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INNOVATIVE TREATMENTS FOR RESOURCE RECOVERY FROM WASTE ELECTRICAL AND ELECTRONIC EQUIPMENT

TRATTAMENTI INNOVATIVI PER IL RECUPERO DI RISORSE DAI RIFIUTI DI APPARECCHIATURE ELETTRICHE ED ELETTRONICHE

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INDEX

INDEX i
List of figures iii
List of tables vii
Abstract ix
Sommario xiii
Acknowledgments xvii
About the author xviii
1 INTRODUCTION 1
  1.1 Objectives 2
  1.2 Outline 4
2 THE MANAGEMENT OF WEEE 7
  2.1 Production and management practices 9
  2.2 Regulations and policies 15
3 WEEE: "URBAN MINING" AND HAZARDOUS WASTE 21
  3.1 Material composition 21
  3.2 Metal content 24
    3.2.1 Common metals 25
    3.2.2 Precious metals 28
    3.2.3 Rare earth elements 31
4 THE RECOVERY OF METALS FROM WEEE 37
  4.1 Mechanical treatments 39
  4.2 Pyrometallurgy 43
  4.3 Hydrometallurgy 48
    4.3.1 Metal leaching from WEEE 50
  4.4 Biometallurgy 56
    4.4.1 Bioleaching processes for metal recovery from WEEE ... 57
5 RESEARCH EXPERIMENTAL ACTIVITY 65
  5.1 Investigation plan 65
6 MATERIALS AND METHODS 69
  6.1 Material characterization 69
    6.1.1 Sampled materials 69
    6.1.2 Metal content 72

- 6.1.3 Particle size characterization ... 72
- 6.2 Mass flow analysis ... 73
- 6.3 Hydro-biometallurgical processes ... 74
  - 6.3.1 Dust used as source material for leaching tests ... 74
  - 6.3.2 Chemical leaching experiments ... 75
  - 6.3.3 Biological leaching experiments ... 77
  - 6.3.4 Analytical methods ... 83
- 7 RESULTS AND DISCUSSIONS ... 85
  - 7.1 Material characterization ... 85
    - 7.1.1 Metal content ... 85
    - 7.1.2 Size distribution ... 87
  - 7.2 Effectiveness of mechanical treatments ... 89
    - 7.2.1 Metal recovery yields ... 89
    - 7.2.2 Quality of output fractions ... 91
  - 7.3 Hydro-biometallurgical processes for critical metal recovery ... 93
    - 7.3.1 Dust characterization ... 93
    - 7.3.2 Chemical leaching ... 95
    - 7.3.3 Biological leaching ... 102
  - 7.4 Technical aspects and process scale-up opportunities ... 110
- 8 CONCLUSIONS ... 115
- References ... 119

LIST OF FIGURES

Figure 2.1 Theoretical circular economy scheme for WEEE management: (1) WEEE collection; (2) WEEE treatment; (3) Return of recovered materials into the market; (4) manufacturing of new EEE; (5) commercialization of new EEE (Chagnes et al., 2016). 8
Figure 2.2 WEEE generated in 2014 in non EU countries (www.step-initiative.org) 11
Figure 2.3 WEEE generated in 2014 in EU countries (www.step-initiative.org) 11
Figure 2.4 Benefits of WEEE recycling (Priya and Hait, 2017) 12
Figure 2.5 Steps involved in WEEE recycling chain with output products and economic impacts (Tanskanen, 2013) 13
Figure 2.6 Stakeholders in WEEE management system 17
Figure 2.7 EPR strategy implementation in several countries for WEEE management (Li et al., 2013) 19
Figure 3.1 Schematic distribution of WEEE composition in terms of items (Kaya, 2016) 22
Figure 3.2 WEEE material composition (adapted from Widmer et al. 2005 and (Tuncuk et al., 2012) 23
Figure 3.3 Critical raw materials for the EU's economy (European Commission 2014) 33
Figure 3.4 Medium-term criticality matrix defined by U.S. Department of Energy (U.S. Department of Energy, 2011) 33
Figure 4.1 General flowchart of processes involved in the metal recycling from WEEE (Priya and Hait, 2017) 38
Figure 4.2 Schematic flowchart of typical WEEE mechanical treatments (Tuncuk et al., 2012) 40
Figure 4.3 Grade-recovery curve (Meskers et al., 2009) 41
Figure 4.4. Noranda schematic smelting process (Cui and Zhang, 2008) 45
Figure 4.5 Boliden Rönnskår schematic smelting process (Chagnes et al., 2016) 46
Figure 4.6 Flowsheet of the recovery process at Umicore (www.umicore.com) 47

Figure 4.7 General flowchart of hydrometallurgical processes for metal recovery from WEEE (adapted from Chagnes et al., 2016) 50
Figure 6.1 Schematic flowchart of the mechanical process under investigation 70
Figure 6.2 Sampled material: (a) plastic, (b) dust, (c) aluminium grains, (d) copper grains 71
Figure 6.3 Reflux condenser system for sample digestion prior ICP-OES analysis 72
Figure 6.4 Dust material used for hydro-biometallurgical tests 74
Figure 6.5 Schematic flowchart of the chemical leaching process performed 75
Figure 6.6 Schematic flowchart of the biological leaching process performed 79
Figure 6.7 Bioleaching medium containing active growing cultures of *A. thiooxidans* (a), inoculated and non-inoculated bioleaching medium (b), bioleaching medium containing active cultures and dust material at different pulp density (c), bioleaching experiments (d) 80
Figure 6.8. Inoculated bioleaching medium containing active growing cultures of *P. putida* and non-inoculated flasks (a), colour reaction proving the CN^- production of *P. putida* (b) 81
Figure 6.9 Cyanide production of *P.putida* as function of various glycine concentrations (5 g/L, 7,5 g/L, 10 g/L) and time of inoculation (Işıldar et al., 2016) 82
Figure 7.1 Particle size distribution of Al and Cu grains 88
Figure 7.2 Metal distribution in the output fractions from the mechanical treatment process under investigation 89
Figure 7.3 Mass flows of valuable and critical metals throughout the mechanical treatment under investigation 91
Figure 7.4 XRD pattern of dust material 95
Figure 7.5 Extraction yields of selected metals after 6 h chemical leaching using sulphuric acid and hydrogen peroxide 96
Figure 7.6 Extraction yields of gold over thiourea leaching runs 99
Figure 7.7 Results of ANOVA (RStudio) 100
Figure 7.8 Results of the multiple linear regression (RStudio) 101
Figure 7.9 Results of Shapiro and Bartlett tests for checking ANOVA assumptions 102
Figure 7.10 pH (a) and ORP (b) profiles during *A. thiooxidans* bioleaching at different pulp density 103

Figure 7.11 Extraction yields of selected metals after 8 days bioleaching using *A. thiooxidans* at different pulp densities 104
Figure 7.12 REE leaching profile over 8 day bioleaching process.........105
Figure 7.13 pH profile during bioleaching experiment using *P.putida* for washed (a) and unwashed (b) dust material..107
Figure 7.14 Gold mobilization during bioleaching experiment using *P. pudita* for washed and unwashed dust...108
Figure 7.15 Gold extraction during chemical leaching at different cyanide concentrations..110
Figure 7.16 A circular economy approach for the management of dust coming from WEEE mechanical treatments 112
Figure 7.17 Comparison of capital costs (a) and operating costs (b) for smelting and bioleaching processes for copper mining recovery (OECD, 2001)..113

LIST OF TABLES

Table 3.1 Hazardous components and substances of concern commonly found in WEEE (Tsydenova and Bengtsson, 2011) 24
Table 3.2 Concentrations of selected common metals in PCBs of different equipment types (Oguchi et al., 2011, 2013) 25
Table 3.3 Common metal content in selected WEEE (elaborated from Cucchiella et al. 2015 and Hagelüken, 2006) 26
Table 3.4 Concentrations of precious metals in PCBs of different equipment types (adapted from Chancerel et al., 2009; Oguchi et al., 2011, 2013) 29
Table 3.5 Precious metal content in selected WEEE (elaborated from Cucchiella et al., 2015 and Hagelüken, 2006) 30
Table 3.6 Percentage distribution of rare earths by application (%)(Binnemans et al., 2013) 32
Table 3.7 Advantages of recycling REEs from waste streams (Tunsu et al., 2015) 34
Table 3.8 End of life products containing REEs (adapted from Tunsu et al., 2015) 34
Table 3.9 REE composition in fluorescent lamp, NdFeB permanent magnets and NiMH batteries (adapted from Tunsu et al., 2015) 35
Table 3.10 REE content of selected WEEE (Cucchiella et al., 2015) 36
Table 4.1 Main features of some mechanical processes (Yu et al., 2009) 42
Table 4.2 Pyrometallurgical plant treating electronic waste (Chagnes et al., 2016) 44
Table 4.3 Literature studies on leaching processes for metal recovery from WEEE 53
Table 4.4 Bioleaching studies for metal recovery from WEEE 62
Table 6.1 Factors and levels under investigation for tiourea leaching tests 77
Table 6.2 Experimental plan for thiourea leaching tests 77
Table 7.1 Average metal concentrations in WEEE fractions under investigation 86
Table 7.2 Size distribution of sampled dust 88
Table 7.3 Metal concentrations detected in the three size fractions of output metallic grains 91

Table 7.4 Average concentration of selected metals in dust (ISO 11466:1995) 94
Table 7.5 Percentage of gold extraction after 1 h using thiourea (TU) ... 99

ABSTRACT

The ever-expanding population, the increasing consumption of resources and the shortage of primary raw materials have addressed the transition of waste management strategies from the linear model based on the "wear and tear" on a circular approach aiming at preventing waste and recycling materials. In this view, the attention has been focused on the use of anthropogenic stock resources in place of virgin materials as promoted by the concept of "urban mining".

Waste electrical and electronic equipment (WEEE) is regarded as the backbone stream in urban mining. It represents the waste stream characterized by the highest grow rate per year (3-5%) and by the most wide-ranging source of materials, since WEEE can contain more than 1000 different substances, including base, precious and critical metals.

The recovery of metals defined critical raw materials as rare earth elements from electronic waste appears, thus, an important opportunity both in economic and environmental terms.

However, the recycling of WEEE is challenged by the complex nature of such waste stream which, beside valuable materials, includes hazardous substances as well. The presence of these toxic components has raised great concern especially in developing countries where the informal recycling sector is still widespread, handling WEEE with unsafe and inadequate practices as a result of a lack of legislation.

In high-income countries, separate collection is the first step of a system pursuing the WEEE sustainable management; mechanical processes are then applied to separate the different materials, including metals which are destined to further recycling by means of metallurgical processes.

The metallurgical treatments currently used for metal recovery from WEEE are, however, claimed to have severe impacts on the environment due to the generation of secondary pollutants. Moreover, the industry of WEEE recycling is still in its early stage, especially if referred to the recovery of rare earth elements.

All these reasons have contributed to increase the interest of both scientific and industrial research in addressing a cost-effective and

environmental friendly treatment of end-of-life electrical and electronic products.
In this background the present research work aimed to:

- the characterization of WEEE in terms of base and critical metal contents, in order to identify and quantify the valuable materials and the hazardous substances for addressing a sustainable recycling strategy;
- the assessment of critical metal fate during the conventional mechanical treatments of WEEE with reference to the sorting effectiveness and the recycling potential;
- the evaluation of the feasible application of innovative treatments in the field of hydro- and bio-metallurgy for the recovery of valuable and critical metals from WEEE.

To this end, the experimental activity was developed in three main steps, matching the specific objectives of the research project:

- the first phase was focused on the characterization of WEEE in terms of base and critical metals. Representative samples were collected over the treatment chain of a full scale mechanical treatment plant operating in South Italy and analysed by their metal content;
- the data obtained from the metal characterization were, thus, used in the second phase to carry out a mass flow analysis in order to investigate the fate of metals, particularly the critical ones, during the conventional mechanical treatments;
- the third phase focused on hydro- and bio-metallurgical tests for the recovery of valuable and critical metals from WEEE. As the results from the previous phase pointed out that after the conventional mechanical treatments significant concentrations of precious metals and rare earth elements were gathered in dust stream originating from process air cleaning, dust was used as secondary source of critical metals and tested for the treatments proposed. Both chemical agents, including a non-conventional one as thiourea, and biological species were used to perform leaching processes. The use of dust, actually destined to landfill disposal, as well as the treatments investigated for the recovery of critical metals marked the novelty of the research.

The first two phases were carried out at the Sanitary Environmental Engineering Division (SEED) of Salerno University. The

hydrometallurgical tests included in the third phase were performed at SEED laboratory as well, whereas the biometallurgical tests were conducted at the laboratory facility of the Institute for water education Unesco-IHE in Delft (Netherlands).

Results of the experimental activity showed that rare earth elements contained in WEEE at trace concentrations do not enter the recovery chain as around 80% in mass were lost in dust streams during the conventional mechanical treatments. Similarly, 24% of precious metals entering the mechanical treatments were conveyed in the dust fraction. Therefore, this matrix appears a potential secondary source of valuable and critical metals to be further processed for metal recovery.

Chemical and biological leaching processes proved their great potential in extracting up to 99% of the critical metals contained in the dust. These promising outcomes suggested that both hydro- and bio-metallurgical processes can be regarded as a suitable option for the management of the dust fractions, which currently represents a cost for the treatment plant. The treatment of dust through these processes provides, indeed, a way to reintroduce this matrix, actually sent to landfill, in the "loop" of product lifecycle, thus limiting the losses of resources in accordance with the new circular economy approach. Moreover, the results of this study are of relevant interest as they highlighted the potential of recovering valuable and critical metals from waste streams using low-cost and environmentally friendly processes in the filed of biometallurgy as an effective alternative to both pyrometallurgical and conventional chemical processes, especially for treating low grade materials as WEEE.

SOMMARIO

La popolazione in continua espansione, il crescente sfruttamento delle risorse e la conseguente carenza di materie prime hanno orientato negli ultimi anni le strategie di gestione dei rifiuti da un approccio lineare basato sul modello del “estrai-produci-usa-getta” verso una visione circolare in cui i rifiuti di un’attività diventano materie prime per un’altra. L’attenzione è stata, pertanto, sempre più incentrata sulla possibilità di utilizzare i residui delle attività antropiche come scorte di materie secondarie in sostituzione di materiali vergini, così come promosso dal noto concetto dell’ “urban mining” o “miniere urbane”.

In tale contesto, i rifiuti di apparecchiature elettriche ed elettroniche (RAEE) costituiscono ad oggi delle vere e proprie miniere urbane. Tale flusso di rifiuti è caratterizzato dai maggiori tassi di crescita per anno (3-5%) e dalla più varia composizione di materiali dal momento che i RAEE possono contenere più di 1000 differenti sostanze, tra cui metalli di base, metalli preziosi e metalli critici.

La possibilità di recuperare dunque “materie prime critiche”, quali le terre rare presenti all’interno dei rifiuti elettronici, si configura come una importante opportunità sia in termini economici che ambientali.

Tuttavia, il riciclaggio dei RAEE è ostacolato dalla loro complessa natura che, accanto a materiali di valore, prevede anche sostanze pericolose. La presenza, difatti, di componenti tossiche è motivo di grande preoccupazione specialmente in riferimento ai paesi in via di sviluppo dove il “canale informale” è ancora ampiamente diffuso ed i RAEE vengono gestiti in maniera inadeguata in conseguenza di una mancanza di riferimenti normativi.

Nei paesi sviluppati, la raccolta differenziata è il primo step di un sistema che mira a perseguire una gestione sostenibile dei RAEE; processi di trattamento meccanico sono poi implementati per separare i metalli dai restanti materiali per il loro successivo recupero mediante processi metallurgici.

I trattamenti metallurgici attualmente utilizzati per il recupero dei metalli dai RAEE hanno tuttavia gravi impatti sull’ambiente a causa della produzione di rifiuti secondari. Inoltre, l’industria del riciclo dei RAEE è

ad oggi ancora nella sua fase iniziale soprattutto in riferimento al recupero delle terre rare.

Tutte queste ragioni hanno contribuito ad accrescere l'interesse sia del mondo scientifico che di quello industriale verso lo sviluppo di tecnologie a basso costo e minor impatto per il trattamento dei RAEE.

In tale contesto, il presente progetto di ricerca è stato mirato a:

- caratterizzare i RAEE in termini di metalli di base e metalli critici, in modo tale da identificare e quantificare il contenuto di materiali di valore e sostanze pericolose per sviluppare una valida e sostenibile strategia di trattamento;
- valutare il destino dei metalli critici nel corso dei convenzionali trattamenti meccanici dei RAEE con particolare riferimento all'efficienza di selezione e al potenziale di recupero;
- investigare la fattibilità dell'applicazione di trattamenti innovativi nel campo dell'idro- e della bio-metallurgia per il recupero dei metalli critici e di valore dai RAEE.

A tale scopo, l'attività sperimentale è stata sviluppata secondo tre fasi principali, funzionali al raggiungimento degli obiettivi specifici del progetto di ricerca:

- la prima fase è stata incentrata sulla caratterizzazione dei RAEE in termini di metalli di base e metalli critici. Campioni rappresentativi di RAEE sono stati prelevati presso un impianto di trattamento a scala reale localizzato nel Sud Italia e analizzati nel loro contenuto di metalli;
- i dati ottenuti dalla caratterizzazione sono stati quindi utilizzati nella seconda fase dell'attività, al fine di condurre un bilancio di massa per investigare il destino dei metalli, in particolare di quelli critici, durante i convenzionali trattamenti meccanici;
- la terza e ultima fase è stata focalizzata sull'applicazione dei processi idro- e bio-metallurgici per il recupero dei metalli critici e di valore dai RAEE. Dal momento che i risultati della fase precedente hanno evidenziato che a seguito dei convenzionali trattamenti meccanici significative concentrazioni di metalli preziosi e terre rare vengono raccolte nelle polveri originate dal processo di trattamento dell'aria, tale matrice è stata utilizzata come fonte secondaria di metalli critici per testare i trattamenti proposti. Sia agenti chimici, tra cui un agente non convenzionale come la tiourea, che agenti biologici sono stati utilizzati per eseguire le prove di lisciviazione. L'uso della polvere, al

momento destinate a smaltimento a discarica, ed i trattamenti proposti per il recupero dei metalli critici hanno segnato l'innovazione della ricerca.

Le prime due fasi sono state svolte presso la Divisione di Ingegneria Sanitaria Ambientale (SEED) dell'Università degli studi di Salerno. Le prove idrometallurgiche incluse nella terza fase dell'attività sperimentale sono state anch'esse condotte presso il laboratorio SEED mentre le prove biometallurgiche sono state svolte presso il laboratiorio dell'Istituto Unesco-IHE di Delf (Paesi Bassi).

I risultati dell'attività sperimentale condotta hanno mostrato che le terre rare presenti in tracce all'interno dei RAEE non entrano nella catena di recupero, dal momento che circa l'80% in massa risulta concentrato in flussi, quali le polveri, non destinati al successivo recupero. In maniera analoga, il 24% dei metalli preziosi contenuti nei RAEE in ingresso al trattamento meccanico sono raccolti all'interno di tale frazione. Le polveri si configurano, pertanto, come una potenziale fonte secondaria di materiali critici e di valore da essere sottoposta a successivo recupero.

I processi idro- e biometallurgici applicati hanno mostrato il loro grande potenziale nel recupare fino al 99% dei metalli critici concentrati nelle polveri. Tali promettenti risultati hanno evidenziato che i processi idro- e biometallurgici possono essere considerati come una valida opzione di gestione delle polveri derivanti dal trattamento meccanico dei RAEE che attualmente rappresentano un costo di smaltimento per l'impianto. Il trattamento delle polveri mediante tali processi fornisce una strategia per reintrodurre tale matrice, al momento smaltita in discarica, nella spirale del ciclo di vita dei prodotti, limitando la perdita delle risorse in essa contenute in accordo con l'approccio promosso dall'economia circolare.

Inoltre, i risultati del presente studio sono di rilevante interesse dal momento che hanno mostrato, in particolare, il potenziale di recupero di metalli critici e di valore dai RAEE mediante processi a basso costo e basso impatto nel campo della biometallurgia, come valida alternativa ai convenzionali trattamenti piromentallurgici ed idrometallurgici.

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1 INTRODUCTION

As a consequence of the shorter lifespan of many electrical and electronic equipment (EEE) due to the continuous replacement of obsolete devices with new technologically advanced versions, the generation of waste electrical and electronic equipment (WEEE) has continuously increased over time (Tanskanen, 2013). In 2014 approximately 41.8 million tons of WEEE were estimated to be globally generated (Baldé et al., 2015) and around 65.4 million tons have been predicted in 2017(UNEP, 2013).

Beside the large volume of WEEE produced, accounting for about 8% of total municipal waste (Widmer et al., 2005), the composition of electronic waste requires the identification of proper management strategies due to the presence of both valuable materials and hazardous components. Some harmful substances, as heavy metals and flame retardants, contained in certain parts or components of electronic appliances can pose risk for environment and human health in consequence to an improper management of such waste stream (Tsydenova and Bengtsson, 2011). On the other hand, as the electronic waste contains relatively high concentrations of metals, it can represent a potential secondary source of these materials (Lee and Pandey, 2012; Tuncuk et al., 2012). In this respect, WEEE is regarded as a backbone stream in “urban mining”, especially for the presence of rare earth elements (REEs) which are classified as critical raw materials with high industrial interest (Cossu and Williams, 2015). The recycling of these strategic metals from WEEE is, thus, a relevant opportunity in both environmental and economic terms (Cui and Zhang, 2008), specifically in the transition towards a circular economy approach aiming at the sustainable management of the resources.

In European Union and in most high-income regions worldwide the management of WEEE is covered by regulations encouraging its separate collection and recycling.

Mechanical processes, pyrometallurgy and hydrometallurgy are the technologies currently involved in the recycling of WEEE (Cui and Zhang, 2008; Khaliq et al., 2014; Priya and Hait, 2017).

Mechanical treatments play a significant role in the WEEE recycling as they determine the amount of material entering the further recovery chain. Although these processes are well designed to recovery base metals, precious metals are often lost as a result of the shredding action of size reduction processes (Bachér et al., 2015; Chancerel et al., 2009). Moreover, the fate of rare earth elements during mechanical treatments has not been addressed yet.

Pyrometallurgy and hydrometallurgy are techniques coming from the mineral sector. Pyrometallurgy is a well-consolidated thermal treatment which has been used in the past years for the recovery of base metals as well as precious metals from WEEE (Cui and Zhang, 2008). Hydrometallurgy is a technique for extracting the metal of interest from the solid matrix by means of acid or alkaline solutions. Both these metallurgical treatments are claimed to produce significant impacts on the environment due to the generation of secondary pollutants, including gaseous emission in the case of pyrometallurgical processes and toxic effluents for hydrometallurgical ones. For this reason, the necessity to set environmental friendly treatments has directed the scientific research towards the biometallurgy as a low cost and minor impact technique (Cui and Zhang, 2008; Das et al., 2009; Ilyas et al., 2010; Pant et al., 2012; Tuncuk et al., 2012).

Biometallurgy exploits the ability of certain microorganisms or biomass either for leaching metals through oxidation-reduction reactions (bioleaching) or for binding metals present in solutions (biosorption). Although bioleaching has been successful used for the extraction of metals from sulphide minerals and biosorption has resulted effective for the removal of metals from wastewater (Cui and Zhang, 2008), the application of these processes for recovering metals from WEEE needs to be deeply investigated, especially with reference to rare earth elements (Ilyas and Lee, 2014) whose recovery rate from secondary resources as electronic waste is still very low (Binnemans et al., 2013).

1.1 OBJECTIVES

The general aim of the present research project is the investigation of innovative solutions for resource recovery from WEEE.

As a comprehensive understanding of the characteristics of the material to be treated is essential in order to set a sustainable recycling strategy (Chancerel and Rotter, 2009; Cui and Forssberg, 2003), the material composition of WEEE was deeply studied with a focus on the contents of both base and special metals, as precious metals and rare earth elements. In this regard it is worthy outlining that data on REE concentrations in electronic waste are rather fragmented due to trade secrets which often cover some devices (Buchert et al., 2012). The analysis of the scientific literature pointed out that valuable metals are mainly found in small household electronic equipment (Chancerel and Rotter, 2009; Oguchi et al., 2011). For this reason, a full scale facility treating mechanically electronic waste coming from this equipment category was selected for the experimental purposes.

Although base metals, which represent the greatest portion of the metallic components in electric and electronic devices, can be successfully sorted from WEEE through mechanical treatments, literature studies highlighted that these processes do not allow the effective recovery of precious metals, which are often lost in wrong output streams, remaining attached to other components, or in dust fractions as a result of shredding actions (Meskers and Hagelüken, 2009; Meskers et al., 2009). Moreover, the fate of rare earth elements during these processes has not been fully investigated. To this end, a mass flow analysis was conducted based on the mechanical process performed at the plant under investigation in order to point out the effectiveness of mechanical treatments in critical metal sorting and recovery.

Since the results of the substance flow analysis revealed that significant concentrations of precious metals and rare earth metals ended up in the dust fraction originated from air process treatment, the dust was used as source material for testing the innovative treatments proposed. Both chemical and biological leaching processes were chosen in order to compare their effectiveness and evaluate their feasibility in extracting critical metals. In this view, a sustainable management approach promoting the recovery of valuable resources from materials actually disposed of in landfill was proposed.

The use of dust fractions as secondary source of rare earth elements and the application of biometallurgical treatments for the recovery of critical metals mark the novelty of the work.

Under this framework, the specific objectives of the research can be summarised as follow:

- the characterization of WEEE in terms of base and critical metal contents, in order to identify and quantify valuable materials and hazardous substances for addressing a cost-effective and environmental friendly recycling strategy;
- the assessment of the fate of critical metals during the mechanical pre-treatment of WEEE, with reference to the sorting effectiveness and the recycling potential;
- the evaluation of the feasible application of both hydro- and bio-metallurgical processes for the recovery of valuable and critical metals from WEEE.

In order to achieve these objectives, an experimental activity was developed in the following three steps matching the specific objective of the research project:

- Phase 1: WEEE characterization in terms of base and critical metals;
- Phase 2: Mass flow analysis of critical metals in WEEE mechanical treatments;
- Phase 3: Hydro- and bio-metallurgical tests for critical metal recovery from WEEE.

The first two phases were carried out at the Sanitary Environmental Engineering Division (SEED) of Salerno University. The hydrometallurgical tests included in the third phase were performed at SEED laboratory as well, whereas the biometallurgical tests were conducted at the laboratory facility of the Institute for water education Unesco-IHE in Delft (Netherlands).

1.2 OUTLINE

The thesis is organized in eight chapters.

The management of waste shaped around material recovery is addressed by legislation and further promoted by clearly identified economic drivers boosting the business. In this view, the first chapters aimed at providing the regulatory framework for WEEE handling, including its recovery, as well as data indicating the economic potential for WEEE recovery. To this end, Chapter 2 introduces the management of WEEE and the strategies legally established to ensure its sustainability in European Union as well as in other high-income countries.

The material composition of WEEE is deeply examined in the third chapter with a special focus on the metal content in terms of common metals, precious metals and rare earth elements as the recovery of metals is considered the major economic driver in WEEE recycling.

Technologies conventionally used to sort and recover metals from WEEE, including mechanical treatments, pyrometallurgical and hydrometallurgical processes are overviewed in Chapter 4. Advantages and drawbacks are highlighted and the current status of their application is provided as well. Moreover, recent developments in the novel field of biometallurgy are discussed, so as to identify the main aspects to be analysed for their application in the field of WEEE.

Chapter 5 describes the overall investigation plan and the three main phases that were developed to pursue the research objectives.

The experimental set up and the analytical methods followed to carry out the research were outlined in Chapter 6. The chapter includes three sections referring to the three phases of the experimental plan.

In the Chapter 7 the results of the research activity are discussed. Wider considerations on technical aspects and process scale up opportunities are provided as well. On the basis of these outcomes, conclusive remarks and future perspectives were outlined in the last chapter.

2 THE MANAGEMENT OF WEEE

The increasing global production of electrical and electronic equipment (EEE) and its continuous consumption have led to the rapidly growth of the amount of obsolete electronic devices becoming waste electrical and electronic equipment (WEEE) (Tanskanen, 2013). The terminology "electronic waste" or "e-waste" is also widely used to identify WEEE.

WEEE includes a wide variety of end-of-life items and equipment which results in an extremely variable composition of such waste stream in terms of both materials and components (Chancerel and Rotter, 2009).

The presence of hazardous substances, such as heavy metals and flame retardants, in certain components or parts of electronic waste is cause of concern as an improper management of such waste can lead to the release of these substances into the environment (Tsydenova and Bengtsson, 2011). Nevertheless, WEEE contains valuable and critical materials whose recovery in recycling processes is profitable (Tanskanen, 2013). For instance, in 2014 it was estimated an intrinsic material value of global WEEE accounting for about 48 billion euro (Baldé et al., 2015).

The increasing amount of WEEE generated because of the continuous expansion of EEE market and the shorter life-cycle of electronic products represents a matter of concern as well. Although in European Countries as well as in most high-income regions the management of WEEE is well regulated, in many nations, especially developing countries, there is still a lack of legislation and the management of this waste stream, often illegally exported, is implemented by an "informal" sector with uncontrolled recycling practices (Tanskanen, 2013).

All these aspects, thus, point out the importance of organizing and optimizing the management system of WEEE with the opportunity for valuable materials to return back to the economy through the widely promoted approach of the "circular economy". This new strategy aims at "closing the loop" of product lifecycle, encouraging its recycling and re-use in order to bring benefits for both the environment and the economy (www.ec.europa.eu).

A theoretical circular economy scheme for WEEE management is reported in Figure 2.1. It basically includes the collection of end-of-life EEE, its treatment, the return of recycled materials into the market, the manufacturing of new EEE and its distribution.

Figure 2.1 Theoretical circular economy scheme for WEEE management: (1) WEEE collection; (2) WEEE treatment; (3) Return of recovered materials into the market; (4) manufacturing of new EEE; (5) commercialization of new EEE (Chagnes et al., 2016).

However, the adoption of a circular economy approach to WEEE management faces some challenges, which currently limit its real implementation (Chagnes et al., 2016).

The efficiency of WEEE recycling chain is highly challenged by its heterogeneity which poses some technical obstacles. Moreover, the resale of recovered materials is extremely affected by the market prices that can fluctuate over time, especially for critical raw materials, influencing the recycling chain. Recycled materials need also to be accepted by the consumers. Indeed, social aspects play a key role for the recycling system as well. In this case, the awareness of consumers can significantly contribute to an effective WEEE collection that is the earlier step of the overall recycling chain (Chagnes et al., 2016). For instance, a relevant portion of small electronic devices, such as mobile phones, is still stored by consumers at home and kept out of the potential recovery or disposed of together with other municipal waste (Baldé et al., 2015).

Therefore, an integration of social, cultural, economic, environmental and technical aspects is a fundamental prerogative for developing an effective and sustainable WEEE management system (Chagnes et al., 2016).

This chapter deals with the main aspects related to the management of electronic waste. E-waste production is explored in order to outline the magnitude of the problem. WEEE management practices are further discussed with particular reference to recycling as important option of management. A brief overview of regulations and policies addressing the management of WEEE is provided as well.

2.1 PRODUCTION AND MANAGEMENT PRACTICES

WEEE is considered one of the faster growing waste stream in EU, with an annual increasing rate of 3-5% (www.ec.europa.eu).

Although the quantification of WEEE flows is a fundamental prerequisite for developing effective and sustainable management solutions, the global monitoring of such waste streams is challenged by lack of reliable data. The difficulty of mapping e-waste flows is related to several factors as: (i) the collection outside official take-back systems in developed countries; (ii) the transboundary movement of electronic waste mostly from developed to developing countries; (iii) the informal collection systems in developing countries. A limited number of countries has actually an official take-back system. However, the existence of a legal take-back system does not imply the existence of a sufficient management system as it often covers in some countries only few e-waste categories. Furthermore, a significant issue is represented by the untracked export of second hand EEE as well as the illegal export of WEEE in developing countries, where electronic waste are treated and handled under unsafe conditions. Moreover, the different lifespan of electronic devices within the several categories and the habitual accumulation of obsolete small equipment in households contribute to the challenge of WEEE quantification (Baldé et al., 2015; Bigum et al., 2012).

A first kind of e-waste world-map was provided by the Step Initiative (www.step-initiative.org). This map includes data on both the amount of EEE put on market and WEEE generated by most countries worldwide. Amount of WEEE produced in 2014 by some nations both including non EU countries and EU countries is displayed in Figure 2.2 and Figure 2.3, respectively.

Values reported in figures refer to domestic WEEE and do not include import and export of electronic waste as well as its components and fractions. In 2014 United States were the major WEEE producer with 7072 kilo tons of electronic waste generated. China follows the top of the ranking, generating 6033 kilo tons of WEEE; Japan and India were just behind with a production of 2200 and 1641 kilo tons, respectively. As evident, e-waste generation is positively correlated with population. Considering the production of WEEE per inhabitant, it is clearly dependent on the wealth of populations (Priya and Hait, 2017). Hence, the amount of e-waste generated per capita varies considerable among high-income countries and less rich ones. For instance in Denmark, Sweden, France, Austria, Germany, Belgium, Norway and Switzerland the WEEE pro-capita production reaches values above 20 kg per inhabitant while in countries as India, Philippines and Africa it remains rather low.

In 2014 41.8 million tons of WEEE have been estimated to be globally generated. This production, corresponding to 5.9 kg per capita, is expected to rise up to approximately 50 million tons in 2018. However, only 6.5 million tons of WEEE have been reported to be formally treated in the same year, corresponding to the 15.5% of the totally generated WEEE (Baldé et al., 2015).

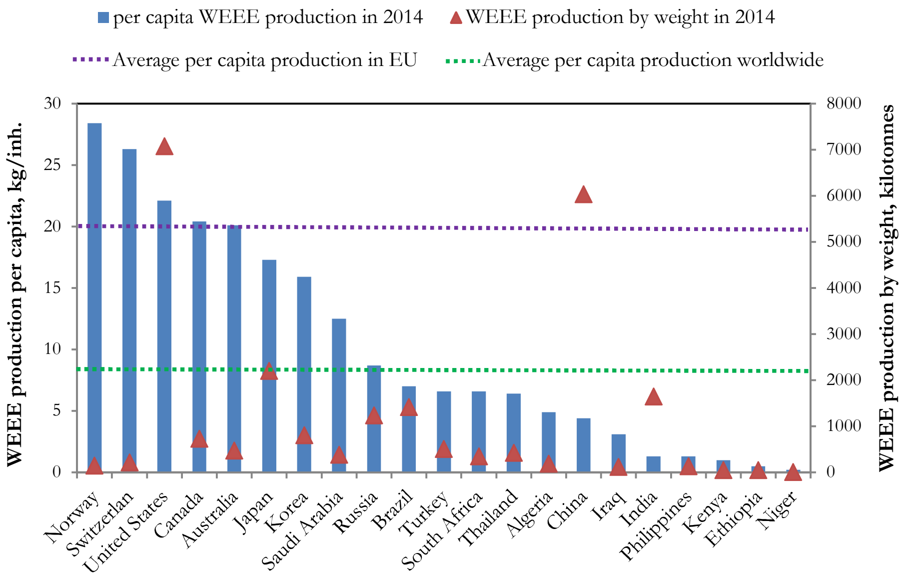


Figure 2.2 WEEE generated in 2014 in non EU countries (www.step-initiative.org)

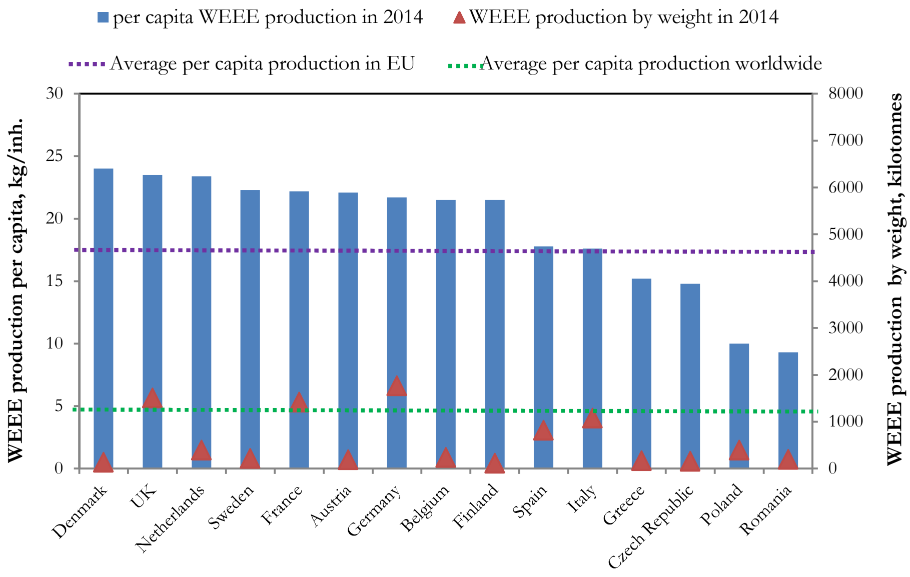


Figure 2.3 WEEE generated in 2014 in EU countries (www.step-initiative.org)

The management of e-waste involves the following options: reuse, remanufacturing, recycling, incineration and landfilling. According to the principles of “waste hierarchy”, the reuse of end-of-life appliances is encouraged as a first priority in WEEE management. The product remanufacturing, consisting in rebuilding, repairing, and restoring the equipment, is recommended as second option, followed by material recovery through recycling techniques. Incineration and landfilling are finally regarded as the least disposal options (Cui and Zhang, 2008; Priya and Hait, 2017). Nevertheless, open dumping is the most widespread practice of management used in many developing countries where an improper WEEE handling is widely practised. Open burning and uncontrolled acid/cyanide leaching activities are carried out in these territories as well, endorsing the existence of an informal recycling sector dealing with serious risks for both human health and environment (Kaya, 2016). This sector, consisting mainly of small workshops or backyard workshops, is primarily encouraged in regions where lack of measures of environmental pollution control, low labour costs and large demand of low-price secondary materials occur (Ongondo et al., 2011).

The recycling of WEEE represents an important option of management as it offers several benefits (Figure 2.4) from the point of waste treatment as well as of resource recovery (Cui and Zhang, 2008; Priya and Hait, 2017).

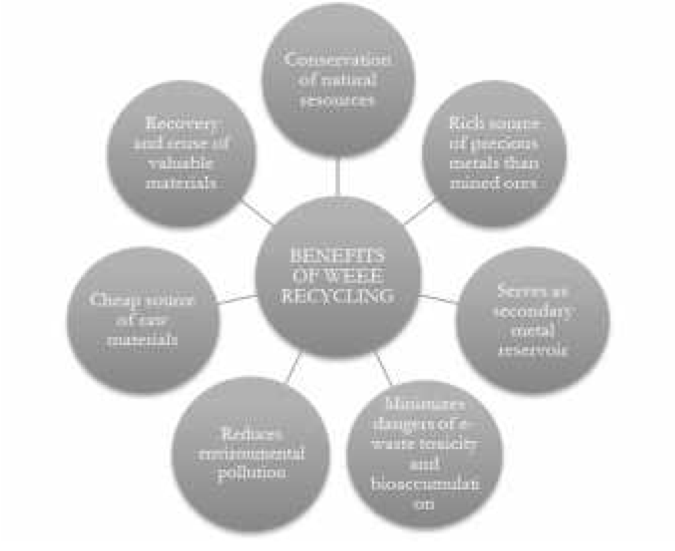


Figure 2.4 Benefits of WEEE recycling (Priya and Hait, 2017)

As WEEE is composed by a relevant quantities of metals, its recycling is of particular interest. Metals can be, indeed, eternally recycled maintaining their quality and functionality. Moreover, recycling metals from secondary source instead of using virgin materials results in energy saving: the extraction of these materials from waste is less energy intensive than their mining as the metal concentration in certain equipment is higher than in ores (i.e. for precious metals). Furthermore, burdens related to primary mining are reduced and the conservation of resources is pursued, especially for critical raw materials. Environmental impacts are reduced as well since avoiding landfill and incineration of metals means prevent both the loss of valuable materials and the release of harmful substances into the environment (Cui and Zhang, 2008; Hageluken, 2006; Khaliq et al., 2014; Priya and Hait, 2017).
Currently the WEEE recycling chain consists of three major steps (Meskers and Hagelüken, 2009; Tanskanen, 2013): (i) collection, (ii) pre-processing, (iii) end-processing (Figure 2.5).

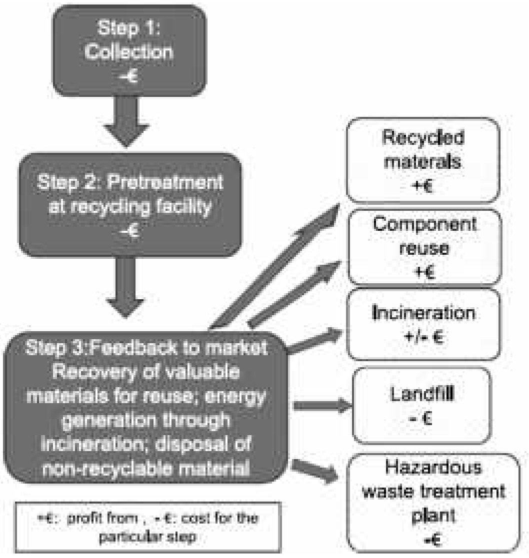


Figure 2.5 Steps involved in WEEE recycling chain with output products and economic impacts (Tanskanen, 2013)

The collection of electronic waste is a fundamental step as it determines the amount of materials entering the overall chain (Meskers and

Hagelüken, 2009). It requires a high level of consumer awareness in order to make the obsolete electronic devices available for recycling (Tanskanen, 2013). This step takes place locally and it is promoted by government policies, advertisement for public awareness and separate collection facilities installed at public places (Khaliq et al., 2014). Municipalities and citizens are the most important actors in WEEE collection operations (Favot and Marini, 2013).

Pre-processing includes pre-treatments such as mechanical processes and disassembly in order to upgrade the material for further refining processes. During pre-processing re-usable parts as well as hazardous components are separated by manually sorting and dismantling. Then mechanical treatments are carried out in order to achieve the separation of metals from non-metals using techniques such as screening, magnetic separation, eddy current and density separation (Khaliq et al., 2014). As for the collection, several costs are involved in this step. Depending on the presence of treatment facilities, pre-treatments usually occur on a local or regional scale (Tanskanen, 2013).

During end-processing recyclable materials coming from the previous steps are further processed in order to be fed back into the market. Non-metallic fractions can be treated through processes as gasification, pyrolysis, supercritical fluid de-polymerization and hydrogenolytic degradation with the main aim of producing chemical substances and fuels (Khaliq et al., 2014). Metallic fractions are recovered using techniques coming from the metallurgical sector, such as pyrometallurgy and hydrometallurgy (Cui and Zhang, 2008). Differently from what observed for both collection and pre-treatment, end processing steps are able to produce profits from the sale of recovered materials. As refining processes require special techniques, they are implemented on national or international level (Tanskanen, 2013).

In order to successfully "closing the loop", a technical and economical optimization along the recycling chain is of specific relevance. This means that all the steps need to work properly as any weakness of a single stage could negatively influence the effectiveness of the overall chain. For instance, an high efficiency for end-processing is not relevant if e-waste is poorly collected or pre-processing is not able to address the fractions containing valuable and critical metals towards the most appropriate metallurgical refining processes. Moreover, good cooperation and coordination among the stakeholders involved into the system is fundamental as well as the role of regulations and policies.

Another relevant aspect is related to the recycling costs as they should be kept at reasonable level by economies of scale (Hagelüken et al., 2016). Although e-waste treatment has achieved a good degree of specialization in some European countries (Li et al., 2013), the recycling of metals from WEEE is still in its early stage (Huang et al., 2009; Priya and Hait, 2017) with recycling rates below 15% for precious metals (Hagelüken et al., 2016) and 1% for critical metals (Binnemans et al., 2013). Addressing all the challenges mentioned is, thus, crucial for WEEE management.

2.2 REGULATIONS AND POLICIES

In European Union, the management of WEEE has been addressed by key directives which mainly refer to the Directive on waste electrical and electronic equipment, known as WEEE Directive, and the Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment or RoHS Directive. WEEE Directive acts mainly at the end-of-pipe whereas RoHS Directive sets the beginning-of-pipe of EEE lifecycle (Schluep, 2014).

The first WEEE Directive, namely Directive 2002/96/EC, entered into force in February 2003, promoting for the first time the collection and the recycling of such waste stream. In the same period the legislation restricting the use of hazardous substances in WEEE, named RoHS Directive 2002/95/EC, was issued as well. According to the latter directive, harmful substances including heavy metals (lead, mercury, cadmium, and hexavalent chromium) and flame retardants (polybrominated biphenyls or polybrominated diphenyl ethers) were required to be substituted in EEE by safer alternatives.

The Directive 2002/96/EC has been then revised by the European Commission which proposed the new WEEE Directive 2012/19/EU, entered into force on 13 August 2012 and being effective since 14 February 2014. The RoHS Directive has been revised as well (www.ec.europa.eu).

As the market for electric and electronic products is wide and a great variety of appliances is produced over time, the first key point to be legally faced dealt with the identification of WEEE. The currently enforced Directive defines WEEE as electrical and electronic equipment, including appliances powered by electric currents or electromagnetic fields as well as equipment for the generation, transfer or measurement of such currents and fields, which “the holder discards or intends or is required to discard” (Directive 2012/19/EU). All items belonging to the e-waste stream are grouped into 10 product categories:

1. Large household appliances;
2. Small household appliances;
3. IT and telecommunications equipment;
4. Consumer equipment and photovoltaic panels;
5. Lighting equipment;
6. Electrical and electronic tools (with the exception of large-scale stationary industrial tools);
7. Toys, leisure and sports equipment;
8. Medical devices (with the exception of all implanted and infected products);
9. Monitoring and control instruments;
10. Automatic dispensers.

From 15 August 2018, these categories shall be regrouped into 6 new categories as follow:

1. Temperature exchange equipment;
2. Screens, monitors, and equipment containing screens having a surface greater than 100 cm^2;
3. Lamps;
4. Large equipment with any external dimension more than 50 cm;
5. Small equipment with external dimensions no exceeding 50 cm;
6. Small IT and telecommunication equipment.

WEEE Directive introduced the adoption of extended producer responsibility (EPR) as key aspect for the management of electronic waste. According to this policy approach, the producers of EEE are responsible, physically and/or economically, for the take back and the recycling of their post-consumer products. Such responsibility aims at promoting the development of sustainable design of electric and electronic products, namely eco-design, in order to make reuse or recycle easier. The implementation of eco-design for EEE would indeed promote recycling and result in the reduction of the waste management costs that are assigned to producers. According to the Directive, producers can address their duties individually or creating producer responsibility organizations (PROs), thus setting up either individual or collective take-back systems. In Italy, for instance, where the Recast Directive has been transposed by the Legislative Decree n. 49/2014, EEE producers have formed 17 PROs, namely consortia or collective systems, coordinated by a national clearing house named "Coordination Centre for WEEE" (CdCRAEE). These collective organisations manage transport, treatment and recycling of WEEE on the national territory. Municipalities remain the responsible for waste collection but they get a financial contribution from the collective organizations (Favot and Marini, 2013).

However, for developing an efficient and sustainable management system, not only producers but all the stakeholders and the operators, from governments to consumers as well as recycling industry (Figure 2.6), need to be involved (Tanskanen, 2013). In this view, it is worth pointing out that the European WEEE Directive introduced also a responsibility for distributors, namely any natural or legal person who makes an EEE available on the market. Distributors have to ensure that the obsolete EEE can be returned at least free of charge on a one-to-one basis when a new equal equipment is supplied. The role of consumers has been outlined as well: they have to actively contribute to the successful collection of WEEE and should be encouraged to its return.

Figure 2.6 Stakeholders in WEEE management system

In order to prevent environmental degradation and losses of valuable raw materials, WEEE Directive fixed mandatory targets for the separate collection of household WEEE. Higher collection targets have been introduced by the Recast WEEE Directive. From the 4 kg per capita of household WEEE established by Directive 2002/96/EC, the new collection targets fixed by Directive 2012/19/EU were applied to all WEEE and based on volumes placed on the market: 45% of the average weight of EEE placed on market in the past three years must be collected by 2016 and 65% in 2019.

Moreover, Member States should ensure that WEEE collected is then treated in an environmental way achieving an high level of recycling and recovery. To this end, recovery targets have been set as well.

Although the management of WEEE in European Countries is regulated by law, only one-third of electrical and electronic waste is reported to be separately collected and properly treated, whereas the remain portion is still potentially sent to landfill disposal or illegally exported abroad in developing countries (www.ec.europa.eu).

Beyond EU and US, analogues regulations are enforced or under development in many countries, including Canada, China, South Africa, Mexico, Argentina, Chile, Colombia, Ecuador, Morocco, Algeria, Tunis, Turkey, Saudi Arabia, Australia, New Zeeland, Vietnam, Thailand and Indonesia (Tanskanen, 2013).

Figure 2.7 displays an overview of EPR implementation in some non European countries, with reference to both existing government legislation, intended as permitted or banned WEEE import/export system, and recycling facilities (either formal or informal).

As shown, South Africa, Kenya and Nigeria are the only African countries that have recently implemented the EPR strategy (Li 2013). However, in Africa informal sector plays still a relevant role in WEEE processing (Ongondo et al., 2011). Moreover, 88% of African destinations countries involved in the transboundary movements of electronic waste have not yet established regulation on WEEE import (Li et al., 2013).

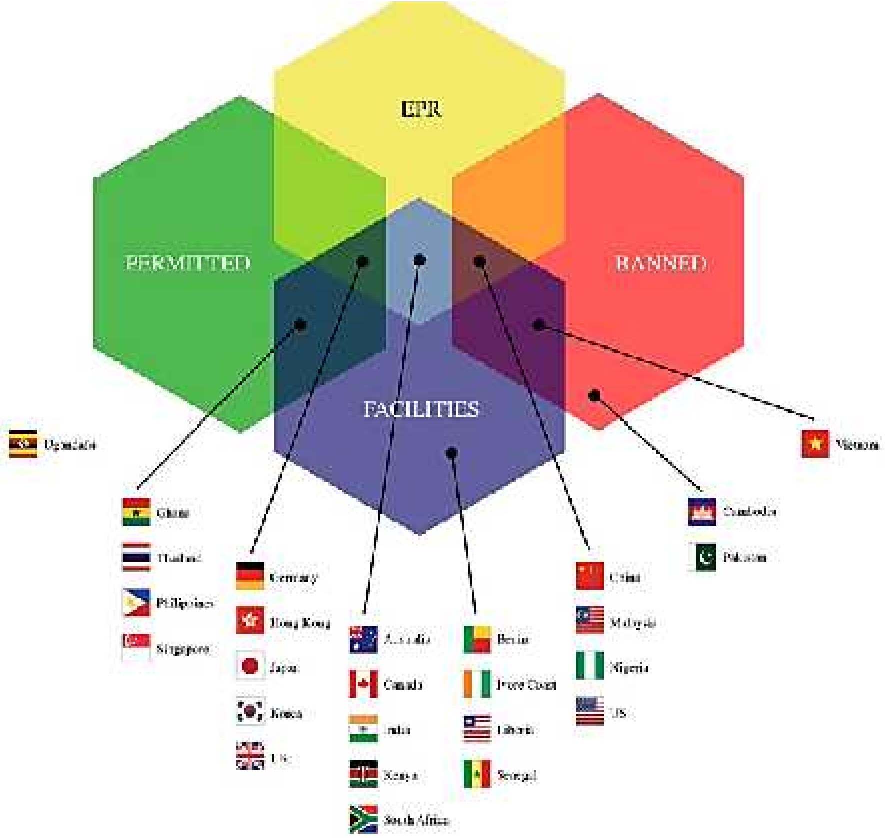


Figure 2.7 EPR strategy implementation in several countries for WEEE management (Li et al., 2013)

Among Asian countries, China, Malaysia, India, Hong-Kong, Japan and South Korea have enforced EPR regulations. Some of these countries banned the import of WEEE whereas other ones permitted imports. In countries as Vietnam and China the illegal traffic is still prevalent even though WEEE imports have been banned. The Japanese WEEE management is characterized by recycling fees which consumers are obligated to pay at time of disposal. This situation stimulated illegal dumping of WEEE as well as intensive end-of-life export as second-hand goods (Ongondo et al., 2011). Beyond recycling fees, the Japanese system has other two unique aspects: the limited number of target appliances and the physical responsibility rather than financial for manufactures towards their end-of-life products (Aizawa et al., 2008).

However, the presence of government regulations as well as company practices such as the example of Sony Corporation have produced in Japan high recycling rates (Li et al., 2013).

EPR strategy has been adopted also in several countries of South America, as Argentina, Brazilm, Colombia and Peru as well as in Canada and Australia (Li et al., 2013). In United States the management of e-waste has occurred mainly via municipal waste service; 18 states have adopted EPR regulation and few voluntary producer take-back programs (i.e., Dell, HP, Toshiba, and Apple) can be mentioned (Wagner, 2009).

However, it is worth pointing out that the same EPR model applied in a specific country cannot be completely extended to other countries due to endogenous and exogenous factors. In order to improve the performance of informal sector as well as the recovery rates in destination countries involved in WEEE transboundary movements, additional responsibility promoted via "full Extended Producer Responsibility" has been proposed as possible solution. In this case, the producer responsibility is not limited to the take-back process in its own country but is also extended to the export of the product (Li et al., 2013).

3 WEEE: "URBAN MINING" AND HAZARDOUS WASTE

Waste electrical and electronic equipment represents a complex and heterogeneous waste stream in terms of both materials and components (Chancerel and Rotter, 2009; Cui and Zhang, 2008). Although a standard composition cannot be outlined for the entire waste stream, metals are the predominant fraction (Widmer et al., 2005).

Due to the relatively high concentrations of metals in electronic devices, WEEE is regarded as a potential secondary source of metals (Hagelüken, 2006). Moreover, it is considered the backbone stream in "urban mining" as electronic waste contains special metals, such as rare earth elements and platinum-group metals, which have been defined as critical raw materials of industrial interest (Cossu and Williams, 2015). However, electronic waste is simultaneously considered as hazardous waste due to the presence of heavy metals, flame retardants and other potentially harmful substances that can lead to health and environment risks if this waste is improperly managed (Tsydenova and Bengtsson, 2011).

The characterization of WEEE in terms of material composition is, thus, a fundamental step in order to develop suitable recycling and management strategies. This approach is known as "recycling oriented categorization" (Chancerel and Rotter, 2009).

To this end, the present chapter deals with the material composition of WEEE with a special focus on its metal content in terms of common metals, precious metals and rare earth elements as the recovery of metals is considered the major economic driver in WEEE recycling.

3.1 MATERIAL COMPOSITION

As a consequence of the continuously change in design and function of electronic equipment, the material composition of obsolete electronic devices is highly variable and heterogeneous. The variability and the heterogeneity are both related to the wide number of different appliances put on market and the different composition of any appliance. Indeed, it has been demonstrated that the material and chemical composition of WEEE varies not only among equipment types with different functions, but also among single appliances belonging to the same equipment type (Chancerel and Rotter, 2009). Half of WEEE generally comes from electrical appliances while the remaining part is composed by electric goods (Kaya, 2016). A schematic distribution of the composition of electronic waste is provided in Figure 3.1. The year of production, the origin and the manufacturer of the electronic equipment contribute to its variable composition as well (Cui and Zhang, 2008).

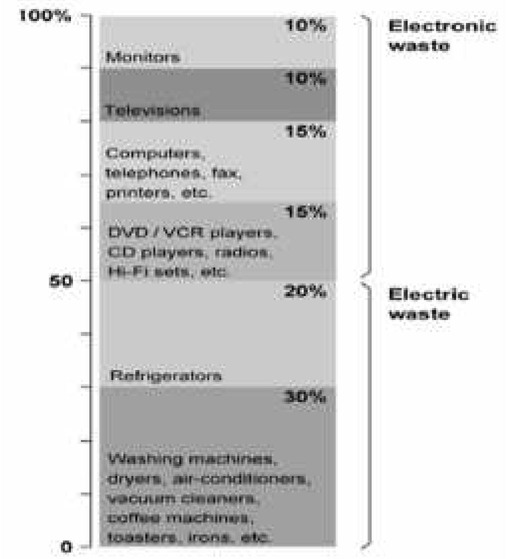


Figure 3.1 Schematic distribution of WEEE composition in terms of items (Kaya, 2016)

Electronic waste can contain more than 1000 different substances, including toxic and valuable materials. Due to this high variability, no generalised material composition exists for WEEE. However, materials found in WEEE can be classified into five main categories: ferrous metals, non-ferrous metals, glass, plastics and other materials. Iron and steel are the most common metals used in electronic devices, accounting for almost 50% of the total appliance weight, while non-ferrous metals, including copper, aluminium and precious metals, represent the 13%. Metals cover, thus, the dominant fraction by weight (around 60%), while plastics represent the second largest component (up to 21%) (Figure 3.2) (Widmer et al., 2005).

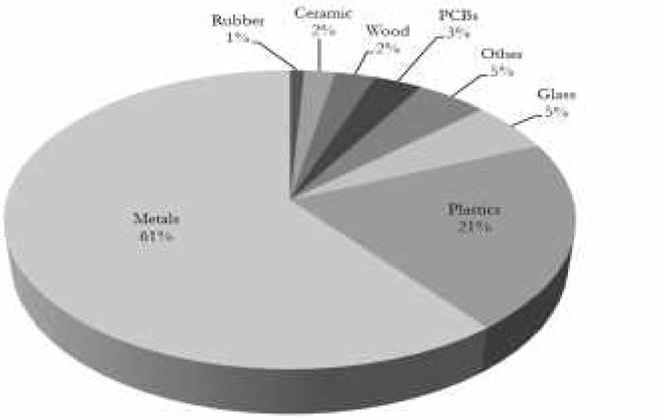


Figure 3.2 WEEE material composition (adapted from Widmer et al. 2005 and (Tuncuk et al., 2012)

WEEE plastic fractions may consist of 15 different polymers: polystyrene (PS), acrylonitrile–butadiene–styrene (ABS), polycarbonate blends (PC/ABS), high-impact polystyrene and polypropylene (HIPS) were found the predominant polymers in small WEEE (Martinho et al., 2012). In addition to polymers, plastics contain some additives and filler, such as brominated flame retardants and heavy metals, which are classified as hazardous (Chancerel and Rotter, 2009).

Heavy metals, brominated flame retardants (BFRs) and other toxic and hazardous substances are generally included in the non-metallic fraction (Wang and Xu, 2014). However the majority of hazardous substances contained in WEEE are found in certain components/parts of electronic appliances (Tsydenova and Bengtsson, 2011). An overview of the substances of concern in WEEE is provided in Table 3.1.

Beyond metals and plastics, the remaining portion of materials present in WEEE is made of composite and interconnected components like cables, printed circuit boards (PCBs) and motors (Chancerel and Rotter, 2009). Most of the hazardous as well as valuable metals are concentrated in PCBs (Hagelüken, 2006).

Table 3.1 Hazardous components and substances of concern commonly found in WEEE (Tsydenova and Bengtsson, 2011)

Components	Equipment type	Substances of concern
Cathode ray tubes	TV sets, PC monitors	Pb in cone glass Ba in electron gun getter Cd in phosphors
PCBs	Ubiquitous (from beepers to PCs)	Pb and Sb in solder Cd and Be in contacts Hg in switches BFRs in plastics
Batteries	Portable devices	Cd in Ni-Cd batteries Pb in lead acid batteries Hg in Hg batteries
Gas discharge lamps	Backlights pf LCDs	Hg in phosphors
Plastics	Wire insulation, plastic housing, circuit board	PVC BFRs

PCBs=printed circuit boards; Pb=lead; Ba=barium; Cd=cadmium; Sb=antimony; Be=beryllium; Hg=mercury; BFRs= brominated flame retardants; Ni=nickel; PVC= polyvinyl chloride.

Over the years the concentration of non-ferrous and precious metals in electronic scraps has been gradually decreased for the use of modern circuits (Cui and Zhang, 2008). Moreover, the content of pollutants and hazardous components have been reduced as well due to European Directives which restricted the use of hazardous substances (RoHS Directive 2002/95/EC).

3.2 METAL CONTENT

The industry of electrical and electronic equipment is a large consumer of metals, both common metals and special metals such as precious ones and rare earth elements.

Different studies have been carried out on WEEE characterization in terms of metal content. However, most investigations have been focused on PCBs as these components, which are included in almost all electronic devices, contain the major fraction of metals (Chancerel, 2010). The metal fraction in PCBs accounts for about the 28% of its weight (Ghosh et al., 2015). Conversely only few study are available on the average content of metal in the entire WEEE.

In the following sections an overview of the concentrations of common metals, precious metals and rare earth elements in WEEE is provided both with reference to PCBs and overall appliances when available.

3.2.1 Common metals

Electronic waste is composed by a variety of common metals, including aluminium (Al), copper (Cu), iron (Fe), lead (Pb), nickel (Ni), tin (Sn) and zinc (Zn). These metals are mainly concentrated in circuit boards which are contained in the major part of electronic devices. PCBs obtained from end-of-life electric equipment, thus, may be considered as a high value waste as they can represent a secondary source of these metals (Das et al., 2009).Copper and zinc are the base metals with the higher economic value (Cui and Zhang, 2008). For this reason, much has been done in literature with reference to the content of common metals in PCBs. Copper generally makes of around 10-20% of the PCB total weight; 4-6% consists of Pb/Sn solders while the remaining metallic fraction is composed by other metals, including the precious ones (Ghosh et al., 2015).

Oguchi et al. (2011) reported the average concentrations of selected common metals in PCBs for several equipment type (Table 3.2).

Table 3.2 Concentrations of selected common metals in PCBs of different equipment types (Oguchi et al., 2011, 2013)

Equipment type	Common metal concentrations in PCBs (mg/kg)					
	Al	**Cu**	**Fe**	**Pb**	**Sn**	**Zn**
Refrigerator	16000	170000	21000	21000	83000	17000
Washing machine	1000	70000	95000	2200	9100	2400
Air conditioner	6900	75000	20000	5800	19000	4900
CRT TV	62000	72000	34000	14000	18000	5300
PDP TV	38000	210000	20000	7100	15000	12000
LCD TV	63000	180000	49000	17000	29000	20000
Desktop PC	18000	200000	13000	23000	18000	2700
Notebook PC	18000	190000	37000	9800	16000	16000
VCR	35000	160000	38000	20000	18000	16000
DVD player/recorder	54000	220000	11000	12000	22000	26000

Stereo system	29000	150000	12000	19000	22000	14000
Radio cassette recorder	61000	140000	58000	17000	24000	11000
Facsimile	37000	120000	11000	19000	7400	7700
Telephone	67000	96000	150000	19000	34000	8600
Printer	180000	140000	17000	10000	16000	4200
Mobile phone	15000	330000	18000	13000	35000	5000
Digital camera	24000	270000	30000	17000	39000	8800
Camcorder	29000	210000	45000	30000	38000	13000
Portable CD player	68000	200000	46000	12000	50000	20000
Portable MD player	27000	330000	45000	9300	48000	11000
Video games	40000	190000	77000	13000	26000	12000
Microwave oven	14000	320000	400000	17000	15000	28000
Rice cooker	20000	350000	200000	5400	29000	39000
Electric pot	40000	230000	74000	22000	33000	30000

Iron, copper and aluminium were found to be the metals with the highest concentrations. Based on the metal content in the PCB of each equipment type and the annual amount of each end-of-life equipment, the authors obtained a sort of categorization of the selected products in terms of potential secondary resource of metals. In details, refrigerators, washing machines, air conditioners, and CRT TVs resulted the most important equipment for Al, Cu and Fe.

Besides PCBs, common metals can be found also in other WEEE components. A metal composition related to the entire electronic device was reported by Cucchiella et al. (2015)(Table 3.3).

Table 3.3 Common metal content in selected WEEE (elaborated from Cucchiella et al. 2015 and Hagelüken, 2006)

Equipment type	**Common metal concentrations (mg/kg)**						**Ref.**
	Al	**Cu**	**Ni**	**Fe**	**Sn**	**Zn**	
LCD notebooks	-	38571	1029	-	-	1	[1]
LED Notebooks	-	38571	1029	-	-	1	[1]
CRT TVs	2680	26240	-	83520	1280	344	[1]
LCD TVs	-	82400	-	-	1800	-	[1]
LED TVs	-	82400	-	-	1800	-	[1]

CRT Monitors	15125	59500	12438	207625	1250	-	[1]
LCD Monitors	26000	-	-	506000	4800	-	[1]
LED Monitors	26000	-	-	506000	4800	-	[1]
Cell Phones	150000	325000	12500	137500	12500	50000	[1]
	10000	130000	1000	50000	5000	-	[2]
Smart Phones	24167	116667	12500	66667	8333	8333	[1]
PV Panels	17125	975	-	-	1	5	[1]
HDDs	760345	25862	-	106897	-	-	[1]
SSDs	1102500	37500	-	155000	-	-	[1]
Tablets	-	54000	1444	-	-	-	[1]
Portable audio	10000	210000	300	230000	1000	-	[2]
DVD player	20000	50000	500	620000	2000	-	[2]
Calculator	50000	30000	5000	40000	2000	-	[2]

[1] Cucchiella et al. (2015); [2] Hagelüken, (2006)

However, few data on metal content are available if we shift the focus from single components as PCBs to the entire WEEE. In this case, some references were given by Morf et al. (2007) and Oguchi et al. (2012). Morf et al. (2007) detected around 49000 mg/kg of Al, 41000 mg/kg of Cu, 360000 mg/kg of Fe, 10300 mg/kg of Ni, 2900 mg/kg of Pb, 1700 mg/kg of Sb and 5100 mg/kg of Zn in small WEEE entering a recycling plant in Switzerland. In roughly agreement with these values, Oguchi et al. (2012) found Fe (480000 mg/kg) as the most prevalent metal in input WEEE at a Japanese municipal waste treatment plant, treating large and small household appliances, information technology and communications equipment, consumer and lighting equipment. They found a content of Cu and Al one order of magnitude lower than iron whereas Pb, Sn and Zn were on the order of 10^3 mg/kg. However it should be pointed out that different proportions of items in input WEEE determine different metal content.

Moreover, WEEE contains less common metals, as bismuth (Bi), cobalt (Co), gallium (Ga), strontium (Sr) and tantalum (Ta), as well as other metals defined as toxic metals, including barium (Ba), beryllium (Be), cadmium (Cd), chromium (Cr), lead (Pb) and antimony (Sb), which raise great concern and set the need for an appropriate management of this waste stream (Oguchi et al., 2011, 2013).

3.2.2 Precious metals

Gold (Au), silver (Ag) and platinum-group metals (PGMs), including platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), iridium (Ir) and osmium (Os), are defined as precious metals (PMs). These elements are characterized by high economic values and specific chemical and physical properties (i.e. low electron affinity, high resistance to corrosion) which make them suitable for usage in electronic industry. For instance, gold is employed in conductor materials for communication and information transfer equipment. Silver finds application as conductor and electrode material due to its high electrical and thermal conductivity. Palladium is a component of pastes for multilayer capacitors production. Platinum is mainly used for data storage in hard disk drives and as barrier layers and contact pads on semiconductor chips (Chancerel, 2010).

Precious metals are mainly present in PCBs, where they occur connected or mixed with other metals in contacts, cables, solders and hard disk drives or with ceramics in multi-layer capacitors, integrated circuits and hybrid ceramics or, furthermore, with plastics in PCB-tracks, interboard layers and integrated circuits (Hagelüken, 2006). However PCBs represent only 3-6% of the WEEE mass (Cucchiella et al., 2015).

Although the concentration of PMs in WEEE is rather low, the recovery of these metals from electronic waste has both a high economic and environmental relevance. It has been demonstrated that more than 70% of the value of cell phones, calculators and PCBs is related to their content in precious metals whereas for TV boards and the DVD player the contribution of PMs make up around the 40% of the appliance value (Cui and Zhang, 2008). Moreover, the concentration of PMs in PCBs is generally much higher than the concentration in mineral ores and the environmental impacts associated with the production from secondary sources is much lower than their primary production. For instance, the material intensity (MIT) of gold is very high as approximately 540 tonnes of virgin material have to be used in order to produce just one gram of this metal (Chancerel, 2010).

The content of PMs in PCBs has been widely investigated. The average concentrations of Au, Ag, Pd and Pt obtained for different type of equipment from previous studies is summarised in Table 3.4. As highlighted by the reported values, PCBs from mobile phones, telephones, personal computers and small electronic equipment, such as digital cameras, camcorder and player audio appliances, are characterized by the highest contents in precious metals followed by CRT and LCD of TV and PC.

Table 3.4 Concentrations of precious metals in PCBs of different equipment types (adapted from Chancerel et al., 2009; Oguchi et al., 2011, 2013)

Equipment type	Precious metal concentrations in PCBs (mg/kg)				Ref.
	Ag	Au	Pd	Pt	
Refrigerator	42	44	-	-	[1,2]
Washing machine	51	17	-	-	[1,2]
Air conditioner	58	15	-	-	[1,2]
CRT TV	120	5	20	-	[1,2]
	280	17	10	-	[3]
	1600	110	41	-	[4]
CRT PC	150	9	3	-	[4]
PDP TV	400	300	-	-	[1,2]
LCD TV	600	200	-	-	[1,2]
	250	60	19	-	[4]
LCD PC	1300	490	99	-	[4]
Desktop PC	570	240	150	-	[1,2]
Notebook PC	1100	630	200	-	[1,2]
PC	1000	250	110	-	[3]
	1000	230	90	-	[4]
VCR	210	23	50	-	[1,2]
DVD player/recorder	710	150	20	-	[1,2]
	700	100	21	-	[4]
Stereo system	57	6	-	-	[1,2]
Radio cassette recorder	170	26	34	-	[1,2]
Radio set	520	68	8	-	[4]
Facsimile	69	35	110	-	[1,2]
Telephone	2400	-	-	-	[1,2]
Printer	70	38	21	-	[1,2]
	350	47	9	-	[4]
Mobile phone	3800	1500	300	-	[1,2]
	3573	368	287	-	[5]
	5540	950	285	7	[6]
Digital camera	3200	780	200	-	[1,2]
Camcorder	5000	530	970	-	[1,2]
Portable CD player	3700	370	10	-	[1,2]
Portable MD player	3400	940	550	-	[1,2]
Video games	740	230	43	-	[1,2]
Microwave oven	2000	-	-	-	[2]

Rice cooker	840	-	-	-	[2]
Electric pot	2500	-	-	-	[2]

[1] Oguchi et al., (2011); [2] Oguchi et al., (2013); [3] Hagelüken, (2006); [4] Huisman et al. (2007); [5] Ernst et al. (2003); [6] Huisman and Buchert, (2008).

Considering the precious metal content in PCBs of several equipment type and the total amount of each end-of-life equipment annually generated, Oguchi et al. (2011) categorized the selected equipment into five groups in order to discuss their potential as secondary resources of precious metals. Desktop PCs, notebook PCs, LCD TVs, mobile phones, and video games were identified as the most important types of equipment in terms of secondary resources of Au and Ag. The highest potential was in particular associated to video games. Furthermore the results obtained from this study showed that small digital equipment, such as portable audio players, digital cameras, and camcorders, should be considered as potential secondary sources of precious metals as well.

Apart from PCBs, precious metals are known to be included also in other WEEE components as connectors, contacts, cables, and solders (Hagelüken, 2006). However only few studies are available with reference to the entire WEEE. Cucchiella et al. (2015) analysed the composition of selected electronic products not considering PCBs as an independent component. The concentrations of precious metals reported in this study are provided in Table 3.5, along with some other references. It is evident that the metal concentration in the total device results lower than the concentration in corresponding PCB, as the mass of the selected metal is related to a greater weight. This evidence is, however, much relevant for heavier appliances. Moreover, Chancerel et al., (2009) estimated a concentration of precious metal of 67.7 mg/kg of Ag, 11.2 mg/kg of Au and 4.4 mg/kg of Pd entering a full-scale facility treating IT, telecommunications, and consumer equipment whereas Oguchi et al. (2012) reported an average content of 5-11 mg/kg for Au, Ag and Pd in WEEE entering a Japan municipal treatment plant.

Table 3.5 Precious metal content in selected WEEE (elaborated from Cucchiella et al., 2015 and Hagelüken, 2006)

Equipment type	**Precious metal concentrations (mg/kg)**				**Ref.**
	Ag	**Au**	**Pd**	**Pt**	
LCD notebooks	71	63	11	1	[1]
LED Notebooks	71	63	11	1	[1]

LCD TVs	45	11	4	-	[1]
LED TVs	45	11	4	-	[1]
CRT Monitors	78	19	-	-	[1]
LCD Monitors	104	40	8	-	[1]
LED Monitors	104	40	8	-	[1]
Cell Phones	12500	300	113	-	[1]
	1340	350	210	-	[2]
Smart Phones	2033	317	125	33	[1]
HDDs	53	9	5	-	[1]
SSDs	78	13	8	-	[1]
Tablets	100	88	16	-	[1]
Portable audio	150	10	40	-	[2]
DVD player	115	15	4	-	[2]
Calculator	260	50	5	-	[2]

[1] Cucchiella et al. (2015); [2] Hagelüken (2006)

3.2.3 Rare earth elements

The rare earth elements (REEs), also named rare earths or rare earth metals, are a group of 17 metallic elements, including 15 lanthanides, namely lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu) plus scandium (Sc) and yttrium (Y). Expect for scandium, rare earths can be divided into two subgroups: the group of light rare earths (LREEs), from lanthanum to europium, and the group of heavy rare earths (HREEs), including the remaining lanthanides together with yttrium. Despite the term "rare", these elements are relatively abundant in the earth's crust but are not easily exploitable as they are often found dispersed and not concentrated in mineral ores. Due to the similarity in their chemical properties (i.e. ionic radii), REEs are very difficult to be separated. The decrease in ionic radii alongside the lanthanide series is the most important aspect for their separation as heavier REEs form stronger complexes than lighter ones in the aqueous solution. Moreover, REEs generally occur in ores together with radioactive elements as uranium and thorium, contributing to make the extraction of these elements extremely challenging (Jha et al., 2016).

Due to their unique and specific physical or electro-chemical characteristics (Bakas et al., 2014), the application of REEs is dominantly expanding in many high-tech components and green technologies as hybrid cars and wind turbines (Jha et al., 2016). An average distribution of rare earth element consumption by application is shown in Table 3.6. However, the distribution can vary depending on product manufacturers (Binnemans et al., 2013).

Table 3.6 Percentage distribution of rare earths by application (%)(Binnemans et al., 2013)

Application	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Others
Magnets	-	-	23.4	69.4	-	-	2	0.2	5	-	-
Battery alloys	50	33.4	3.3	10	3.3	-	-	-	-	-	-
Metallurgy	26	52	5.5	16.5	-	-	-	-	-	-	-
Auto catalysts	5	90	2	3	-	-	-	-	-	-	-
FCC	90	10	-	-	-	-	-	-	-	-	-
Polishing powders	31.5	65	3.5	-	-	-	-	-	-	-	-
Glass additives	24	66	1	3	-	-	-	-	-	2	4
Phosphors	8.5	11	-	-	-	4.9	1.8	4.6	-	69.2	-
Ceramics	17	12	6	12	-	-	-	-	-	53	-
Others	19	39	4	15	2	-	1	-	-	19	-

The high demand of REEs coupled with its scarce worldwide production, mainly limited to China that currently manages over the 90% of the market share, entail the critical status of these elements. In 2010 REEs were classified by the European Commission as the most critical raw materials at supply risk. Their criticality assessment has been then confirmed in 2014, splitting the rare earth elements into heavy and light categories. In this case, HREEs have been defined as the most critical materials (Figure 3.3), followed by the LREEs (European Commission, 2014, 2010).

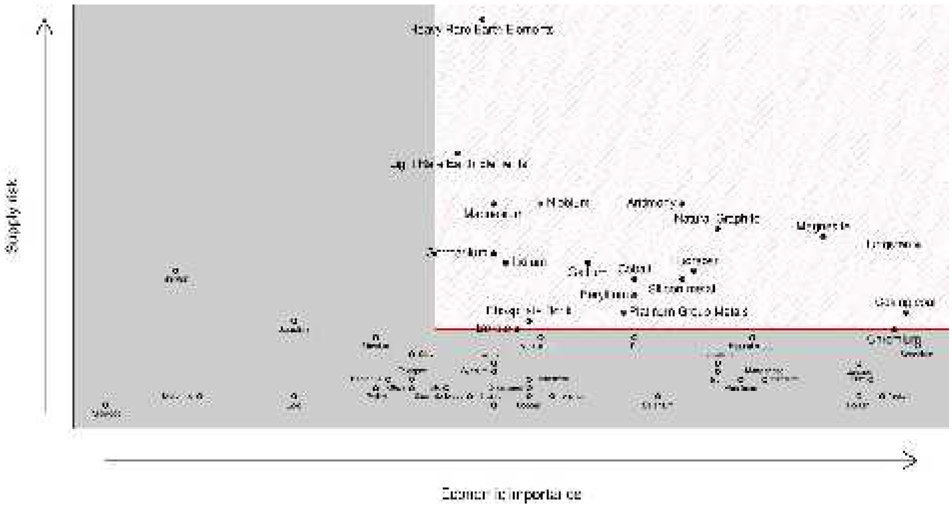


Figure 3.3 Critical raw materials for the EU’s economy (European Commission 2014)

Moreover, the U.S. Department of Energy has defined a medium-term criticality matrix in which neodymium, europium, terbium, dysprosium and yttrium are identified as the five most critical REEs (Figure 3.4).

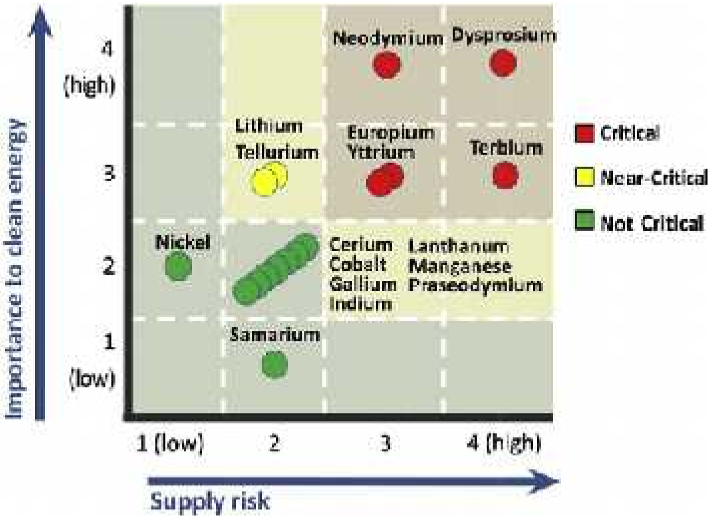


Figure 3.4 Medium-term criticality matrix defined by U.S. Department of Energy (U.S. Department of Energy, 2011)

Because of these aspects, the concept of recovering REEs contained in end-of-life products appears as an important chance in order to achieve a sustainable circular economy. Mining REEs from waste products obviously has several benefits, related to environment, material supply and economy. These advantages are summarized in Table 3.7. However, drawbacks can be mentioned as well, connected to logistics, collection, sorting, treatment and generation of secondary waste (Tunsu et al., 2015).

Table 3.7 Advantages of recycling REEs from waste streams (Tunsu et al., 2015)

Aspect	Benefits
Environment	Spreading prevention of radioactive elements (i.e. uranium and thorium) present in REE minerals Reduction of landfilling disposal both for mining residues than for discarded products Conservation of resources
Material supply	Material recycling Increasing availability of materials as metal concentration in discarded products is generally higher compared to ores
Economy	Cost reduction of raw materials by creating additional supply

Among the end-of-life REE-containing products, WEEE is considered an important "urban mining" target (Tunsu et al., 2015). Rare earths are widely used in electronic devices. For instance, REEs can be found in cathode ray tube (CRT), fluorescent lamps, magnets, accumulators, electrodes, semi-conductors, capacitors and electric contacts (Menad and van Houwelingen, 2011). However, the research on REE recycling has been mainly focused on three categories of end-of-life products: products containing phosphors which are capable of luminescence; products containing permanent magnets and batteries due to their REE contents (Table 3.8) (Tunsu et al., 2015).

Table 3.8 End of life products containing REEs (adapted from Tunsu et al., 2015)

Category	Products	REEs used in the stream
Phosphors-containing products	Fluorescent lamps	Eu, Y, Tb, La, Ce, Gd
	LEDs	Ce, Y, Gd, Eu
	Plasma display panels	Eu, Y, Gd
	CRT screen	Y, Eu, Tb, Ce, Nd, Sm

Permanent magnet-containing products	Products containing NdFeB magnets (HDDs, speakers, headphones, electric motors, electric generators for wind turbines etc.)	Nd, Dy, Pr, Gd, Tb
Batteries	NiMH batteries	Ce, La, Nd, Pr, Y

Products containing phosphors include fluorescent lamps, LED lamps, CRTs and plasma screens. These products mainly contain yttrium and europium but small amounts of other REEs such as cerium, lanthanum, terbium and gadolinium can also be present. Yttrium is the prevalent rare earth in fluorescent lamps as reported in Table 3.9, in which the REE content is displayed for the three phosphor types used in fluorescent lamps (red, green and blue).

The most common REE-based permanent magnets are the neodymium-iron-boron (NdFeB) magnets which can be found in hard disk drives, speakers, headphones, mobile phones, electric motors and generators. Neodymium is the principal REE component but minor amounts of dysprosium, praseodymium, gadolinium and terbium have been reported as well (Table 3.9).

Many electronic devices are powered by rechargeable batteries. The most used are the nickel-metal hybrid batteries (NiMH) which replaced the nickel-cadmium ones due to their technological and environmental advantages. NiMH batteries are made up of about 7% of a mixture of REEs, namely lanthanum, cerium, praseodymium and neodymium (Table 3.9). This REE-containing alloy replaced the toxic cadmium of the old batteries as it is less harmful (Tunsu et al., 2015).

Table 3.9 REE composition in fluorescent lamp, NdFeB permanent magnets and NiMH batteries (adapted from Tunsu et al., 2015)

Products		**Composition (% wt)**							**Ref.**
		Y	Eu	Ce	Nd	Dy	La	Pr	
Fluorescent lamps	Red phosphor	67.2	6.5						[1]
	Green phosphor			9.5					
	Blue phosphor		1.9						
NdFeB magnets	HDD Voice coil				29	2.3			[2]
	HDD Spindle motor				29				
	Loudspeaker				31				
NiMH Batteries	Anode	0.7		7.4	2.4		20.2	1	[3]

[1] Mei et al., (2009); [2] Buchert et al. (2012); [3] Larsson et al., (2013)

Besides these components, data on REE concentrations in electronic waste are rather fragmented. A further obstacle is also posed by trade secrets which cover some devices (Buchert et al., 2012).

A characterization in terms of critical materials of selected WEEE has been provided by Cucchiella et al. (2015). As reported in Table 3.10, the concentration of rare earth elements present in WEEE is however quite low. Furthermore a reference for these less common metals has been provided by Oguchi et al. (2012) who reported a general concentration of rare earth metals ranging from 10^{-1} and 10^{2} mg/kg in WEEE discarded in the city of Hitachi.

Table 3.10 REE content of selected WEEE (Cucchiella et al., 2015)

Equipment type	REE concentrations (mg/kg)								
	Ce	Dy	Eu	Gd	La	Nd	Pr	Tb	Y
LCD notebooks	<0.3	17	<0.3	<0.3	<0.3	600	78	<0.3	0.6
LED Notebooks	<0.3	17	<0.3	<0.3	-	600	78	-	0.6
LCD TVs	0.5	-	0.8	<0.1	0.7	-	<0.1	0.2	11
LED TVs	<0.1	-	<0.1	0.2	-	-	-	-	0.5
CRT Monitors	-	-	-	-	-	-	-	-	62
LCD Monitors	<0.2	-	0.2	<0.2	<0.2	-	<0.2	<0.2	3.2
LED Monitors	<0.2	-	<0.2	0.4	-	-	-	-	<0.2
Smart Phones	-	-	-	-	-	417	83	-	-
HDDs	-	103	-	-	-	1724	250	-	-
Tablets	<2	24	<2	<2	<2	854	110	<2	<2

4 THE RECOVERY OF METALS FROM WEEE

The continuously increasing generation of WEEE and its heterogeneous composition, which makes this waste both a potential source of secondary materials and a vehicle of hazardous substances if improperly handled, require the implementation of sustainable management strategies (Rubin et al., 2014).

In European countries the management of WEEE is regulated by directives, promoting its collection and recycling.

The recycling of WEEE represents an important option of management as it offers several benefits (Cui and Zhang, 2008; Priya and Hait, 2017). Environmental protection, energy saving, resource conservation and economic value of recoverable materials are among the main reasons for processing electronic waste (Khaliq et al., 2014). However, the complex and heterogeneous nature of WEEE represents a relevant obstacle for recycling treatments (Cui and Zhang, 2008). For instance, recycling is still hindered by the product design: the component assembly often makes difficult its separation as in the case of hard disk drivers (HDDs), in which the magnet is strongly glued to the bulk of the entire product (Chagnes et al., 2016). Moreover, the challenge of recycling is not only technical but related to politics, economics, legislation, society and culture as well (Tanskanen, 2013).

The value of the metallic fraction is the main driver for WEEE recycling (Wang and Xu, 2014). The recycling of metals from electronic waste consists of several steps, including physical, chemical and biological processes. A flowchart of the steps involved in the recycling of metals from WEEE is shown in Figure 4.1. After a first step of manual dismantling aiming to separate hazardous components as well as reusable parts, the waste is processed through mechanical treatments. Size reduction, shredding and physical separation processes are employed to pursue an high metal liberation in order to concentrate and separate the metallic fraction from the non-metallic one. Metals are then further sent to refining processes for the effective metal recovery. These processes are mainly based on metallurgical techniques as pyrometallurgy and hydrometallurgy. In the last years the need to develop economical feasible and environmental friendly treatments has moved to biometallurgy as promising technique for metal recovery from WEEE (Cui and Zhang, 2008; Khaliq et al., 2014; Priya and Hait, 2017).

The choice of the suitable recycling technique is addressed by factors as metal grade, economic feasibility and environmental compatibility. However, the recycling of electronic waste is in its early stage with a large amount of this waste still managed by the informal sector in an uncontrolled manner (Huang et al., 2009; Priya and Hait, 2017).

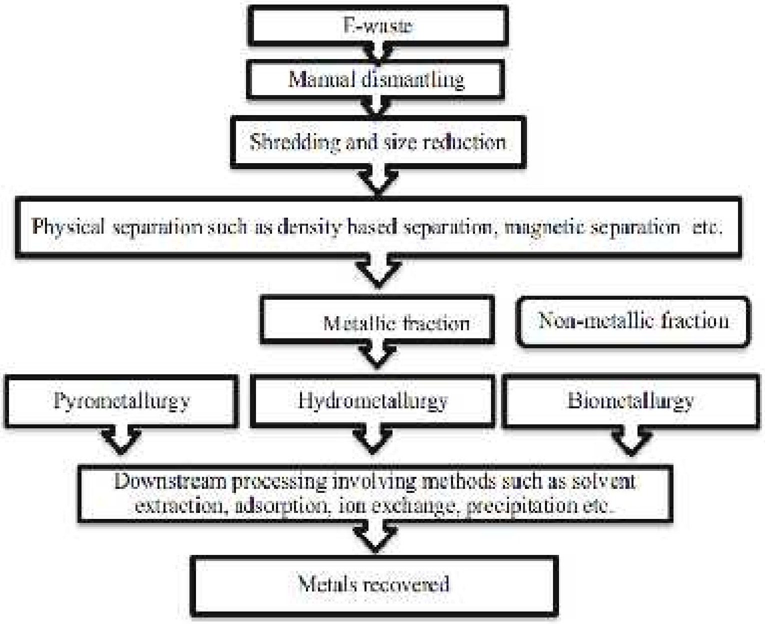


Figure 4.1 General flowchart of processes involved in the metal recycling from WEEE (Priya and Hait, 2017)

In the following paragraphs an overview of the state of art of metal recycling processes from electronic waste is provided. Conventional technologies, including mechanical treatments, pyrometallurgical and hydrometallurgical processes, are deeply discussed. Recent research developments in the field of biometallurgy are outlined as well, with particular emphasis on bioleaching processes. Advantages and drawbacks of the metallurgical processes examined are highlighted.

4.1 MECHANICAL TREATMENTS

Mechanical processes are generally employed as WEEE pre-treatments.

The pre-treatment of WEEE aims at selectively removing larger valuable and hazardous components as well as upgrading material fractions which are further routed to end-refining processes (Cui and Zhang, 2008). The techniques used for WEEE mechanical treatments have been transferred from the mineral sector (Chagnes et al., 2016).

Disassembly is commonly the first step of the chain. The objectives of the process are: (i) to separate re-usable parts; (ii) to eliminate components containing hazardous substances; (iii) to dismantle components (i.e. PCBs or cables) containing high valuable materials in order to avoid their losses through the chain (Cui and Forssberg, 2003). Dismantling is mainly performed manually due to its flexibility (He et al., 2006). However, the increasing amount of waste generated has set the necessity to automate this stage at least using semi-automatic lines (Chagnes et al., 2016).

Shredding processes are used to reduce the size of particles pursuing their liberation. Crushing/shearing machines or hammer grinders are commonly involved in WEEE treatments. After shredding, particles are then further separated via selection techniques based on size, density, electrical or magnetic properties of the incoming waste material (Yu et al., 2009).

Screening is generally performed for classifying shredded particles. Vibrating screen and trommel are in general common in WEEE treatment processes. The material entering the screening section is separated at least into two fractions: the oversize material, namely the particles that remain on the screen surface, and the undersize material, including particles that pass through the screen (Chagnes et al., 2016). The aim of this stage is to return output fractions uniformed in size as well as enriched in metals (Cui and Forssberg, 2003).

The different electromagnetic properties of the feeding material are exploited by separation techniques such as magnetic separation, eddy current separation and corona electrostatic separation (Yu et al., 2009). Magnetic separators, specifically low-intensity drum separators, provide the separation of ferromagnetic metals, as iron scraps, from non-ferrous metals and other non-magnetic materials (Cui and Forssberg, 2003). Eddy current separation and corona electrostatic separation base the selection criteria on the conductivity properties of the material. The former separation technique uses alternative magnetic fields in order to originate eddy currents in non-ferrous particles. These currents induce in turn a secondary magnetic field which, reacting with the first one, results in repulsive forces able to separate the conducting particles from the product stream. The latter technique employs an high voltage electric field which provides the separation of metals from non-conductor materials as plastics (Chagnes et al., 2016).

Density-based techniques basically divide the coming product mixture into light, mixed and heavy fractions. Pneumatic table or air table are the equipment commonly used (Chagnes et al., 2016). These techniques are widely applied for the metals/non-metal separation (Cui and Forssberg, 2003).

A schematic flowchart of a typical WEEE mechanical treatment line is reported in Figure 4.2.

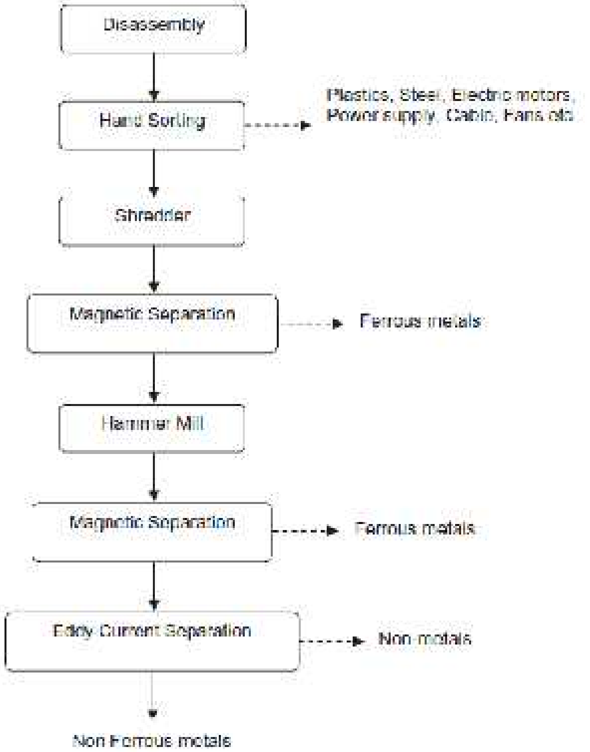


Figure 4.2 Schematic flowchart of typical WEEE mechanical treatments (Tuncuk et al., 2012)

As mechanical treatments determine the effective concentration of materials entering the final recovery processes, they play a fundamental role in WEEE recycling chain (Chancerel et al., 2009; Meskers and Hagelüken, 2009; Meskers et al., 2009).
The amount of the output material obtained and its quality are important processing parameters. These parameters are used to delineate the grade-recovery curve which defines the maximum expectable recovery (Figure 4.3). The curve is delimited by two extreme points: point 1, which indicates high amount of recovered material but with low quality, and point 2 representing conversely the situation of high grade quality and low amount of recovered material. The optimum condition is clearly between these extreme points (Meskers et al., 2009).

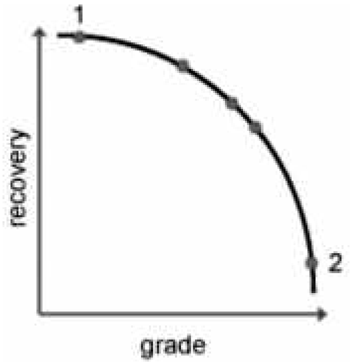


Figure 4.3 Grade-recovery curve (Meskers et al., 2009)

During pre-processing material losses can occur as 100% of recovery is an ideal situation. These losses can be related to several factors: (i) the type as well as the combination of the selection techniques; (ii) the thermodynamic of the process performed; (iii) an incorrect sorting which determines the presence of metals of interest in output streams not directly involved in the recovery process (Meskers and Hagelüken, 2009; Meskers et al., 2009) (Meskers et al., 2009; Meskers and Hagelüken, 2009).
Moreover, the physical characteristics of the waste material, such as particle size and shape, can strongly affect the metal extraction as well as the process selectivity (Cui and Forssberg, 2003; Sun et al., 2015; Veit et al., 2002). For instance, Zhang and Forssberg (1997) highlighted that a comminution below 2 mm is sufficient to achieve a complete liberation of copper particles. The selectivity of the process is affected by the size

of particles as separation techniques are characterized by a workable size particle ranges (Zhang and Forssberg, 1997). These ranges are pointed out in Table 4.1. Moreover, the separation process is influenced by the shape of particles (Veit et al., 2002) as well as by the product design (Bachér and Kaartinen, 2016).

Table 4.1 Main features of some mechanical processes (Yu et al., 2009)

Process	Particle size	Sorting task	Efficiency	Application situation
Vertical vibration separation	150-300 µm	Copper, lead, tin, aluminium/ others	85% metal recovered, out of which 50% is copper	Experimental stage
Gravity separation	5-150 mm	Non-metal/ metal	A large part of heavy metals are separated	Widely used in nonmetal and metal separation
Eddy current separation	>5mm	Nonferrous metal/ non-metal separation	Recovery in excess of 90% is possible	Limited applications in PCB recycling
Corona electrostatic separation	0.1–5 mm	Metal/ non-metal separation	Cu 99% Epoxy resin 99.5%	Some applications in PCB recycling
Magnetic separation	-	Ferromagnetic metals/ others	43% of iron on average is recovered	Widely used in recycling ferromagnetic metals, but not suitable for PCB recycling

Mechanical treatments are characterized by relative low capital and operating costs (Tuncuk et al., 2012). However, the main drawback is represented by the losses of valuable metals as well as significant dust generation (Kaya, 2016). Mechanical processes are well designed to recover mass relevant metals, as iron and copper, with yields up to 80% whereas they fail in the recovery of precious metals which are often lost in dust streams (Bachér et al., 2015; Chancerel et al., 2009; Cui and Zhang, 2008; Lu and Xu, 2016; Oguchi et al., 2012; Veit et al., 2002).

Previous investigations reported around 60-70% of losses in terms of gold and up to 80% of palladium. These losses are mainly ascribed to the shredding processes as they act dispersing precious metals in stream extraneous to metal recovery (Bachér et al., 2015; Chancerel et al., 2009). Research is, thus, currently directed towards the optimization of these processes in order to ensure the recovery of precious metals as well as rare earth elements whose fate has not been addressed yet.

4.2 PYROMETALLURGY

Pyrometallurgy is a well-established thermal treatment which has been traditionally used in the past two decades for recovering both non-ferrous metals and precious metals from WEEE (Cui and Zhang, 2008). During pyrometallurgical treatments, electronic components are burned in specially designed incinerators, blast furnace, or plasma arc furnace. At the end of the thermal process the plastics are removed while metals are concentrated in a metallic phase and extraneous materials in a slag one (Cui and Zhang, 2008; Hoffmann, 1992; Khaliq et al., 2014; Priya and Hait, 2017). The main output product is the copper ingot which is further processed through electrorefining or hydrometallurgical processes in order to produce high purity metals. Slimes collected from the electrolytic process are then finally refined for recovering precious metals (Tuncuk et al., 2012). Incineration, smelting, drossing, sintering, melting and reactions in a gas phase at high temperatures are included among pyrometallurgical processes (Sum, 1991). Smelting is the prevalent route used for e-waste recycling (Zhang and Xu, 2016). As WEEE is principally composed by copper and lead beyond iron and aluminium, copper and lead smelters have been successfully employed for recycling electronic waste (Khaliq et al., 2014). Several smelting industrial applications treating electronic waste can be mentioned worldwide as well as patented applications (Cui and Zhang, 2008). A list of the most known plants is reported in Table 4.2, with a description of the main features of the process performed and the recovered metals.

Table 4.2 Pyrometallurgical plant treating electronic waste (Chagnes et al., 2016)

Process	Recovered metals	Process description
Noranda, Canada	Cu, Au, Ag, Pt, Pd, Se, Te, Ni	Cu smelting → converting → anode casting → electrorefining → Cu+PMs → PMS refinery → PMs+Se,Te
Boliden Rönnskår, Sweden	Cu, Ag, Au, Pd, Ni, Se, Zn, Pb	Copper line: smelting → zinc fume+molten black copper → converting → u electrorefining → u+residue containing PMs→ PMs refinery → PGMs+Se Lead line: Kaldo furnace → fraction containing PMs (for Cu converting)+Pb fraction → Pb refinery → Pb
Umicore, Belgium	Cu, Ni, As, Pb, Sn, Sb, Bi, Au, Ag, Pd, Pt, Ir, Ru, Rh, In, Se, Te	Copper line: Cu smelting (IsaSmelt) → Cu bullion → Cu refinery → Cu+residue containing PMs Lead line: Pb blast fornace → Pb bullion + speiss (Ni, As) → Pb refinery → Pb, Sn, Sb, Bi+residue containing PMs PMs recovery: residue from Cu line and Pb line → cupellation → PMs refinery → PGMs+In, Se, Te

A custom copper smelter processing electronic waste as well as copper concentrates and precious metal-bearing materials is the Horne Smelter located in Rouyn-Noranda, Quebec (Canada). Electronic waste represents the 14% of the total plant working rate (around 100.000 tons of obsolete electronics per years). Figure 4.4 shows the schematic diagram of the process. The raw materials are immersed in a molten metal bath at 1250°C. During the smelting process two layers take form in the reactor. Lead, zinc and iron are converted into oxides and are trapped in an upper silica-based slag. This slag floats over a metallic lower layer, consisting of copper matte, that conversely is heavier. The copper matte is collected and sent to the converting. The output from the converter, named blister copper, is then refined in the anode furnaces and casted to form anodes at 99,1% of purity. The precious metals contained in the remaining 0,9% are finally recovered by anodes electrorefining. The slag obtained from the smelting process is further refined for metal recovery as well (Cui and Zhang, 2008; Khaliq et al., 2014).

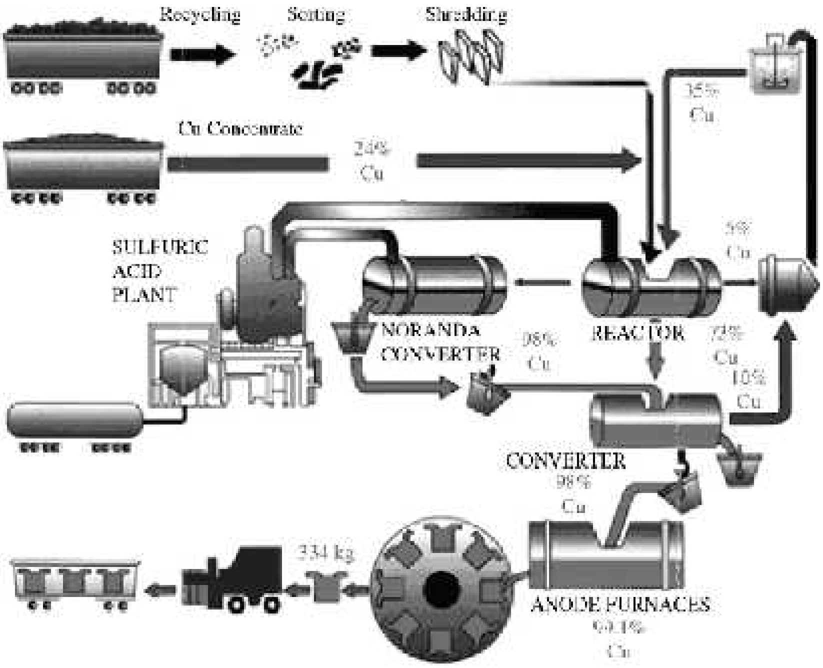


Figure 4.4. Noranda schematic smelting process (Cui and Zhang, 2008)

The Boliden Ltd. Rönnskår Smelter in Sweden provides an integrated system for smelting both copper and lead scraps, including electronic waste. A schematic diagram of the processes is displayed in Figure 4.5. Raw materials containing high grade copper are directly sent to the smelting and converting processes while low grade scraps, as electronic waste, are used to feed the Kaldo furnace along with lead concentrates. The Kaldo technology does not require any external energy as the plastics contained in the scraps are able to provide the sufficient energy for the process. The product of the Kaldo reactor is a mixed copper alloy which is further sent to the converting process, together with the output from the copper smelting process, for the recovery of metals as Cu, Ag, Au, Pt, Pd, Ni, Se and Zn. Dusts originating from the Kaldo furnace are sent to separate refining operations for recovering Pb, Sb, In and Cd. A line for treating off gas emissions is provided as well: in this way the sulphur dioxides produced during the smelting process are reduced in sulphuric acid and other sulphur products (Chagnes et al., 2016; Cui and Zhang, 2008; Khaliq et al., 2014; Zhang and Xu, 2016). In 2015 the plant processed 814.000 tons of copper, concentrates and secondary materials, producing 206.000 tons of copper cathodes, 26.000 tons of lead, 36.000 tons of zinc clinker, 13 tons of gold, 539 tons of silver and 533.000 tons of sulphuric acid (www. boliden.com). As of 2014, around 120.000 tons entering the plant were made of electronic waste (Chagnes et al., 2016).

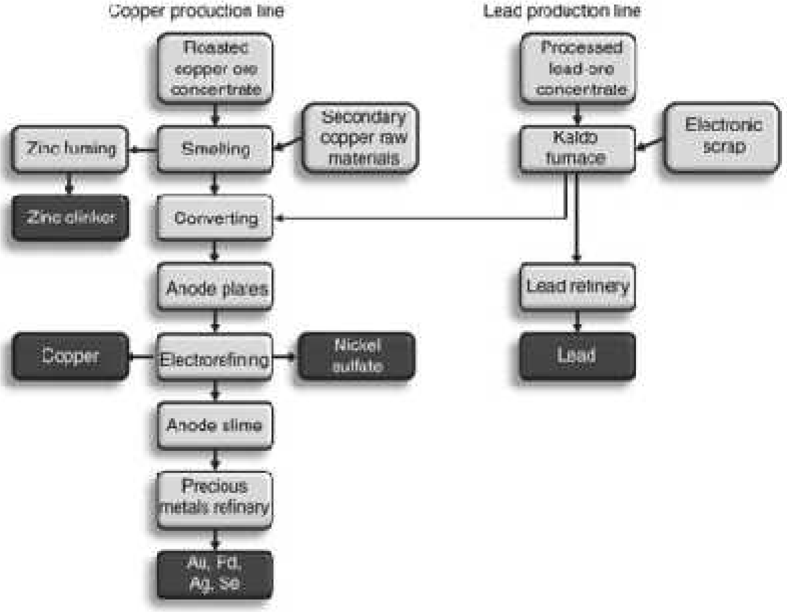


Figure 4.5 Boliden Rönnskår schematic smelting process (Chagnes et al., 2016)

Another pyrometallurgical process for recovering precious metals as well as base metals from electronic waste has been developed at the Umicore plant in Hoboken, Belgium. The complex flowsheet of the processes involved at Umicore's plant is displayed in Figure 4.6. Over 250.000 tons of feed-materials, including various industrial wastes, residues containing precious metals, spent industrial catalysts as well as car exhaust catalysts and printed circuit boards, are treated annually in this integrated smelter and refinery plant. Electronic waste represents the 10% of the total feed-material. Around 50 tons of platinum-group metals, 100 tons of gold and 2400 tons of silver are produced every year. In total seventeen different metals, including base, precious and special metals, can be recovered through two processing lines: one for precious metal recovery, namely precious metal operations (PMO), and the other sets for base metal operations (BMO). PMO include an IsaSmelt furnace which produces as outputs a copper bullion, a lead slag and sulphur gases. The copper bullion is further sent to leaching and electrowinning processes and the residue is finally treated for the recovery of precious metals. Gases are fed to a sulphuric acid plant. Instead, the lead slag is treated along with the high grade lead residues in BMO, which basically consist of a lead blast furnace. The lead furnace produces in turn both a lead bullion, further treated in the lead refinery with the aim of recovering special metals as In, Se and Te, and a copper matte which returns to the PMO. The IsaSmelt furnace is equipped with an emission control system as well. During smelting, plastics and other organic substances contained in the feeding material act as reducing agent and energy source in place of coke (Chagnes et al., 2016; Cui and Zhang, 2008; Hagelüken, 2006; Zhang and Xu, 2016).

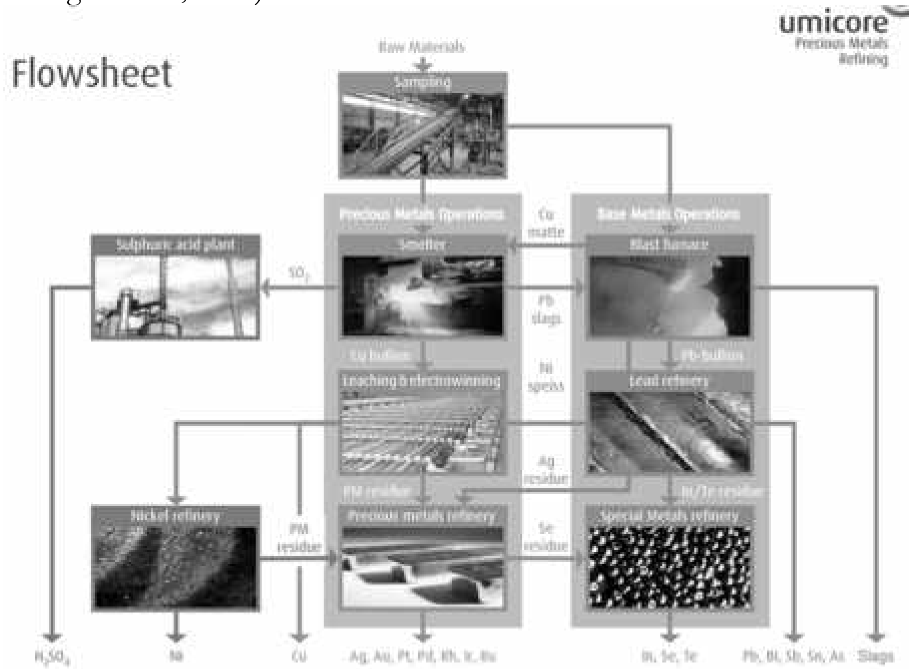


Figure 4.6 Flowsheet of the recovery process at Umicore (www.umicore.com)

Pyrometallurgical processes have also been considered for recycling rare earth elements from end-of-life products as magnets, batteries and lamp phosphors (Binnemans et al., 2013). Several high temperature processes, including melting, extraction with liquid magnesium, electroslag remelting, chlorination, fluorination, or electrolysis of molten salts can be performed depending on the type of treated waste (Polyakov and Sibilev, 2015). However, REEs are easily lost during pyrometallurgical processes as they are usually trapped into the slag phase due to the strong oxygen affinity of this group of metals. In this case, further hydrometallurgical processes are required in order to recover REEs from the slag (Binnemans et al., 2013; Haque et al., 2014). Although the several research efforts in developing effective routes for REE recycling, industrial applications are still limited. Regarding pyrometallurgical routes, in 2011 Umicore and Rhodia developed the first industrial process for recycling rare earths contained in Nickel Metal Hydride (NiMH) rechargeable batteries. This process combines the metallurgy experience of the Umicore group and the rare earth refining competences of Rhodia company. The batteries are processed using the patented Ultra High Temperature (UHT) smelting technology developed by Umicore. At the bottom of the furnace, nickel and iron are collected in a metal alloy and separated from the rare earths which end up in the slag phase together with oxides of Ca, Al, Si, and Fe. The rare earth-bearing slag is then refined and converted into rare earth materials at Rhodia's plant in La Rochelle (France) (Binnemans et al., 2013).

Over the years pyrometallurgy has been proved to effectively recover metals from WEEE. Although it offers the advantage to treat any form of scraps (Ghosh et al., 2015), several limits hinder the application of this technology. The generation of hazardous emission is the major challenge along with the high-energy requirements which make the process suitable only for high grade materials. Mechanical treatments are thus generally required before pyrometallurgical treatments in order to process metal enrich components (Tuncuk et al., 2012; Zhang and Xu, 2016). Moreover, the outputs from pyrometallurgical processes need to be further refined through hydrometallurgical and/or electrochemical techniques in order to obtain the pure metal (Cui and Zhang, 2008; Tunsu et al., 2015).

4.3 HYDROMETALLURGY

The several limits associated with pyrometallurgical processes have increased the interest in hydrometallurgy as potential alternative route for metal recovery from WEEE. Compared to pyrometallurgy, hydrometallurgy is a more predictable and controllable process, characterized by low energy consumption, low or no gasses emissions and high recovery rates (Cui and Zhang, 2008; Tuncuk et al., 2012). However, large amount of toxic, highly acidic or alkaline effluents can be produced as hydrometallurgy involves chemical lixiviants (Priya and Hait, 2017).

A hydrometallurgical process typically consists in the following steps: (i) a leaching step using a suitable lixiviant in order to extract and dissolve the metal of interest, (ii) a purification procedure aiming at concentrating the metal in the solution and (iii) a final step for the effective metal recovery (Cui and Zhang, 2008).

As metals in WEEE are generally encapsulated by or covered with plastics or ceramics, a mechanical pre-treatment of the waste is necessary in order to allow the exposure of metals to the lixiviant action, making the extraction phase easier (Cui and Zhang, 2008; Sun et al., 2015). A series of acid or caustic lixiviants are then involved in the extraction step: in this phase an oxidative leaching process takes place. The leaching solution is, therefore, directed to processes of purification such as precipitation of impurities, solvent extraction, adsorption or ion exchange in order to isolate and concentrate the metal of interest. The metal is further recovered from the concentrated solution through electro-refining processes, chemical reduction or crystallization (Cui and Zhang, 2008). A general flowchart of hydrometallurgical processes for metal recovery from WEEE is provided in Figure 4.7.

Compared to the recovery of base metals, the hydrometallurgical recovery of precious metals and rare earth elements appears more attractive, due to their price, scarcity, low availability and high demand. However, despite the numerous studies carried out on hydrometallurgical processes for metal recovery from WEEE, their industrial application is still limited, especially with reference to critical metals. Moreover, in this field the information retrieval is hindered by competition as well as trade secrets. Hydrometallurgical treatments are actually integrated with pyrometallurgical or electrometallurgical processes as for instance at Hoboken plant (Umicore) and at La Rochelle plant (Rhodia). For large scale applications, leaching agents as sulphuric acid and cyanide are preferred whereas regarding the processes for metal separation from the leachate solvent extraction is generally the most used (Chagnes et al., 2016).

In the overall hydrometallurgical process, the leaching step assumes a key role as it determines the metal transport from the solid matrix into the aqueous phase, affecting the yield of the entire recovery process (Zhang et al., 2012). The following sections, thus, focus on the leaching phase examining the main factors which control the process.

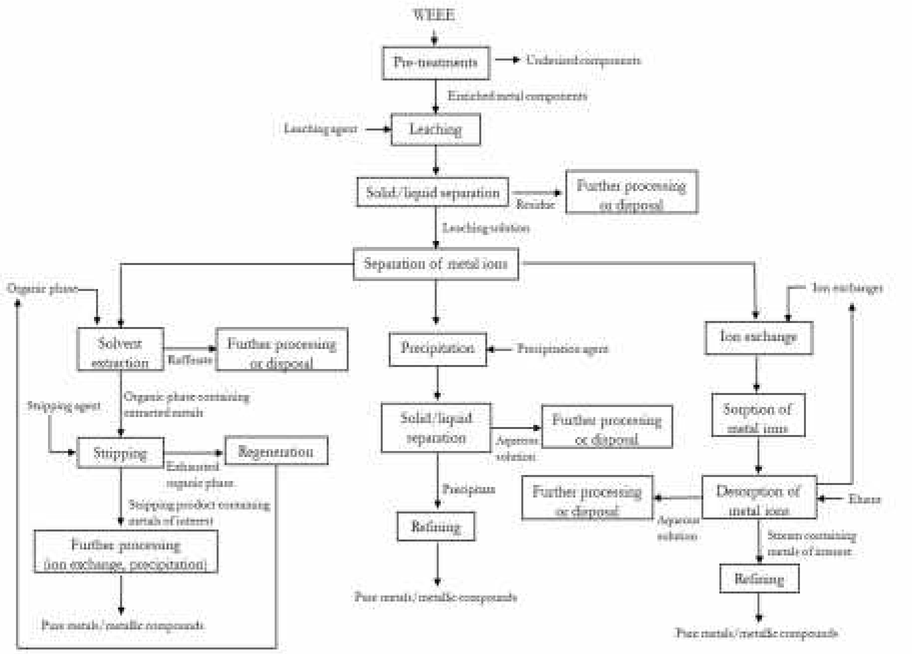


Figure 4.7 General flowchart of hydrometallurgical processes for metal recovery from WEEE (adapted from Chagnes et al., 2016)

4.3.1 Metal leaching from WEEE

Several acid or alkaline solutions have been used as hydrometallurgical lixiviants for the recovery of base metals, precious metals and rare earth elements from WEEE.

Mineral acids, as hydrochloric acid, sulphuric acid and nitric acid, have been widely investigated for the extraction of base metals, especially copper, from PCBs (Table 4.3). In combination with acids a strong oxidant, including H_2O_2, O_2, Fe^{3+} and Cl_2, is generally used in order to enhance the metal extraction (Tuncuk et al., 2012). Although the effectiveness of nitric and hydrochloric acid in metal leaching is well proved, these leaching agents are not suitable for industrial applications due to their corrosive nature. In comparison, sulphuric acid (H_2SO_4) is less corrosive and less toxic and, therefore, more applicable at industrial scale (Yang et al., 2011). Moreover, H_2SO_4 is a cheap reagent and it showed good efficiency on metal dissolution in presence of hydrogen peroxide (H_2O_2) (Birloaga et al., 2014; Oh et al., 2003; Yang et al., 2011). Organic acids (citric and oxalic acid) and alkaline solutions (ammonium and sodium hydroxide) have been considered for base metal leaching as well (Birloaga et al., 2014; Pant et al., 2012).

Base and alkaline solution have also been considered for leaching rare earth elements from both primary and secondary resources (Jha et al., 2016). Hydrochloric, nitric and sulphuric acid are, however, the mineral acids generally used for REE leaching (Tunsu et al., 2015).

Cyanide, thiourea, thiosulfate and halide are the most common leaching agents tested for the extraction of precious metals from WEEE (Cui and Zhang, 2008). Generally the leaching of precious metals is carried out after the dissolution of base metals in order to improve the efficiency of the extraction process and reduce the impurities (Birloaga et al., 2013; Ghosh et al., 2015; Zhang et al., 2012).

Cyanidation has been used in the mining industry of gold for centuries due to its high efficiency and easily technical application as it is based on a simple process. The dissolution of gold is achieved through an electrochemical process: gold dissolves in the alkaline cyanide solution and forms gold cyanide as in the following equation (1) (Akcil et al., 2015):

$$4A \quad + 8C \quad ^{-} + O_2 + 2H_2O \rightarrow 4A \quad (C \quad)_2^{-} + 4OH^{-} \qquad (1)$$

The process is pH dependent. Optimum rates are reached at pH over 10.5 as in this condition "free cyanides" are mainly present in solution in form of cyanide anion (CN^-). Conversely at pH lower than 8.5, cyanide is present as aqueous hydrogen cyanide (HCN) which is a volatile substance (Akcil et al., 2015). Cyanide complexes can be formed with other precious metals as well, following this order of activity: Au>Ag>Pd>Pt (Cui and Zhang, 2008). Moreover, complexation can occur even with base metals. Thus, as copper and other common metals contained in WEEE may tie up cyanide making it no more available for gold dissolution, a chemical pre-treatment aiming at dissolving base metals is necessary. Same highlights can be even extended to the other lixiviant agents involved in precious metal dissolution (Akcil et al., 2015). Studies on precious metal leaching from electronic waste using cyanide solutions are included in Table 4.3. However, the high toxicity related to cyanide and its environmental pressure have increased the interest for using non-cyanide lixiviants, as thiourea, thiosulfate and halide.

Thiourea ($(NH_2)_2CS$), even known as sulfurized urea, is an organic complexing agent able to form soluble cationic complexes with gold under acidic conditions (Cui and Zhang, 2008; Zhang et al., 2012):

$$A \quad + 2C \quad (NH_2)_2 \rightarrow A \quad (C \quad (NH_2)_2)_2^+ + e \tag{2}$$

Several research studies on thiourea leaching of precious metal from WEEE have demonstrated its promising application (Table 4.3) due to its faster kinetics and its lower toxicity compared to cyanide (Akcil et al., 2015). Conversely, thiourea has a very poor stability as it can be easily decomposed, leading to a high consumption of the reagent. In order to prevent thiourea decomposition, a suitable oxidant needs to be selected for obtaining the maximum oxidation of gold and the minimum oxidation of thiourea (Zhang et al., 2012). Ferric ions have been proved to be the most convenient oxidant (Birloaga et al., 2013). The greater consumption of the reagent along with its higher cost make the process more expensive, hindering its application at full scale. A further limitation is represented by the final step of gold recovery which requires further developments (Cui and Zhang, 2008; Zhang et al., 2012).

Thiosulfate ($S_2O_3^{2-}$) has been investigated as cyanide substitute for precious metal leaching from electronic waste (Table 4.3). Sodium and ammonium thiosulfate are the two kinds of thiosulfate commonly used (Zhang et al., 2012). The dissolution of gold in thiosulfate solution is an electrochemical reaction which requires the presence of ammonia and cupric ions in solution. Ammonia helps to stabilize the system in order to prevent the decomposition of thiosulfate whereas cupric ions act as a catalyst enhancing the gold dissolution. In this conditions, thiosulfate forms stable complexes with gold following the equations (3) and (4) (Cui and Zhang, 2008).

$$\begin{aligned} &A \quad + 5S_2O_3^{2-} + C \quad (NH_3)_4^{2+} \\ &\rightarrow A \quad (S_2O_3)_2^{3-} + 4NH_3 + C \quad (S_2O_3)_3^{5-} \end{aligned} \tag{3}$$

$$2C\ \ (S_2O_3^{2-}) + 8NH_3 + 1/2\,O_2 + H_2O \\ \rightarrow 2C\ \ (NH_4)_4^{2+} + 2OH^- + 6S_2O_3^{2-} \qquad (4)$$

Thiousulfate is less toxic and less expensive compared to cyanide. However, relatively low recovery rates and high reagent consumption are the main drawbacks of the process (Akcil et al., 2015).

Halide lixiviants include chloride, bromide and iodide solutions. Although high leaching rates have been reported, the use of these leaching agents is limited since they require special stainless steel and rubber-line equipment. Moreover, the formation of chlorine gases needs to be controlled as they are highly poisonous (Cui and Zhang, 2008). However, only chlorine has been currently applied at industrial scale. The mixture of hydrochloric acid and nitric acid in 3:1 ratio, known as aqua regia, has been successfully used for the extraction of precious metals from PCBs (Sheng and Etsell, 2007)(Table 4.3).

Table 4.3 Literature studies on leaching processes for metal recovery from WEEE

Leaching agent	Source matrix	Process parameters	Leaching rates	Refs
Nitric acid	PCBs	T: 80°C S/L: 33% w/v Lixiviant concentration: 6 M Leaching time: 6 h	Cu: 95%	Mecucci and Scott (2002)
Nitric acid	PCBs	T: ambient S/L: 33% w/v Lixiviant concentration: 1 M Leaching time: 6 h	Pb: 90%	Mecucci and Scott (2002)
Nitric acid	scrap TV boards	T: 70°C S/L: 6% w/v Lixiviant concentration: 2–3 M Leaching time: 2 h	Cu: 88.5–99.9%	Bas et al. (2014)
Sulfuric acid	PCBs	T: ambient S/L: 10% w/v Lixiviant concentration: 15% wt H_2SO_4 - 10 mL 30% H2O2 Leaching time: 3 h	Cu: 95%	Yang et al. (2011)
Sulfuric acid	PCBs	T: 85°C S/L: 1% w/v Lixiviant concentration: 2 M H_2SO_4 - 0.2 M H_2O_2 Stirring rate: 150 rpm Leaching time: 12 h	Cu, Fe, Zn, Ni, Al: 95%	Oh et al. (2003)

Sulfuric acid	PCBs	T: 30°C S/L: 10% w/v Lixiviant concentration: 2 M H_2SO_4 - 20 ml 30% H_2O_2 Stirring rate: 200 rpm Leaching time: 3 h	Cu: 76.12% in one step) Cu: 90% in double step)	Birloaga et al. (2013)
Sulfuric acid	NiHM battery	T: 20°C S/L: 10% w/v Lixiviant concentration: 2 M Leaching time: 2 h	REEs: 80%	Pietrelli et al. (2002)
Sulfuric acid	Fluorescent powder	T: 90°C S/L: 20% w/v Lixiviant concentration: 4 N Leaching time: 3 h	Y: 85%	De Michelis et al. (2011)
cyanide	electronic scrap	pH: >10 T: 25°C	Au: 95%	Quinet et al. (2005)
cyanide	mobile phone PCBs	pH: 12.5 T: 25°C S/L: 5% w/v Lixiviant concentration: potassium cyanide at 6-8% Leaching time: 2-4 h	Au: 60-70%	Petter et al. (2014)
thiourea	PCBs	pH: 1 T: ambient S/L: 12.5% w/v Lixiviant concentration: 10 g/L Stirring rate: 500 rpm Leaching time: 2 h	Ag: 94% Au: 97%	Ficeriová et al. (2008)
thiourea	PCBs	pH: 1 T: 25°C Lixiviant concentration: 24 g/L Leaching time: 2 h	Ag: 50% Au: 90%	Jing-ying et al. (2012)
thiourea	PCBs	pH: 1.4 T: ambient S/L: 10% w/v Lixiviant concentration: 20 g/L Stirring rate: 600 rpm Leaching time: 3.5 h	Au: 69%	Birloaga et al. (2013)
thiourea	PCBs	T: 45°C S/L: 0.3% w/v Lixiviant concentration: 0.5 M Stirring rate: 150 rpm Leaching time: 2 h	Au: 3.2 mg/g	Gurung et al. (2013)
thiourea	PCBs	T: 60°C S/L: 2% w/v Lixiviant concentration: 0.5 M Stirring rate: 150 rpm Leaching time: 2 h	Ag: 6.8 mg/g	Gurung et al. (2013)
(ammonium) thiosulfate	PC PCBs	pH: 10 T: 40°C S/L: 0.5% w/v	Ag: 100% Au: 95%	Oh et al. (2003)

		Lixiviant concentration: 0.2 M Stirring rate: 250 rpm Leaching time: 24h (Ag), 48 h (Au)		
(ammonium) thiosulfate	mobile phones scraps	pH: 10 T: 25°C Lixiviant concentration: 0.12 M Stirring rate: 200 rpm Leaching time: 2 h	Au: 98%	Ha et al. (2010)
(ammonium) thiosulfate	mobile phone PCBs	pH: 10 T: 25°C Lixiviant concentration: 0.12 M Stirring rate: 200 rpm Leaching time: 10 h	Au: 90%	Ha et al. (2010)
(ammonium) thiosulfate	PCBs	pH: 9 T: 40°C S/L: 9% w/v Lixiviant concentration: 0.5 M Stirring rate: 500 rpm Leaching time: 48 h	Ag: 93% Au: 98%	Ficeriová et al. (2011)
(sodium) thiosulfate	mobile phone PCBs	pH: 9 T: 25°C S/L: 5% w/v Lixiviant concentration: 0.1 M Leaching time: 4 h	Au: 15% Ag: 3%	Petter et al. (2014)
aqua regia	PC PCBs	T: 90°C S/L: 50% w/v Leaching time: 0.5 h	Au: 100%	Sheng and Etsell (2007)
aqua regia	PCBs	T: 20°C S/L: 2.5% w/v Leaching time: 3 h	Ag: 7.2% Au: 100% Pd: 7.8%	Park and Fray (2009)

A critical comparison of the lixiviant agents used for precious metal recovery from WEEE was given by Cui and Zhang, (2008). Considering the economic feasibility of the leaching process as summary of the score from leaching rate, leaching kinetics, reagent cost and corrosive properties, cyanide results the best leaching agent. The assessment is overturned when the environmental impact due to the lixiviant toxicity is considered. However, cyanide and thiourea got the same final results, although thiourea leaching is still at low research levels.

The leaching process is influenced by several factors, including type of leaching agent and its concentration, pH, temperature, leaching time, stirring rate, ratio between the amount of solid and the leaching solution, size of solid particles and their mineral phase (Chagnes et al., 2016).

Temperature is recognised to have a positive effect on kinetic reaction making it faster. However, the oxidative leaching has been successfully applied also at room temperature as an increasing in temperature resulted in the degradation of hydrogen peroxide in water and oxygen (Birloaga et al., 2014; Yang et al., 2011). Similarly, high temperature (above 40°C) led to the decomposition of thiourea (Birloaga et al., 2013). Besides the effect of the leaching agents, temperature affects the dissolution of the chemical elements as well. For instance, elevated temperature decreased the solubility of rare earths in sulphuric acid solution leading to their precipitation (Tunsu et al., 2015). Ambient temperature is, moreover, desirable for economic aspects.

A degradation of H_2O_2 was also reported when the leaching process is carried out at high stirring rates. Thus, the oxidative leaching must be performed either without shaking or at low stirring rates. Conversely, higher shaking rates were necessary for acidothiourea leaching as the process depends on a strong mixing (Birloaga et al., 2013).

Moreover, optimum leaching conditions generally require smaller particle size as this ensure the exposure of larger metallic areas to the leaching agents (Birloaga et al., 2013).

4.4 BIOMETALLURGY

The environmental burdens related to both pyrometallurgical and hydrometallurgical processes have set the need for developing eco-friendly techniques for metal recovery from secondary materials. For this reason, in the last years the attention has been directed toward a low cost and minor impact technology named biometallurgy (Cui and Zhang, 2008; Das, 2010; Ilyas et al., 2010; Pant et al., 2012; Tuncuk et al., 2012).

Bioleaching and biosorption are the two main areas of biometallurgy (Cui and Zhang, 2008). Bioleaching has been successfully used over the years for the extraction of metals from ores exploiting the capacity of some microorganism to solubilise metals as a result of bacterially assisted reactions (Cui and Zhang, 2008). Biosorption is based on the ability of living as well as death biomass, including algae, fungi, yeast and bacteria, to bind the metal species present in solution. This process has been efficiently used for the removal and/or the recovery of metals from liquid effluents (Andrès et al., 2003; Das, 2010; Vijayaraghavan and Yun, 2008; Wang and Chen, 2009).

Biometallurgical processes offer several advantages related to low capital costs, less environmental impacts and less energy consumption in comparison to conventional metallurgical technologies (Priya and Hait, 2017). Conversely, biometallurgy provides slow leaching kinetics resulting in a time consuming process (Pant et al., 2012). However, the application of biometallurgical technologies is of relevant interest especially for low grade material recovery. For instance, as REEs are contained in electronic waste at trace concentrations the recovery of these elements through biometallurgical approaches appears economically sustainable compared to conventional treatments (Beolchini et al., 2012).

Although some investigations have demonstrated the feasibility of biometallurgy in recovering metals from electronic waste (Beolchini et al., 2012; Bhat et al., 2012; Brandl et al., 2001; Creamer et al., 2006; Ilyas et al., 2007, 2010; Işıldar et al., 2016; Macaskie et al., 2007; Pant et al., 2012), most of the applications are still at laboratory scale (Zhang and Xu, 2016) and the potential of metal recovery from WEEE through biometallurgical processes is yet to be fully explored (Ilyas and Lee, 2014), especially with reference to rare earth elements (Barmettler et al., 2016).

As the metal extraction phase from the solid matrix is of fundamental importance for its further recovery, the following paragraph is mainly focused on bioleaching processes aiming to mobilize metals from WEEE.

4.4.1 Bioleaching processes for metal recovery from WEEE

Bioleaching is a mature technique applied in mining industry for metal extraction from mineral sulphides. The first application dates back to the 1950s with regard to the extraction of copper but after the mid-1980s it has been extended also to other metals as gold (Brierley and Brierley, 2001). The extraction of these metals form mineral ores is performed at industrial scale piling the material and sprinkling the leaching water in it. Basically three main procedures are used, consisting of dump leaching, heap leaching and underground or in situ leaching. The use of tank leaching has been tested as well (Bosecker, 1997).

Besides mineral ores, the ability of some microorganisms to enhance the mobilization and the dissolution of metals contained in solid matrices into their soluble form has been proved to be effective even for secondary sources as electronic waste (Beolchini et al., 2012). However, the bioleaching processes for metal recovery from WEEE are still at infancy stage of development as electronic waste presents a form physically and chemically different from other solid waste. The literature studies available on WEEE bioleaching are currently limited (Ilyas and Lee, 2014) and mainly restricted at bench scale applications with only few attempts on column bioreactor at laboratory scale (Chen et al., 2015; Ilyas et al., 2010; Lee and Pandey, 2012).

WEEE bioleaching studies have been mostly focused on PCBs using autotrophic and heterotrophic microbes belonging to bacterial and fungal strains. The major microbes investigated include iron and sulfur-oxidizing chemolithotrophic acidophiles such as *Acidithiobacillus* and *Leptospirullum,* heterotrophs such as *Chromobacterium* and *Pseudomonas*, and fungi such as *Aspergillus* and *Penicillium*.

Bioleaching processes for metal recovery from e-waste have been mainly focused on the extraction of base metals as well as precious metals. Both autotrophic bacteria and heterotrophic microorganisms have been also used for REE leaching from native minerals (Brisson et al., 2016; Desouky et al., 2016; Ibrahim and El-Sheikh, 2011; Shin et al., 2015); however, only a limited number of studies is currently available on REE leaching from secondary sources including electronic waste (Beolchini et al., 2012; Muravyov et al., 2015; Qu and Lian, 2013; Reed et al., 2016). Moreover, the REE microbe-interaction is not well understood (Barmettler et al., 2016).

The mechanism which governs the bioleaching process is still debated. In principle bioleaching can involves two dissolution mechanisms: direct bioleaching and indirect bioleaching. The former mechanism is based on the direct action of the bacteria that oxidize enzymatically the metal sulphide in sulphate via the intimate contact with the mineral surface. The latter mechanism provides the oxidation of metals through leaching agents biologically produced (Bosecker, 1997). Nevertheless, Sand et al., (2001) limited the bioleaching model only to the indirect mechanism proposing a pathways based on the production of sulfur intermediates, namely thiosulfate and polysulfide.

However, the bioleaching-based principles are recognised to be essentially attributed to: (i) oxidation-reduction reactions, (ii) production of organic and inorganic acids, (iii) excretion of microbial metabolites, chelators and complexing agents. Redoxolysis, acidolysis and complexolysis mechanisms are therefore responsible of metal bioleaching (Brandl, 2001; Priya and Hait, 2017) and can occur even simultaneously (Ilyas and Lee, 2014).

During bioleaching processes oxidation-reduction reactions take place. These reactions are catalysed by bacteria including iron-oxidizing strains which are able to oxidize ferrous iron (Fe^{2+}) in ferric iron (Fe^{3+}). Ferric ion is a powerful oxidizing agent (E_h=0.77 V) that can attack metals, generally contained in the electronic waste in zero-valent form, converting them into their soluble form. Once metals are chemically oxidized, Fe^{3+} is again reduced to Fe^{2+}. Then the generated Fe^{2+} is re-oxidizes in Fe^{3+} by bacteria in a continuous cycle following the reactions reported below (Bosecker, 1997):

$$2Fe^{2+} + 0.5O_2 + 2H^+ \xrightarrow{\text{Bacteria}} 2Fe^{3+} + H_2O \tag{5}$$

$$Fe^{3+} + M^0 \rightarrow Fe^{2+} + M^{2+} \tag{6}$$

where: M^0 stands for metal.

The biogenic production of inorganic as well as organic acid contributes to the leaching of metals from WEEE. For instance, microorganisms as sulphur-oxidizing ones are able to produce sulfuric acid by the oxidation of elemental sulfur providing protons for the hydrolytic attach of metals (Bosecker, 1997):

$$S^0 + 1.5O_2 + H_2O \xrightarrow{\text{Bacteria}} 2H^+ + SO_4^{2-} \tag{7}$$

$$M^0 + H_2SO_4 + 0.5O_2 \rightarrow M^{2+} + SO_4^{2-} + H_2O \tag{8}$$

where: M^0 stands for metal.

Besides inorganic acids, the dissolution of metals can be moreover assisted by organic acids, such as acetic, citric and oxalic acid produced by some heterotrophic bacteria and fungi. In this condition, both a mechanism of acidolysis and complexolysis can take place as some of these acids have chelating properties which lead to the formation of metallic complexes with the metals contained in the solid matrix (Ilyas and Lee, 2014). Complexolysis is the general leaching mechanism that involves also the microbial metabolites excreted by some microbes. Bacteria strains as *Chromobacterium violaceum* and *Pseudomonas fluorescent* were found to solubilize gold from PCBs due to the secretion of biogenic cyanides forming complexes as follow (Priya and Hait, 2017):

$$4Au + 8CN^- + O_2 + H_2O \xrightarrow{\text{Bacteria}} 4A\ \ (C\ \ )_2^- + 4OH^- \quad (9)$$

Complexation can take place in presence of rare earth cations (RE_2O_3) and organic acids as well. For instance, oxalic acid fully dissociated in solution (equation 10-11) can form rare earths oxalate complexes as reported in equation 12-13.

$$C_2H_2O_4 \rightarrow (C_2HO_4)^{1-} + H^+ \quad (10)$$

$$C_2H_2O_4 \rightarrow (C_2O_4)^{2-} + 2H^+ \quad (11)$$

$$3(C_2HO_4)^{1-} + R\ \ {}_2O_3 \rightarrow R\ \ (C_2HO_4)_3 \quad (12)$$

$$3(C_2O_4)^{2-} + R\ \ {}_2O_3 \rightarrow R\ \ (C_2O_4)_3 \quad (13)$$

A bioleaching process is affected by various biotic factors as well as abiotic ones (Priya and Hait, 2017).

Biotic factors include type of microorganism, inoculum size, maximum metal tolerance and adaptability of microbes to the e-waste toxicity (Ilyas and Lee, 2014; Priya and Hait, 2017). The most investigated group of bacteria in metal leaching from e-waste is represented by chemolithoautotrophic acidophilic bacteria, including *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans* and *Leptospirillum ferroxidans*. These microbes derive energy from oxidation of ferrous iron and reduced sulfur compounds. Besides autotrophic microorganisms, heterotrophs are exploited as well. They use organic carbon as energy source producing metabolites and organic acids able to leach out metals. The most used heterotrophic bacteria in WEEE bioleaching are *Chromobacterium violaceum*, *Pseudomonas fluorescens* and *Pseudomonas aeruginosa*, also known as cyanogenic bacteria whereas *Aspergillus niger* and *Penicillium simplicissimum* are the fungi mostly investigated (Ilyas and Lee, 2014; Priya and Hait, 2017). Compared to autotrophs, heterotrophic microorganisms can tolerate high pH conditions created by the alkaline nature of electronic waste and their ability of chelating metals represents an important advantage as the metal toxicity is reduced in solution by the formation of metal complexes (Burgstaller and Schinner, 1993). As greater amount of microorganisms involves faster leaching of metals, the size of inoculum was found to positively affect the leaching process (Yang et al., 2009) as well as the use of mixed cultures, instead of pure ones, that have been proved to have synergic effects resulting in more effective leaching rates (Brandl et al., 2001; Ilyas et al., 2007; Işıldar et al., 2016). Moreover, a pre-growth strategy consisting in microorganism cultivation in absence of electronic waste demonstrated a more efficient metal mobilization due to the reduction of the toxic effects of the waste material for the microbes (Brandl et al., 2001; Işıldar et al., 2016). Conversely, a prolonged time of adaptation is needed (Brandl et al., 2001; Ilyas et al., 2007).

Abiotic factors influencing metal bioleaching consist of pH, temperature, particle size of the solid matrix, leaching time, aeration or stirring rate and composition of leaching media (Ilyas et al., 2007; Wang et al., 2009). Metal leaching has been proved to be highly sensitive to pH (Yang et al., 2009). pH represents a fundamental parameter as it regulates the condition for optimum microorganism growth as well chemical metal solubilisation (Bosecker, 1997). Same consideration can be ascribed to temperature which is crucial for both microbial growth and metal dissolution. Microbes exploited in bioleaching processes belong mainly to mesophilic and thermophilic class: the formers act at temperature ranging between 25–30°C whereas the last mobilize metals at optimum temperature of 40–45°C (Ilyas et al., 2007). However, a recent investigation demonstrated the feasibility of leaching copper even at room temperature using a mixed culture of *A. ferrooxidans* and *A. thiooxidans* (Işıldar et al., 2016).

The characteristics of the source material affect the process as well. The size of solid particles influences the leaching process as it determines the material surface exposure to the leaching attack (Sun et al., 2015). Efficient metal leaching has been achieved using particle size ranging between 40–200 μm (Ilyas et al., 2007; Priya and Hait, 2017; Yang et al., 2009). The toxic nature of e-waste imposes the amount of solid in the pulp: a pulp density above 1-2% w/v generally resulted in the inhibition of the microbial growth (Beolchini et al., 2012; Priya and Hait, 2017). Moreover, washing the solid material prior to bioleaching experiments in order to remove the non-metallic components could enhance the bioleaching performances (Ilyas et al., 2007).

Compared to chemical processes, bioleaching is recognised to require longer operation time. However, an average leaching time of 7 days was reported by several studies. The bioleaching experiment needs to be carried out at shaking conditions providing enough aeration for microorganisms without producing friction and abrasion conditions due to an excessive agitation (Priya and Hait, 2017). Optimum stirring rate ranged between 120–175 rpm (Beolchini et al., 2012; Ilyas et al., 2007; Yang et al., 2009).

The rate of bioleaching is moreover affected by the composition of leaching media in terms of nutrients supporting the microbial growth. The concentration of Fe^{2+} as well as S^0 influences the activity of autotrophic microorganisms (Ilyas et al., 2007; Yang et al., 2009; Zhu et al., 2011) due to its relevant role in bioleaching processes whereas the concentration of organic compounds regulates the growth of heterotrophs as for glycine with reference to cyanogenic bacteria (Işıldar et al., 2016).

An overview of bioleaching studies for metal recovery from WEEE is reported in Table 4.4.

Table 4.4 Bioleaching studies for metal recovery from WEEE

Microrganism	Source matrix	Process parameters	Leaching rates	Refs
A. ferrooxidans + *A. thiooxidans*	Dust from WEEE shredding processes	pH: 2.1 - 0.9 T: 30°C S/L: 0.5-1% w/v Stirring rate: 150 rpm Leaching time: 10 d	Al: 90% Cu 90% Ni: 90% Zn: 90%	Brandl et al. (2001)
S.thermosulfidooxidans + acidophilic isolate	PCBs	pH: 2 T: 45°C S/L: 1% w/v Stirring rate: 180 rpm Leaching time: 18 d	Ni: 81% Cu: 89% Al: 79% Zn: 83%	Ilyas et al. (2007)
A. ferrooxidans	PCBs	pH: 2 T: 30°C S/L: 2.5% w/v Stirring rate: 165 rpm Leaching time: 4 d	Cu: 100%	Yang et al. (2009)
Mixed Acidophilic bacteria	PCBs	pH: 2, T: 30°C S/L: 1.2% w/v Stirring rate: 160 rpm Leaching time: 1.8 d	Cu: 96.8% Zn: 91.6% Al: 88.2%	Zhu et al. (2011)
A. ferrooxidans + *L. ferrooxidans* +	TV PCBs	pH: 1.7 T: 35°C	Cu: 89%	Bas et al. (2013)

A. thiooxidans		S/L: 1% w/v Stirring rate: 175 rpm Leaching time: 4.8 d		
A. ferrooxidans + *A. thiooxidans*	PCBs	pH: 1. 5 T: 32°C S/L: 3% w/v Stirring rate: 180 rpm Leaching time: 10 d	Cu: 90%	Liang et al. (2010)
A. ferrooxidans	PC PCBs	pH: 3 T: 30°C S/L: 2% w/v Stirring rate: 170 rpm Leaching time: 0.8 d	Cu: 100% Ni: 100%	Arshadi and Mousavi (2014)
A. thiooxidans	PCBs	pH: 1 T: 30°C S/L: 1% w/v Leaching time: 5 d	Cu: 60%	Hong and Valix (2014)
A. ferrooxidans	PC PCBs	pH: 2.2 T: 30°C S/L: 1.5% w/v Stirring rate: 170 rpm Leaching time: 3 d	Cu: 96.8% Zn: 83.8% Al: 75.4%	Yang et al. (2014)
A. ferrooxidans + *A. thiooxidans*	PCBs	pH: 1.0–1.6 T: ambient S/L: 1% w/v Stirring rate: 150 rpm Leaching time: 7 d	Cu: 98%	Işıldar et al. (2016)
A. ferrooxidans + *A. thiooxidans*	PCBs	pH: 1.5 - 2.2 S/L: 1% w/v Leaching time: 28 d	Cu: 100% Ni: 92% Zn: 89% Al: 20%	Mrazikova et al. (2015)
Penicillium simplicissimum	PCBs	pH: 6 – 3 T: 30°C S/L: 1% w/v Stirring rate: 150 rpm Leaching time: 21 d	Cu: 30% Al: 60% Ni: 100% Zn: 100%	Brandl et al. (2001)
Apergillus niger	PCBs	pH: 6 – 4 T: 30°C S/L: 5% w/v Stirring rate: 150 rpm Leaching time: 21 d	Cu: 65%	Brandl et al. (2001)
C. violaceum	PCBs	pH: 7.2 – 9 T: 30°C S/L: 1% w/v Stirring rate: 150 rpm Leaching time: 7 d	Au: 14.9%	Faramarzi et al. (2004)
C. violaceum	electronic scrap	S/L: 0.5% w/v, Leaching time: 7 d	Au: 11.5%	Pham and Ting (2009)
P. fluorescens	electronic scrap	S/L: 0.5% w/v Leaching time: 7 d	Au: 10.5%	Pham and Ting

				(2009)
C. violaceum	PC PCBs	pH: 7.2 – 9 S/L: 1% w/v Leaching time: 7 d	Au: 69%	Pradhan and Kumar (2012)
C. violaceum + *P. aeruginosa*	PC PCBs	pH: 7.2 – 9.3 S/L: 1% w/v Leaching time: 7 d	Au: 73%	Pradhan and Kumar (2012)
C. violaceum	electronic scrap	pH: 7 – 9 T: 30°C S/L: 0.5 % w/v Stirring rate: 170 rpm Leaching time: 8 d	Au: 11.3%	Natarajan and Ting (2015)
P. putida	PCBs	pH: 7.3 – 8.6 T: 30°C S/L: 0.5 % w/v Stirring rate: 150 rpm Leaching time: 2 d	Au: 44%	Işıldar et al. (2016)
A. ferrooxidans + *A. thiooxidans* + *L. ferrooxidans*	CRT fluorescent powder	T: 30°C S/L: 10% w/v Stirring rate: 175 rpm Leaching time: 16 d	Y: 70%	Beolchini et al. (2012)
Gluconobacter oxydans	CRT fluorescent powder	T: 30 °C S/L: 1.5% w/v Stirring rate: 150 rpm Leaching time: 1 d	Total REEs: 2%	Reed et al. (2016)

5 RESEARCH EXPERIMENTAL ACTIVITY

As the industry of electronic devices is a large consumer of metals, the recycling of these materials from obsolete equipment reaching their end-of-life represents an important opportunity in both economic and environmental terms (Cui and Zhang, 2008). Recycling entails an efficient way to feed materials back to economy, lowering the environmental impacts and the energy consumptions of material supply (Hagelüken et al., 2016). This aspect is especially relevant for electronic waste due to the rapidly increasing volume of waste generated as well as the simultaneous presence of valuable metals, such as precious metals and rare earth elements, and hazardous materials.

Conventional treatments for metal recovery from WEEE, including pyrometallurgy and hydrometallurgy, are recognised to provide several limits mainly related to high costs and secondary-produced pollutants (Cui and Zhang, 2008). Compared to these processes, biometallurgy is claimed to offer an eco-friendly treatment with low costs and minor environmental impacts (Priya and Hait, 2017). Although the feasibility of biometallurgical processes in base metal extraction from ores and in metal recovery from aqueous solutions is well documented (Cui and Zhang, 2008), the application of this technique to electronic waste needs to be thoroughly investigated, especially with regard to rare earths (Ilyas and Lee, 2014).

In this background, the present research aims at evaluating the potential application of innovative biotechnological treatments for valuable and critical metal recovery from WEEE. To this end, the presence of these materials, as well as their fate during conventional pre-treatments, was firstly investigated, as described in the following paragraph.

5.1 INVESTIGATION PLAN

The experimental activity was developed in steps matching the specific objectives of the research. The experimental set up and the materials and methods were outlined on the basis of an in-depth analysis of the scientific literature. As previous studies revealed that small household electronic equipment contains components rich in valuable metals (Chancerel and Rotter, 2009; Oguchi et al., 2011), a WEEE industrial facility mainly treating electronic waste coming from this category was selected for the experimental purposes. Therefore WEEE samples were collected from the selected plant and used for the laboratory activity.

The experimental plan developed through the following three phases:

- PHASE 1: WEEE characterization in terms of base and critical metals. Material characterization represents a crucial aspect for developing a sustainable treatment for WEEE recovery, as the extreme heterogeneity of this waste stream is a challenge for its effective recycling (Cui and Zhang, 2008). The main factors affecting the efficiency of WEEE treatment processes are the distribution of elements in the material as well as the dimensional characteristics of the electronic scraps destined to recovery (Cui and Forssberg, 2003; Sun et al., 2015; Veit et al., 2002). The sampled materials were thus characterized by their metal content, both in terms of base metals and critical metals, as well as by particle size distribution.
- PHASE 2: Mass flow analysis of critical metals in WEEE mechanical treatment. As pre-treatments involving mechanical processes are generally the first step of WEEE recycling chain, the effectiveness of these treatments influences the further material recovery (Chancerel et al., 2009; Meskers and Hagelüken, 2009; Meskers et al., 2009). Although mechanical treatments are well-designed for recovering base metals, precious metals are often lost (Bachér et al., 2015; Chancerel et al., 2009; Cui and Zhang, 2008; Oguchi et al., 2012; Veit et al., 2002), while the fate of critical metals is not yet well addressed. For this reason, a conventional mechanical treatment was investigated by means of a mass flow analysis conducted in order to point out the effectiveness of these processes in critical metal sorting and recovery.
- PHASE 3: Hydro-biometallurgical tests for critical metal recovery from WEEE. Since the results from the previous phase highlighted that after pre-treatments the major part of critical metals contained in WEEE is not concentrated in the fraction destined to further metal recovery but ends up in the dust material originated from mechanical units, dust was used as secondary source material of critical metals and tested for innovative biometallurgy treatments. Both the use of

dust, actually destined to landfill disposal, and the proposed biotechnological treatment for the recovery of critical metals outlined the novelty of the research.

The experimental activity was mainly focused on the leaching step that determines the effective extraction of metals from the solid matrix. To this purpose, both acid solutions and microorganisms were tested as leaching agents. The chemical leaching experiments were carried out at the laboratory facility of the Sanitary Environmental Engineering Division (SEED) of Salerno University. The operating conditions were based on previous studies and the experimental tests were planned using the strategy of the design of experiment (DOE). The biological leaching experiments were performed at the laboratory facility of the Institute for water education Unesco-IHE in Delft (Netherlands).

6 MATERIALS AND METHODS

In the following paragraphs a description of the experimental set up and the analytical methods followed to carry out the research is outlined.
To this end, the chapter is divided into three main sections:

- the first section deals with the methods adopted to characterize the materials used for the experimental activity. WEEE samples were collected at a full scale mechanical treatment plant and characterized in terms of metal content and particle size distribution.
- the second section describes the principles followed to conduct the substance flow analysis involving the mechanical treatment under investigation. The data obtained from the metal characterization were, thus, used to carry out a mass flow analysis in order to investigate the fate of metals, particularly the critical ones, during the conventional mechanical treatments. The quality of the output fractions was also discussed pointing out the effectiveness of the mechanical process.
- the last section is focused on the application of innovative treatments for metal recovery from WEEE. Since in conventional pre-treatment special metals were mainly concentrated in dust fraction produced by the mechanical units, dusts were selected as source material for investigating the efficiency of bio-hydrometallurgical processes in critical metal extraction. Both chemical and biological leaching processes were considered and tested.

6.1 MATERIAL CHARACTERIZATION

6.1.1 Sampled materials

The materials used for the experimental activity were collected at a full-scale treatment plant located in the South of Italy. The facility under investigation treats 2 ton per hour of electronic waste coming from small electronic equipment, IT and consumer appliances. The treatment line includes mechanical processing units which basically enable the separation of metallic fractions from plastic ones. The input WEEE is subject to a two-stage size reduction pre-treatment which includes both a shredding and a granulator; each unit is followed by a magnetic separator. At the end of this section, the particles of the incoming waste have been reduced below 20 mm and the iron scraps have been sorted out from the waste stream that is further processed through the separation section. The half-processed waste, thus, enters into a patented selection device which uses high-speed to separate metals from plastics. Due to this high-speed, the waste beats the walls of the device. As a result of the continuous impacts, the plastic-based materials flake off, while metals form small grains. A further separation of metallic and plastic fractions is provided via sieving, fluid bed and electrostatic separation. Metallic grains are finally split into two fractions, one mainly made of copper and the other one of aluminium. The treatment line is also equipped with bag filters which remove dust particles from off-gases. The schematic flowchart of the process under investigation is plotted in Figure 6.1.

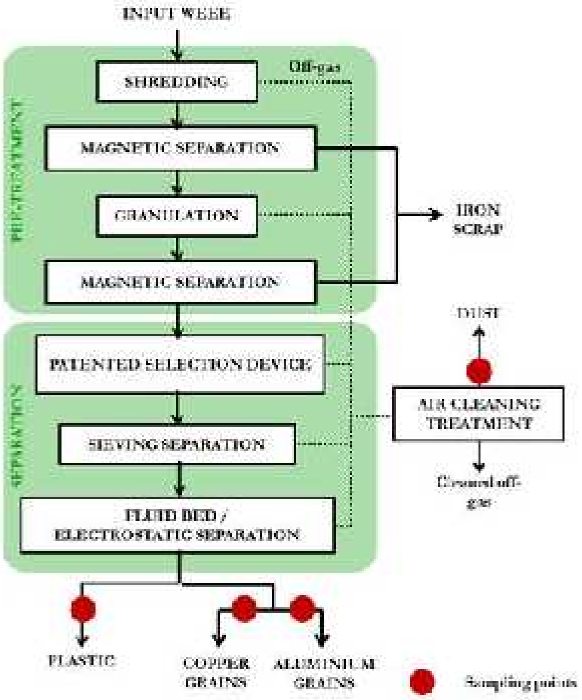


Figure 6.1 Schematic flowchart of the mechanical process under investigation

At the end of the mechanical process, five output fractions are obtained:

i) iron scraps, destined to material recovery. This fraction accounts for about 50% by weight of the incoming waste;
ii) plastic material, actually sent to incineration due to its great heterogeneity, which represents a challenge for its effective recycling. This material stands for almost the 30-35% of the input WEEE;
iii) dust fraction, disposed of in landfill. It is around 5-8 % of the processed WEEE;
iv) copper grains, destined to further refining processes. This fraction represents around 3.5-6% of the treated waste;
v) aluminium grains, accounting for 2.5 – 4% of the incoming waste, sent to recycling processes.

Metallic granules, both copper and aluminium ones, plastic material and dust fraction were sampled for the experimental activity (Figure 6.2). Large iron scraps were not included among the sampled fractions as the visual inspection provided their classification as ferrous materials. Samples were collected from the plant stockpiles using a composite sampling method. The sampling campaigns for characterization purposes covered one year.

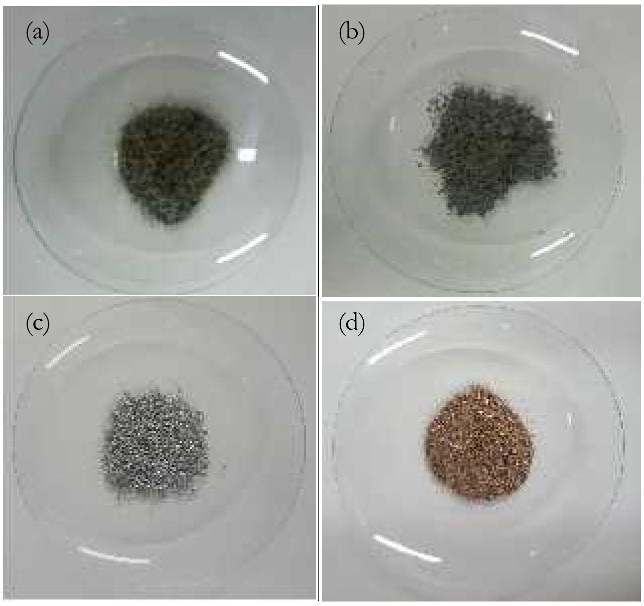


Figure 6.2 Sampled material: (a) plastic, (b) dust, (c) aluminium grains, (d) copper grains

6.1.2 Metal content

The collected fractions were analysed in terms of metal content using the aqua regia extraction procedure according to ISO 11466:1995. Approximately 3 g of each fraction were transferred into 100 mL conical flasks and a slurry was created adding small amount of water. Then 7 mL concentrated HNO_3 and 21 mL concentrated HCl were added in several portions. The flasks were covered by a watch glass and left to stand for 16 h. Then the solutions were gently boiled for 2 h under a reflux condenser mounted on the top of each flasks (Figure 6.3). After the samples had cooled down, the condenser was rinsed with 2% HNO_3 and the samples filtered. The solutions were made up to 100 mL with 2% HNO_3 and the concentration of selected base metals (Al, Cd, Cu, Fe, Ni, Pb, Zn), precious metals (Au, Ag, Pd, Pt) and rare earth elements (Ce, Eu, La, Nd, Y) was determined by means of using inductively coupled plasma-optical emission spectroscopy (ICP-OES, Thermo iCap 6000 series). Each analysis was done in triplicate.

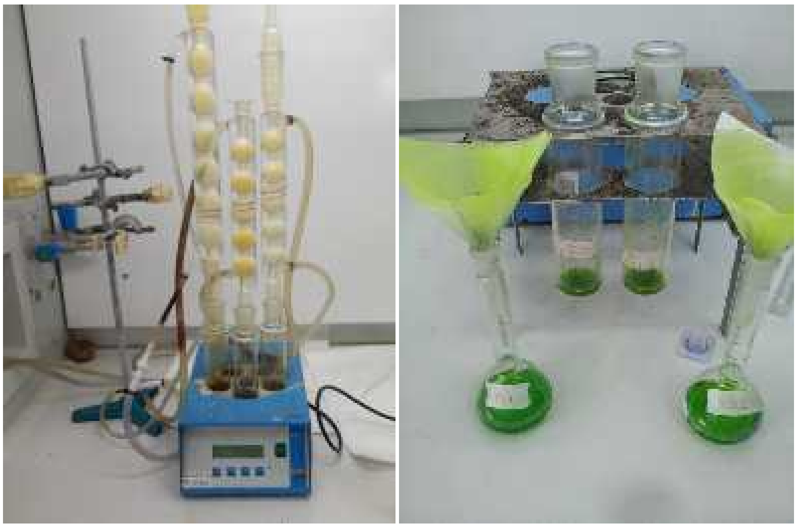


Figure 6.3 Reflux condenser system for sample digestion prior ICP-OES analysis

6.1.3 Particle size characterization

Metallic grains and dust fraction were characterized in terms of particle size distribution by employing ASTM Retsch testing sieve series.

Metallic granules were further separated by size into three fraction, namely F1 (smaller than 1.18 mm), F2 (between 1.18 and 2 mm) and F3 (larger than 2 mm), according to previous literature studies (Veit et al., 2002; Zhang and Forssberg, 1997). The obtained fractions were then characterized in terms of metal content following the aqua regia digestion procedure in order to evaluate the effect of particle size on metal liberation via mechanical treatments.

6.2 MASS FLOW ANALYSIS

A mass flow analysis was conducted with the aim of evaluating the effectiveness in metal recovery of the mechanical process under investigation. In order to develop the analysis, the following assumptions were considered:

- as dust particles coming from the different treatment units end up in a single flow, dust samples were collected from this flow. Its composition was assumed to be representative of the entire line;
- large iron scraps were entirely classified as Fe by visual inspection and the concentrations of other metals in this fraction were thus assumed to be negligible.

Considering the concentration of the i-th metal in the j-th output flow, known from the material characterization, and the mass of that flow, the mass flow of the i-th metal concentrated in the j-th output flow can be calculated with the following equation, as previous done by Chancerel et al., (2009):

$$M_i = C_i \cdot M_j \tag{14}$$

with: M_{ij}= mass flow of metal i concentrated in flow j, mg;
C_i= concentration of metal i in flow j, mg/kg;
M_j= mass of flow j, kg.

The potential recovery R of the i-th metal in the j-th flow was thus obtained using the following equation:

$$R_i = {}^{M_{ij}}\!\Big/_{M_{i-in}} \cdot 100 \tag{15}$$

with: R_{ij}= recovery of metal i in the flow j, %;
M_{ij}= mass flow of metal i contained in flow j, mg;
$M_{i\text{-input}}$ = mass of metal i in the input, mg.

Moreover, the mass of the metals in the input WEEE was determined as sum of the metal contents in the outputs (Oguchi et al., 2012).

6.3 HYDRO-BIOMETALLURGICAL PROCESSES

6.3.1 Dust used as source material for leaching tests

As the early steps of the research activity revealed that a significant amount of special metals is concentrated in dust fraction conventionally produced in mechanical treatments, dust was used as source material for testing the applicability of hydro-biometallurgical processes (Figure 6.4). Dust fraction is actually sent to landfill disposal and the potential recovery of critical metals from this waste matrix is of particular interest in the transition to a circular economy.

Figure 6.4 Dust material used for hydro-biometallurgical tests

Before leaching experiments, a secondary sample of dust was obtained from the primary collected sample and afresh characterized in terms of metals following the aqua regia extraction procedure (ISO 11466:1995).
For a deepen characterization, a mineral phase analysis on dust material was carried out as well, using a X-ray powder diffractometer (XRD, Bruker D8 advance). The following conditions were set up: Cu Kα radiation, 35 keV accelerating voltage, 40 mA current, 10–80° scanning range, 0.5 s/step (0.0296°/step) scan speed.
The laboratory research was mainly focused on the leaching step involved in these processes, as it plays a key role in metal extraction (Zhang et al., 2012). Both chemical and biological leaching processes

were tested in order to evaluate and compare their effectiveness. Batch leaching experiments were performed in two separate steps (two-step leaching process) using different leaching agents in order to pursue the selective recovery of the metals of interest, avoiding the consumption of reagents by other metals.

6.3.2 Chemical leaching experiments

A two-step chemical leaching process was carried out, using first an acid reagent and then a precious metal lixiviant. Among acid reagents, sulfuric acid was selected as it is recognised to be less toxic and corrosive as well as cheaper than nitric and hydrochloric acid (Yang et al., 2011). Thiourea was chosen as precious metal lixiviant due to its promising effectiveness and minor toxicity compared to the most used cyanide (Akcil et al., 2015). The performances of sulfuric acid, well-known with regard to base metal extraction, were tested for the leaching of rare earths, while thiourea was used for evaluating the extraction of precious metals from low-grade matrix. A schematic flowchart of the chemical leaching process performed is displayed in Figure 6.5.

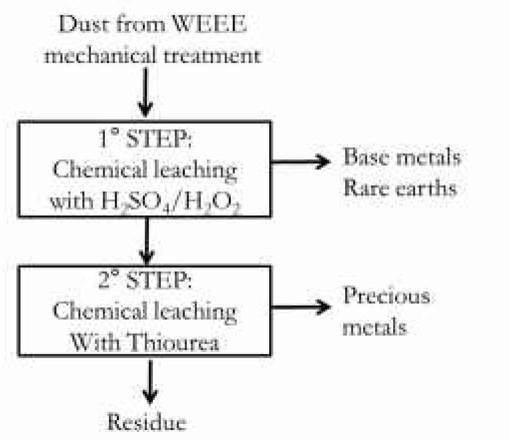


Figure 6.5 Schematic flowchart of the chemical leaching process performed

In detail, the first step was performed using sulfuric acid as leaching agent and hydrogen peroxide as oxygen source, following the study of Birloaga et al., (2013). 10 g of dust were immersed in 100 ml solution of 2M sulfuric acid and 20% v/v of hydrogen peroxide. Operating conditions were set to ambient temperature, 150 rpm and 6 h through a double-oxidative step (3h+3h). The experiments were run in triplicate. The solid residue from this step was collected, dried and used for the second leaching step.

For the second step, using thiourea as lixiviant, the strategy of design of experiment (DOE) was adopted to define the optimal experimental conditions. Differently from the sulphuric acid, thiourea leaching is at low research stage. For this purpose, a full factorial design was performed by varying the factor all together, instead of one at time, in order to investigate the effects of the input parameters or factors on the process response, identifying the significant ones (Montgomery, 1991).

The factors which mainly influence the leaching process include thiourea concentration, pulp density, stirring rate, shaking time, pH, temperature, particle sizes, presence or absence of external oxidant (Gurung et al., 2013). Since thiourea acts in acid condition (Akcil et al., 2015; Cui and Zhang, 2008), the pH of the leaching solution was kept around 1 with sulfuric acid according to previous studies (Birloaga et al., 2013; Ficeriová et al., 2008; Jing-ying et al., 2012). The temperature of the experiment was set at ambient room as higher values were demonstrated to decompose thiourea in sulfur species (Birloaga et al., 2013). The metal extraction was found to be significantly improved by smaller particles due to the high surface area (Gurung et al., 2013; Jing-ying et al., 2012). However, in the present study the size of particles was not considered a key factor as dust used in the leaching experiments was made up of tiny particles. Ferric ions have been indicated as the most convenient oxidant able to enhance the gold dissolution rate, speeding up the thiourea leaching reaction (Birloaga et al., 2013). For instance, Gurung et al. 2013 found that in presence of ferric ions the extraction of gold from PCB samples reached the maximum rate after 2 h while in absence of oxidant the shaking time ensuring the complete leaching of gold corresponded at 6 h. However, in our experience preliminary leaching tests revealed significant analytical interferences related to the use of ferric sulfate. For this reason, the thiourea leaching tests were further carried out in absence of oxidant but increasing the shaking time up to 6 h. Moreover, samples were collected at different intervals: 1h, 3h and 6 h.

Definitively, three operating factor were selected for the experimental design: pulp density, thiourea concentration and stirring rate. These factors were assumed to vary between two levels, namely “low” (-) and “high” (+). In this way, a 2^3 factorial design was defined with eight test combinations. No central points were added to the design assuming the linearity of the effects and the absence of quadratic terms in the model. The levels were set up on the basis of previous literature studies. The selected factors and levels are reported in Table 6.1.

Table 6.1 Factors and levels under investigation for tiourea leaching tests

Factors	Levels		Reference
	Low (-)	High (+)	
Pulp density	0.2 g/70 ml	2 g/70 ml	[1]
Thiourea (TU) concentration	0.25 M	0.5 M	[1], [2]
Stirring rate (rpm)	150	600	[1], [2]

[1] Gurung et al., (2013); [2] Birloaga et al., (2013)

After defining factors and levels as well as organizing the experimental plan (Table 6.2), the single tests were carried out. The data collected from each run were then analysed using the ANOVA technique and the significant factors were evaluated conducting F-tests.

Table 6.2 Experimental plan for thiourea leaching tests

Run	Pulp density (g/ml)	TU Concentration (M)	Rpm	Response (% extraction)
1	-1 (0.2/70)	-1 (0.25)	-1 (150)	Y_1
2	+1 (2.0/70)	-1 (0.25)	-1 (150)	Y_2
3	-1 (0.2/70)	+1 (0.50)	-1 (150)	Y_3
4	+1 (2.0/70)	+1 (0.50)	-1 (150)	Y_4
5	-1 (0.2/70)	-1 (0.25)	+1 (600)	Y_5
6	+1 (2.0/70)	-1 (0.25)	+1 (600)	Y_6
7	-1 (0.2/70)	+1 (0.50)	+1 (600)	Y_7
8	+1 (2.0/70)	+1 (0.50)	+1 (600)	Y_8

6.3.3 Biological leaching experiments

Similarly to the chemical leaching, the biological leaching or bioleaching involved firstly an acidophilic strain, *Acidithiobacillus thiooxidans*, to extract both base metals and rare earth elements and then a cyanide producing one, *Pseudomonas putida*, for the recovery of precious metals.

Acidithiobacillus thiooxidans is an autotrophic bacteria, as it uses carbon dioxide as carbon source, and strictly chemolithotrophic, as it derives energy by the reduction and oxidation of inorganic sulfur compounds. It belongs to the genera of *Acidithiobacillus* which includes essentially iron and sulfur oxidizers. These microbes, mesophilics in nature, grow in low pH environment and due to their ability in leaching metals from sulfidic ores they have been also investigated for the extraction of metals from waste material as electronic waste (Ilyas and Lee, 2014). In this case, the role of *A. thiooxidans* in bioleaching process is to oxidize elemental sulfur (S^0), which is added externally as it is not found in the waste material, to sulfuric acid (H_2SO_4). Metals contained in WEEE are then solubilized by biogenic H_2SO_4 as a result of an indirect bioleaching mechanism following the equations (Nguyen and Lee, 2015):

$$S^{o} + H_2O + 1.5O_2 \rightarrow H_2SO_4 \qquad (16)$$

$$H_2SO_4 + M \qquad\qquad - M \ \rightarrow M \qquad\qquad - 2H + M \quad O_4 \qquad (17)$$

where Me stands for metal.

Compared to *Acidithiobacillus ferroxidans,* which are the most used microbes in bioleaching processes, the research on *Acidithiobacillus thiooxidans* is limited (Travisany et al., 2014). In the present study, *A. thiooxidans* was selected for its well-known ability in base metal bioleaching and in order to test this strain for rare earth extraction.

Pseudomonas putida belongs to *Pseudomonas* strains. These microbes have the ability of producing cyanides in aqueous medium via oxidative decarboxylation of glycine. The biogenic cyanides act leaching gold under alkaline conditions (Ilyas and Lee, 2014) and minimizing the issues related on cyanide environmental toxicity. The microbially-produced cyanides occur indeed only for a short period at late exponential or early stationary phase of bacterial growth (Knowles, 1976). Although they showed weak CN^- production compared to the most used cyanogenic microorganism in precious metal bioleaching from WEEE namely *Chromobacterium Violaceum*, *Pseudomonas* can be easily employed for industrial application as they are common among rhizosphere microbial communities and moreover they have strong ability of acclimation (Ruan et al., 2014). As the effective ability of *P.putida* has been demonstrated for gold mobilization from PCBs (Işıldar et al., 2016), it was chosen as cyanogenic bacteria for being tested on the selected material.

A schematic flowchart of the biological leaching process performed is displayed in Figure 6.6.

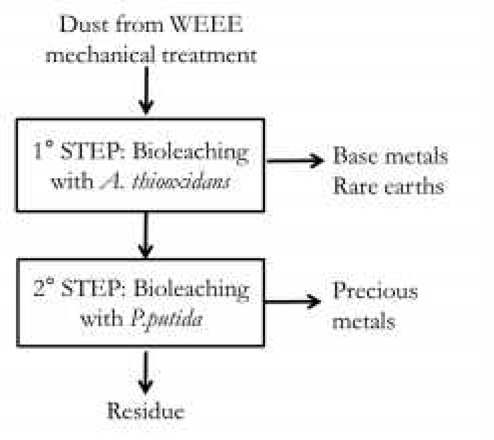


Figure 6.6 Schematic flowchart of the biological leaching process performed

A pre-growth strategy was used as WEEE were found to inhibit bacterial growth due to its hazardous compounds (Liang et al., 2010). In order to reduce the toxic effect of the waste, the microorganisms were firstly grown in absence of WEEE and subsequently, when optimum bioleaching conditions were reached, the waste material was added (Brandl et al., 2001; Işıldar et al., 2016).

Acidithiobacillus thiooxidans (DSM 9463) were ordered from the Leibniz Institute (DSMZ), Braunschweig (Germany) and grown in a mineral medium containing (g/L): $(NH_4)_2SO_4$ (2.0), $MgSO_4x7H_2O$ (0.25), K_2HPO_4 (0.1), KCl (0.1) and S^0 (5.0). The pH was set to 3.5 with sulfuric acid. The cultures were inoculated with 10% in v/v in 100 mL growth medium and incubated at 30˚C and 150 rpm for 10 days prior to the bioleaching experiments (Figure 6.7a). *A. thiooxidans* cells were enumerated using the spread plate method (Starosvetsky et al., 2013). Thiobacillus agar containing 0.4 g $(NH_4)_2SO_4$, 0.5 g $MgSO_4$ x $7H_2O$, 0.25 g $CaCl_2$, 4 g KH_2PO_4, 0.01 g $FeSO_4$, 5 g $Na_2S_2O_3$, 12.5 g agar in 1 L distilled water was used. Samples were serially diluted up to 10^{-7} using saline solution (0.85% NaCl) and plated on the agar plates. The Petri dishes were then incubated for 7-10 days at 31±0.5 °C.

The first leaching step was performed adding the dust, previously dried at 80°C overnight (Brandl et al., 2001), in the bioleaching medium containing active growing cultures of *A. thiooxidans* ($2.1 \pm 0.3x10^7$ CFU/mL) (Figure 6.7c). Three different solid/liquid ratio were tested (0.5%, 1% and 2% w/v). Bioleaching experiments were carried out for 8 days in a controlled temperature room at 30°C using an orbital shaker (Brunswick Innova 2000, USA) set to 150 rpm (Figure 6.7d). During bioleaching, samples were taken at different time intervals (2 days, 4 days, 6 days, 8 days) and analysed in terms of metal concentrations. Each test was done in duplicate and control experiments, namely negative control as they contained non-inoculated bioleaching medium, were run as well (Figure 6.7b). pH and oxidation reduction potential (ORP) were measured to indirectly monitor both the pre-growth and the bioleaching process.

Figure 6.7 Bioleaching medium containing active growing cultures of *A. thiooxidans* (a), inoculated and non-inoculated bioleaching medium (b), bioleaching medium containing active cultures and dust material at different pulp density (c), bioleaching experiments (d)

After the first step, the solid residue was collected, washed twice in order to remove any traces of sulfuric acid, dried and used for the second bioleaching step involving *Pseudomonas putida*. Unwashed samples were tested as well.

P. putida (WSC361) were kindly provided by Dr. Peter Bakker from Utrecht University (the Netherlands) and grown in a nutrient broth containing (g/L): meat extract (1.0), yeast extract (2.0), peptone (2.0), and NaCl (5.0). The pH was set to 7.3 with sodium hydroxide. The cultures were inoculated with 1% in v/v in 150 mL growth medium supplemented with 10 g/L of glycine (Işıldar et al., 2016) and incubated at 30˚C and 150 rpm for 18 h prior to the bioleaching experiments (Figure 6.8a).

Figure 6.8. Inoculated bioleaching medium containing active growing cultures of *P. putida* and non-inoculated flasks (a), colour reaction proving the CN^- production of *P. putida* (b)

The bacterial growth was monitored recording the optical density (OD) at 600 nm. As it is known that the maximum cyanide production is generally achieved in the late exponential/early stationary phase (16-20 h) and after that it starts to decrease (Işıldar et al., 2016; Natarajan and Ting, 2015), the dust derived from the first leaching step was added 18 h after inoculation (OD_{600}=0.9). Işıldar et al. (2016) found that in this condition, *P. putida* are able to produce approximately 20 mg/L of CN^- (Figure 6.9).

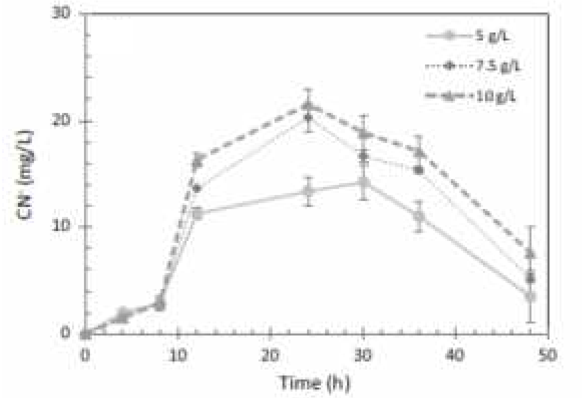


Figure 6.9 Cyanide production of *P.putida* as function of various glycine concentrations (5 g/L, 7,5 g/L, 10 g/L) and time of inoculation (Işıldar et al., 2016)

However, the ability of *P. putida* in producing CN^- was proved using a modified colorimetric method (Işıldar et al., 2016; Ruan et al., 2014). *P.putida* were plated on nutrient agar supplemented with glycine. A sterile filter paper soaked in a solution of 0.5% picric acid and 2% sodium carbonate was fixed to the underside of the Petri dish lid. The dishes were covered with paraffin film and incubated at 30°C (Işıldar et al., 2016). The CN^- production determined a colour reaction of the filter paper which turned from yellow to red (Figure 6.8b), proportionally to the cyanide concentration (Ruan et al., 2014).

Operating bioleaching conditions of pulp density, temperature, agitation rate and leaching time were set to 1% (w/v), 30°C, 150 rpm, and 30 h, respectively. Samples were taken at different intervals (3 h, 8h, 20h, 24 h, 30 h) and analysed in terms of metal concentrations. pH was measured to indirectly monitor both the pre-growth and the bioleaching process. As for the previous biological leaching step, each flask experiment was done in duplicate and control experiments containing non-inoculated bioleaching medium were run as well (Figure 6.8a).

Moreover, the biogenic cyanide leaching was compared with a chemical leaching using a solution of potassium cyanide at 5, 10, 25 mg/L cyanide concentrations and 1% w/v pulp density. The operating conditions were set to ambient temperature, 150 rpm and 30 h. Prior to the cyanide leaching, a chemical leaching using sulphuric acid was carried out for removing base metals.

6.3.4 Analytical methods

During each leaching step, the collected samples were chemically analysed in order to evaluate the leaching ability in terms of metals. The concentrations of the selected base metals, precious metals and rare earth elements were obtained by means of metal analysis using inductively coupled plasma optical emission spectrometry (ICP-OES).

Prior to the ICP-OES analysis, the samples obtained from the chemical leaching, namely chemical samples, were filtered via nylon membrane 0.45 μm (Whatman), acidified with concentrated HNO_3 at 2% for base metals and rare earths analysis and with 5% HCl for precious metal detection. Proper dilutions were also applied for analytical purposes. Conversely, the samples collected from the biological leaching experiments were centrifuged at 12000g for 10 min, then filtered at 0.45 μm, acidified according the detection of the metal of interest and finally diluted prior to ICP-OES analysis.

The leaching ability (Li) shown for the i-th metal was calculated taking into account the mass of the source material used for the experiment (M), the volume of the leaching solution (V) and the concentration of the selected metal (Ci) in the leachate.

$$L_i = \frac{C_i \cdot V}{M} \tag{18}$$

where: Li= leaching ability for the i-th metal (mg/g);

Ci= concentration of the i-th metal detected in the leaching solution (mg/L);

M= mass of the dust used for the experiment (g);

V= volume of the leaching solution (mL).

Thus, the recovery (Ri), or extraction efficiency, was expressed in percentage with reference to the initial concentration (Cin,i) as reported in the following equation:

$$R_i = \frac{L_i}{C_{i\ ,i}} \cdot 100 \tag{19}$$

where: Ri= recovery of the i-th metal (%);

Li= leaching ability for the i-th metal (mg/g);

Cin,i= concentration of the i-th metal in dust (mg/kg).

7 RESULTS AND DISCUSSIONS

In the present chapter the results of the research activity are presented and discussed into four main sections:

- the first section deals with the characterization, in terms of metal contents and size distribution, of the WEEE samples used for the experimental activity;
- in the second section the effectiveness of conventional mechanical treatments for metal recovery is evaluated, with particular reference to both the fate of critical metals and the quality of the output metallic fractions;
- the third section focuses on the innovative treatments proposed. The results of hydro- and bio-metallurgical tests are discussed and the recovery rates of selected metals for both chemical and biological processes are compared;
- in the last section the experimental results obtained were discussed to address wider considerations on the technical implications. A focus on the processing scale-up of the treatments performed is outlined as well.

7.1 MATERIAL CHARACTERIZATION

7.1.1 Metal content

The output fractions from a full scale mechanical plant treating e-waste, namely aluminium grains, copper grains, plastic and dust were analysed by their metal content. The average metal concentrations detected in the investigated fractions are reported in Table 7.1. The concentration of the selected metals in WEEE stream entering the plant was provided as well, calculating the metal content in input WEEE as sum of the metal contents in the outputs (Oguchi et al., 2012).

Table 7.1 Average metal concentrations in WEEE fractions under investigation

Investigated fraction	Common metal concentrations (mg/kg)						
	Al	**Cd**	**Cu**	**Fe**	**Ni**	**Pb**	**Zn**
Input WEEE*	31982	40	60290	504424	712	3743	8463
Aluminium grains	332173	66	192350	24090	5257	20449	73217
Copper grains	4297	35	761106	31354	5956	2273	71944
Plastic	48756	62	14998	1829	195	2538	1825
Dust	35436	196	26624	12423	1028	24705	7926

Investigated fraction	Precious metal concentrations (mg/kg)			
	Au	**Ag**	**Pd**	**Pt**
Input WEEE*	5.1	32.4	3.0	4.1
Aluminium grains	35.0	102.6	22.3	<DL
Copper grains	21.6	204.4	6.8	2.8
Plastic	4.6	23.8	2.3	12.1
Dust	11.0	105.5	11.7	<DL

Investigated fraction	Rare earth element concentrations (mg/kg)				
	Ce	**Eu**	**La**	**Nd**	**Y**
Input WEEE*	4.4	0.5	4.5	5.6	6.2
Aluminium grains	1.7	0.03	1.4	1.9	0.2
Copper grains	<DL	0.1	1.4	0.4	0.1
Plastic	3.0	0.2	2.2	3.0	1.9
Dust	42.5	5.1	45.8	56.6	69.6

* Calculated values; DL=detection limit

As highlighted in Table 7.1, the input WEEE consisted mainly of Fe (504000 mg/kg), Cu (60000 mg/kg) and Al (32000 mg/kg) as also extensively reported in other investigations (Meskers and Hagelüken, 2009; Widmer et al., 2005). Although different proportions of input materials provide different metal composition, the concentrations determined in the input WEEE were found to be in good agreement with the values of previous studies (Morf et al., 2007; Oguchi et al., 2012). However, high standard deviations were recorded among the sampling campaigns as a result of the wide heterogeneity which generally characterizes the e-waste stream.

Precious metals and rare earth elements were found to be present at trace concentrations in input WEEE. As precious metals are reported to be mainly concentrated in specific components such as PCBs, literature studies are mostly focused on the quantification of these valuable metals in those components (Chancerel et al., 2009). Therefore, data on precious metal concentrations are principally referred to PCBs and not to the generic WEEE as in the present study. However, the value obtained were in the same order of magnitude of the study of Chancerel et al. 2009 who reported around 67.7 g of Ag, 11.2 g of Au and 4.4 g of Pd per ton of WEEE entering a mechanical plant treating IT, telecommunications and consumer equipment. Similarly the concentrations calculated in input WEEE for rare earth elements were found to be roughly consistent with the study of Oguchi et al. (2012), who estimated a general concentration of rare earth metals ranging from 10^{-1} and 10^{2} mg/kg in WEEE discarded in the city of Hitachi.

Among the investigated fractions, the higher metal concentrations were detected in the metallic granules, namely aluminium and copper grains, which are the output fractions of the mechanical process destined to further refining treatments. For instance, aluminium grains recorded a concentration of Al around 330000 mg/kg as well as copper grains reported a Cu concentration of 760000 mg/kg. However, relevant concentrations of metals were found both in plastic stream and in dust fraction which are actually not involved in the metallurgical recovery process. This condition is particularly relevant for rare earth elements which were found in the dust stream in concentrations one order of magnitude higher than in input WEEE. Such evidence points out that losses of critical metals occur in WEEE pre-processing.

7.1.2 Size distribution

The size of particles was classified for both output metallic grains and dust fraction based on sieve analysis results.

Figure 7.1 shows the particle size distribution of Al grains and Cu grains expressed as cumulative weight against particle diameters.

As can be seen from the curves, Al grains presented granules with larger particles: around 90% in mass of Al grains revealed a diameter size smaller than 8 mm while for Cu grains 90% of particles was smaller than 2 mm.

This different composition in size distribution between the two metallic fractions pushes their separation by size as the finest fraction (<1 mm) consists mainly of copper while the coarse one (up to 15 mm) is mostly composed of aluminium.

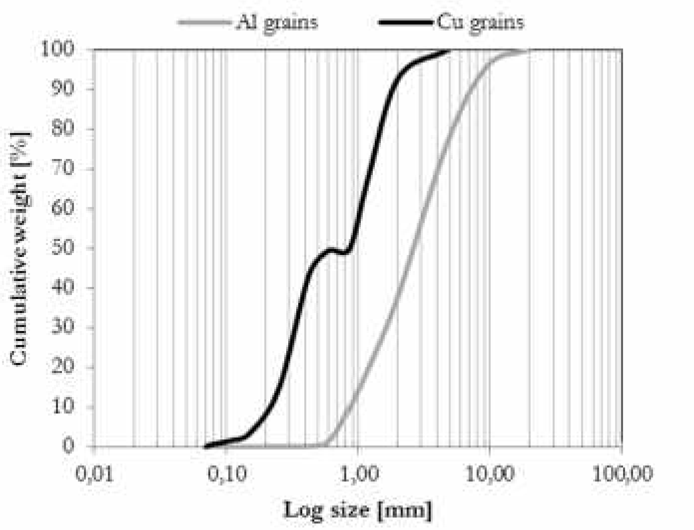


Figure 7.1 Particle size distribution of Al and Cu grains

The particle size distribution of dust material is reported in Table 7.2. More than 90% by weight of sampled dust was composed of tiny particles with a diameter smaller than 0.5 mm. This fraction can be considered homogeneous. The remain portion, accounting for about 10% of the total weight, consisted of fluffy material and capacitors foils coated by aluminium which is the most abundant metal found in this fraction as confirmed by the metal characterization. The obtained classification by size is roughly consistent with the characterization reported by Brandl et al. (2001).

Table 7.2 Size distribution of sampled dust

Fraction (mm)	% w/w	Description
<0.5	92.6	Homogeneous dust
0.5 - 1	2.2	Fluffy material
1 - 2	0.6	Fluffy material
>2	4.6	Al-coated capacitor foils

7.2 EFFECTIVENESS OF MECHANICAL TREATMENTS

7.2.1 Metal recovery yields

The data obtained from the metal characterization of the output fractions were used to evaluate the recovery yields of the mechanical process under investigation. The fate of valuable and critical metals in WEEE pre-processing was discussed as well. To this end, a mass flow analysis was carried out and the distribution of the selected metals was calculated as percentage in the output fractions.
The distribution of the metals under investigation in the various output fractions is plotted in Figure 7.2.

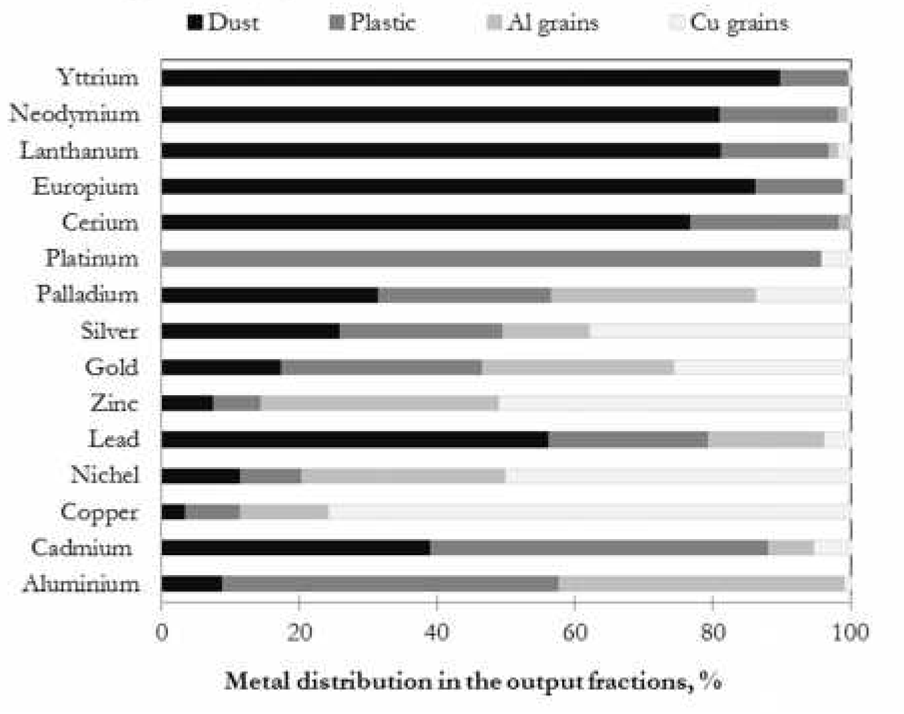


Figure 7.2 Metal distribution in the output fractions from the mechanical treatment process under investigation

As can be seen from the graph, base metals were mainly concentrated in the output metallic fractions, namely copper grains and aluminium grains, which are destined to further recovery.

More than 70% of copper was effectively collected in the corresponding output fraction sent to the metallurgical processes of recovery. This evidence confirmed that mechanical treatments allow the effective recovery of base metals, especially copper (Veit et al., 2002). However, the recovery yield obtained for aluminium was lower compared to that of copper. Only around 40% of aluminium was concentrated in Al grains while approximately half was found in the plastic stream, not involved in the metallurgical refining process. The selection treatment, thus, was found to be poorly effective for aluminium. This outcome can be ascribed to the form in which the metals are present in WEEE. Differently from copper, aluminium is mainly present as alloy or entrapped in multi material layers providing a minor degree of liberation as proved by other investigations (Sun et al., 2015).

Regarding precious metals, approximately half of gold, silver and palladium were distributed between the metallic output fractions while platinum was almost completely lost in the plastic stream. Mechanical processes have been demonstrated to be unfavourable for precious metal recovery (Chancerel et al., 2009). As these metals are mainly present in small contactors or multi-layered ceramic compound, they can be easily pulverized by shredding and crushing processes (Meskers and Hagelüken, 2009; Meskers et al., 2009). Moreover, this negative action is particularly evident for palladium (Bachér et al., 2015; Chancerel et al., 2009) as confirmed from the experimental activity.

Similarly, almost all the rare earth elements were found to be mainly distributed in the dust fraction, actually disposed in landfill.

Referring to the potential recovery rates of valuable and critical metals, significant losses of these materials occur in WEEE pre-processing.

As shown in Figure 7.3, only 30% of precious metals, including silver, gold, platinum and palladium, ended up in the metallic fraction destined to further recovery whereas more than 50% remained concentrated in both plastic and dust stream. These losses are roughly consistent with other studies (Bachér et al., 2015; Chancerel et al., 2009). However, significant losses were recorded especially for rare earth metals. In this case, more than 80% of all REEs contained in WEEE were lost through the dust stream.

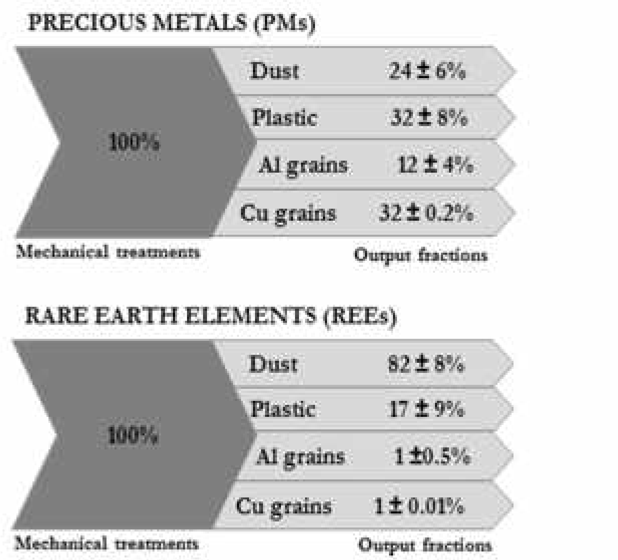


Figure 7.3 Mass flows of valuable and critical metals throughout the mechanical treatment under investigation

7.2.2 Quality of output fractions

As previous studies revealed that a complete metal liberation is achieved shredding particles below 2 mm (Zhang and Forssberg, 1997), the output metallic granules were separated into three fraction, namely F1<1.18 mm (fine fraction), 1.18 mm<F2<2mm (medium fraction), F3>2 mm (coarse fraction), and analysed by their metal contents in order to discuss the quality of the products of the mechanical treatments with particular reference to the effect of particle sizes on the process performances.

The metal concentrations detected in each granule fraction are reported in Table 7.3.

Table 7.3 Metal concentrations detected in the three size fractions of output metallic grains

Investigated fraction		Common metal concentrations (mg/kg)						
		Al	**Cd**	**Cu**	**Fe**	**Ni**	**Pb**	**Zn**
Al grains	F1	857434	<DL	6922	4619	69	517	1512
	F2	502951	6.2	1890	2852	40	11	368
	F3	124402	283	63530	83339	9601	530	74183

Cu grains	F1	1635	<DL	404175	12140	3667	4253	48004
	F2	1490	141	237021	36118	6180	<DL	107948
	F3	4011	252	232551	96277	13013	<DL	13546

Investigated fraction		**Precious metal concentrations (mg/kg)**			
		Au	**Ag**	**Pd**	**Pt**
Al grains	F1	100	113	306	<DL
	F2	8.1	15.5	26.9	<DL
	F3	<DL	20.6	<DL	<DL
Cu grains	F1	78.3	121	25.4	24.4
	F2	15.6	105	7.0	<DL
	F3	<DL	104	<DL	<DL

Investigated fraction		**Rare earth element concentrations (mg/kg)**				
		Ce	**Eu**	**La**	**Nd**	**Y**
Al grains	F1	0.3	1.8	<DL	0.4	<DL
	F2	<DL	<DL	1.1	<DL	0.04
	F3	<DL	<DL	<DL	<DL	<DL
Cu grains	F1	<DL	0.2	5.3	0.2	0.1
	F2	<DL	<DL	<DL	<DL	<DL
	F3	<DL	<DL	<DL	<DL	<DL

DL=detection limit

As can be observed, Al was mainly concentrated in the finest fraction (F1<1.18 mm) of aluminium grains while the other common metals were mainly concentrated in the coarse one. Similarly the higher concentration of Cu was found in the fine fraction of Cu grains whereas the other base metals were distributed in the fraction with diameter greater than 2 mm. Same considerations can be outlined with regard to the precious metals that were principally found in the fraction with diameter less than 1.18 mm. The small portion of REEs which ended up in the metallic granules, was distributed in the fine fraction as well.

This evidence demonstrated that the finest fraction was characterized by a major degree of purity. Conversely, the coarse fraction (F3>2 mm) contained a greater amount of impurities.

However, the relationship between the size of particle and the quality of the output materials can be ascribed in the present study to the treatment technology applied, with peculiar reference to the patented device included in the mechanical line of the facility under investigation. In this device the separation of plastics from metals is pursed forcing the waste at high-speed so that plastics flake off while metals form small grains as a consequence of the continuous impacts against the device walls. Once metals form granules, quantities of impurities can be incorporated in the grains proportionally to the granule size. Thus, relevant concentrations of other metals can be found in the coarse fractions and this is especially relevant for the aluminium fraction as it is characterized by grains with a larger size. The major degree of purity revealed by the finest metallic fraction outlined that refining treatment could be focused on the fraction with a particle diameter less than 2 mm.

7.3 HYDRO-BIOMETALLURGICAL PROCESSES FOR CRITICAL METAL RECOVERY

7.3.1 Dust characterization

As significant portions of valuable and critical metals end up in dust stream originated from WEEE mechanical treatments, dust was employed as source material for testing hydro-biometallurgical processes in order to extract and recover these materials.

The metal characterization of the dust fraction further used for hydro-biometallurgical assays is displayed in Table 7.4.

As highlight in the section of material characterization, relevant concentrations of metals were detected in the dust stream collected from the WEEE treatment plant under investigation. Due to the action of the shredding process, precious metals and rare earth elements were mainly concentrated in this waste flow which can be regarded as worthy for recovery as well as harmful for the environment due to the relatively high concentration of lead (Wang et al., 2015).

Table 7.4 Average concentration of selected metals in dust (ISO 11466:1995)

	Element	[mg/kg]	
Common metals	Al	31797	± 1476
	Cd	236	± 36
	Cu	33501	± 4063
	Fe	16003	± 3890
	Ni	1294	± 154
	Pb	22100	± 2689
	Zn	8202	± 597
Precious metals	Ag	271	± 85
	Au	8.7	± 0.6
	Pd	23	± 5.6
	Pt	< DL	
Rare earths	Ce	72	± 1.1
	Eu	2	± 0.2
	La	87	± 11.6
	Nd	88	± 1.9
	Y	42	± 8.0

For a deepen characterization, a mineral phase analysis was conducted on this fraction. The results of XRD analysis are reported in Figure 7.4. As the presence of organic matter in dust as well as the high content in iron would widen the background of the diffraction profile and enhance the fluorescent effect, an accurate analysis of XRD patter is quite hard (Wang et al., 2015). However, in our study the presence of amorphous material in dust mainly related to plastic matter was clear, as evidenced by the background noise. The several peaks recorded indicated that different phases are included in the mixture confirming the complex composition of the matrix. The pattern suggested that SiO_2, metallic copper, aluminium, iron and lead are present in dust material, mostly in their simple substance form as also reported by a previous study (Wang et al., 2015). REE compounds were found as well, but in form of oxides. While base metals are mainly present in their native form or as alloy (Tuncuk et al., 2012), REEs can be found in electronic equipment as oxides and phosphates in fluorescent lamps or as alloy in permanent magnets and these different chemical structure influence the dissolution of rare earths in acid media. REE oxides can be easily extracted in mild acid solution compared to phosphates which conversely require severe leaching conditions in terms of acid concentration and temperature (Han et al., 2014). The presence of REE oxides in the dust suggests a potential for effective extraction by hydrometallurgical processes.

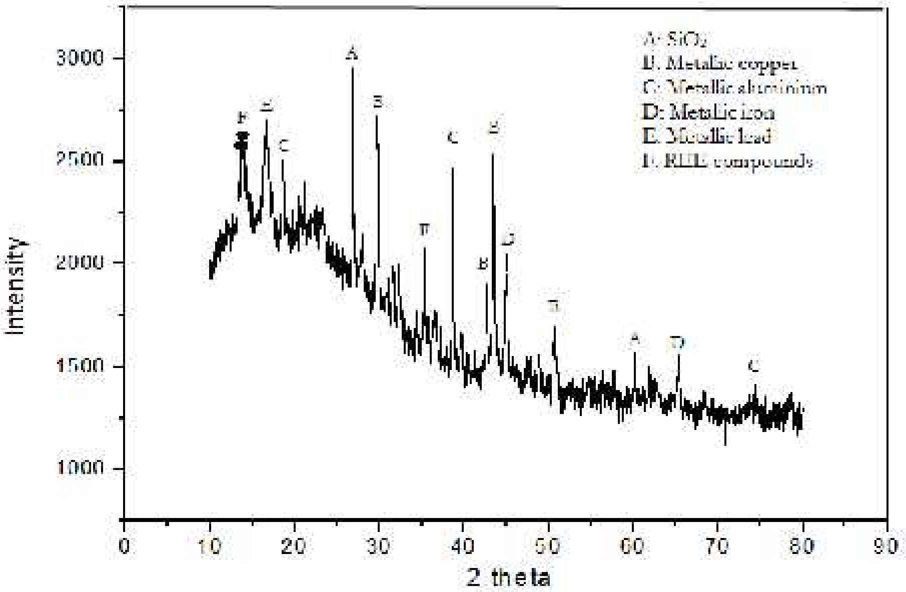


Figure 7.4 XRD pattern of dust material

7.3.2 Chemical leaching

Dust material was subjected to a chemical leaching process following two steps: the former using sulphuric acid and hydrogen peroxide as leaching agents and the latter testing thiourea as non-conventional lixiviant.

The metal extraction yields after chemical leaching using sulphuric acid and hydrogen peroxide are reported in Figure 7.5.

As can be observed from the graph, base metals such as aluminium, cadmium, iron, nickel and zinc were almost entirely leached into solution. Copper achieved an extraction yield of about 80% while lead was not detected in solution. Similar extraction efficiencies were reported by the study of Oh et al. (2003) even though at operating condition involving higher temperature that are less desiderable from an economic point of view compared to the ambient temperature used in the present study.

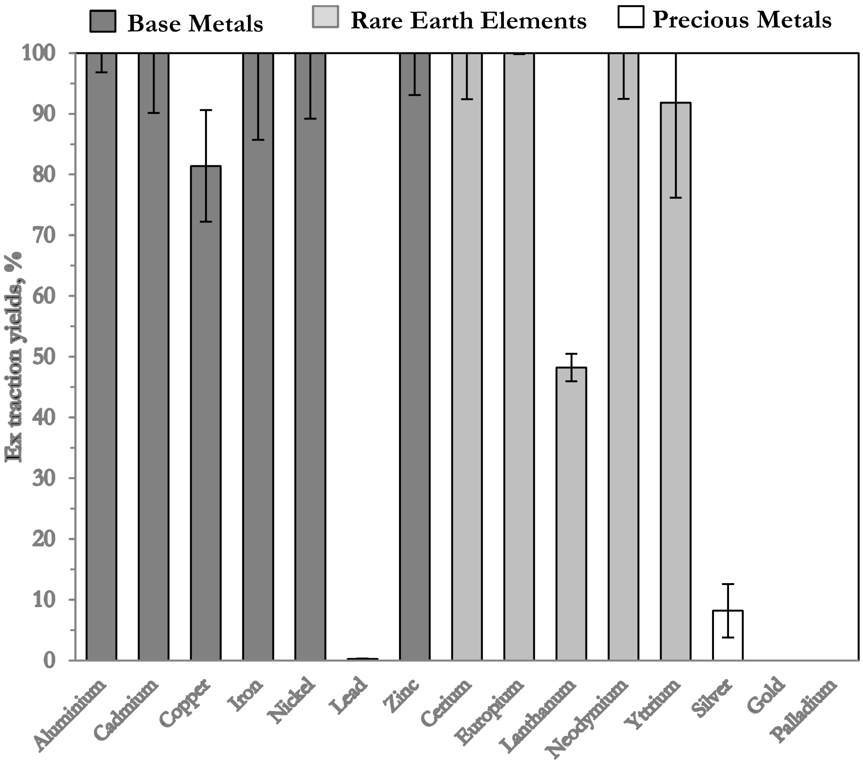


Figure 7.5 Extraction yields of selected metals after 6 h chemical leaching using sulphuric acid and hydrogen peroxide

In the leaching process under investigation, metals are solubilised in acidic sulphate media via the oxidation provided by H_2O_2 (Nguyen and Lee, 2015). The process feasibility depends on the thermodynamic driven force of the oxidative reactions, namely Gibbs free energy (ΔG). ΔG measures the tendency of the reaction to occur and it can assume either negative and positive values: if $\Delta G<0$ the reaction is spontaneous and it evolves towards the products, whereas if $\Delta G>0$ the reaction is disfavoured and it is driven in the reverse direction.

$\Delta G=0$ means that the reaction is at equilibrium (Nicol et al., 1987).

During the leaching dissolution of Cu, Zn, Fe, Ni with sulphuric acid and hydrogen peroxide the following reactions can take place (Birloaga et al., 2013):

$$C \quad + H_2S \quad {}_4 + H_2O_2 \rightarrow C \quad O_4 + 2H_2O \qquad \Delta G^{\circ} = -77.94\, k \quad /m \qquad (20)$$

$$Z \quad + H_2S \quad {}_4 + H_2O_2 \rightarrow Z \quad O_4 + 2H_2O \qquad \Delta G^{\circ} = -127.96\, k \quad /m \qquad (21)$$

$$F \quad + H_2S \quad {}_4 + H_2O_2 \rightarrow F \quad O_4 + 2H_2O \qquad \Delta G^{\circ} = -115.85\, k \quad /m \qquad (22)$$

$$N \quad + H_2S \quad {}_4 + H_2O_2 \rightarrow N \quad O_4 + 2H_2O \qquad \Delta G^{\circ} = -101.24\, k \quad /m \qquad (23)$$

These reaction are associated to largely negative standard-state free energy ($\Delta G°$) values, which indicate that they will evolve towards products. The results obtained from the leaching experiment are, thus, consistent with thermodynamic data, confirming the potential of sulphuric acid in base metal extraction from solid matrices. The mobilization of certain metals is, moreover, influenced by their electrochemical interactions, as the metal dissolution is an electrochemical process. Therefore, metals with lower standard electrode potential, such as aluminium and zinc ions, are preferentially dissolved compared to copper ions (Hong and Valix, 2014).

Furthermore the effectiveness of the extraction process highly depends on the solubility of the metal ions in the leaching media. As lead is insoluble in sulphate media, it was no detected in the leaching solution.

As expected, sulphuric acid and hydrogen peroxide were not able to leach out precious metals, which remained in the solid matrix (Birloaga et al., 2014; Oh et al., 2003) since noble metals are known to be soluble only in strong leaching media as aqua regia (Oliveira et al., 2009). However, silver showed a slight extraction yield (8%).

According to literature (Jha et al., 2016; Tunsu et al., 2015), REEs were soluble in sulphuric acid media as well. Cerium, europium and neodymium were almost completely extracted as well as yttrium which showed a leaching rate of 92±16% while lanthanum did not exceeded 48±2%. The leaching extraction yield is generally influenced by the chemical form in which metals are present in WEEE (Tunsu et al., 2015). The good extraction extent is in accordance with the characterization results, pointing out the presence of REEs in the dust as oxides.

The solid residue from the first leaching step mainly containing precious metals was then collected and used for the second leaching step involving thiourea as non conventional leaching agent.

An overall number of 8 leaching tests with two replications, hereafter named “Rep I” and “Rep II”, were performed by statistical design. During each run, samples were collected after 1h, 3h and 6h.

Although the effectiveness of thiourea has been reported in literature also for silver (Ficeriová et al., 2008; Gurung et al., 2013; Jing-ying et al., 2012), in the present study the leaching process showed effect only on gold extraction. However, the poor mobilization of silver could be ascribed to the operating conditions, likely more favourable for gold. Gurung et al. (2013) reported indeed an efficient extraction of silver at higher temperature (60°C). A further reason could be identified in the competition with other metals consuming thiourea. The metal characterization of the leaching solution pointed out that the copper which had not been leached out by sulphuric acid was indeed dissolved in thiourea. Concentrations of REEs even low were recorded in the leachate as well. This evidence was ascribed to the sulphuric acidic condition used for preventing thiourea decomposition, which facilitated a further leaching of the residual rare earths (Yörükoğlu et al., 2003).

Figure 7.6 reports, for each run, the average extraction yield of gold over the 6 h leaching process.

Lower leaching rate were recorded in the present investigation compared to previous literature studies (Birloaga et al., 2013; Ficeriová et al., 2008; Gurung et al., 2013; Jing-ying et al., 2012). Although the leaching process was carried out in absence of ferric sulphate as oxidant due to analytical interferences, the best leaching extraction was achieved after only 1 h. However, even though not externally provided, ferric ions are partially supplied by the dust material as it contains significant concentrations of iron. As can be seen by the leaching profile reported in Figure 7.6, an increase in leaching time resulted in a decrease in leaching rate, demonstrating the poor stability of thiourea in solution as well as its reaction with other metal ions. The best leaching efficiency was achieved during run 5: 53.5±15% of gold was extracted with a solid/liquid ratio of 0.2g/70 mL, a thiuorea concentration of 0.25 M and a stirring rate of 600 rpm.

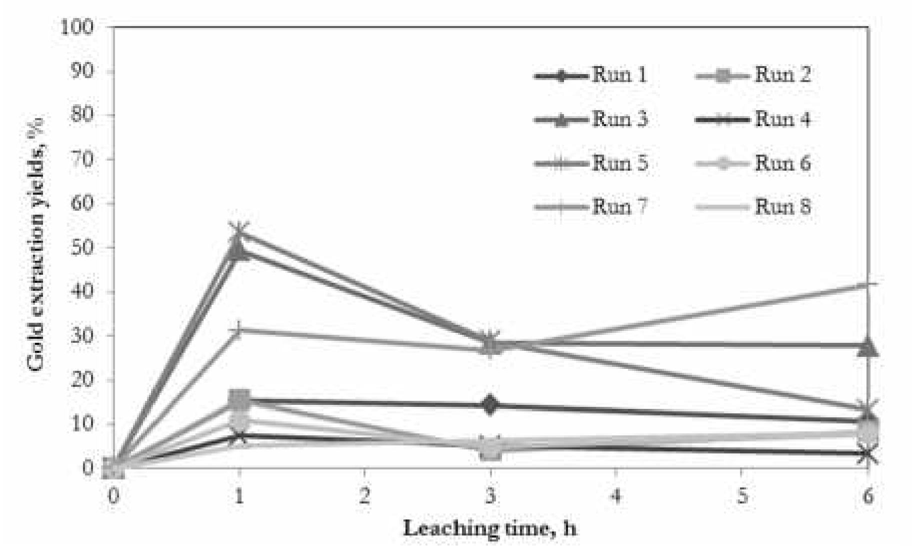


Figure 7.6 Extraction yields of gold over thiourea leaching runs

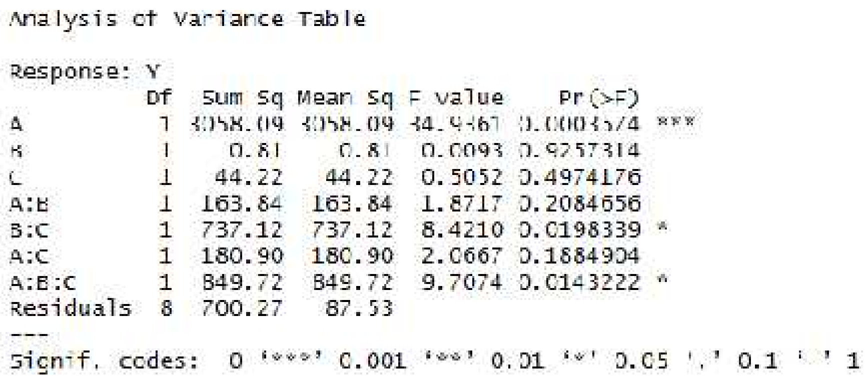
Values obtained at 1 h leaching time were, thus, used in the statistical evaluation of the results. The response in terms of gold extraction for each run and each replication is given in Table 7.5.

Table 7.5 Percentage of gold extraction after 1 h using thiourea (TU)

Run	Pulp density (g/ml)	TU Concentration (M)	Rpm	Gold extraction, Rep I (%)	Gold extraction, Rep II (%)
1	-1 (0.2/70)	-1 (0.25)	-1 (150)	19.6	11.0
2	+1 (2.0/70)	-1 (0.25)	-1 (150)	20.2	10.5
3	-1 (0.2/70)	+1 (0.50)	-1 (150)	44.1	54.7
4	+1 (2.0/70)	+1 (0.50)	-1 (150)	9.6	5.4
5	-1 (0.2/70)	-1 (0.25)	+1 (600)	38.5	68.5
6	+1 (2.0/70)	-1 (0.25)	+1 (600)	13.6	8.3
7	-1 (0.2/70)	+1 (0.50)	+1 (600)	37.9	24.7
8	+1 (2.0/70)	+1 (0.50)	+1 (600)	4.9	5.3

The significance of the input factors under investigation, namely pulp density (A), thiourea concentration (B) and stirring rate (C), was analysed using ANOVA technique and conducting F-tests at 95% confidence level. Data were processed via RStudio software.

The results of the statistical analysis are displayed in Figure 7.7.



```
Analysis of Variance Table

Response: Y
          Df  Sum Sq Mean Sq F value    Pr(>F)    
A          1 3058.09 3058.09 34.9367 0.0003574 ***
B          1    0.81    0.81  0.0093 0.9257314    
C          1   44.22   44.22  0.5052 0.4974176    
A:B        1  163.84  163.84  1.8717 0.2084656    
B:C        1  737.12  737.12  8.4210 0.0198339 *  
A:C        1  180.90  180.90  2.0667 0.1884904    
A:B:C      1  849.72  849.72  9.7074 0.0143222 *  
Residuals  8  700.27   87.53                      
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

Figure 7.7 Results of ANOVA (RStudio)

The significance of the input factors was statistically determined on the basis of "p-value", which represents the probability to obtain a result equal to or more extreme than actually observed results (Pr(>F)) when the null hypothesis is true. The null hypothesis for ANOVA states that the average value of the factors is the same in each run or treatment, meaning that the different operating factors have no significant effect on the process response. Fixed a confidence level of 95% (α=0.05), if p-value<α, the null hypothesis can be rejected and then the effect of the factors is statistically significant for the process response.

The factors statistically significant are indicated towards an asterisk in the ANOVA table obtained from RStudio software (Figure 7.7). Therefore, for the thiourea leaching process pulp density (A) was found to be statistically significant as well as the interaction between thiourea concentration and stirring rate (BC) and the interaction between all the three factors under investigation (ABC).

Using a multiple linear regression function, the following mathematic model returning the percentage extraction of gold via thiourea leaching process was constructed on the basis of the results of the model fitting function (Figure 7.8):

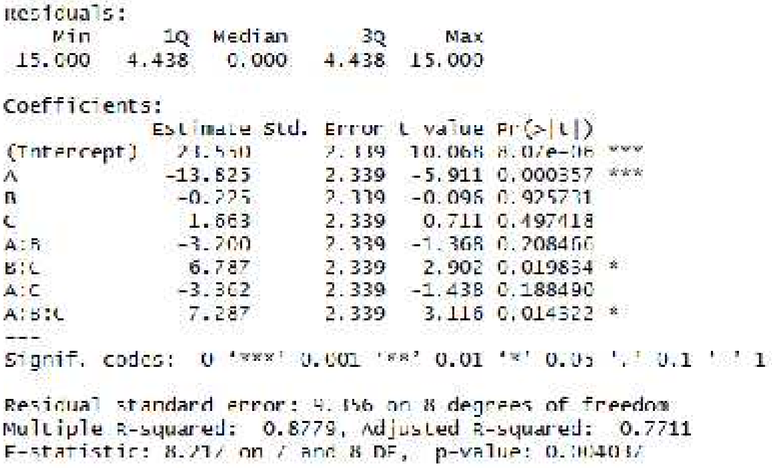
$$G \quad e \quad (\%) = 23.5 - 13.8\,A - 6.8\,B \quad + 7.3\,A \tag{24}$$

where: A= pulp density (g/mL);

B= concentration of thiourea (M);

C= stirring rate (rpm).

The model, including only the factors statistically significant (Deveci et al., 2010), was statistically acceptable at a confidence level of 99.6% with a R-squared of 0.88.



```
Residuals:
    Min      1Q  Median      3Q     Max 
 15.000   4.438   0.000   4.438  15.000 

Coefficients:
            Estimate Std. Error t value Pr(>|t|)    
(Intercept)   23.550      2.339  10.068 8.07e-06 ***
A            -13.825      2.339  -5.911 0.000357 ***
B             -0.225      2.339  -0.096 0.925731    
C              1.663      2.339   0.711 0.497418    
A:B           -3.200      2.339  -1.368 0.208466    
B:C            6.787      2.339   2.902 0.019834 *  
A:C           -3.362      2.339  -1.438 0.188490    
A:B:C          7.287      2.339   3.116 0.014322 *  
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 9.356 on 8 degrees of freedom
Multiple R-squared:  0.8779, Adjusted R-squared:  0.7711 
F-statistic: 8.217 on 7 and 8 DF,  p-value: 0.004037
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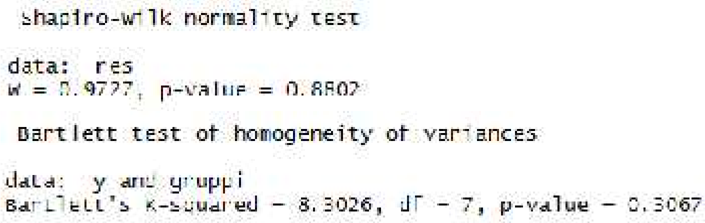
Figure 7.8 Results of the multiple linear regression (RStudio)

As can be observed from the coefficients of the model, pulp density held a negative coefficient, confirming the negative effect that an increase of this factors has generally on the leaching process. Not surprisingly, the best leaching rate was achieved when pulp density assumed the low level. A negative coefficient was gathered for thiourea concentration as well. As for pulp density, the maximum gold extraction was reached at low level of thiourea concentration. Gurung et al. (2013) revealed that only a proper thiourea concentration was effective on gold leaching, pointed out that for instance an increase from 0.5M to 1M was not so efficacious. Conversely, the stirring rate showed a positive coefficient as the leaching process is positively influenced by an effective mixing (Birloaga et al., 2013).

However, the statistical analysis conducted is based on the assumptions that residuals are normally and independently distributed (normality) with the same variance in each treatment or factor level (homogeneity). These assumptions must be checked for the reliability of the analysis. For this purpose, both a Shapiro and Bartlett test were performed: the former for checking the assumption of the normal distribution and the latter for verifying the equality of variances, as a measure of the homogeneity. Results of those tests are reported in Figure 7.9. Fixed a confidence level of 95% (α=0.05), the assumptions can be assumed true, as the p-values obtained were greater than 0.05.



```
 Shapiro-Wilk normality test

data:  res
W = 0.9777, p-value = 0.8802

 Bartlett test of homogeneity of variances

data:  y and gruppi
Bartlett's K-squared = 8.3026, df = 7, p-value = 0.3067
```

Figure 7.9 Results of Shapiro and Bartlett tests for checking ANOVA assumptions

7.3.3 Biological leaching

Dust material was used for testing a biological leaching process as well. The bioleaching assays were carried out using a pre-growth strategy in order to reduce the toxic effects of the waste material on the microorganisms. Therefore, microorganisms were initially growth in absence of dust (Brandl et al., 2001; Işıldar et al., 2016). After reaching the optimum conditions for bioleaching experiments, indirectly monitored through parameter such as pH and ORP, dust material was added to the bioleaching medium. This strategy was followed for both the first leaching step exploiting *A. thiooxidans* and the second one using *P. putida*. *A. thiooxidans* were grown for 10 days prior to bioleaching experiments, whereas *P. putida* for 18 hours.

Figure 7.10 shows both the pH and the ORP profiles during the bioleaching experiments using *A. thiooxidans* at different pulp density.

The bioleaching experiments began when the pH of the inoculum was around 1. After adding dust at t=0, the pH increased due to the alkalinity of the solid material (Brandl et al., 2001). Conversely, the ORP decreased. Higher material load showed higher pH increasing as can be seen in Figure 7.10. However, 2 days later the pH remained roughly constant: a balance between the H+ ions provided by the biogenic oxidation of elemental sulphur in sulphuric acid and the H+ ions consumed by the oxidation of metals was reached. As reported in literature, the bioleaching of metals from a non-sulphide waste as the electronic waste involves mainly indirect leaching mechanism, whereas the direct oxidation of metals is marginal. The role of *A. thiooxidans* in bioleaching processes is to catalyse the oxidation of elemental sulphur in H_2SO_4 which is, in turn, responsible of the metal solubilisation (Hong and Valix, 2014; Zhu et al., 2011).

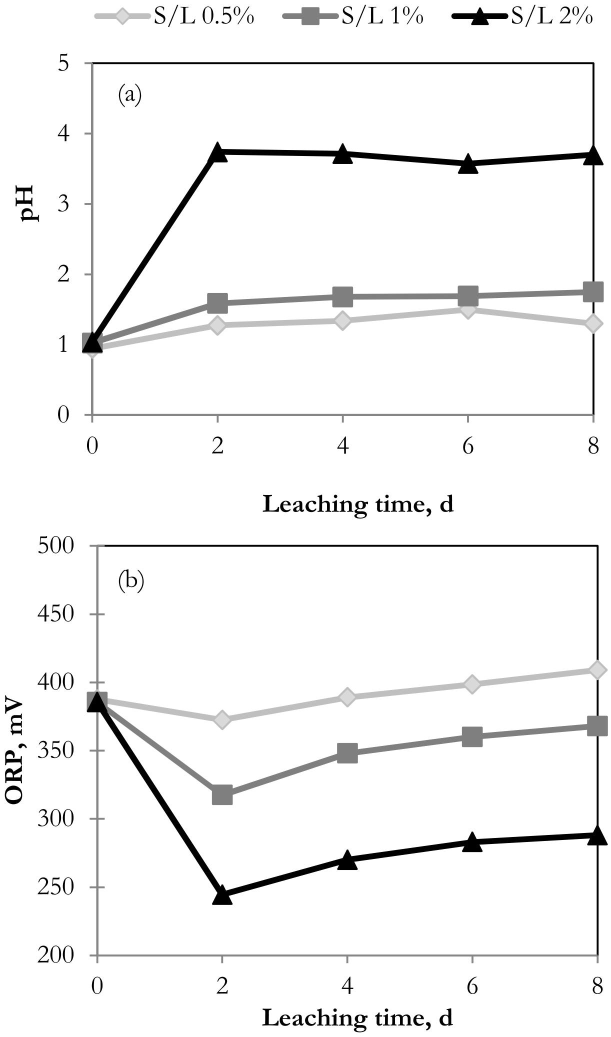


Figure 7.10 pH (a) and ORP (b) profiles during *A. thiooxidans* bioleaching at different pulp density

The extraction efficiencies of the selected metals after 8 days bioleaching, performed at different pulp densities using *A. thiooxidans*, are reported in Figure 7.11.

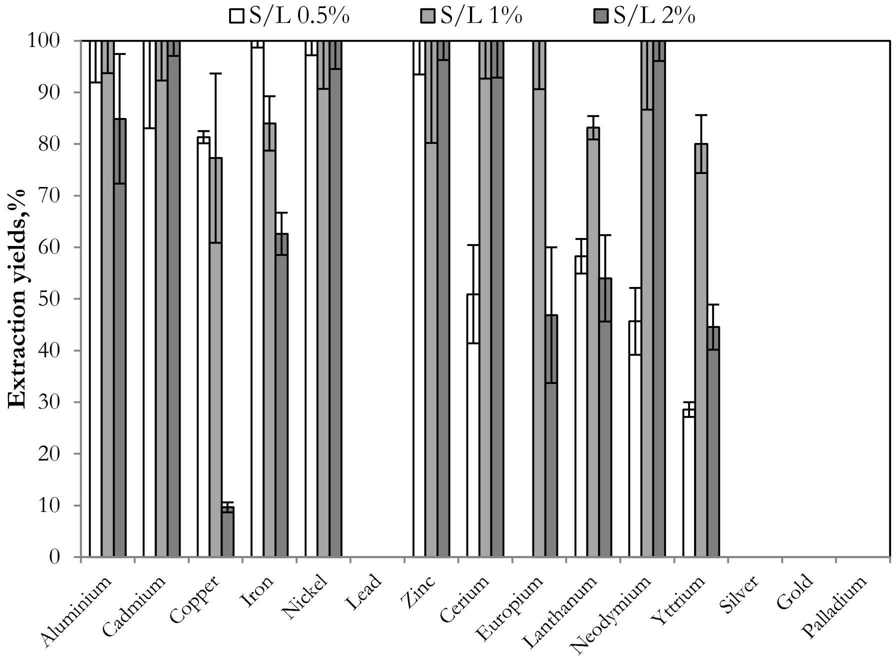


Figure 7.11 Extraction yields of selected metals after 8 days bioleaching using *A. thiooxidans* at different pulp densities

As can be seen from the graph, a pulp density lower than 2% w/v showed a more efficient mobilization. Due to the toxic nature of e-waste, a higher pulp density inhibited the bioleaching performances (Işıldar et al., 2016) or at least would require an extension of the time needed to the microorganism adaptation. Although the leaching process resulted in different leaching efficiencies according to the metal of interest, 1% w/v pulp density revealed the best overall leaching rates in agreement with previous studies (Bas et al., 2013; Brandl et al., 2001; Hong and Valix, 2014; Ilyas et al., 2007; Işıldar et al., 2016). In this condition aluminium, cadmium, nickel and zinc were almost entirely leached out from the solid matrix. Relative lower extraction yields were achieved for iron (84±5%) and copper (77±16%). Lead was not detected in the leaching solution: its precipitation as $PbSO_4$ can be speculated as reported by other similar investigations (Brandl et al., 2001; Ilyas et al., 2007).

A. thiooxidans were able to leach rare earth elements as well. After 8 days at 1% pulp density cerium, europium and neodymium were mobilized at high percentages (>99%) whereas lanthanum and yttrium reached approximatively an extraction yield of 80%. Cerium and neodymium were in particular almost leached out after 2 days while the remaining rare earths under investigation were mobilized at higher extent after 8 days as shown by the bioleaching profile of Figure 7.12. Although the bioleaching process required longer leaching time compared to the chemical process, a better leaching rate was observed for lanthanum which was extracted at yield of 83% after the biological process compared to the 48% of the chemical one.

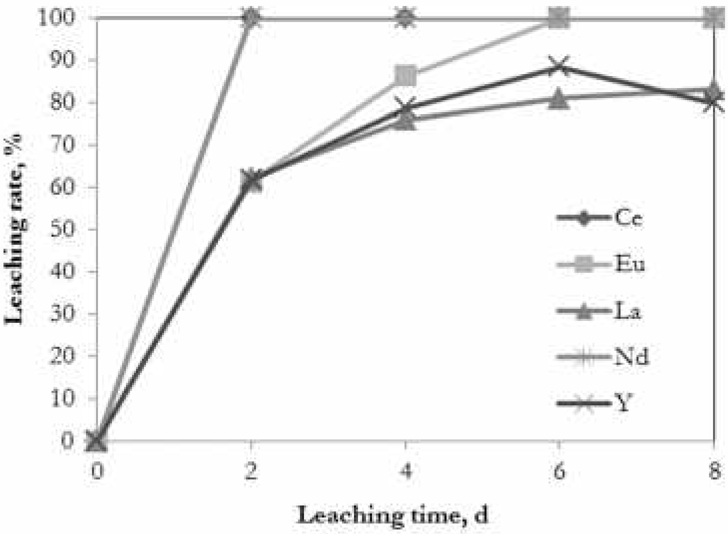


Figure 7.12 REE leaching profile over 8 day bioleaching process

The extraction yield obtained for yttrium was roughly consistent with a recent study of Beolchini et al. (2012) who reported an yttrium mobilization of 70% from cathode ray tube fluorescent powders using a mixed culture of Fe/S-oxidizing bacteria. However, it is worth pointing out that bioleaching processes are quite difficult to be compared as the several leaching factors affecting the process highly influence its extraction effectiveness.

Although the ability of these microorganisms in leaching base metals from e-waste has been deeply investigated (Bas et al., 2013; Brandl et al., 2001; Hong and Valix, 2014; Ilyas et al., 2007, 2007; Liang et al., 2010; Mrazikova et al., 2015; Zhu et al., 2011), poor information are currently available in literature with reference to the microbe interaction with rare earths (Beolchini et al., 2012). Nevertheless, a leaching process involving rare earth elements can be assumed to be dominated by the same general mechanisms of acidolysis, redoxolysis and complexolysis (Barmettler et al., 2016). Moreover, in the present study the good bioleaching efficiencies reported for REEs using sulphur oxidazing bacteria confirmed the solubility of REEs in sulphuric acid media and the effective role of *A. thiooxidans* in producing sulphuric acid.

Conversely, no precious metals were detected in the leaching solution since the role of acidophilic bacteria in gold mining operations, namely bio-oxidation processes, is to solubilize copper leaving the valuable material in the solid matrix for its further recovery (Brandl, 2001; Pham and Ting, 2009).

In the non-inoculated control experiment metals were not detected. Only slight concentrations of copper were recorded due to the mild presence of sulphuric acid in the leaching medium for pH adjustment as also observed in other studies (Brandl et al., 2001; Işıldar et al., 2016). This evidence confirmed that the mobilization of metals was the result of the microbial activity.

The dust collected from the first bioleaching step with *A. thiooxidans* was then used for a second bioleaching stage involving *P. putida*. Differently from *A. thiooxidans* working in acidic condition, the activity of these microorganisms is promoted in alkaline environments. Both washed and unwashed dusts were thus tested in the bioleaching experiments, in order to evaluate the influence on the process of the potential acidity of the dust coming from the first step.

As for *A. thiooxidans, P. pudita* were firstly grown in absence of dust. Dust was then added 18 h after the incubation (corresponding to t=0 for bioleaching experiment) which is supposed to be the time of maximal cyanide production as previously demonstrated by the study of Işıldar et al. (2016). In the same growth conditions, a cyanide production of 20 mg/L was reported by those authors. The cyanogenic production of *P. putida* was, however, confirmed by the colorimetric method applied which resulted in an intense red colour (Figure 6.8b).

During the bioleaching experiments among precious metals only gold was detected in solution. Therefore, the process was not efficient with regard to silver and palladium. Rare earth metals were not detected in the leaching solution as well, confirming that cyanides cannot form stable complexes with these transition elements (Barnes et al., 2000; Faramarzi et al., 2004).

The pH profile and the gold mobilization during bioleaching experiments are shown in Figure 7.13 and Figure 7.14, respectively.

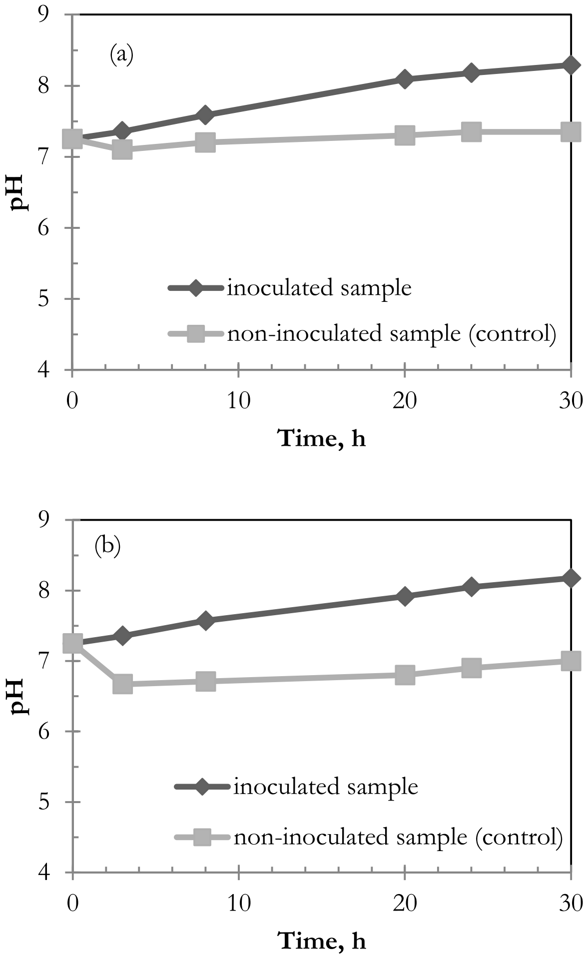


Figure 7.13 pH profile during bioleaching experiment using *P.putida* for washed (a) and unwashed (b) dust material

Although unwashed sample revealed a lower pH as demonstrated in the non-inoculated control sample, the pH profiles during the bioleaching experiments were similar for both washed and unwashed dust samples. The gold bioleaching took place at pH around 7-8, which is considered physiological for cyanogenic bacteria growth (Pham and Ting, 2009). As the pH during the bioleaching experiments did not exceeded the value of 8.4, it was reasonable to assume that cyanides were partially lost through volatilization as the concentration of cyanide ions in solution is highly dependent on pH. Cyanide is completely dissociated in its ions only at pH 11, while at a pH of 9.36 50% of cyanide is present in form of hydrocyanic acid gas that can easily evaporate (Barnes et al., 2000).

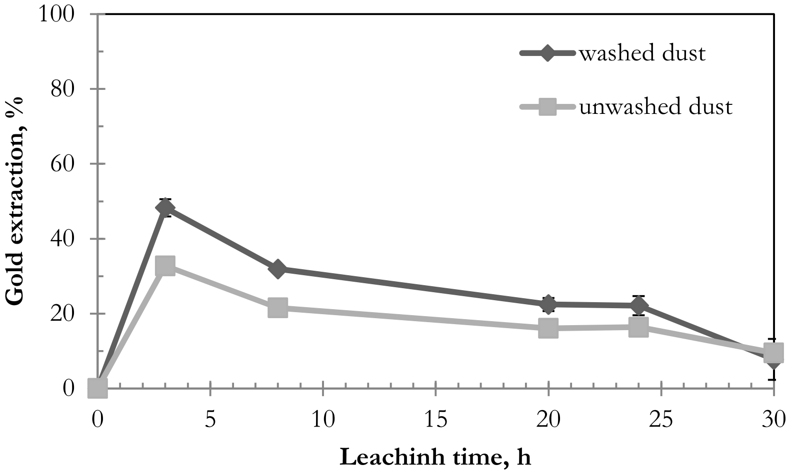


Figure 7.14 Gold mobilization during bioleaching experiment using *P. pudita* for washed and unwashed dust

As highlighted in the bioleaching profile (Figure 7.14), the maximum gold mobilization was achieved after only 3 hours. Later on, the concentration of gold detected in the solution decreased: gold complexes resulted less stable with a prolonged leaching time. This condition might be ascribed either to sorption processes onto biomass or to the biodegradation of metal cyanides which serve as carbon or nitrogen source (Brandl et al., 2008). However, it is worth pointing out that the biological decomposition of cyanides makes bioleaching processes environmental friendly as it provides a way to overcome the toxicity concerns related to the chemical processes (Işıldar et al., 2016).

Higher extraction yields were obtained using washed dust compared to unwashed dust: 48% of gold was leached out from washed dust samples after 3 hours whereas 33% of gold was extracted from unwashed samples. This better efficiency could be related to the action of the washing treatment as it might contribute to the removal of toxic substances for microbes (Ilyas et al., 2007). However, the washing treatment did not change significantly the metal composition of the residue: only around 2% of copper was lost in the washing solution.

Although copper was mainly removed from the dust material through the first bioleaching step using *A. thiooxidans*, it was found in the leaching solution of the second stage as well. Around 15% of copper was indeed mobilized both for washed and unwashed samples confirming the prevalent reactivity of cyanide ions with copper that set the necessity to remove this metal prior to cyanidation process. The leaching rate recorded for gold likely did not exceeded 50% as cyanides were partially consumed by the residual copper.

In the non-inoculated control experiment no gold was detected confirming that its extraction was provided by the microbial activity.

The biogenic cyanide leaching was compared with a chemical cyanide leaching process. Results of the chemical leaching tests using a solution of potassium cyanide are displayed in Figure 7.15. During the cyanide leaching process the pH remained around 12.

As can be seen from the graph, the cyanide concentration had a positive correlation with the gold mobilization: higher concentration extracted more gold. Differently from the biological process, the gold extraction via chemical leaching showed a profile increasing over time. Moreover, silver was mobilized as well. After 3 hours, more than 95% of the silver contained in the dust material was extracted even at low cyanide concentration. As the biogenic cyanide production of *P. putida* can be speculate to be around 20 mg/L (Işıldar et al., 2016), the gold extraction profile during the bioleaching process can be compared with the gold chemically mobilized using a solution of 25 mg/L CN^-. Although the chemical process resulted in a more effective mobilization of gold (70% after 30 h), the environmental burdens related to the chemical process cannot be overlooked. However, the extraction efficiency provided after 3 h by the cyanides biologically produced is similar to the extraction yield reported by the corresponding chemical process.

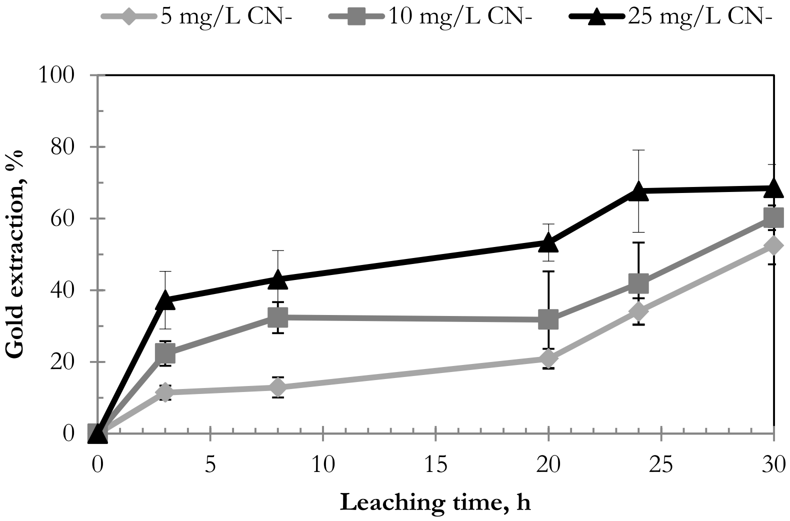


Figure 7.15 Gold extraction during chemical leaching at different cyanide concentrations

7.4 TECHNICAL ASPECTS AND PROCESS SCALE-UP OPPORTUNITIES

Based on the results obtained from the experimental activity, several technical implications can be highlighted with reference to the recovery of metals from electronic waste.

The research study confirmed that conventional mechanical treatments provide an effective recovery of base metals and revealed that both precious metals and rare earth elements are mainly subjected to material losses. These metals are especially conveyed in the dust stream originated from shredding and crushing processes. These treatments, which are essential to deliver the liberation of metals from the other materials (Guo et al., 2011) and to gather the liberated materials into small particles (Bachér et al., 2015; Chancerel et al., 2009) negatively affect the recovery of precious metals and rare earth elements from WEEE.

In this regard, the selective disassembly of valuable components from e-waste could reduce the losses of these materials during the recycling chain. However, the benefits in terms of material recovery need to be weighed up against the costs of the process, as selective dismantling is characterized by prolonged operating time and lower treatment capacities compared to mechanical automated processes.

A key role in material recovery improvement is played by eco-design strategies which address the design of the electronic device for its easier recycling (Ardente et al., 2014). Selective disassembly and eco-design can be, thus, regarded as upstream-oriented strategies to effectively extract the raw material before its processing. On the other hand downstream strategies or "end of pipe" techniques could be set as well. In this view, dust fractions containing significant concentrations of strategic metals might be further processed via metallurgical treatments. Although dust collected from the treatment system generally accounts just for low mass percentages (~3.7%) of its capacity (Bachér and Kaartinen, 2016; Wang et al., 2015), it represents a cost for the plant as actually dust is disposed of in landfill. If dust production may not promote mass-based recycling due to its relative low rates, its composition makes this fraction worthy for valuable metals recovery (Bachér and Kaartinen, 2016; Wang et al., 2015). Moreover, the treatment of dust pursues the removal of a relevant portion of base metals that contributes to the toxic nature of this fraction. In this respect, the concentration of heavy metals could be reduced and the quality of this matrix improved for its sustainable disposal.

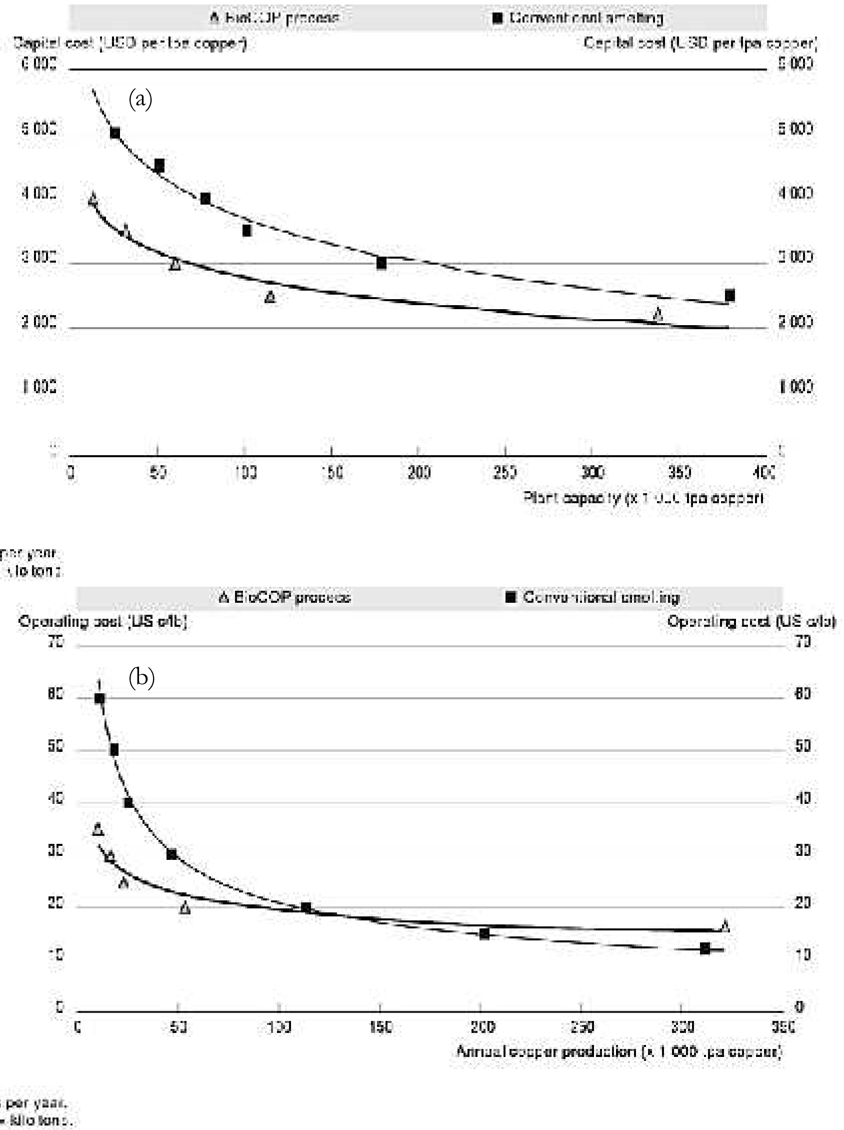
The experimental activity showed the feasibility of recovering valuable and critical metals from dust through both chemical and biological leaching processes developed in two steps: the former for extracting base metals and rare earth elements and the latter for gold mobilization. The results obtained in terms of extraction efficiencies were similar for both the chemical and the biological process. The biological treatment employed more time: while applying a chemical process for leaching base metals and rare earth elements only few hours were required, some days were necessary for leaching the same metals using a biological treatment. Conversely, for gold extraction this difference was not so evident as cyanogenic bacteria showed a faster leaching kinetic.

The research pointed out the opportunity of managing a waste material such as the dust fraction in a "circular economy" approach as reported in Figure 7.16, involving hydrometallurgical or biometallurgical processes. In this way, valuable materials ending up in such stream can return back to the market leading to benefits, both for the environment and the economy, particularly relevant for rare earth elements due to their price, low availability and high demand.

Figure 7.16 A circular economy approach for the management of dust coming from WEEE mechanical treatments

However, the present research has been conducted at laboratory scale and further studies need to be carried out in order to establish the application of these technology at larger scale, especially for biometallurgy. In this regard, the economic feasibility of these processes should take into account both capital and operating costs as well as the value of the recovered materials. Capital costs include direct costs as reactors and agitators and indirect costs related to engineering and construction management. Operating costs cover reagent, power, labour and maintenance costs. As biometallurgy has not been yet applied at industrial scale for WEEE recovery, no references are currently available in order to make a reliable cost analysis evaluation; some economic considerations can be, however, outlined referring to the bioleaching processes for the mining recovery of copper.
The capital costs of bioleaching processes are generally 50% less than the conventional smelting processes while the operating costs can be considered competitive with the unit costs of smelting (www.web.mit.edu).

A comparison between smelting and bioleaching is provided in Figure 7.17 for both capital and operating costs as a function of the plant capacity.



1. tpa: tons per year.
2. x 1 000 = kilo tons.

1. tpa: tons per year.
2. x 1 000 = kilo tons.

Figure 7.17 Comparison of capital costs (a) and operating costs (b) for smelting and bioleaching processes for copper mining recovery (OECD, 2001)

Considering the reagent costs, the continuous delivery to the plant is not necessary for a bioleaching process as these reagents are biologically produced (Beolchini et al., 2012). This advantage makes this process economic and environmental competitive compared to hydrometallurgical treatments. Conversely, hydrometallurgical processes require an incentive maintenance due to the corrosive nature of the used reagents (OECD, 2001).

Although bioleaching is known as a low cost and environmental friendly technique, some aspects actually hinder the application of this technology at industrial scale. The main limitations of bioleaching are related to the prolonged leaching time and the lower loading capacity in terms of solid material to be treated over time due to the toxic effects on the microorganisms. However, the latter aspect is not limiting for dust treatment as this fraction is produced at low mass percentages. The leaching time can vary according to the microorganism exploited as well as to the scale of operation. For instance, bioleaching processes using cyanogenic bacteria were faster than processes involving acidophilic strains. Furthermore, bioleaching could require from few days at laboratory scale to 3-18 months in case of heap bioleaching system at full scale (OECD, 2001).

However, the successful application of biometallurgy depends on the integration of both microbiological and hydrometallurgical engineering. In addition, regulations and policies promoting the use of “green technology” could significantly contribute to the development of such processes, especially when considering that the low cost of the bioleaching process makes them particularly convenient for treating low grade waste materials as electronic waste (Beolchini et al., 2012).

8 CONCLUSIONS

The management of waste electric and electronic equipment is attracting increasingly interest as WEEE is one of the waste stream characterized by faster growing rates and handling issues due to its heterogeneous and potentially hazardous composition.

As WEEE contains valuable and critical metals of relevant economic interest, such as rare earth elements, it represents a potential source of raw materials as well. The recovery of these metals from electronic waste is regarded as a charming opportunity to pursue both environmental and economic benefits. However, the recycling industry of WEEE is still in its early stage and it is mostly dominated by smelting processes or emerging hydrometallurgical treatments addressing mainly the recovery of base metals and precious metals while the recycling technologies for REEs recovery are not yet consolidated.

Moreover, the metallurgical treatments currently applied are claimed to have several impacts on the environment due to the generation of secondary pollutants. In this respect, the development of environmental friendly and cost-effective treatments is strongly required, especially with reference to critical metals which are actually recycled at low rate.

Under this framework, the research discussed in the present work dealt with innovative and sustainable solutions for resource recovery from WEEE. As the characterization of WEEE is fundamental in order to develop a cost-effective and environmental friendly strategy of recycling, the fist step of the research activity aimed at the identification and the quantification of valuable and critical materials contained in such waste stream. To this end, representative samples were collected from a full scale plant treating mechanically small electronic waste. Results from this step confirmed the presence of precious metals as well as rare earth elements in WEEE at trace concentrations.

The data obtained from the metal characterization were then used for evaluating the fate of the strategic metals during the conventional mechanical pre-treatments which cover the fist stage of the WEEE recycling chain. A mass flow analysis revealed that at the end of the mechanical treatments 56% of precious metals, including gold, silver and palladium, were concentrated in output fractions not involved in the subsequent metallurgical processes. Moreover, approximately 80% of all the rare earths were mainly gathered in the dust fraction originating from process air cleaning which is actually destined to landfilling.

The performed analysis highlighted that during the conventional mechanical treatments losses of precious metals and rare earth elements can occur as a result of the action of shredding processes which easily pulverize these materials, conveying them in the dust stream not entering the recycling chain. Although crushing treatments are fundamental and economically attractive for the metal liberation and its further recovery, an optimum compromise should be set between the size reduction and the effective metal liberation in order to avoid losses of materials. In this view, the selective dismantling of valuable components from input WEEE as well as the eco-design of electronic appliances could act as upstream-oriented strategies aiming to pursue the effective recovery of these strategic materials before their processing. However, this approach could turn to be not economically competitive towards automated mechanical sorting as selective disassembly is time consuming and provides a lower treatment capacity. Thus, downstream strategies acting conversely at the end-of-pipe could be considered as suitable alternatives to upstream approaches. In this case, dust fraction could be regarded as a target matrix to be further processed for valuable and critical metal recovery from WEEE. Such approach would give valuable materials back to the market avoiding their losses, while ensuring the higher sustainability of the landfilling of dust residues.

According to this outcome, dust was used as source material for testing the innovative treatments proposed. In this regard, the experimental activity was mainly focused on the leaching process that determines the effective extraction of metals from the solid matrix. To this end, both chemical and biological leaching processes were carried out in two separate steps in order to achieve a selective mobilization of the metals of interest: the former step aimed at extracting base metals and rare earth elements while the latter one at gold mobilization.

Results from the hydro- and bio-metallurgical tests revealed the feasibility of extracting valuable and critical metals from WEEE shredding dust by means of these processes.

The chemical process involving sulphuric acid and hydrogen peroxide was efficient in extracting base metals and rare earth elements. Aluminium, cadmium, iron, nickel and zinc were almost entirely leached after 6 hours. In the same conditions copper achieved an extraction yield of about 80%. Moreover, rare earths were also mobilized. Cerium, europium and neodymium were almost completely extracted, yttrium showed a leaching rate of 92±16% while the extraction yield of lanthanum did not exceeded 48±2%. In the further chemical leaching step, the thiourea extracted 53.5±15% of the gold contained in the dust matrix in only 1 hour. The solid/liquid ratio, the concentration of thiourea and the stirring rate were found to be the factors significantly affecting the leaching process. Based on these outcomes, a mathematical model was constructed for the gold extraction as function of the significant operating factors using thiourea as non conventional and less toxic lixiviant compared to the common cyanide.

During the bioleaching process, aluminium, cadmium, nickel and zinc were almost entirely leached out from the solid matrix using *A. thiooxidans*. Relative lower leaching yields were obtained for iron (84±5%) and copper (77±16%). Lead was not detected in the leaching solution due to its precipitation. Moreover, *A. thiooxidans* showed good leaching capacity also with regard to rare earth elements. After 8 days at 1% pulp density cerium, europium and neodymium were mobilized at high percentages (>99%) whereas lanthanum and yttrium reached an extraction yield of 80%. In the second leaching step, *P. putida* mobilized 48% of gold after 3 hours.

The research findings were of relevant interest as they proved that valuable and critical metals can be extracted and recovered from WEEE shredding dust trough both chemical and biological processes. The processes were effective with regard to rare earth elements whose recovery is particularly attractive due to their price, scarcity, low availability and high demand. This management strategy provides a way to reintroduce the dust fraction, actually sent to landfill, in the "loop" of the product lifecycle avoiding the losses of these resources as promoted by the new circular economy approach. Moreover, the results of the study pointed out the potential of using biological processes for leaching base metals, precious metals as well as rare earth elements. These processes appear as an effective alternative to the chemical processes due to their minor impacts on the environment and their lower cost which makes them particularly convenient for treating low grade waste materials as WEEE. The potential treatment of the dust stream and the innovative biometallurgical processes investigated marked the novelty of the research work.

As the research activity highlighted the feasibility of using biometallurgical processes for resource recovery from WEEE at laboratory scale, further studies should be addresses towards the following aspects:

- the subsequential recovery of the extracted metals from the leaching solutions;
- the evaluation of the fate of hazardous substances under the processes proposed;
- the application of these processes at larger scale and for treating other secondary materials.

Further investigations should be addressed to the strategies for recovering the metal extracted and concentrated in the leaching solution. In this regard, bioleaching would be followed by biological processes still in the field of biometallurgy, such as biosorption, in order to preserve the cost-effectiveness as well as the environmental compatibility of the treatment process.

However, it is worthy pointing out that the benefits related to a recycling system cannot be focused only on the recovered materials but additional aspects should be considered such as the toxicity control associated to recycling practises. To this end, deeper considerations should be examined with particular regard to both the content of harmful elements in the dust fraction and the fate of these substances in the treatments proposed as their toxicity is strongly related to their mobilization.

As the feasibility of bioleaching has been proved in the present research at laboratory scale, further studies should investigate the application of this technology at larger scale. The research activity highlighted that bioleaching processes required prolonged time of treatment and provided lower loading capacity compared to chemical processes. These factors could, thus, hinder the process scale-up. In this view, an interesting aspect to be further investigated is however the development of hybrid technologies based on the integration of both chemical and biological processes in order to overcome their limits coupling the faster kinetic of the chemical treatment with the eco-friendly advantages of the biological approach. Moreover, future developments could be addressed towards the application of these processes to different kinds of metal bearing materials in order to exploit the ability revealed in extracting valuable and critical metal even for other secondary sources.

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