle 42,5% of the WEEE produced, while Asia only 11,7%, Americas 9,4%, Oceania 8.8% and Africa with the lowest rate of 0,9%.[13]. These rates only consider the WEEE collected officially in each country and do not account for exports from developed countries to developing countries, that poses a problem by itself.

In these developing countries the WEEE management infrastructure is not yet fully developed and, in some cases, is entirely absent. Therefore, WEEE is managed by the informal sector (see Figure 3). where dismantlers manually break the equipment down into usable marketable components and materials, and burn, using methods that are harmful to their health and the environment. In some cases, metals are then shipped back towards industries in developed countries [13].

Figure 3 - Typical recycling processes applied in the informal sector of developing countries, adapted from [15], *from left to right: open burning for copper recovery, hand pinking of components, burning for desoldering of PCBs.*

Despite this problem persisting worldwide, there are already countries, especially in the developed world, that have higher quotas of recycling and recovery largely enforced by legislation along with prohibition of the disposal of PCBs in landfills, increasing interest in the end-of-life management of e-waste [16].

For these reasons strategies to deal with WEEE are gaining attention. Different methods can be held, but as usual in complex problems, multidisciplinary approaches are important for optimal resource usage. The World Economic Forum, for instance, propose, as result of the annual meeting in Davos 2019 [17], different strategies that involve, **Design of products**, **Reintegration of manufacturing scrap**, **Repair, second life and durability**, **Improve of collection rates and Advances in recycling technologies**, as illustrated in Figure 4.

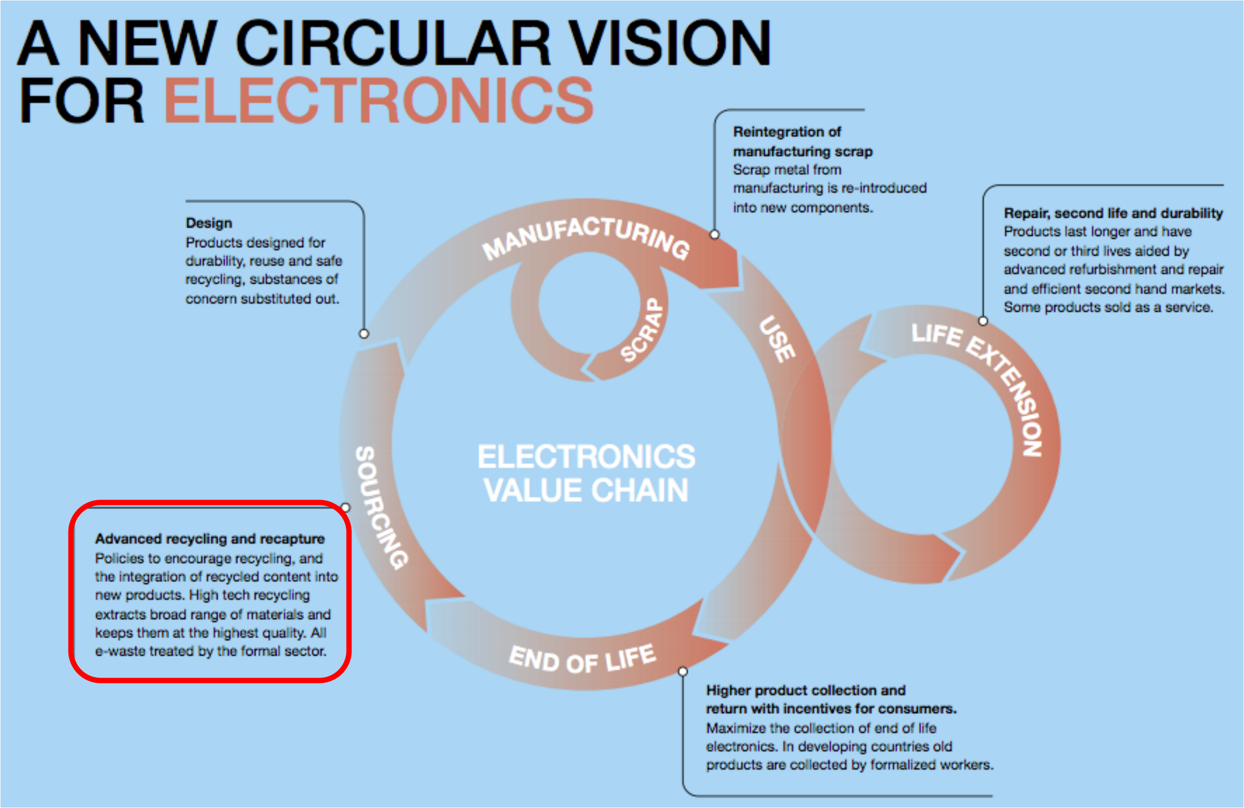
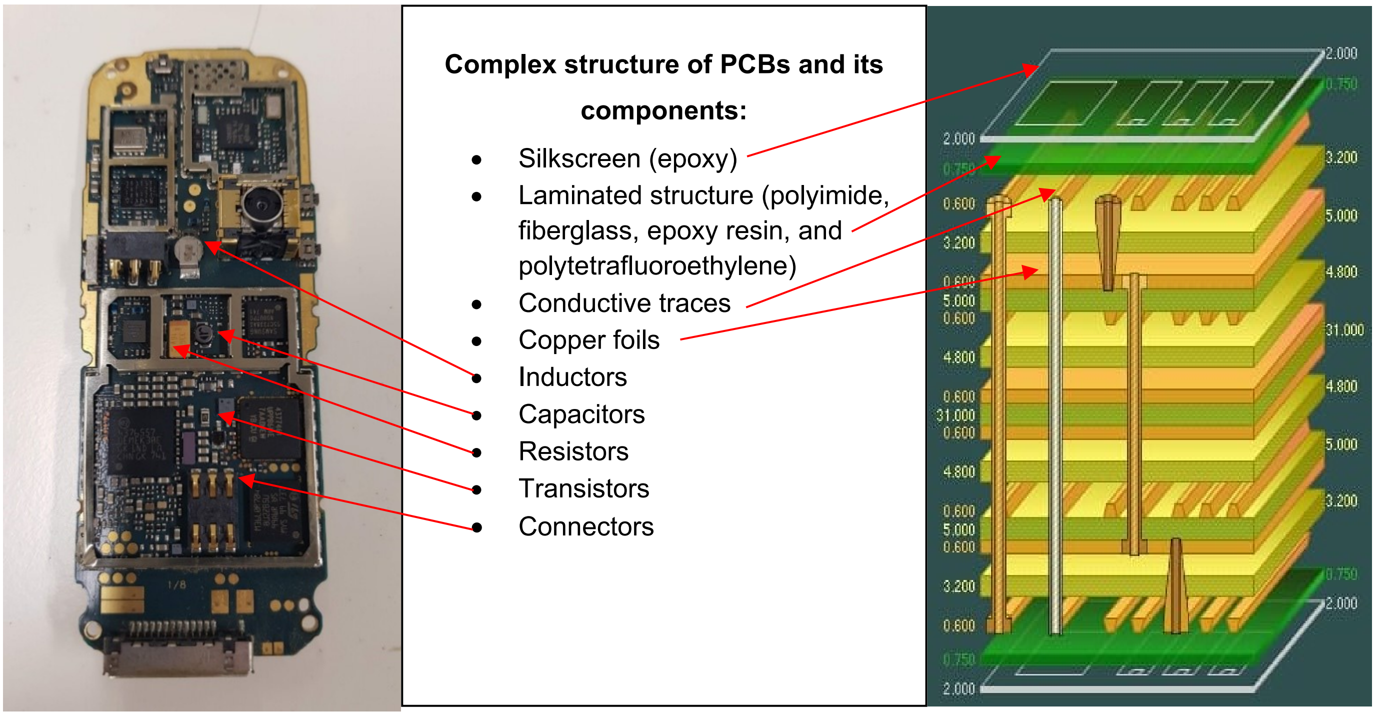


Figure 4 - Multidisciplinary approach for WEEE management - Source World Economic Forum 2019

In this context, it can be said that this work falls within the **'Advanced Recycling'** approach identified by the World Economic Forum and highlighted in Figure 4, where the use of alternative leaching agents may contribute to high-tech recycling, enabling the extraction of a broad range of materials while maintaining them at the highest possible quality.

2.2. WEEE RECYCLING PROCESS

Recycling WEEE is challenging, especially PCBs, due to their complex material constitution and intricate structure, resulting in a demanding recycling process and a considerable portion is difficult to recycle or reuse being disposed of in landfills [18].



Complex structure of PCBs and its components:

- Silkscreen (epoxy)
- Laminated structure (polyimide, fiberglass, epoxy resin, and polytetrafluoroethylene)
- Conductive traces
- Copper foils
- Inductors
- Capacitors
- Resistors
- Transistors
- Connectors

Figure 5 – On the left a mobile phone PCB used in trials. On the right a cross-section view of the PCB showing its complexity. In the middle PCBS components and materials. Images credits from PCB producer Ventura Electronics.

Within the range of sources, PCBs from mobile phones are the ones that contain higher amounts of valuable metals, as disclosure by Sahan and colleagues in 2019 [19]. Therefore, this specific type of PCBs was chosen for the current work not only due to its high concentration of valuable metals but also for the easy access to this equipment, abundant in households.

Due to its complex composition, PCBs recycling requires a multistep approach, generally a three-step procedure involving **pre-treatment, metal enrichment, and metal recovery**, as represented in **Figure 6** and **Figure 7**.

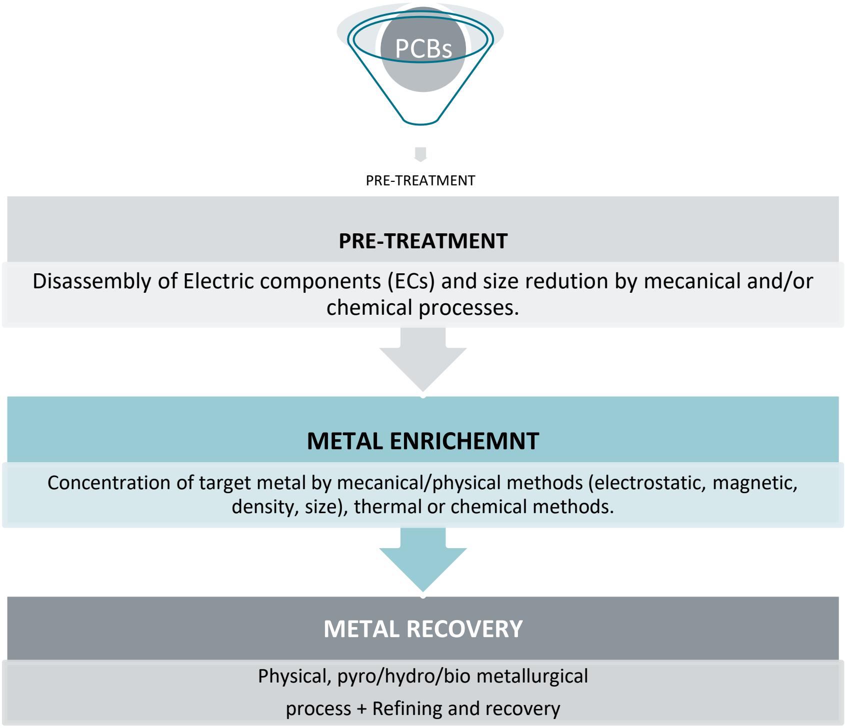


Figure 6 - The multiple steps involved in the recycling process of PCBs.

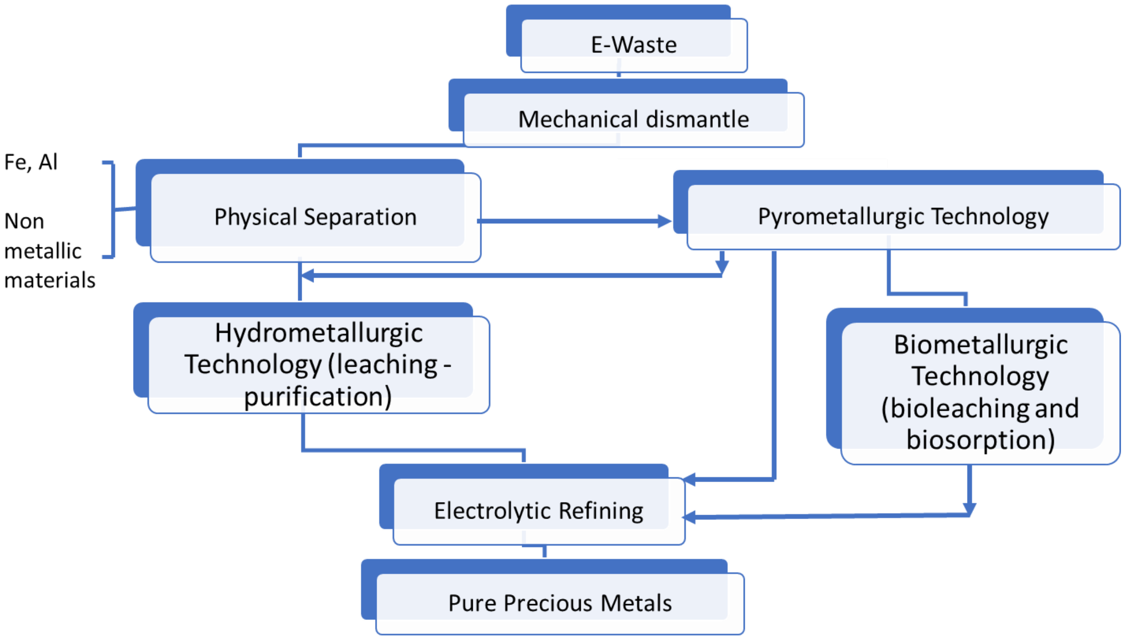


Figure 7- Diagram illustrating the various steps and processes employed in the recovery of precious metals from WPCBs (adapted from [20])

2.3. PRE-TREATMENT

Depending on the recovery process (metal recovery step), pre-treatment importance varies, but is recommended due to the existence of hazardous components, cell batteries, capacitors, and electric components (ECs) that have different recycling routes and should be removed before the main recycling process takes place [21]. Pretreatment can also be carried out on different levels depending on the metal concentration target and the subsequent recovery technique For instance, hydrometallurgy and bioleaching routes are more demanding on pretreatment because of the interference of base metals (like copper, aluminum, lead, nickel, tin, and zinc) when aiming to the recovery of precious metals [22].

Pretreatment of PCBs can be either mechanical, chemical or a combination of both:

Mechanical methods, manual, semi-automatic or automatic, normally are destructive involving a combination of impact, shearing, vibration forces to open-soldered connections, and heating up to temperature of 40-50 °C (melting point of the solder) [16]. In Figure 8 it is possible to observe an example of a dismantling machine that uses crushing and sieving as separation techniques.

Figure 8- PCB dismantling machine from Doing Co Ltd manufactory.

The benefit of mechanical separation process is the low capital and operation costs when compared with dedicated chemical pre-treatment [12]. The main disadvantages are the high energy consumption, dust pollution (high temperatures that might occur during the dismantling, with a potential for dioxin formation), and high valuable metal loss (10–35%) due to insufficient metal liberation [12] [23]. More complex machinery, automatic and semi-automatic disassemblers are expensive and ideally suited for high-metal content waste [24]. In developing countries, where informal recycling is conducted, techniques such as manual dismantlement, oven heating, and open burning furnaces are used, but increasing pollution and health problems (as well as large amount of metals are lost) [25].

Chemical pretreatment can also be used to separate the laminated structure (such as polyimide, glass fiber reinforced epoxy resin, and polytetrafluoroethylene) from the electronic components (ECs) in a efficient way [23]. Zeng and colleagues mention that a bath in several heated liquids (water soluble ionic liquids (WSIL)), assisted by mechanical vibration, could be a promising technology for opening solder connections [26].

Different solvents can be used, beside the ionic liquids such as alkali and acid solvents or supercritical fluids [23].

In comparison with mechanical methods, chemical pre-treatments hold several advantages, such as higher selectivity, lower energy consumption, higher metal recovery yields [27], [28], however, mechanical pretreatment is a more common method, due to a more cost-effectiveness since they require less specialized equipment and are generally simpler to set up and operate.

However, it's essential to note that the choice between mechanical and chemical pretreatment depends on the specific goals of the recycling process, the types of materials involved, and environmental considerations. In some cases, a combination of mechanical and chemical methods may be employed to achieve optimal results in PCB recycling.

2.4. METAL ENRICHMENT

The importance of metal enrichment is related with the improvement of the efficiency for the recovery, helping to reduce the amount of solvent or energy necessary for metal recovery. Physical treatment is generally used to enrich metals according to their physical properties. The common methods include, screening, electrostatic separation, magnetic separation, density separation. In these approaches, the sizes of particles had to be milled below 150 µm to ensure no interlocking of metallic and non-metallic particles [12].

The drawbacks of physical separation processes include loss of valuable metals and high cost due to small sample size needed. Furthermore, the metals could not be sufficiently liberated from their intimate association with plastics. Chancerel and colleagues [29] studied the effect of shredding on the loss of precious metals (Ag, Au, and Pd). They measured the concentration of precious metals in unshredded, preshredded (<8 mm), and shredded (<2.5 mm) PCBs. They found that there is 7% loss in preshredded PCBs compared to unshredded PCBs, and 62% loss in shredded PCBs compared to preshredded PCBs.

These findings highlight the importance of adopting efficient metal enrichment methods.

2.5. METAL RECOVERY

Metal recovery it's the final step of a multistep approach for recovering metals from PCBs. At this point operators select the recovery method depending on expertise and resources availability. Different approaches can be adopted: **pyrometallurgical, hydrometallurgical,** and **biometallurgical** process, as well as some hybrid processes [30].

2.6. PYROMETALLURGY

Pyrometallurgy is the metal recovery technique that involves the use of high temperatures to extract and refine metals from ores or raw materials. Smelting is the key pyrometallurgical process where heat is applied to a metal ore or a mixture of ores and other materials to separate the desired metal from its impurities. Pyrometallurgical processing, has become a traditional method to recover metals from WEEE in the last three decades [12]. In the pyrometallurgic process, metal is melted by incineration, smelting in plasma arc furnace, blast furnace or Cu smelter, high temperature roasting in presence of selective gases.

Well-established plants such as Noranda (at Quebec, Canada), Boliden (at Rönnskår, Sweden) or Umicore (Hoboken, Belgium) use a combination of pyrometallurgical, complemented with electrochemical refining, to recover precious metals such as gold (Au), silver (Ag) and palladium (Pl) [31] from WEEE. As represented in Figure 9 Umicore's integrated metal refinery, electronic scraps are treated in the Cu-Smelter furnace, primarily to produce Copper (Cu) through Copper leaching and electrowinning followed by precious metals recovery from Cu-leached residue in precious metal refinery [32].

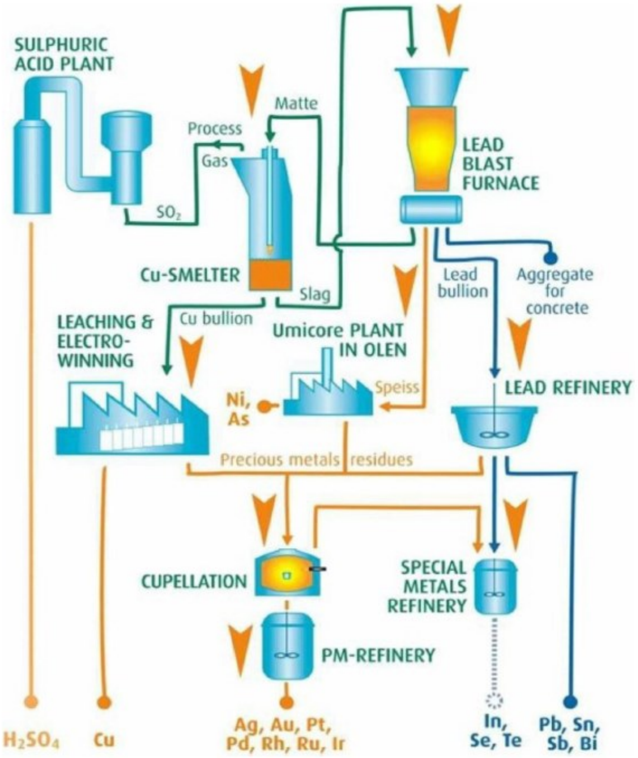


Figure 9-Process flow diagram for Umicore's integrated precious metal smelting (source: [33])

Pyrometallurgy is considered the most common adopted method in a big scale operation, but pyrometallurgy isn't completely independent from hydrometallurgy since the final steps of the process is usually complemented with an electro-chemical process to enrich and separate metals from unpurified metal bullions.

The main advantage of pyrometallurgical treatment is its ability to accept any forms of scrap.[12]. Several authors identify drawbacks on the pyrometallurgy process, as determined by [33] in their work, enormous energy consumption, emission of toxic gases (such as SO_2, Cl2, Br_2, dioxins/furans), volatile metals, dust, solid waste residue [34] and require high capital investment.

2.7. BIOMETALLURGY

Regarding biometallurgy techniques, these comprise bioleaching and biosorption. Bioleaching constitutes a sustainable and eco-friendly approach for metal extraction from ores or e-waste that uses microorganisms (such as bacteria, archaea, eukaryota, or a combination) to oxidize metals making them soluble. These microorganisms secrete acids, ligands or recycle elements through different, well-sequenced biochemical pathways acting as lixiviants to solubilize metals.

At present, research and development is in progress for a few metals, such as copper, nickel, cobalt, zinc, gold, and silver. Bioleaching has been successfully applied in recovery of metals from metallic sulfides (ores), which are the major bearing minerals for many base and precious metals, using bacterially assisted reactions [35]

Three fundamental bioleaching mechanisms are known to this day: acidolysis, redoxolysis, and complexolysis, represented in Figure 17. Having the metal in solid form, and through the action of several bacteria such as *Acidithiobacillus caldus* ou fungi such as Aspergillus niger. the iron III will oxidise the metal, reducing to iron II in redoxolysis. Sulfur is oxidised to sulfuric acid that oxidises the metal in acidolysis [35]. Also, microorganisms such as *Chromobacterium violaceum* or *Pseudomonas aeruginosa* can also produce acids and other organic molecules, named ligands, which can interact with metals forming soluble complexes through complexolysis. An example is glycine, the most simple amino acid, which is produced by these microorganisms and can act as a ligand for gold solubilization [35].

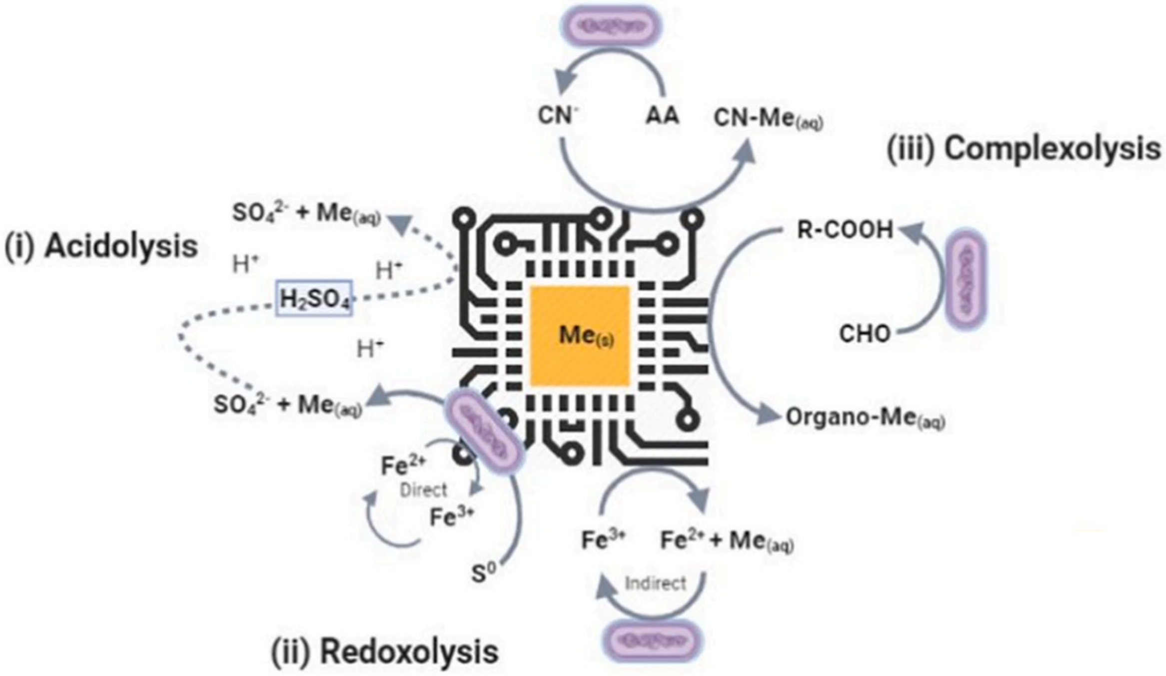


Figure 10-Bioleaching Mechanisms: (i) acidolysis, (ii) direct and indirect redoxolysis and (iii) complexolysis during the bioleaching of metals from WEEE. [35]

Biosorption is the technique that allows us to retrieve the oxidised metals from solution. It is a passive physio chemical interaction between charged surface groups in microorganisms and metal ions in solution. It can use both forms of microorganisms, viable or non-viable form [35]

The focus of the present work is the hydrometallurgy (studies developed to recover Silver from PCBs). The aim in this context is to indorse a depth analysis of the different metal recovery techniques conducted from the point of view of precious metal recovery (Silver) from PCBs through hydrometallurgy.

2.8. HYDROMETALLURGY

Hydrometallurgical process is a metal recovery approach that involves the use of aqueous solutions [33] (usually mineral acids or cyanide-based) to extract (solubilize) and recover metals from primary or secondary sources (mineral ores or WEEE). Recently, hydrometallurgy has emerged as a prominent research area, making significant achievements in the recovery of precious metals from Waste Printed Circuit Boards (WPCBs) using more sustainable solvents [9]. It comprises the leaching process followed by metal concentration/purification and precipitation/recovery.

Leaching plays an important role as it dissolves the precious metals present in the waste-waste, separating them from other components and provides an efficient and selective means. It is particularly advantageous for treating low-grade ores or complex substrates (such as WPCBs), where traditional pyrometallurgical methods may not be suitable [30].

The choice of the leaching solution depends on the specific metal being targeted for recovery. Commonly used lixiviants include mineral acids like sulfuric acid (H_2SO_4), hydrochloric acid (HCl), nitric acid (HNO_3) and aqua regia (HNO_3 + HCl in a 1:3 ratio) as well as cyanide-based solutions and alternative lixiviants like the ones with thiol groups (thiourea, thiosulfate and thiocyanate), and halides (chloride, iodide and bromide) [33].

The leaching solution is usually agitated or circulated through the WEEE material to maximize metal dissolution in a container, such as a reactor, procedure described by several authors ([36][37]. This allows the lixiviants to react with the precious metals and form soluble complexes or metallic ions. The duration of the leaching process can vary depending on the parameters and factors such as the desired metal recovery rate and the leaching kinetics [38].

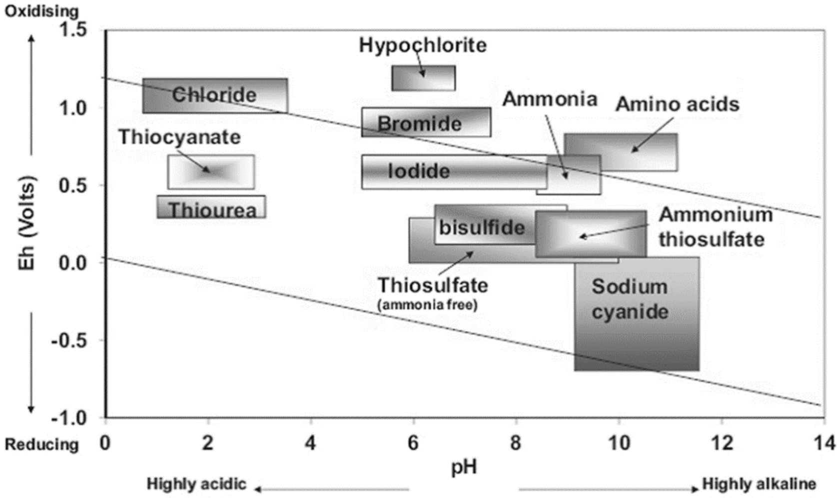


Figure 11-Eh-pH diagram of promising gold lixiviants and their working areas [33]

Regarding efficiency and selectivity for the metal recovery it depends on thermodynamic parameters, especially temperature, pressure, pH, and redox potential (Eh). As Barragan and colleagues demonstrated out in 2021 [39], although the leaching of metals from WPCBs is well known and frequently used, its chemistry is not fully understood. It is important to control and define the thermodynamic parameters in order to promote an optimal leaching, otherwise, the dissolution is not thermodynamically feasible [40]. In Figure 11, it is showed the Eh-pH diagram of promising gold lixiviants and their working areas. In this diagram, also known as Pourbaix diagram, a graphical representation predicts the stability of different chemical species in a system under varying pH and Eh (redox potential) conditions.

In the example shown, in Figure 12, using a solution with nitric acid, silver is soluble as an cation at pH lower than 3 and redox potential higher than 0,5V where the red line indicates the pH restriction, and the blue line indicates the potential Eh(V) restriction for the leaching process.

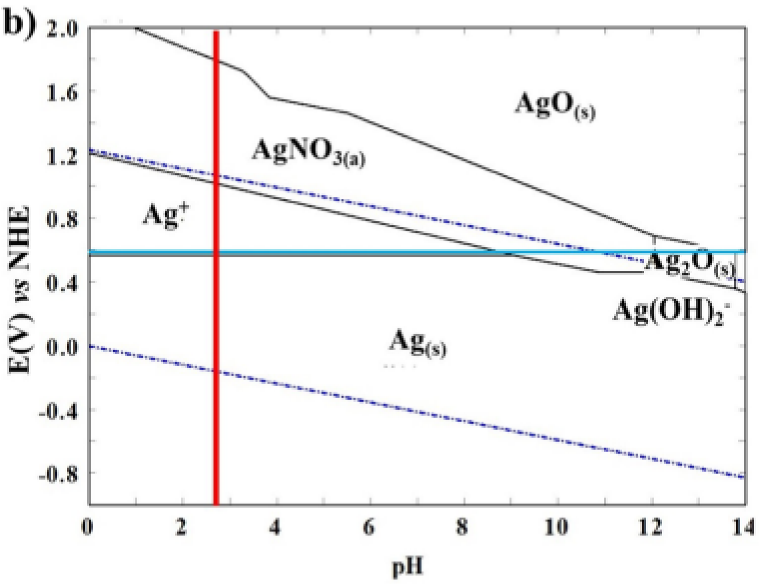


Figure 12 - Pourbaix diagrams, Eh vs pH, in the leaching system of 2 M HNO3 extracted from [39]

In Figure 12 it's possible to observe that the formation of Ag+ or $AgNO_3$ (soluble) is pH and redox potential dependent and needs to be carried out at potentials greater than 0.6 V and lower that 1.6 V and pH lower than 3 to avoid any precipitation reaction. In this example of leaching, HNO_3 acts as oxidizing agent, reacting with metallic Ag (s) to form ions (Ag+) (aq) or $AgNO_3$ (aq) soluble in acid solution, illustrated in the Equation 1:

Equation 1:$3Ag(s)+4HNO_3(aq) \leftrightharpoons 3AgNO_3(aq)+NO(g)+2H_2O(l)$

As an additional note, oxidants can be added to the reaction such as air/O_2, H_2O_2, Cl_2, Cu^{2+}, Fe^{3+} to promote the metal oxidation and stabilize the solution through metal complexation, enhancing the dissolution of other components, and provide control over the leaching process limiting the formation of insoluble salts that these metals usually form [30].

After this step, the resulting solution, called "Pregnant Leach Solution" (PLS), contains the dissolved precious metals along with impurities. Several separation techniques can be employed to isolate and recover the metals. These techniques may include precipitation, solvent extraction, ion exchange, electroplating, or other methods depending on the specific metal and the impurities present. The goal is to selectively separate the target precious metals from the solution and concentrate it for further processing or refining.

To finally recover silver, as metallic silver, several methods can be used [41]. One of this method is the zinc method, where the silver can be recovered through reduction using metallic zinc as reducing agent (Equation 2):

Equation 2: $Zn(s)+2AgNO_3(aq) \leftrightharpoons Zn(NO_3)_2(aq)+2Ag(s)$

In this reaction, the metallic zinc (Zn) reacts with silver nitrate (AgNO3), causing the nitrate to be released as zinc nitrate ($Zn(NO_3)_2$) in the solution. At the same time, elemental silver (Ag) is formed as a solid precipitate.

Although less used as recovery method on the recycling of WPCBs as confirmed by several authors [34] [42] and others, hydrometallurgical route has been identified as the most advantageous since it is the more selective, less energy demanding (lower carbon footprint) and requires lower investments for implementation [43] when compare with big smelting facilities. On the other hand, strong solvents represent a risk for people, equipment's, and environment, with process resulting on a large amount wastewater needing to be managed properly[44].

LEACHING WITH MINERAL ACIDS

As mentioned before (see Equation 1) leaching metals with mineral acids is a possible method for recovering metals from WEEE.

Nitric acid (HNO_3), for instance, has been reported as having the fastest leaching kinetics for copper, silver, and lead, but H_2SO_4 and HCl, have the advantages of low costs, well-investigated leaching mechanism [30].

Aqua regia (HCl and HNO_3 in 3:1 proportion) has the highest gold dissolution rate among different leaching agents, but it is applied usually in a laboratory scale because of aqua regia's strong oxidation and high corrosion potential [45].

LEACHING WITH CYANIDES

Cyanide leaching has extensively been used for extraction of silver and gold from ores for decades, and according with work developed by Akcil and coworkers in 2015 [34] and Hilson and Monhemius in 2006 [46], a large majority of gold and silver mines (>90%) use cyanide as lixiviant. However, in the context of WEEE recycling cyanidation is less common due to environmental and safety concerns [34], [47].

Fundamentals behind the chemistry of cyanidation is similar to other leaching agents and depending on the pH and redox potential. Cyanidation can be either in the form of cyanide anion (CN^-) or hydrocyanic acid (HCN) [34].

Metallic silver (Ag) reacts with cyanide ions (CN^-) to form a soluble complex known as silver cyanide ($Ag(CN)^{2-}$). This complexation reaction occurs in the presence of excess of cyanide ions, typically provided by the addition of sodium cyanide (NaCN).

The reaction is represented in Equation 3:

Equation 3: $Ag(s)+4NaCN \leftrightharpoons 2Na[Ag(CN)_2]+Na_2S$

Cyanidation is primarily associated with the solubilization of gold and silver however, it can also be applied to the extraction of other metals, like Copper (Cu), Zinc (Zn), Nickel (Ni) and Cobalt (Co), although it is less commonly used [48].

The recovery of silver can also be achieved using the Zinc method discussed earlier.

Cyanide is an effective low-cost solution, being the lixiviant preferred by the industry (specially in mining), however, as several studies confirm, cyanide toxicity to humans and environment, with some serious environmental accidents occurring around the world caused by the leakage of cyanide from metallurgical plants [47], stringent environmental regulations and public concerns has promoted the research for more efficient and environmentally friendly methods [49]. Furthermore, the large content of copper in WPCBs consumes excessive cyanide, which increases the cost considerably [23]. However, if the copper is removed in a Pre-treatment step (see Pre-treatment) the cyanide use can be reduced.

LEACHING WITH ALTERNATIVE REAGENTS

Alternative leaching agents have gained attention for their potential in the recovery of PM (precious metals) since the end of the 1990s [50], however since the 1900s that thiosulfate (for instance) is studied as a process for PM recovery [37]. The growing global focus on environmentally responsible practices as promoted the use of more sustainable approach to extract valuable metals from electronic waste in recent years.

Several less toxic reagents have been developed in the pursuit of safer and more environmentally friendly processes, in particular thiol groups (thiourea, thiosulfate and thiocyanate) and halides (chloride, iodide and bromide) [40] have gained attention. Other innovative processes have been developed such as chelating leaching [51] , ionic liquid leaching [26] sub- / supercritical leaching [51], but they will be out of the scope of this work.

THIOL GROUPS REAGENTS (THIOUREA, THIOSULFATE AND THIOCYANATE)

THIOSULFATE LEACHING

Thiosulfate is a polyatomic ion that consists of a central sulfur atom (S) bonded to three oxygen atoms (O) and one sulfur atom (S), resulting in a tetrahedral molecular geometry, represented in Figure 13:

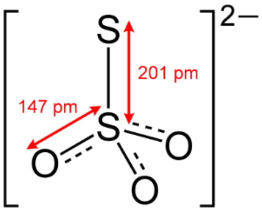


Figure 13-Thiosulfate ion schematic representation with bond distances represented in red. -

Note: (The prefix thio- indicates that the thiosulfate is a sulfate with one oxygen replaced by sulfur.)

Thiosulfate has several industrial uses, but it’s its ability to form stable complexes with various metal ions, such as copper (Cu^{2+}), silver (Ag^{+}), and gold (Au^{+}) that makes it interesting for metal leaching. Both ammonia thiosulfate ($(NH4)_2S_2O_3$) and sodium thiosulfate ($Na_2S_2O_3$) are described as effective lixiviants of silver. The solubility of metals begins in near-neutral solutions and in the presence of a mild oxidant, but the dissolving rates remain low. To enhance solubility, alkaline solutions should be used as they prevent the decomposition of thiosulfate [37]. Also leaching kinetics is increased 20 fold in the presence of ammonia and copper ions, the so-called **thiosulfate-copper-ammonia** system [52] This system was described as complicated, due to the simultaneous presence of complexing ligands such as ammonia and thiosulfate, the Cu(II)-Cu(I) redox couple and the instability of thiosulfate in solution [37].

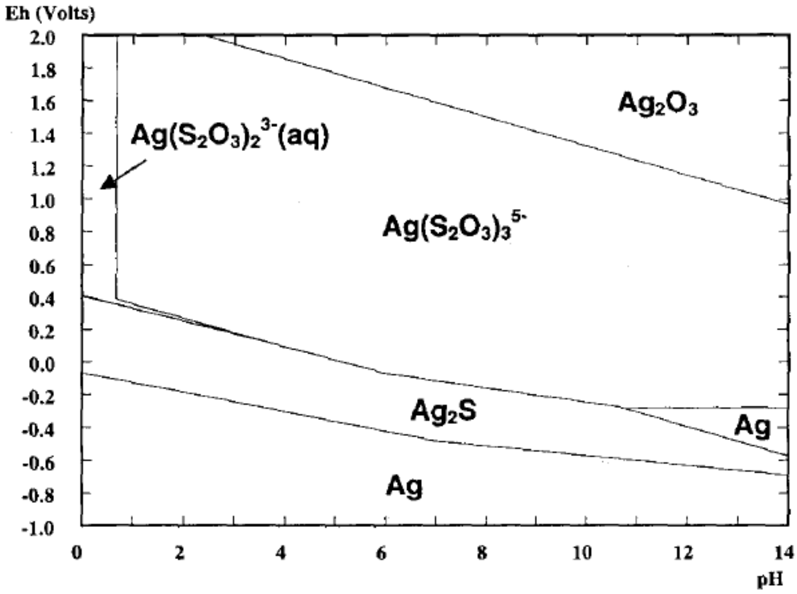
In general terms, ammonia, prevents the buildup of sulfur layers on the metal surface as a result of the decomposition of thiosulfate, bringing metals into solution as an ammine complex. The ammine complex is then converted to thiosulfate complex. Copper ions in solution act as an oxidant, and catalysis reaction promoting metal dissolution. Oxygen or some other oxidants are required to convert copper (I) to copper (II) regenerating thiosulfate.

Regarding thermodynamic equilibrium, the Pourbaix diagram in Figure 13, shows that if the potential is too low, silver remains undissolved or precipitates as a silver sulfide (Ag_2S) over the whole range of pH. At high potentials and pH values (10-14), silver forms oxide (Ag_2O_3) in the form of insoluble precipitates.

The dissolution of silver occurs through the formation of complex silver-thiosulfate species ($(Ag(S_2O_3)_2^{3-}$ which are soluble in aqueous solution. As mentioned before the exact mechanism may vary depending on the specific conditions and presence of other factors, such as thermodynamic conditions and other metals, but in general the dissolution reaction can be represented as follows, Equation 4:

Equation 4: $Ag\,(s) + 2\,[Cu(NH_3)_4]^{2+}\,(aq) + 2\,S_2O_3^{2-}\,(aq) \rightarrow Ag(S_2O_3)_2^{3-}\,(aq) + 2\,SO_4^{2-}\,(aq) + 4\,NH_{3\,(g)} + 2\,Cu^{2+}\,(aq)$

Silver combines preferentially with thiosulfate, while silver ammonia complexes are only stable at low thiosulfate concentrations.



c

Figure 14 Eh-pH diagram for ammoniacal- thiosulfate and silver system

In conclusion, thiosulfate is reported as a promising alternative to cyanide, due to high selectivity, low corrosiveness, low price and reduced environmental risk, as Xu and colleagues showed in their study of 2017, and also Hao and colleagues in 2020),[47][23] however there are significant obstacles which are based on the low reagent stability and high consumption manly caused by its decomposition [37]. This may be the reason for its limited industrial application so far [40].

THIOUREA

Thiourea ($(CS(NH_2)_2)$) is also a sulfur-containing compound where the oxygen atom from the Urea is replaced by a sulfur atom (as implied by the thio- prefix) (Figure 14).

Thiourea has also been used and study as an alternative leaching agent for the dissolution of gold, silver, copper, and other metals from ores and WEEE.

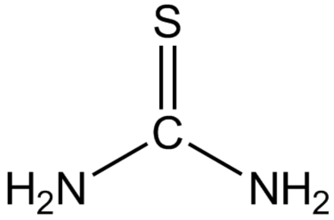


Figure 15 - Thiourea Figure 15 - Thiourea schematic representation (ref?)

Thiourea forms a stable soluble complex with silver ions, [53] as suggested the in Equation 5, in the presence of Fe^{3+} ions as an oxidant:

Equation 5: $Ag\ (s) + 3CS(NH_2)_2\ (aq) + Fe^{3+}\ (aq) \rightarrow Ag\ ((CS(NH_2)_2)^{3+}(aq) + Fe^{2+}(aq)$

The addition of Fe^{3+} enhances the leaching efficiency by promoting the oxidation of thiourea and facilitating the dissolution of silver. This complex remains dissolved in the leaching solution, and solubility is influenced largely by its pH value, redox potential, leaching time, and the concentration of thiourea and Fe^{3+} [46]. Zhang and coworkers in 2012 [54], concluded that, among alternative agents, Thiourea has the highest potential, however, other research demonstrated that the future of thiourea leaching is not so promising due to its higher cost, high-volume consumption, and potentially carcinogenic potential [34] [55].According with same authors Thiourea shows a much poorer stability when compared with other leachants. Also it is common in this system that elemental sulfur produced form a stable passivation layer on the surface of metal reducing lixiviation increasing reagent consumption [54].

Ongoing research is exploring ways to improve the efficiency and reduce the cost of thiourea leaching for commercial applications [30] but is important to note that Thiourea poses significant environmental and health risks, and their use requires careful consideration and management.

THIOCYANATE

Like thiosulfate and thiourea, thiocyanate (SCN^-) can be used as complexing agent that forms stable soluble complexes with silver (and other metals), allowing its solubilization. The complex formed between silver and thiocyanate is typically soluble, allowing effective extraction of silver from the ore or the material being leached.

The thiocyanate leaching process typically involves the following reaction represented in Equation 6:

Equation 6: $Ag(s) + SCN^{-}(aq) \rightleftharpoons [Ag(SCN)]^{-}(aq)$

Thiocyanate as a linear structure with the carbon atom in the center and has two resonance forms (-S-C=N) and S=C=N^{-}), being ambidentante ligant,, it can work as a donor either via the S or the N atom, forming Silver complexes with the S-thiocyanates [56].

As can be observed in the Pourbaix diagram for Ag-SCN-H2O system, in Figure 16, complexes are soluble in the form of $Ag(SCN)_3^{2-}$ and $Ag(SCN)_4^{3-}$ for wide range of pH conditions, but more favorable for acid conditions (pH 1 – 3) and redox potential around 0 – 100mV [56].

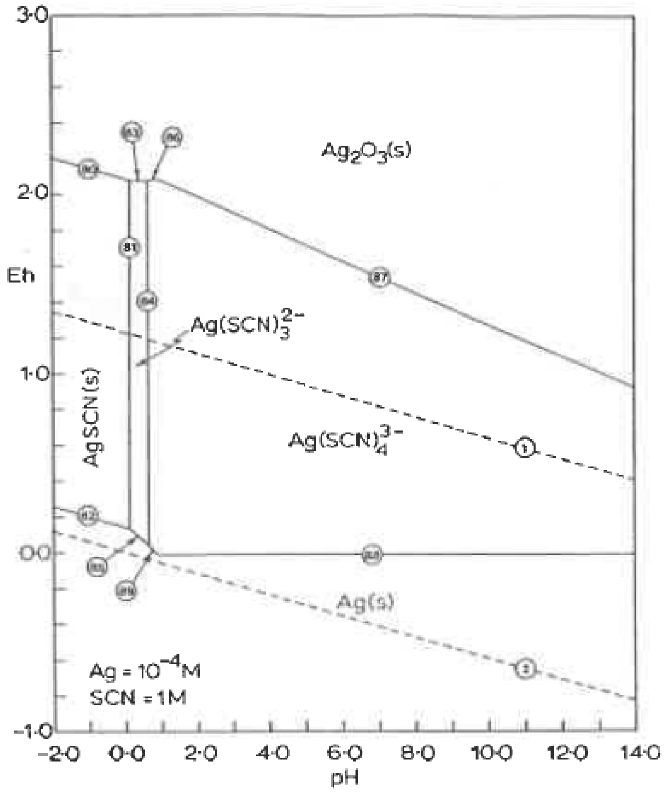


Figure 16 - Pourbaix diagrams, E vs pH, for the Ag-SCN-H2O system source [56]

HALIDES (CHLORINE, BROMINE AND IODINE)

Chlorine, bromine and iodine have been studied to leach precious metals from ores earlier than cyanides. However, little attention has been paid on gold leached from WPCBs as Ghosh and colleagues identified in 2015 [57]. Gold can oxidize both as Au^{+} and Au^{3+} complexes with halides. Chlorine, with high chemical stability, is considered as a relatively safe chemical reagent to leach precious metals. Examples of 100% gold, 71.36% silver and 100% lead leaching recoveries, in three steps were reported using NaClO-HCl-H_2O_2 system [44] However, the main disadvantage to this process is that it requires special equipment and poses potential health hazards to workers. Iodine/iodide, which exhibits non-corrosivity, non-toxicity, good selectivity, and rapid kinetics, have also been used to recover precious metals in alkaline environment [54]Iodide leaching has enabled a 98.5% gold, 97.2% lead, and 99% silver leaching efficiencies [28]. The main disadvantages of iodine–iodide leaching system are high consumption of reagents which can result in significant effluents production. High cost is also mentioned [54].

2.9. METAL RECOVERY (FROM PREGNANT SOLUTION)

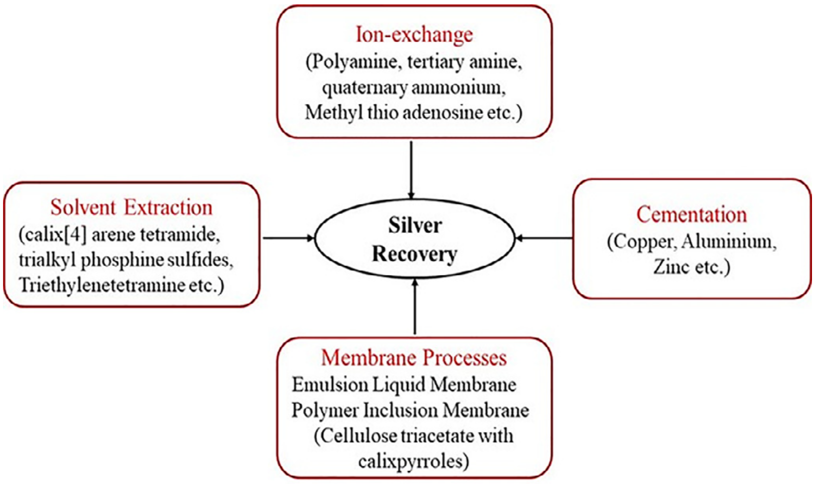


Figure 17 - The recovery of silver through various processes from leach liquor of WPCBs [9]

In the hydrometallurgical route of recovery of silver, the leached liquor is subjected to separation and purification processes. Ray and coworkers in their paper of 2022 describe in detail most used recovery methods, such as electrowinning, cementation, adsorption, precipitation [58] among which the Zinc method previously mentioned. Other authors also describe alternative methods, such as solvent extraction or through membrane filtration [9]. A resume of several techniques can be observed in Figure 17.

Two of the most common methods are electrowinning and electrorefining mostly used in the final steps of pyrometallurgy. While both involve the use of electric current to recover and purify metals, there is a fundamental difference in the location of the impure metal during these processes as can be observed in Figure 18

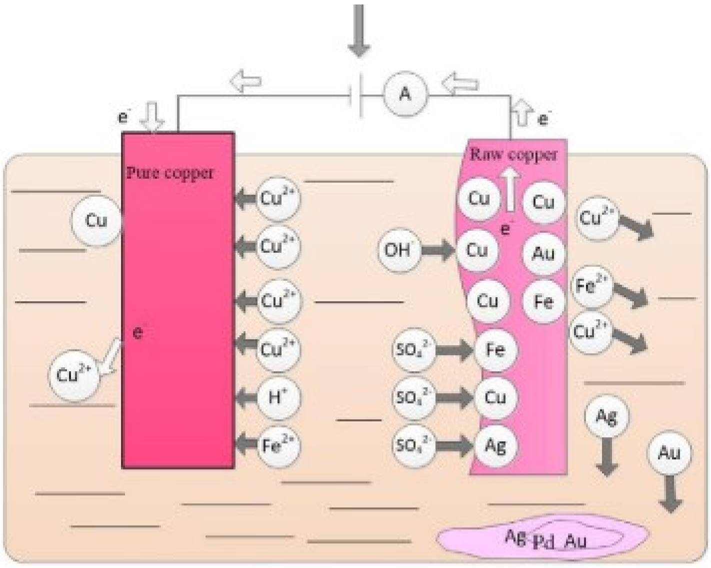


Figure 18 - Diagram of electrorefining of Copper- adapted from [44]

In the electrowinning process, the impure metal is present in the leach solution or electrolyte. On the other hand, in the electrorefining process, the impure metal is intentionally placed at the anode.

2.10. QUANTIFICATION TECHNICS

Accurate quantification of the target metal in solution is essential for assessing leaching behavior and effectiveness of the several strategies.

After leaching metals from PCBs there are several techniques and the choices depend on factors such as the nature of the metals, their concentration, sensitivity requirements, and equipment availability.

The review of literature shows that the most common techniques for quantification in Hydrometallurgy are related with light absorption/light emission, (see Figure 19 and Table 3) where spectroscopy is the dominant technology for analyses, with some variations from technique to technique.

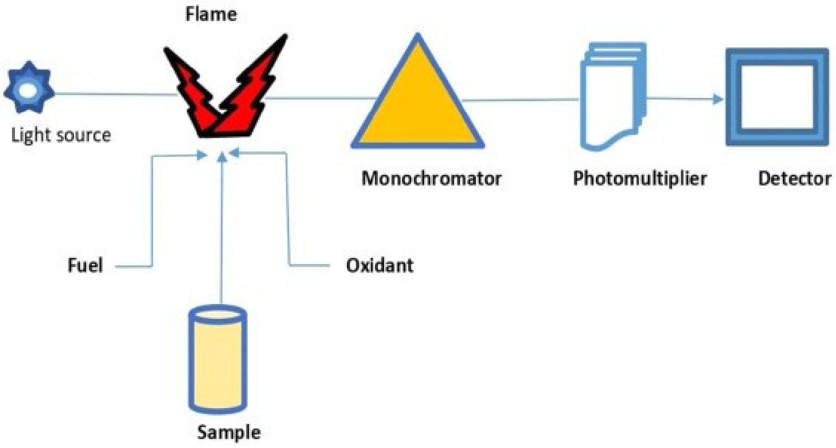


Figure 19 - Working principle of atomic absorption spectroscopy.

Atomic Absorption Spectroscopy (AAS) is a widely used technique for metal analysis. It measures the absorption of light by the metal atoms in the solution to determine their concentration. It uses the phenomenon of atomic absorption, where atoms in the ground state absorb light at specific wavelengths that correspond to their electronic energy transitions. Sample is atomized into vapor to facilitate the absorption of light. The detector measures the intensity of the transmitted light. Figure 19 illustrates the principle behind this technique through a schematic drawing. The amount of absorbed light is directly proportional to the concentration of the element in the sample [59]. In Figure 20, is an Atomic Absorption spectrophotometer.

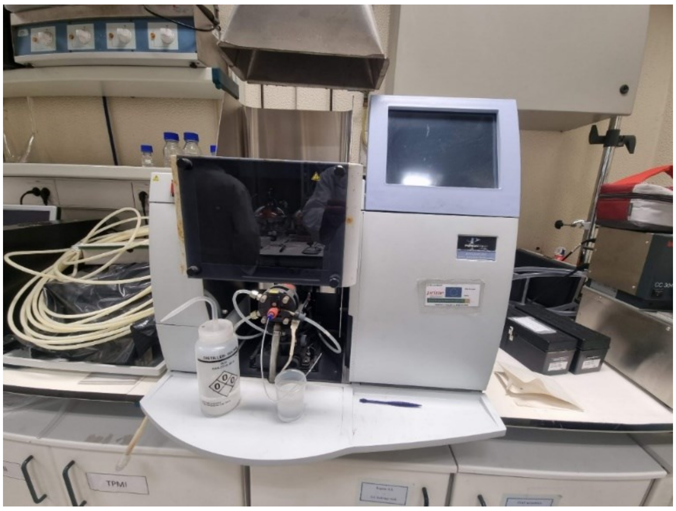


Figure 20 - Atomic Absorption Spectrometer (AAS), @ CERENA - IST

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) is another popular technique for metal analysis. It uses an inductively coupled plasma to atomize and excite the metals in the solution, and then measures the emitted light to determine their concentration. The technique allows for the simultaneous analysis of numerous elements in a single run, offering high throughput and efficiency.[60]. Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) also uses an argon plasma to excite the atoms, resulting in the emission of light at characteristic wavelengths. However ICP-AES (as also AAS) typically analyzes one element at a time. Figure 21 represents the tests conducted for this study using AES.

Figure 21 - Atomic Emission Spectrometer (AES), produce by Horiba model Ultima @ LNEG.

In X-ray Fluorescence Spectroscopy (XRF) the sample is irradiated with high-energy X-rays, typically generated by an X-ray tube. The X-rays cause the atoms in the sample to become excited and promote inner-shell electrons to higher energy levels. When these excited electrons return to their original energy levels, they emit fluorescent X-rays with characteristic energies that are unique to each element [61].

Table 3 – A review of studies, lixiviants, origin, metals and quantification technics used in Hydrometallurgy.

Research article	Leachant	Metal(s)	quantification technique
(Ernst et al., 2003)	Aquaregia	PCBs (several metals, including Ag)	ICP-OES
(Ficeriová et al., 2008)	Thiourea	Gold and Silver	XRF
(Ha et al., 2010)	Thiosulfate	Gold (PCBs from mobile phones)	AAS
(Yamane et al., 2011)	Aquaregia	PCBs (several metals, including Ag)	ICP-OES
(Yang et al., 2011)	Sulfuric acid	Copper from PCBs	ICP-OES
(Kamberovic et al., 2011)	Thiourea	Copper from PCBs	AAS, XRF and ICP-OES
(Gouveia et al., 2014)	Aquaregia	Silver and Gold from PCBs	XRF
(Birloaga et al., 2013)	Thiourea	Copper and Gold from PCBs	XRF
(Porte, 2013)	Aquaregia	Copper and Gold from PCBs	AAS
(Fogarasi et al., 2014)	Sulfuric acid	Copper and Gold from PCBs	AAS
(Birloaga et al., 2014)	Thiourea	PCBs (several metals)	XRF
(Ha et al., 2014)	Thiosulfate	Gold (PCBs from mobile phones)	AAS
(Nascimento Cortês, 2015)	Thiourea	Gold (Computers microprocessors)	AAS
(Holgersson et al., 2018)	Aquaregia	PCBs (several metals, including Ag)	ICP-MS
(Kasper, 2016)	Thiosulfate	Gold (PCBs from mobile phones)	AAS
(Kim et al., 2018)	Aquaregia	PCBs (several metals, including Ag)	ICP-OES
(Kasper & Veit, 2018)	Thiosulfate	silver from photovoltaic modules	AAS
(Huang et al., 2022)	several	Gold WPCBs	ICP-OES

Although any of these studies used Spectrophotometry, the method was also considered due to its relatively simple, cost-effective approach and equipment availability in the laboratory. Spectrophotometry is a technique that measures the absorption or transmission of light by a substance as a function of its wavelength. It is particularly useful for quantitative analysis of molecules that absorb light in the ultraviolet (UV) and visible (VIS) regions of the electromagnetic spectrum.

By measuring the absorbance or transmission of light by the sample at a specific wavelength, the concentration of the substance can be determined using the calibration curve obtained from the reference standards.

LABORATORY ASSAYS

3. MATERIAL AND PROCEDURES

3.1. MATERIALS

Silver powder, 2-3.5 µm, ≥99.9% containing trace metals basis was acquired from Sigma Aldrich (sample a). The PCBs from mobile phones (mobile phone Nokia 5070 from 2007 + smartphone Sony Xperia from 2013) (Sample b) were donated to the studies. Motherboards from Umicore Hoboken ((crushed/calcinated) from Lot 182914) with 40,60% metal content was provided by MetalEspaço. (Sample c).

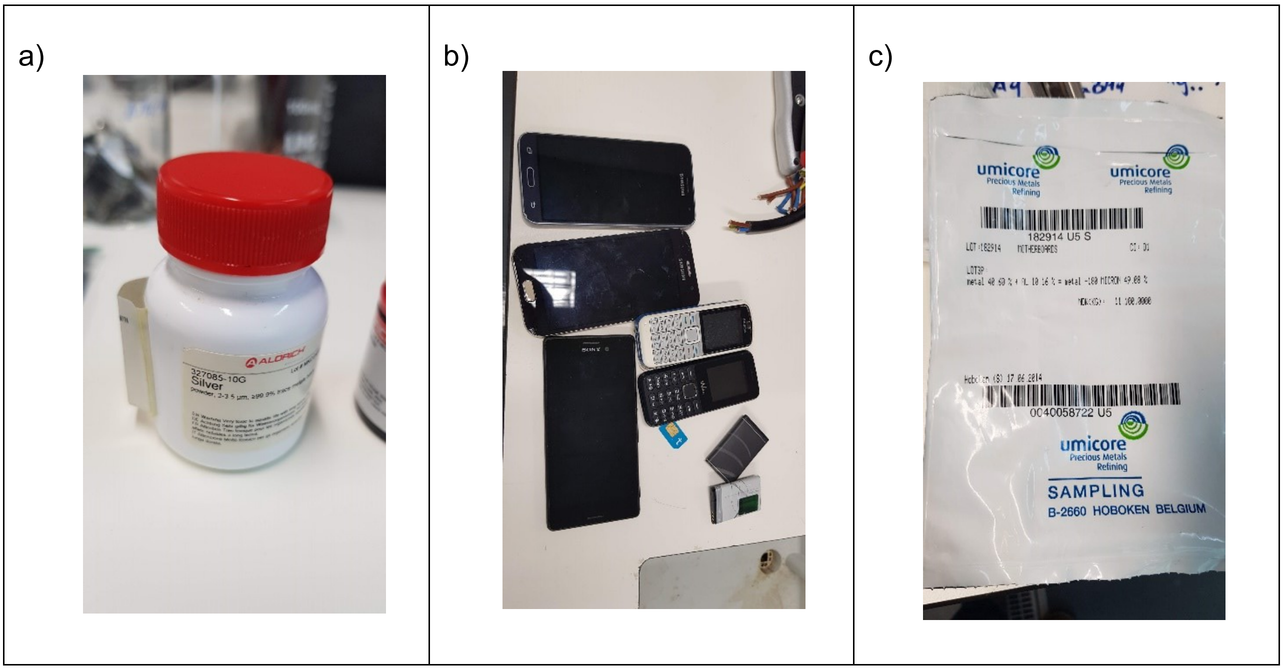


Figure 22 - Samples used for assays a) silver powder; b) Mobile phones source of PCBs; c) Motherboards sample.

Regarding reagents, all were laboratory grade, namely Ammonium thiosulfate, Thiourea and Ammonia buffer solution, pH 10 were supplied by Sigma-Aldrich, Sulfuric acid with 95,0% (m/m) were from Panreac, Hydrogen peroxide 35% (v/v) was supplied by Carlo Erba, Copper (II) sulphate (pentahydrated) was obtained from José Manuel Gomes dos Santos, Iron(II) sulfate heptahydrate was provided by Panreac. Filter papers Laurent 70mm from Prat Dumas.

3.2. EQUIPMENT:

Precision balance with 0.1 mg readability, Orbital shaker ES20 from Grant-bio, pH Meter Mettler Toledo Five Easy, Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), from Horiba Jobin–Yvon model Ultima, Atomic absorption spectroscopy (AAS) from Perkin Elmer model AAnalyst 200, Silver Cathode respective Lamp for Spectroscopy and Multiskan SkyHigh Microplate Spectrophotometer from ThermoFisher.

3.3 Procedures

Based on the knowledge acquired through the literature review, an experimental plan was organized, based on the objectives, research questions, and available resources (*vide* Objectives).

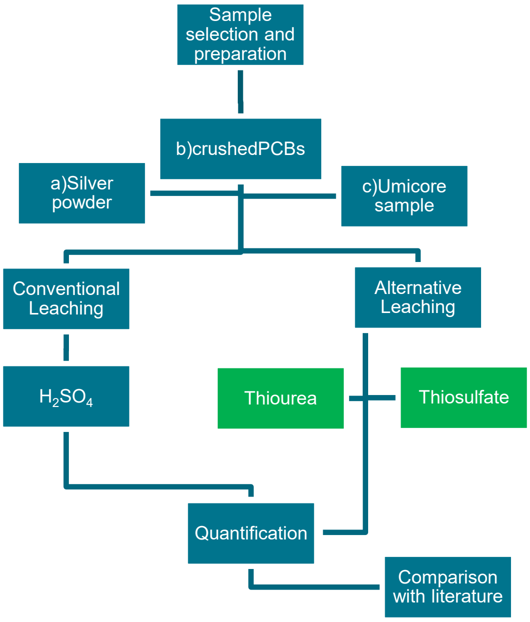


Figure 23 Flowchart outlining the steps of the plan for laboratory work.

Leaching agent selection: Samples, after pretreatment, were subjected to a leaching process (in duplicates) using conventional leaching agents, such as Sulfuric Acid due to its proven ability to leach silver and alternative leaching agents such as Ammonium Thiosulfate and

Thiourea selected due to their leaching potential, availability, low hazard, and reduced ecological impact (see Figure 23).

Quantification techniques: All leaching assays were followed by metal quantification in solution using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), Atomic Absorption Spectroscopy (AAS) and, as an alternative study, the molecular Spectrophotometer.

Pretreatment (Mechanical)- Mobile and smartphones were manually dismantled, the plastic was removed as well as the metallic covers, and electronic components such as batteries, screens, and other smaller components like cameras, using a screwdriver and wire cutters (a). Clean PCBs were then fragmented using cutters into non-calibrated parts of 10mm each (b). These fragments were evenly distributed among the 50ml Erlenmeyer flasks.

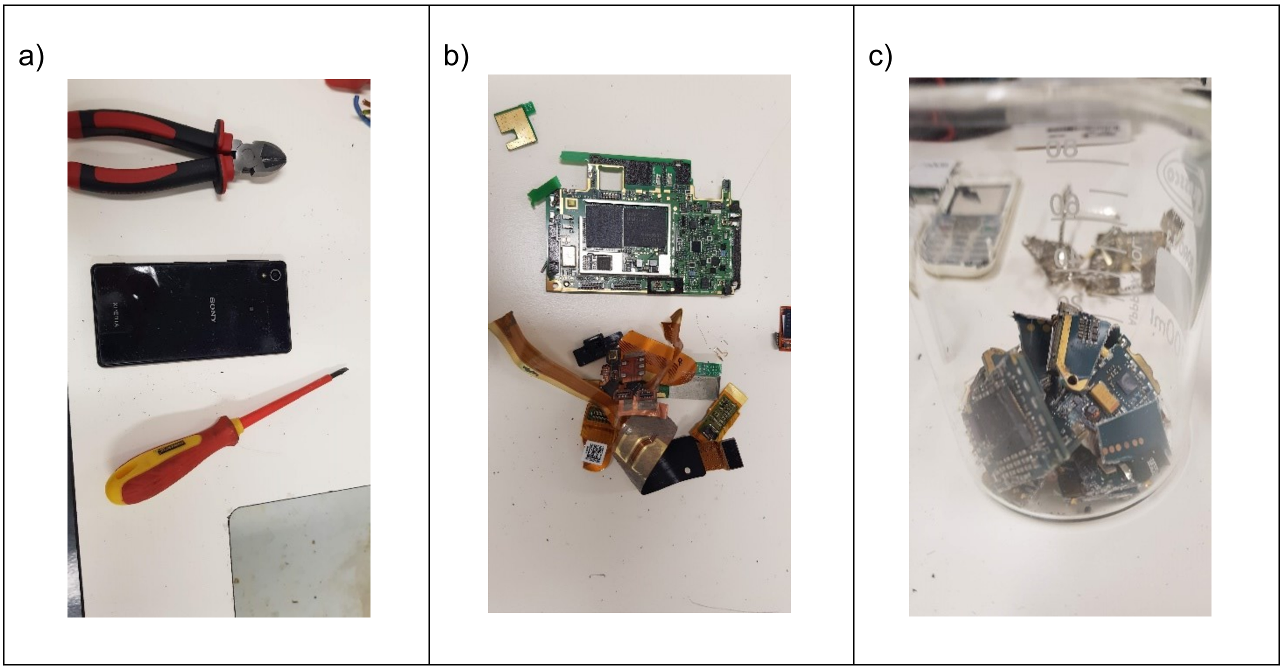


Figure 24 –The 3 stages of sample a) PCBs preparation.

3.3.2 Lixiviant system preparation:

Preparation of **thiosulfate-copper-ammonia leaching system**:

Solution composition: 0.12M $(NH_4)_2S_2O_3$, 0.02M NH_4OH, 0.02M $CuSO_4$

This composition was selected following the work of V.H. Ha and coworkers in 2010 [49] for leaching gold from PCBs. It was inferred that perhaps silver might had a similar behavior.

Ammonia and copper (II) sulfate solutions were firstly mixed [49] and then added to the ammonium thiosulfate solution, and the pH of the solution was monitored to remain in the 10–10.5 range to prevent thiosulfate decomposition.

Preparation of **acidic thiourea solution**:

Solution composition: 0.2M de $CS(NH_2)_2$, 0.02M $FeSO_4$ and 0.1M H_2SO_4

The composition of this solution was chosen based on the studies conducted by A. Behnamfard and colleagues in 2013 [45] This study involved the optimization of several parameters and enabled the attainment of high metal recovery rates.

Preparation of **sulfuric acid solution**:

Solution composition: 2 M H_2SO_4, 35%(v/v) H_2O_2

This composition was selected following the work performed by I. Birloaga and colleagues in 2014 [42] for precious metals extraction from waste printed circuit boards (WPCBs) using a thiourea system (thiourea with the ferric ion in sulfuric acid medium), with promising results.

The leaching experiments were all performed in 50 mL Erlenmeyer flasks using the orbital shaker at 200 rpm at 30ºC, for 15h. The solid/liquid ratio (S/L) for PCBs and Umicore sample was 1/10 (100 g/L) based in the studies of A. Behnamfard and colleagues in 2013 [45], I. Birloaga and colleagues in 2014. Ratio used for pure silver, also 1/10 S/L (1.3 g/L) derived from the work of X. Wang and G. Gaustad in 2012, where a review of several published papers determined that the concentration of Silver in PCBs is 0.0013g/g of PCBs [3] in average.

All samples were subjected to a leaching process with sulfuric acid for control and with thiourea and thiosulfate solutions, separately, for comparison, in duplicates.

After the lixiviation period, leached solutions were filtered using funnels and filter paper Laurent with a pore size of 70mm. Pregnant solutions were kept in a dark box until analyzed (12h).

Figure 25 - Leaching assays in the Orbital shaker ES20 Grant-bio, for 15h at 30ºC and 200 rpm.

The silver concentration in the leaching solutions was determined by ICP-AES, Horiba Jobin–Yvon Ultima), AAS, Perkin Elmer model AAnalyst 200 and Spectroscopy Multiskan SkyHigh Microplate Spectrophotometer from ThermoFisher.

4. RESULTS AND DISCUSSION

After the several approaches for leaching treatments data was summarized in Table 4.

Table 4 – silver Leaching assays where "sample" means the sample number, sample type, the leachant system and the yield determined either by ICP-AES or AAS (n.a. = not analysed).

Silver (Ag) Quantification			Quantification method	
			ICP - AES	AAS
Sample nº	Sample type	Leachant system	yield	yield
1	Ag	Ammonium Thiosulfate	72,56%	4,92%
4	Ag	Thiourea	n.a.	5,00%
5	Ag	Sulfuric acid	99,67%	31,92%
6	Umicore	Ammonium Thiosulfate	0,87%	1,75%
9	Umicore	Thiourea	n.a.	0,17%
10	Umicore	Sulfuric acid	0,06%	0,27%
11	PCBs	Ammonium Thiosulfate	0,61%	0,58%
14	PCBs	Thiourea	n.a.	0,73%

Results presented in Table 4 show a very low yield for silver recovery on PCBs and Umicore samples regardless the lixiviant system used. Higher yields were obtained with the classic lixiviant of Sulfuric acid resulting in 99,7% yield for sample type Ag, followed by Ammonium thiosulfate with a 72,5% yield also for sample type Ag measured in ICP-AES.

The leaching Yield was calculated following Equation 7:

Equation 7:

$$Yield = \frac{[Ag]g/l * D}{[Ag]^t}$$

Were D represents the dilution factor, $[Ag]^t$ the concentration of silver in PCBs (literature based) and [Ag] g/L the measured concentration of silver in solution.

[Ag]t value derived from literature review, in particular the work of X. Wang and G. Gaustad in 2012, where concentration of Silver in PCBs was0.0013g/g of PCBs [3].

Although there were some preliminary studies with the spectrophotometer, all the presented results were analyzed in the ICP and AAS equipment. It is also important to mention that some samples using Thiourea were not analyzed in ICP-AES, since at that time Thiourea wasn't considered to be tested. The results obtained revealed an interesting insight into the efficiency of the different leachants in extracting silver from PCBs and infer that their complex nature could require more pre-treatment steps. Furthermore, the results display substantial variations in yields for silver among different leachants and samples. As seen in the introduction (vide Hydrometallurgy), thiosulfate and thiourea leaching systems exhibit complex chemistry, especially with complex samples such as PCBs. Several authors have mentioned the difficulty of stabilizing the systems, which is highly dependent on thermodynamic conditions [39]. It was also mentioned a high consumption of leaching agent, the easy oxidation of the agent in the presence of other metals in solution (such as copper) [62], or the formation of passivation surfaces, preventing contact between the leaching agent and the metal to be solubilized [47]. For example, thiosulfate can easily be oxidized in aqueous solution and tends to decompose into intermediate products [47], forming others sulfur species including sulfite, sulfate, and polythianates, depending on the pH and Eh [63], consuming the thiosulfate that otherwise would complex with the silver (solubilizing it).

Figure 26 - Decomposition route of thiosulfate, adapted from [47]

The extremely low yields for Thiourea treated samples, especially in comparison to the yields obtained with other leachants, raise questions about the effectiveness of Thiourea in this context. The system used was based on the work of A. Behnamfard and colleagues in 2013 [43] that showed the optimization of several parameters, and it achieved high metal recovery rates, but also refer that copper has the effect to passivate the surface affecting leaching of target metals. This was the main reason to add ammonia and copper (0.02M NH4OH, 0.02M

CuSO4) to thiosulfate system, preventing the buildup of sulfur layers on the metal surface. The same principle is behind the addition of Fe^{3+} to Thiourea system since this oxidant is essential to dissolve sulfides and maintain the stability of thiourea as a leaching agent. Nevertheless, this addition, apparently, didn´t prevent the sulfur layers to form or other unwanted side reactions that didn't oxidized the metal. Also, silver is known to form insoluble complexes with several ions. So perhaps, even if is leached it might react with ions to form insoluble complexes.

For this reason, a first step of base metals leach (especially the copper) seams mandatory in order to effectively leach precious metals such as Gold or Silver, otherwise lixiviants could degrade before reaching the target.

Since this pretreatment wasn't conducted in our assays, it could explain the poor yields obtained when leaching complex samples rich in copper, such as in PCBs and Umicore motherboard samples.

The color variation observed during assays for the same system (in this case Thiosulfate with Sample a) silver, illustrated in Figure 27, could also suggest the degradation reactions of thiosulfate, forming sulfuric precipitates.

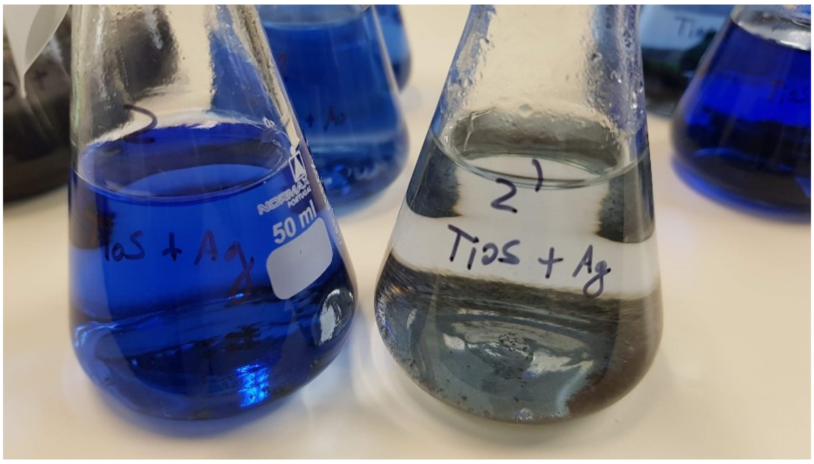


Figure 27 - Color variation illustration, in this case using the same sample a) pure Ag and lixiviant system (thiosulfate).

The existence of intermediate products is related with the decision to exclude results obtained from the spectrophotometer, since for the correct determination of metal ions concentration using this equipment, a suitable chemical reaction or complex formation is necessary, to selectively react with the metal ion of interest and form a colored complex, not compatible with the complex chemistry and instability observed in these trial reactions.

The PCB samples were prepared according to chapter 3 and fragmented using cutters. The obtained fragments (squares) were approximately 10 mm in size. In the literature, it is stated that the optimal particle size is less than 2 mm [64], ensuring an increase in specific surface area. However, the same studies suggest that for particle sizes inferior to 3 mm, the leaching of precious metals is compromised. This can be explained, once again, by the increase of copper in solution, promoted by particle size reduction. The cupric ion oxidizes thiourea and forms a protective layer on the precious metal surface, negatively affecting the intended chemical reaction.

Depending on the target metal and samples, the use of unshared or selected parts of PCBs for leaching precious metals, could be justified, as Kasper and coworkers defend in their work in 2011 [64]. This prevents the liberation of base metals such as copper to the solution and could improve the lixiviation of target metals.

It is also important to mention that the low yields could also be explained by the theoretical concentration of silver in PCBs used for the determination. This concentration is derived from the study of X. Wang and G. Gaustad in 2012 [3] and being an estimation and not a measured value for the samples used in trials. This can influence the results, whether by excess or by defect. Some authors have determined that silver concentration in PCBs could vary from 0.05% to 0.20%, meaning that the concentration predicted (0.13%) could influence the analyze of the results.

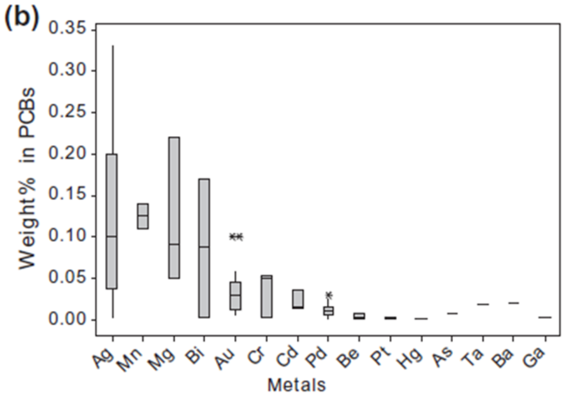


Figure 28 Compositional variation of metals in PCBs adapted from [3] *Gaustad and colleagues work in 2012.*

To avoid this bias a complete digestion and characterization of the samples used should be conducted to determine the exact amount of silver present and enable the exact yield determination.

5. CONCLUSIONS

E-Waste is increasing rapidly, and strategies to deal with it must be improved to reduce impact. Among the several approaches, advancements in recycling technologies hold significant importance.

WEEE, especially PCBs, still holds significant potential, particularly in recycling valuable elements like silver, which is one of the top priorities for recovery.

Due to its complex composition, PCBs recycling requires a multistep approach, generally a three-step procedure involving pre-treatment, metal enrichment, and metal recovery/purification.

Current recycling technologies for the metal recovery in WEEE are pyrometallurgical, hydrometallurgical, biometallurgical processes, as well as some hybrid processes.

Pyrometallurgy is considered the most common and adopted method in big scale operators, The main advantage of pyrometallurgical treatment is its ability to accept any forms of scrap (including complex substrates) but high energy consumption, pollution and implementation cost are appointed as the main disadvantages.

Hydrometallurgy has emerged as a promising approach due to its selectivity, low energy demand and lower implementation costs. However, the use of strong solvents poses risks to both people and the environment. Complex chemistry obligates to carefully control of thermodynamic parameters; otherwise, leaching may not be feasible. Greener options are being studied in order to increase leaching kinetics, as well as lowering the environmental impact.

Biometallurgical techniques offer a great hope in the precious metal recovery, due to their sustainability potential. Nevertheless, it requires enhancement of the metal recovery kinetics, more studies on the microbial community and development of more efficient genetically engineered microorganisms with improved rates for metal solubilization.

Outcomes obtained in the present work showed a substantial variation in silver yields among different leachants and equipment. Sulfuric acid emerges as the most effective, yielding a remarkable 99.7% for pure silver, followed by Ammonium thiosulfate with a 72.5% yield. PCBs are complex samples, and the use of thiosulfate and thiourea solutions for silver extraction, under the conditions tested, did not show positive results.

The complex chemistry of reactions, particularly with complex samples like PCBs, poses challenges to silver extraction. Thiosulfate oxidation, competitive degradation reactions, and the influence of copper as a destabilizing factor contribute to the observed low yields.

This work has demonstrated that the implement of a pre-leaching step specifically targeting base metals before initiating the extraction of precious metals is crucial for precious metal leaching afterwards.

The absence of a complete characterization of the PCBs, prior to the trials may be a source of error in silver determination. Also, the limitations associated with the unknown origin and pre-treatment of the Umicore sample emphasize the importance of complete sample characterization before trails. Also, the low amount of silver in the unknown composition of Umicore samples might just mean that these samples didn't have silver to begin with.

The review of literature shows that the most common techniques for quantification in Hydrometallurgy are ICP-OES and AAS, and results showed that, although theoretically possible, the use Spectrophotometry to determine the concentration of ions in complex solutions is challenging due to the presence of other ions and complexes that might affect the absorbance measurements.

It is crucial to acknowledge that the application of alternative leaching agents for precious metal recovery from WEEE remains an active area of research and development. Despite their promising advantages, certain challenges, including process optimization, scalability, and cost-effectiveness, require careful consideration and future work should be conducted.

6. FUTURE WORK

The work conducted has enabled to identify a set of tasks that can be pursued in the future, aiming to provide further insights into the raised questions and explore alternative leaching agents that are not only efficient but also environmentally sustainable, namely:

Continue research on the thiosulfate system by refining the addition of ammonia and copper to prevent unwanted reactions.

Conduct further experiments to optimize the conditions for Thiourea leaching. Adjust parameters such as concentration, pH, and exposure to ultraviolet light to enhance its stability and potentially improve yields.

Explore and implement a pre-leaching step specifically targeting base metals before initiating the extraction of precious metals.

Explore other possible leachants such as glycine, that can even be produced biologically by certain microorganisms, such as *Chromobacterium violaceum*. These microrganisms can also leach metals, in complexation reactions [65].

Revisit the decision to exclude spectrophotometer. If feasible, explore alternative chemical reactions or complex formations compatible with the observed complex chemistry and instability. This may contribute to achieve a more sustainable and easier to access method to quantify metals in solution.

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