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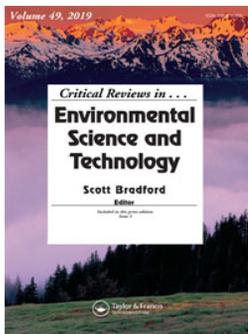
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## Recent advances on hydrometallurgical recovery of critical and precious elements from end of life electronic wastes - a review

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### ABSTRACT

Waste electrical and electronic equipment (WEEE) contains economically significant levels of precious, critical metals and rare earth elements, apart from base metals and other toxic compounds. Recycling and recovery of critical elements from WEEEs using a cost-effective technology are now one of the top priorities in metallurgy due to the rapid depletion of their natural resources. More than 150 publications on WEEE management, leaching and recovery of metals from WEEE were reviewed in this work, with special emphasize on the recent research (2015–2018). This paper summarizes the recent progress regarding various hydrometallurgical processes for the leaching of critical elements from WEEEs. Various methodologies and techniques for critical elements selective recovery (using ionic liquids, solvent extraction, electrowinning, adsorption, and precipitation) from the WEEEs leachates are discussed. Future prospects regarding the use of WEEEs as secondary resources for critical raw materials and its technological and commercial beneficiaries are discussed.

### KEYWORDS

Critical raw materials;  
Critical and precious metals;  
E-Wastes; Hydrometallurgy;  
Metal selective recovery;  
Rare earth elements; WEEEs

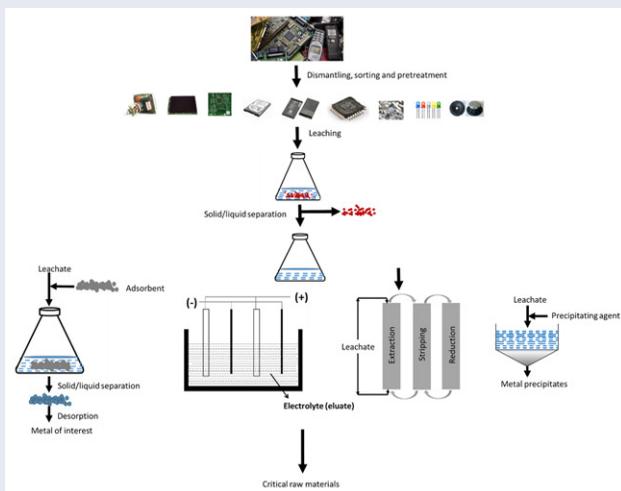
**CONTACT** Manivannan Sethurajan  [biotek\\_mani@yahoo.co.in](mailto:biotek_mani@yahoo.co.in)  Department of Environmental Engineering and Water Technology, IHE Delft Institute for Water Education, Westvest 7, 2611 AX Delft, The Netherlands. Color versions of one or more of the figures in the article can be found online at [www.tandfonline.com/best](http://www.tandfonline.com/best).

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**Abbreviations:** E-Waste: Electronic waste; WEEE: Waste electrical and electronic equipment; CRM: Critical raw materials; PCB: Printed circuit board; LCD: Liquid crystal display; CRT: Cathode ray tube; Fl. Lamp: Fluorescent lamp; HDD: Hard disk drives; LED: Light emitting diode; EU: European Union; UNEP: United Nations Environmental Program; REE: Rare earth element; ITO: Indium-tin oxide; PM: Precious metal; NiMH battery: Nickel-hydride battery; CPU: Central processing unit; RAM: Random access memory; LiBs: Li-ion batteries; SFL: Spent fluorescent lamps

### GRAPHICAL ABSTRACT



Pictorial representation of the hydrometallurgical recovery of critical and precious elements from WEEE

### Highlights

- Review focusing on the utilization of electronic waste as secondary resources
- Different types, origin and composition of WEEE are summarized
- Various lixiviants for critical elements leaching from WEEE are reviewed
- Strategies for critical and precious elements recovery from leachates are discussed
- Techno-economic benefits of hydrometallurgy of electronic waste are highlighted

### 1. Introduction

Enormous amounts of waste electrical and electronic equipment (WEEE) are being generated in recent years. According to recent statistics from

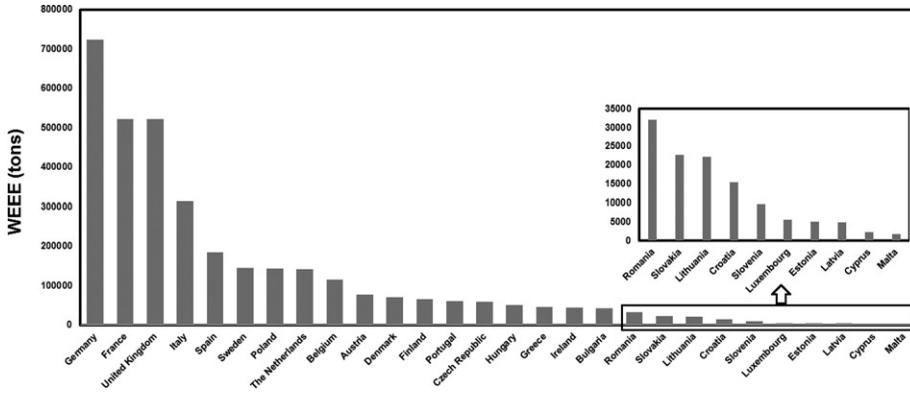


Figure 1. Amount of WEEE generated in EU countries in 2014 (Cyprus - 2013 data) (European Union statistics, 2017).

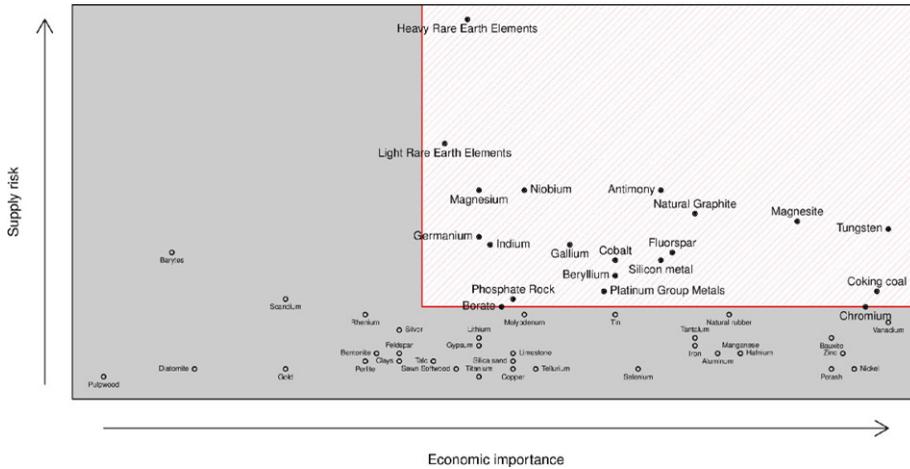


Figure 2. List of critical raw materials (European Commission report, 2014).

European Union statistics institute, approximately 8.3 to 9.1 million tons of WEEE wastes were generated in the EU by 2005 and is expected to increase to 12.3 million tons by 2020 (European commission, 2008) (Figure 1). On the other hand, worldwide WEEE generation will reach 50 million tons by 2018 (Balde, Wang, Kuehr, & Huisman, 2015). These WEEE not only contains organic pollutants (like polybrominated diphenyl ethers, chlorofluorocarbons etc.) but also contains significant concentrations of base, critical and precious metals as well as rare earth elements (Robinson, 2009; Işildar, van de Vossenberg, Rene, van Hullebusch, & Lens, 2017). Therefore, discarded electric and electronic devices have the potential to be a very promising secondary source of critical and precious elements (Ghosh, Ghosh, Parhi, Mukherjee, & Mishra, 2015). The major economic driver for recycling electronic waste is the recovery of critical raw materials (CRM). United Nations

Environment Program (UNEP) and European Union (EU) have classified several elements such as Ga, In, W, Nd, Pd, Ta, REE etc., as critical raw materials which are essential to EU economy (Figure 2) (Buchert, Schüler, Bleher, & Programme des Nations Unies pour l'environnement, 2009; European Commission, 2014). However, the list has been recently updated and 9 new raw materials (such as baryte, bismuth, hafnium, helium, natural rubber, phosphorus, scandium, tantalum and vanadium) have also been addressed as critical raw materials (European Commission, 2017).

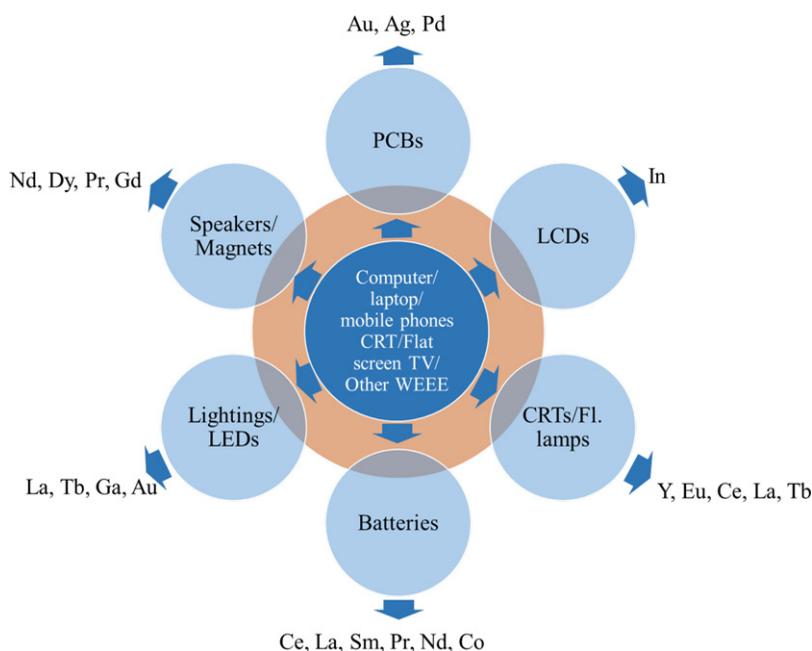
While there is a gradual depletion of primary ores of these critical and precious elements, they are found in relatively high concentrations in electronic wastes. Waste printed circuit boards (PCBs), waste liquid crystal displays (LCDs), spent cathode ray tubes (CRTs), spent fluorescent lamps, waste hard disk drives (HDDs), spent light emitting diodes (LEDs) and spent batteries are the fastest growing WEEE and contain many critical and precious elements (Willner & Fornalczyk, 2013; Askari, Ghadimzadeh, Gomes, & Ishak, 2014; Natarajan, Tay, Yew, & Ting, 2015). For instance, Indium-tin oxide (ITO) forms the basis of LCDs and rise crucial demand for indium (In). European Commission (2014) reported that the total world consumption of yttrium is estimated 7,650 Mg and the main uses of yttrium are 79% and 21% for phosphors and ceramics, respectively. The yttrium demand has been increasing by around 8% per year and its supply is also expected to increase at a similar rate (European Commission, 2014). On the other hand, europium is a fundamental element for phosphors production, almost 96% of the global Eu consumption (425 Mg) is used for phosphors production (European Commission, 2014). Similarly, precious metals such as Au are essential to fabricate PCBs and chip-on-board LEDs. Significant concentration of gold ( $2 \text{ g}\cdot\text{kg}^{-1}$ ) is present in the spent chip-on-board LEDs (Murakami, Nishihama, & Yoshizuka, 2015). WEEEs are highly heterogeneous and practically it is not possible to have a generic recycling technologies.

Currently WEEE is processed at complex smelters by pyrometallurgy, which has demerits such as high energy requirements, non-selectivity, losses of rare earth elements (REE), and high capital costs (Tunsu & Retegan, 2017). However, for low-volume streams (shredder dusts, LEDs, PCBs) which escape from collection chains of pyrometallurgical recyclers, an entirely different technology is needed. On the other hand, high grade resources of critical raw materials are depleting considerably (Hennebel, Boon, Maes, & Lenz, 2015). In order to meet the market demand, it is important to explore other ways of metals recycling and recovery strategies from these WEEE. Pyrometallurgy is not suitable for these kind of wastes because of higher capital costs and energy requirements compared to hydrometallurgical process.

Several studies on the hydrometallurgy of spent WEEE were reported, but drawbacks such as acid toxicity, heavy metal pollution, sludge generation, etc. were highlighted. Cui and Zhang (2008) reviewed pyro and hydrometallurgical processes proposed for the recovery of metals from WEEEs. However, this review is almost a decade old and more novel methodologies were proposed in the recent years. Tuncuk, Stazi, Akcil, Yazici, and Devenci (2012) reviewed the possible applications of hydrometallurgy to recover metals from PCBs but had the drawback of focusing in only one type of WEEE i.e. PCB. Zeng, Li, and Singh (2014) overviewed the recycling of lithium ion batteries, but the emphasis was only on Li and Co. Recycling and recovery of yttrium (Y), europium (Eu), cerium (Ce), lanthanum (La), and terbium (Tb) in phosphors from waste fluorescent lamps were reported (Tan, Li, & Zeng, 2015). In this review, emphasis was given only to REE from fluorescent lamps. Extensive review on hydrometallurgical extraction of gold from different WEEEs were reported by Akcil, Erust, Gahan, Ozgun, Sahin, and Tuncuk (2015) and Göknelma, Birich, Stopic, and Friedrich (2016). In these reviews, gold was given sole attention and did not target many other metals present in WEEE. Zhang, Wu, Wang, Li, Zhang, and Zuo (2015) overviewed different processes reported for the leaching and recovery of In from particular WEEE i.e. LCDs. Similarly, Chagnes and Pospiech (2013) reviewed various hydrometallurgical processes for the recycling of spent lithium-ion batteries. There are also a lot of studies on the biohydrometallurgical approaches for the solubilization of metals from different WEEEs (Erüst, Akcil, Gahan, Tuncuk, & Devenci, 2013; Ilyas & Lee, 2014; Işıldar, van de Vossenberg, Rene, van Hullebusch, & Lens, 2017). In the present review, up-to date reported strategies for the leaching and recovery of critical and precious elements from different end of life electronic wastes are reviewed. Recovery of REE, critical and precious elements bearing WEEEs such as waste printed circuit boards, waste liquid crystal displays, spent cathode ray tubes, spent fluorescent lamps, waste hard disk drives, spent light emitting diodes and spent batteries are given a special attention. Their elemental composition and various hydrometallurgical (leaching and recovery phases) operations proposed for the recovery of critical elements are reviewed.

## **2. WEEE as a secondary source for critical raw materials**

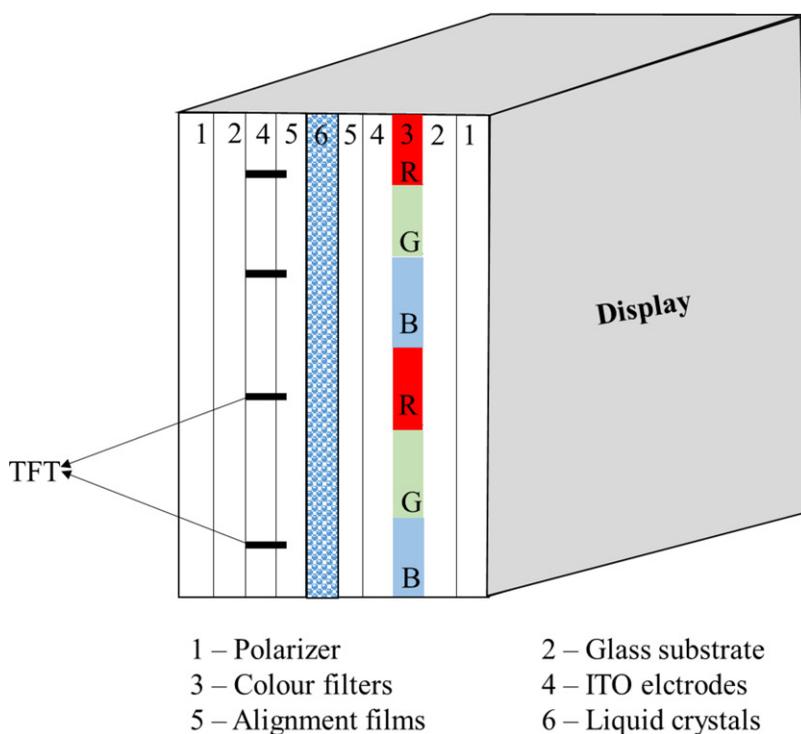
WEEE such as spent PCBs, spent LCDs, spent fluorescent lamps, spent LEDs and spent batteries contain significant concentration of different critical and/or precious metals (Figure 3). Various characteristics (such as the physico-chemical properties and elemental composition) of each of the different WEEE were discussed below in detail.



**Figure 3.** Pictorial representation of different types of WEEE and their major critical raw materials.

### 2.1. Spent LCDs

Indium is a scarcely available metal, which finds application in electronics industry especially in the production of LCD panels. In the recent past decades, LCDs have replaced conventional CRTs because of their lower power consumption capacity (Dodbiba, Nagai, Wang, Okaya, & Fujita, 2012). Indium is used for the fabrication of Indium-Tin-Oxide (ITO) in LCD panels. ITO has some unique characteristics, such as electricity conduction, can bind strongly to glass and is also transparent, which attracts maximum In usage in LCD design (Křištofová, Rudnik, & Miškuřová, 2017). About 70% of total In consumption is accounted to ITO production (Tolcin, 2012). On the other hand, natural In resources in Earth crust is as low as 0.25 ppm (Schwarz-Schampera & Herzig, 2002). Dzhallindite, indium hydroxide mineral is the most common and predominant primary resource of In. In supply will remain for fewer than 14 years based on the current rate of extraction, which urges the necessity of recycling of In bearing wastes (Křištofová, Rudnik, & Miškuřová, 2017). Spent LCDs are one such wastes which contain significant concentration of In. A cross section of a LCD panel is shown in Figure 4. As mentioned earlier, ITO is one of the major parts of spent LCDs (Figure 4). In is present as indium (III) oxide ( $\text{In}_2\text{O}_3$ ), which contributes to 90% (by weight) of in ITO (remaining 10% is made of tin (IV) oxide). Typical spent LCD panels on an average contain  $530 \text{ mg}\cdot\text{kg}^{-1}$  of In,  $346 \text{ mg}\cdot\text{kg}^{-1}$  of As and  $24 \text{ mg}\cdot\text{kg}^{-1}$  of Sb (Savvilotidou, Hahladakis, & Gidaracos, 2015).



**Figure 4.** Cross section of a thin-film-transistor-LCD panel.

## 2.2. Spent batteries

### 2.2.1. Li-ion batteries

Electrical batteries can be classified into two types such as (1) primary batteries (non-rechargeable) and (2) secondary batteries (rechargeable). The primary batteries are mainly made of Zn-C-MnO<sub>2</sub>. These primary batteries can again be divided into two types (1) acidic batteries which uses ammonium chloride and (2) alkaline batteries that use potassium hydroxide. Rechargeable batteries are made of Co and Li and are called as Lithium-ion batteries (LiBs). LiBs are the most used type batteries and are widely used in portable electronic devices such as mobile phones, laptops, recorders, cameras and MP3 players (Shuva & Kurny, 2013). Consumption of Li in the electronics industry continues to grow in the recent past years (Sakultung, Pruksathorn, & Hunsom, 2007). For instance in 2007, 2.04 billion LiB units were produced and in 2010 it went up to about 4.6 billion units (Scrosati, Krebs, Beck, & Bartels, 2007; Zeng, Deng, Luo, Luo, & Zou, 2012). Due to huge increase in production, excessive spent LiB wastes have been generated in the recent decades. Spent LiBs can be considered as hazardous waste, because it can cause adverse effects to the environment, animals and human health (Shin, Kim, Sohn, Yang, & Kim, 2005). On the other hand, these spent LiBs contain significant concentration of valuable

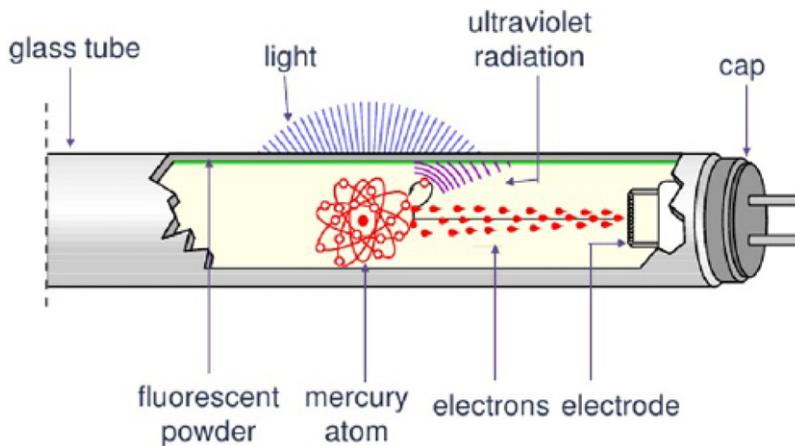
metals like Co and Li. X-ray diffraction studies shows that  $\text{LiCoO}_2$  and  $\text{Co}_3\text{O}_4$  are the major mineral phases present in the spent LiBs. For example, Lee and Rhee (2003) found out that 27.5% (wt%) of  $\text{LiCoO}_2$  is present in spent LiBs (Zheng et al., 2016). There are many different LiB units produced and the concentration of Co and Li present in the spent LiB can vary accordingly. As Co is one of the critical elements, spent LiB wastes can be considered as a potential secondary resource of Co. However, precautions and safety measurements should be taken prior dismantling the spent Li-batteries. Even the spent LiBs contain residual voltage and can produce strong heat and flames due to self-ignition (because of residual charge) and internal short circuit (Nan, Han, & Zuo, 2005; Vieceli et al., 2018). Therefore, precautionary steps like (i) refrigeration using NaCl or water, (ii) cryogenic activities like immersion in liquid nitrogen for 4–6 min and (iii) promoting short circuit and discharging the batteries using electric iron powder were proposed in the literature (Li, Wang, & Xu, 2016; Vieceli et al., 2018).

### **2.2.2. Ni-MH batteries**

Spent NiMH (nickel-hydride) battery scrap is a valuable material for recovery of cobalt and REEs. It is worth to mention that the battery used in hybrid cars contains 3 kg of REEs and 1.5 kg of Co for 11 kg nickel content. Mechanical or thermo-mechanical processing (grinding, separation, roasting) of this waste leads usually to separation of the most valuable fraction often called “black mass.” The black mass is susceptible for hydrometallurgy. Typical elemental composition of the black mass contain from 5 to 15% of REEs, 2–6% of Co, and also other metals like Ni (29–51%), Zn (1–8%) and Mn (2–8%) (Innocenzi & Vegliò, 2012; Becker et al., 2016; Petranikova, Herdzik-Koniecko, Steenari, & Ekberg, 2017).

### **2.3. Spent LEDs**

Light emitting diodes (LEDs) are widely used in electronics industry, especially in television displays. LEDs consume less energy than the traditional illuminants. Zhan, Xia, Ye, Xiang, and Xie (2015) state that the waste LEDs are poly-metallic and contain Ga ( $2.1 \text{ mg}\cdot\text{kg}^{-1}$ ), In ( $1.1 \text{ mg}\cdot\text{kg}^{-1}$ ) and Au ( $16.7 \text{ mg}\cdot\text{kg}^{-1}$ ). Apart from the spent LEDs wastes, there is another Ga containing WEEE gallium arsenide scraps. Gallium arsenide (GaAs) sludges are co-products generated during the production of LEDs and they contain significant concentrations of Ga and As. XRD analysis of these scraps reveal that they contain gallium arsenide (GaAs) and gallium phosphide (GaP) compounds (Hu, Xie, Hsieh, Liou, & Chen, 2015). Approximately 42–50% of Gallium and 25–50% of As were found in the waste GaAs



**Figure 5.** Structure of double-capped linear fluorescent lamp (CREE Inc., 2015).

**Table 1.** The chemical composition of pure tri-chromatic phosphate (adapted from Wu et al., 2014).

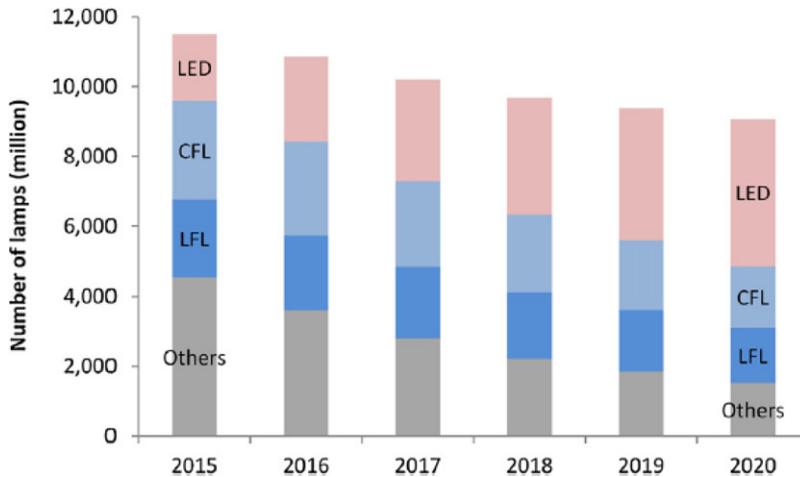
Elements	Rare earth oxide	Contents (%)	Elements	Rare earth oxide	Contents (%)
Y	Y <sub>2</sub> O <sub>3</sub>	46.9–51.2	Ce	CeO <sub>3</sub>	4.1–5.3
Eu	Eu <sub>2</sub> O <sub>3</sub>	3.9–4.4	Tb	Tb <sub>4</sub> O <sub>7</sub>	2.2–2.6
Ce	CeO <sub>3</sub>	4.1–5.3	Mg	MgO	2.7–4.0
Ba	BaO	2.1–3.2	–	–	–

scraps (Lee & Nam, 1998; Chen, Tsai, Tsai, & Shu, 2012; Hu, Xie, Hsieh, Liou, & Chen, 2015).

#### 2.4. Spent fluorescent lamps (SFLs)

The lamp tube contains low-pressure mercury vapor, an inert gas such as argon or helium and tri-chromatic phosphor coating the inner lamp tube surface (Wu, Yin, Zhang, Wang, & Mu, 2014). An electronic discharge by the cathode inside the glass tube stimulates the mercury vapor causing it to emit radiation in the UV range ( $\lambda_{\text{Hg}} = 253.7 \text{ nm}$ ) (Wu, Yin, Zhang, Wang, & Mu, 2014). The inner tube wall is coated with powder containing yttrium and europium doped oxide lattices to absorb the invisible UV radiation emitted from the interaction of mercury (Hg) and electrons for visible wavelength (The Hong Kong Observatory, 2012; Wu, Yin, Zhang, Wang, & Mu, 2014; NEC Lighting, Ltd, 2015) (Figure 5).

Wu, Yin, Zhang, Wang, and Mu (2014) reported that the share of red, green and blue phosphor in standard chemical composition is 55, 30, and 15%, respectively. The elemental composition of standard tri-chromatic fluorescent lamp is reported in Table 1. Expectation of the total global lighting market and lamp type shares are given in Figure 6.



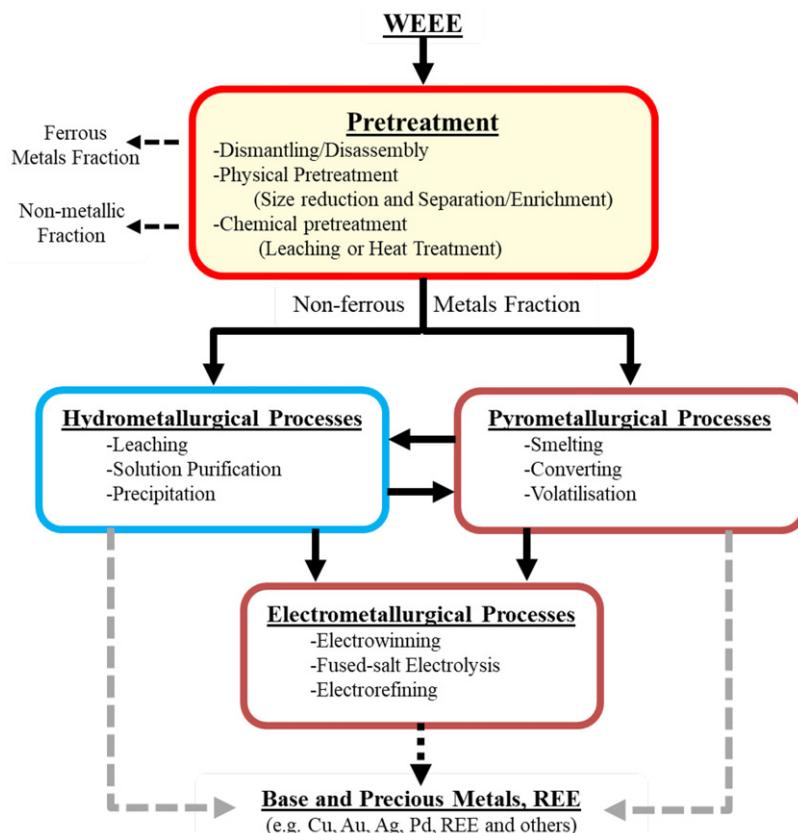
**Figure 6.** Expectation of the total lighting market in terms of lamp type shares (Adopted from McKinsey & Company, 2012). LED: Light emitting diodes; CFL: Compact fluorescent lamps; LFL: Linear fluorescent lamps.

### 2.5. Spent PCBs

Waste printed circuit boards (PCBs) account for about 3% of nearly 50 Mt/year global WEEE generation (Kaya, 2016; Işıldar, van de Vossenberg, Rene, van Hullebusch, & Lens, 2017). They are heterogeneous in nature, which constituted of metals (40%), ceramic (30%) and plastics (30%). Among these fractions, the driving force for recycling waste PCBs is the recovery of precious metals (in particular Au) (Tuncuk, Stazi, Akcil, Yazici, & Deveci, 2012). Because PCBs contain many base (such as Cu, Ni and Fe) and precious metals (PMs), mainly Ag, Au and Pd (Priya & Hait, 2018). PMs concentrations in PCBs are much higher than those found in the natural deposits (Ebin & Isik, 2017). PCBs could be seen as a respectable poly-metallic secondary source for urban mining.

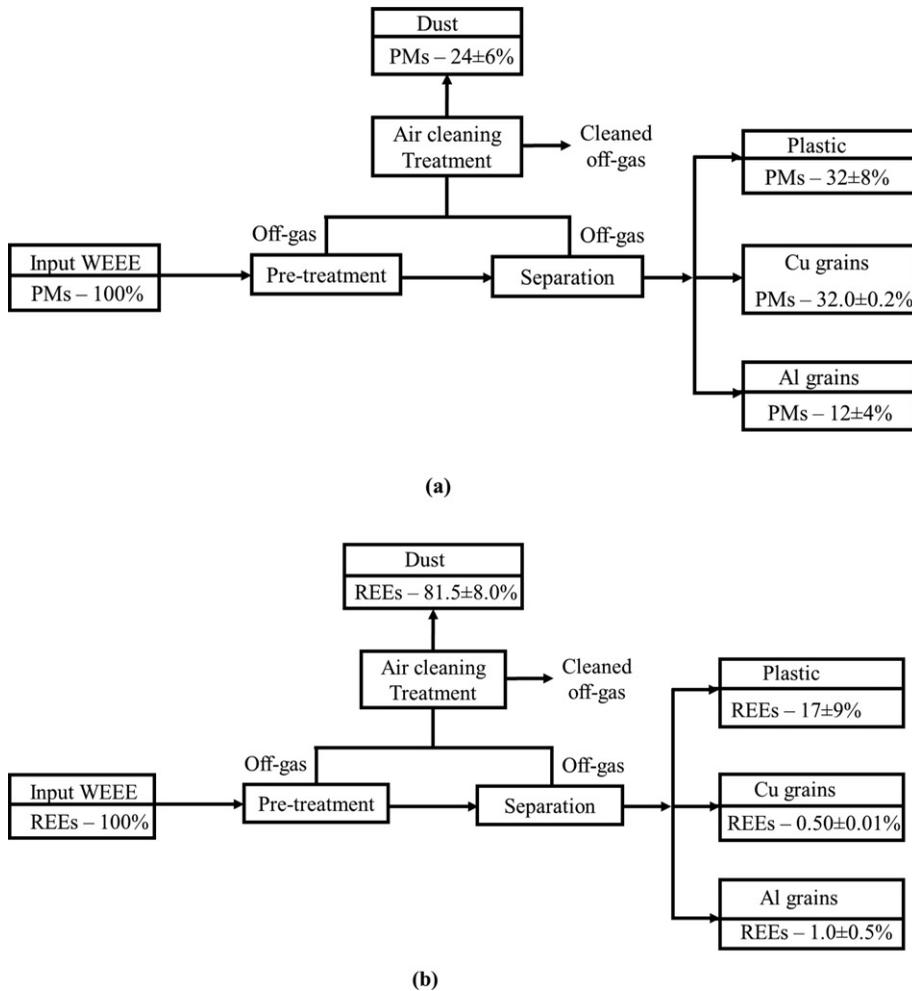
### 3. Pre-treatment of WEEE

Pre-treatment is the first and obligatory step to recover critical and precious elements from WEEE. WEEE is inherently complex and heterogeneous in type and composition with considerable variations in metal and materials content, which makes it extremely difficult to develop and implement recycling processes for selective recovery of the contained elements. In addition to the heterogeneity of the different WEEE, there is also a significant change in the composition of the WEEE, because of the technology developed over the years (Cui & Forsberg, 2003; Stevens & Goosey, 2008; Yazıcı, Deveci, Yazici, & Akcil, 2015; Yamane, de Moraes, Espinosa, & Tenório, 2011; Yazıcı & Deveci, 2009; Kucuker, 2018). Pre-treatment of WEEE is often required prior to metallurgical extraction processes for



**Figure 7.** Unit operations/processes in the treatment of WEEE for recovery of the contained values.

selective recovery/separation of the desired components with economic or pollution potential, increasing the technical effectiveness and reducing the cost of these processes (Yazıcı & Deveci, 2009). Pre-treatment is the first stage of a recycling operation for WEEE feedstock (Figure 7), which involves mainly dismantling/disassembly and physical processes such as size reduction and physical separation. Sufficient liberation and efficient separation of metals/materials are essential in WEEE pre-treatment operations. These processes have been proven as indispensable for the conventional WEEE recycling, i.e., for the recovery of “mass relevant” fractions presented in WEEE, such as ferrous and non-ferrous metals, plastic, glass and other. However, part of precious and critical elements are lost during the pre-treatment processes (Figures 8 and 9). Loss of precious and critical elements in overall recycling chain is mainly caused by the fact that these substances in pre-treatment phase end up in output streams (e.g., shredding dusts (Marra, Cesaro, & Belgiorno, 2018)), which implies that further optimization of WEEE pre-treatment stage is needed (Chancerel, Meskers, Hagelüken, & Rotter, 2009). Chemical pre-treatment for beneficiation of



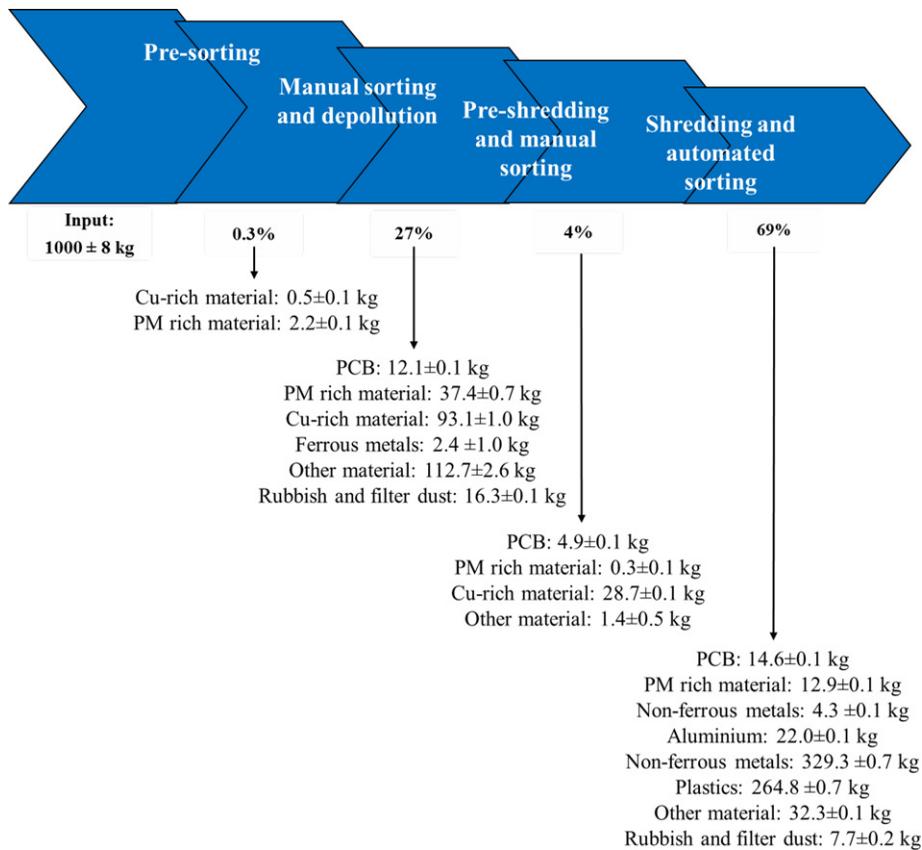
**Figure 8.** Mass flow diagram showing the distribution of (a) PMs and (b) REEs in different fractions (redrawn from Marra et al., 2018).

the contained values, removal of hazardous components, energy recovery etc. can be also exploited before the extraction of metals. In general, pre-treatment phase consists of:

- Manually disassembly/dismantling
- Mechanical treatment processes
- Combination of manual and mechanical pre-processing

### 3.1. Manually disassembly/dismantling

Dismantling/disassembly of WEEE is essentially the first step of recycling for selective recovery of components and devices (capacitors, batteries, screens, PCB etc.) for re-use and/or further treatment. The main focus of



**Figure 9.** Mass balance of the pre-processing of 1,000 kg of input WEEE (redrawn from Chancerel et al., 2009).

manually dismantling phase is to ensure removal of hazardous or otherwise environmentally relevant components defined in Annex VII of the WEEE Directive 2012/19 (EC Directive, 2012). In addition, more specific dismantling targeting the most valuable parts/units such as central processing unit (CPU), random access memory (RAM) etc. and/or hazardous components can be performed to obtain high value products (Lee, Chang, Fan, & Chang, 2004). From processing point of view, dismantling allows pre-separation and enrichment of valuable metal-bearing parts from non-metallic parts such as plastics and ceramics, increasing their potential for recycling and improving economics of the overall recycling process (Cui & Forsberg, 2003). It is always difficult and costly to process, separate and recover values downstream from such heterogeneous and complex mixtures. Dismantling/disassembly is often carried out manually, making this step labour intensive, while automated systems are also developed for specific applications (Elo & Sundin, 2014; Park, Kim, Han, & Park, 2015; Kopacek, 2016).

### 3.2. Mechanical treatment processes

Manual sorting and dismantling is usually followed by a traditional recycling processes, where metals and materials contained in WEEE are liberated and separated based on their specific physical characteristics such as weight, size, shape, density, and electrical and magnetic characteristics (de Oliveira, Bernardes, & Gerbase, 2012). After selective sorting/recovery through dismantling, metal bearing components such as printed circuit boards (PCBs) are often subjected to physical pre-treatment essentially for improving the technical and economic aspects of the following treatment processes. The first stage of physical pre-treatment is the size reduction of WEEE down to a suitable size for the selected treatment process. Shredders and hammer mills are extensively used for size reduction of WEEE (Dalrymple et al., 2007; Kaya, 2016). In a recent study, Electro Dynamic Fragmentation of PCB was demonstrated as an unconventional method for size reduction and liberation of components (Martino, Iseli, Gaydardzhiev, Streicher-Porte, & Weh, 2017).

The degree of size reduction required is determined by the following process/operation. In this regard, fine grinding (typically  $<200\ \mu\text{m}$ ) is prerequisite for stirred tank leaching as the main stage of a hydrometallurgical process while relatively coarse material can be fed to pyrometallurgical processes such as smelting. In a similar way, physical separation processes as pre-treatment is more effective at relatively coarse sizes; albeit, their separation efficiency relies essentially on the degree of liberation of target phases (Yazıcı & Devenci, 2009). Degree of liberation is often a function of particle size also depending on the type of WEEE. In this regard, reducing the size of waste computer PCB down to  $-5\ \text{mm}$  was reported to be required for a high degree of liberation ( $\geq 97\%$ ) of metals e.g., copper, aluminium and ferromagnetics (Zhang & Forssberg, 1997; 1998). Notwithstanding this, even very fine grinding (e.g.,  $<75\ \mu\text{m}$ ) could not be sufficient for complete liberation of metals from PCB (Ogunniyi, Vermaak, & Groot, 2009; Yazıcı, Devenci, Alp, Akcil, & Yazıcı, 2010).

After size reduction for achieving the required degree of liberation, physical separation methods can be readily exploited for the separation of metals from WEEE prior to the pyrometallurgical and hydrometallurgical extraction processes. The main advantages of physical separation include their simplicity and low-costs. A variety of separation methods are available based on the differences in physical properties including specific gravity, conductivity, magnetic susceptibility, brittleness and hydrophobicity of the phases (Wills & Finch, 2015). Table 2 summarises physical separation methods available/studied for beneficiation of WEEE. Magnetic separation, which is usually performed with low intensity

**Table 2.** Physical separation methods available for recovery of metals from WEEE (adapted from Cui & Forssberg, 2003; Yazıcı & Deveci, 2009).

Method	Exploited property	Separation of materials	Particle size	References
<b>Magnetic Separation</b>	Magnetic susceptibility	Ferrous (ferromagnetic) metals from non-ferrous metals and non-metals (para-/dia-magnetics)	<5 mm	Zhang and Forssberg (1997); Zhang and Forssberg (1998); Veit et al. (2005); Yazıcı and Deveci (2015); Zhang et al. (2017)
<b>Electrostatic Separation</b>	Electrical conductivity	Metals (conductive) from non-metals	0.1–5 mm	Zhao, Wen, Li, and Tao (2004); Li, Lu, Guo, Xu, and Zhou (2007); Wen et al. (2005); Zhang et al. (2017)
<b>Eddy-current Separation</b>	Electrical conductivity/specific gravity	Light metals i.e. Al from conductive but heavy (base and precious) metals and non-conductive materials (plastics and ceramics)	>5 mm	Zhang and Saito (1998); Yazıcı, Deveci, Alp, Akcil, and Yazıcı (2010)
<b>Gravity Separation</b>	Specific gravity	Metals from non-metals	0.05–10 mm	Galbraith and Devereux (2002); Zhao, Wen, Li, and Tao (2004); Eswaraiah, Kavitha, Vidyasagar, and Narayanan (2008); Duan et al. (2009); Veit, Juchneski, and Scherer (2014)
<b>Flotation</b>	Surface properties	Non-metals (hydrophobic) from metals	0.075–1 mm	Ogunniyi and Vermaak (2009); Vidyadhar and Das (2013); Gallegos-Acevedo, Espinoza-Cuadra, and Olivera-Ponce (2014)

magnetic drum separators, is often used as the first stage of physical separation for removal of ferrous metals as magnetic fraction (Yazıcı & Deveci, 2009; Tuncuk, Stazi, Akcil, Yazıcı, & Deveci, 2012). Air classification can be used to separate essentially fluffy material or fine light plastics (Lee, Chang, Fan, & Chang, 2004; Zhao, Wen, Li, & Tao, 2004; Eswaraiah, Kavitha, Vidyasagar, & Narayanan, 2008). Light metals such as Al with a high ratio of conductivity/density ( $>10$ ) are separated by eddy-current separation from non-conductive (non-metallic) fraction and heavy non-ferrous metals i.e. base and precious metals, are recovered through electrostatic separation based on their conductivity (Table 2), and using permanent magnets, such as iron-boron-neodymium magnets (Zhang & Forssberg, 1998). Finally, due to differences in specific density of different materials contained in WEEE, gravity separation techniques such as shaking tables, heavy media separation, jigging, etc., can be used to separate materials of different specific gravity by their relative movement in response to gravity (de Oliveira, Bernardes, & Gerbase, 2012).

Despite the improved liberation of metals, the effectiveness of physical separation methods tends to deteriorate with decreasing particle size, this also depends on the difference in magnitude of the physical property of

fractions (Veit et al., 2005; Yazici & Deveci, 2015; Zhang et al., 2017). In effect, each separation method can be most effective in a certain size range (Table 2) (Wills & Finch, 2015). Size reduction operations inevitably generate fine/dust fraction from which recovery of metals by most conventional separation methods such as magnetic, eddy-current or electrostatic separation is difficult and inefficient (Zhao, Wen, Li, & Tao, 2004; Li, Lu, Guo, Xu, & Zhou, 2007; Yazıcı, Deveci, Alp, Akcil, & Yazıcı, 2010; Yazıcı & Deveci, 2015). This inefficiency of physical separation processes can lead to prohibitively high metal losses (10–35%) (Goosey & Kellner, 2002; Hagelüken, 2006; Marra, Cesaro, & Belgiorno, 2018). However, there are potential beneficiation methods such as flotation and centrifugal gravity separation for recovery of metals from fine size fractions (Galbraith & Devereux, 2002; Wen et al., 2005; Duan et al., 2009; Ogunniyi & Vermaak, 2009; Veit, Juchneski, & Scherer, 2014).

### **3.3. Fate of critical and precious elements in pre-treatment processes**

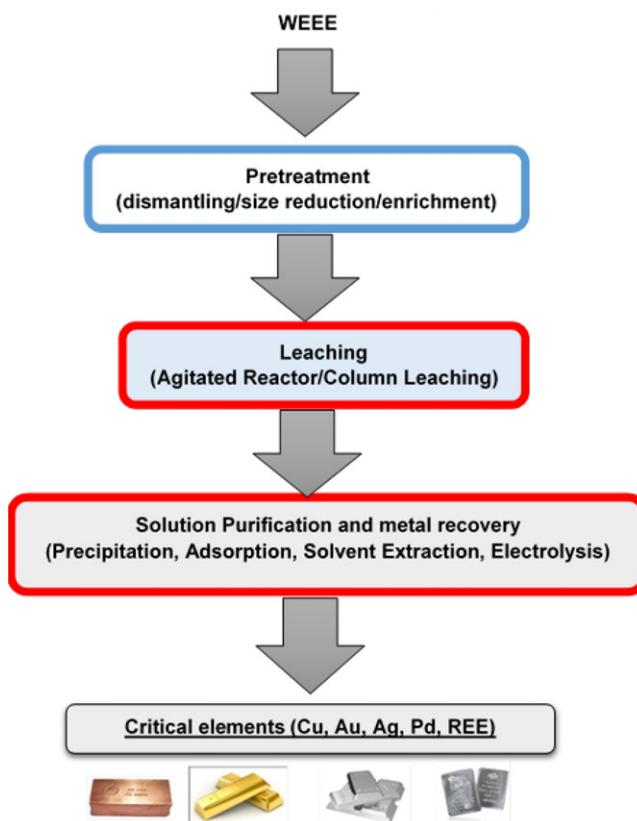
The recovery of a specific material from end-of-life WEEE input stream increases with decreasing of impurities in the final material after the pre-treatment stage (Chancerel, Meskers, Hagelüken, & Rotter, 2009; Meskers & Hagelüken, 2009). Loss of precious and critical elements through the manual dismantling, and/or shredding processes result in the overall reduction of the recycling efficiency (Bigum, Brogaard, & Christensen, 2012). Fully automated disassembly is not currently technically feasible and not expected to become economically viable in near future (Duflou et al., 2008). Technical optimization with focus to ameliorate manual disassembly during the pre-treatment stage is crucial. Also, generally standard practice to shredding whole WEEE devices leads to significant losses of precious metals - which cannot be compensated by the downstream sorting and refining processes (Buchert, Manhart, Bleher, & Pingel, 2012).

Losses of precious metals in PCBs caused by shredding was examined through an industrial test (Chancerel, Meskers, Hagelüken, & Rotter, 2009), where the difference in concentration between unshredded and pre-shredded PCBs was determined. The results showed 7% less precious metals after the pre-shredding phase, while the difference between pre-shredded PCBs and shredded PCBs indicated additional loss of 62% precious metals in the PCBs. Ueberschaar, Otto, and Rotter (2017) showed that relatively small shares of gallium bearing components on PCBs or in LEDs lead to a dilution with other materials in conventionally applied recycling processes. Ending in the pyrometallurgical process for copper and precious metals refining, gallium is transferred as oxidized form to the slag. Thus, gallium rich components must be separated prior to any mechanical

processing with other material. Mechanochemical technology can be used as a means of pre-treatment, and then hydrometallurgical technology to recycle metals from some specific wastes, including WEEE. Through this way, the recovery rate of metal was significantly higher than ordinary hydrometallurgy (Zhang & Xu, 2016). This was demonstrated by Lee et al. (2013) in their study on indium recycling from waste LCD panels, Zhang and Saito (1998) for recovering yttrium (Y) and europium (Eu) in waste phosphor, Lee, Zhang, and Saito (2000) on recovering Co and Li from spent lithium – ion batteries. Marra, Cesaro, and Belgiorino (2018), demonstrated that about 80% of REE will be trapped up in dusts (because of these conventional pre-treatment techniques) and then the dusts have to be treated by other specific processes (Figure 8).

Although major losses of precious and critical elements are occurring during the pre-treatment phase, in order to enhance their recovery, some of the crucial improvements should be implemented even in steps that precede pre-treatment phase (Figure 9). Besides increasing the collection rates for all product groups that contain precious and critical elements, more reliable and transparent information about the content of these metals in different equipment groups and their components, should be available. Also, structure and design of electrical and electronic products in order to facilitate manual disassembly and recycling processes need to be additionally optimized.

Within pre-treatment phase, it is necessary to optimize processes by improvement of manual disassembly and separation of target components in WEEEs (which are rich in precious and critical elements). Besides removal of the WEEE components that are legally stipulated (Annex VII of the WEEE Directive 2012/19, EC Directive, 2012), parts of equipment such as batteries containing cobalt, neodymium hard disk magnets, small PCBs, etc., should also be removed and fed into a suitable recycling process (Buchert, Manhart, Bleher, & Pingel, 2012). Outputs from pre-treatment phase must be fractions with characteristics appropriate for end-processing facilities. More investments and further research should be focused on promising technologies for automatic recognition, sorting, and dismantling of WEEE, in order to recover precious and critical elements from heterogeneous WEEE flows, more efficiently (Chancerel, Meskers, Hagelüken, & Rotter, 2009; Buchert, Manhart, Bleher, & Pingel, 2012). Finally, quantitative targets for the recycling of WEEE (Annex V of the WEEE Directive 2012/19, EC Directive, 2012), are not formulated specifically in terms of material or components, but relate to the weight percent of the complete devices, which leads to negative incentives for the recovery of precious and critical elements. Therefore, revision of the WEEE Directive in terms of setting targets for the recycling rates for specific critical metals and/or product groups, is recommended (Buchert, Manhart, Bleher, & Pingel, 2012; Chancerel, Meskers, Hagelüken, & Rotter, 2009). In



**Figure 10.** General flowsheet of hydrometallurgy of WEEE.

general, a compromise between the quality and quantity of grade-recovery fraction has to be carried out to minimize the losses of valuable metals and the distribution of precious metals over the outputs of the operating conditions for WEEE pre-processing.

#### **4. Hydrometallurgical treatment of WEEE for recovery of critical elements**

Hydrometallurgy of WEEE consists of at least two main unit operations, namely (1) leaching (solubilization of metals from WEEE into leachates using aqueous chemicals) and (2) recovery (selectively recovering the dissolved metals from the leachates) (Figure 10). Various leaching and recovery processes for the extraction of critical raw materials from WEEE is described below in detail.

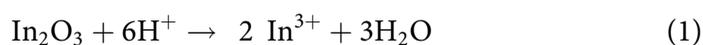
##### **4.1. Leaching of critical elements from WEEE**

Various hydrometallurgical processes have been described in the literature for the leaching of REE, precious and critical metals from WEEE. There

are various process parameters such as (1) particle size, (2) lixiviant type, (3) concentration of the lixiviant, (4) temperature, (5) pH, (6) solid to liquid ratio, (7) agitation and (8) redox potential that control the leaching kinetics and extent. In some cases, addition of oxidants and reductants will also be provided to improve the leaching efficiency. In the below sections, leaching of REE, critical and precious metals from different WEEE will be discussed in detail.

#### **4.1.1. Leaching of critical elements from WEEE**

**4.1.1.1. Indium leaching from LCD.** Several studies on the effect of mineral acids on the leaching of Indium from LCDs have been published (Li, Liu, Li, Liu, and Zeng, 2011; Dodbiba, Nagai, Wang, Okaya, & Fujita, 2012; Silveira, Fuchs, Pinheiro, Tanabe, & Bertuol, 2015; Savvilotidou, Hahladakis, & Gidarakos, 2015) (Table 3). Yang, Kubota, Baba, Kamiya, and Goto (2013) studied the effect of individual mineral acids (such as HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>) on the leaching of Indium from LCD panel glass. The results showed that the hydrochloric acid leached more In than sulfuric and nitric acids at lower solid to liquid ratio (Yang, Retegan, & Ekberg, 2013). On the other hand, Li, Liu, Li, Liu, and Zeng (2011) reported that both sulfuric and hydrochloric acid leach more than 99% of In from ITO targets (at a given time). However, information regarding the pre-treatment (i.e., removal of the plastic films) was not clearly mentioned. Mixture of different acids (like HCl + HNO<sub>3</sub> and HCl + H<sub>2</sub>SO<sub>4</sub>) was also investigated to solubilize In from LCDs. Hydrochloric acid and nitric acid mixture found to have higher leaching capacity than the sulfuric acid mixture (Savvilotidou, Hahladakis, & Gidarakos, 2015). The main reactions of acidolysis of ITO are illustrated as follows (Li, Liu, Li, Liu, and Zeng, 2011):



Leaching efficiency of In from LCDs can be influenced by particle size, temperature, solid to liquid phase ratio and lixiviant (acid) concentration. Increase in acid concentration leads to increase in the leaching efficiency of In from LCDs (Silveira, Fuchs, Pinheiro, Tanabe, & Bertuol, 2015). Indium leaching from LCDs is temperature and pulp density dependent (Savvilotidou, Hahladakis, & Gidarakos, 2015). Lower the pulp density, higher is the leaching efficiency from LCDs. Usually, maximum leaching of In was achieved in higher temperature range (80 °C–90 °C) (Křištofová, Rudnik, & Miškufová, 2017).

**4.1.1.2. Cobalt leaching from spent Batteries.** Various chemical leaching processes were reported to leach out Co from spent batteries (Table 3). Since Co is present as Co(III) in LiCoO<sub>2</sub>, reductive leaching by reductive

**Table 3.** Different hydrometallurgical approaches proposed for the leaching of critical metals from WEEE.

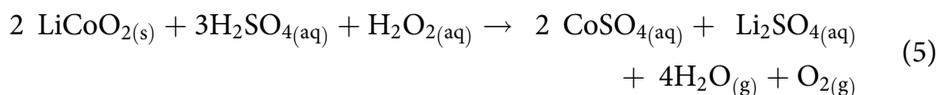
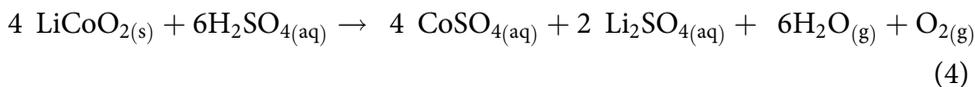
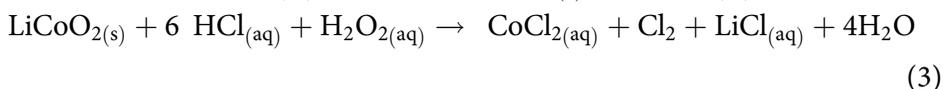
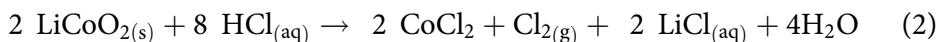
WEEE type	Metal content (w/w %)	Leachant	Optimum conditions	Leaching yield	Reference
ITO powders	In - 71.21%	H <sub>2</sub> SO <sub>4</sub>	0.75 M H <sub>2</sub> SO <sub>4</sub> , 1:100 solid/liquid ratio, 90 °C, 150 min, and stirring at 500 rpm.	Maximum 99 % of In	Li, Liu, Li, Liu, and Zeng (2011)
LCD	In - 0.02%	HCl	1.5 M HCl, 1:100 solid/liquid ratio, 90 °C, 150 min, and stirring at 500 rpm.	Maximum 98 % of In	Yang et al. (2013)
LCD from mobile phones	In - 0.61%	H <sub>2</sub> SO <sub>4</sub>	1.0 M H <sub>2</sub> SO <sub>4</sub> , 1:2 solid/liquid ratio, 20 °C, 24 h, and stirring at 350 rpm.	More than 85% of In was leached	Yang et al. (2013)
LCD from computers	In - 0.05%	HCl	1.0 M HCl, 1:2 solid/liquid ratio, 20 °C, 24 h, and stirring at 350 rpm.	Maximum 80% of In was leached	Silveira, Fuchs, Pinheiro, Tanabe, and Bertuol (2015)
Mobile phone batteries	Co - 30.5%	HCl	1.0 M H <sub>2</sub> SO <sub>4</sub> , 1:50 solid/liquid ratio, 90 °C, 1 h, and stirring at 500 rpm.	A maximum of 96.4 wt.% In	Savvilitidou, Hahladakis, and Gidarakos (2015)
Lithium ion batteries	-	HCl + H <sub>2</sub> O <sub>2</sub>	HCl:H <sub>2</sub> O (3:2), 1:5 solid/liquid ratio, 80 °C, 1 h, and under a mild agitation.	Approximately of 60% of In leached	Sakultung, Pruksathorn, and Hunsom (2007)
Lithium ion batteries	Co ≈ 33.20%	H <sub>2</sub> SO <sub>4</sub> + H <sub>2</sub> O <sub>2</sub>	5 M HCl, 80 °C, 1.5:100 solid-liquid ratio and 60 min	Maximum 84% of Co was leached	Shuva and Kurny (2013)
Lithium ion batteries	-	HCl + H <sub>2</sub> O <sub>2</sub>	3 M HCl + 3.5% H <sub>2</sub> O <sub>2</sub> , 80 °C, 1:20 solid-liquid ratio, 400 rpm and 40 min.	Maximum 79% of Co was leached	Nayl, Elkhashab, Badawy, and El-Khateeb (2014)
Lithium ion batteries	LiCoO <sub>2</sub> - 27.5%	HNO <sub>3</sub> + H <sub>2</sub> O <sub>2</sub>	1 <sup>st</sup> step - Decomposition with NH <sub>4</sub> OH to leach Al and Cu 2 <sup>nd</sup> step - 2 M H <sub>2</sub> SO <sub>4</sub> + 4% H <sub>2</sub> O <sub>2</sub> , 70 °C, 1:10 solid-liquid ratio, 400 rpm and 60 min.	Maximum 99% of Co was leached	Lee and Rhee (2003)
Lithium ion batteries	-	Citric acid + H <sub>2</sub> O <sub>2</sub>	1 M HNO <sub>3</sub> + 1.7 % H <sub>2</sub> O <sub>2</sub> , 1:50 solid to liquid ratio, 400 rpm, 30 min and 75 °C.	More than 95% of Co was leached	Zheng et al. (2016)
Lithium ion batteries	-	Citric acid + H <sub>2</sub> O <sub>2</sub>	4 M C <sub>6</sub> H <sub>8</sub> O <sub>7</sub> + 1% H <sub>2</sub> O <sub>2</sub> , 1.5:100 solid to liquid ratio, 5 h and 90 °C.	More than 99% of Co was leached	

(continued)

Table 3. Continued.

WEEE type	Metal content (w/w %)	Leachant	Optimum conditions	Leaching yield	Reference
Lithium ion batteries	Co - 53.8%	Malic acid + H <sub>2</sub> O <sub>2</sub>	1.5 M C <sub>4</sub> H <sub>5</sub> O <sub>6</sub> + 2% H <sub>2</sub> O <sub>2</sub> , 1:50 solid to liquid ratio, 40 min and 90 °C.	More than 90% of Co was leached	Li et al. (2010)
Lithium ion batteries	Co - 35.52%	Tartaric acid + H <sub>2</sub> O <sub>2</sub>	2 M C <sub>4</sub> H <sub>6</sub> O <sub>6</sub> + 4% H <sub>2</sub> O <sub>2</sub> , 1.7:100 solid to liquid ratio, 30 min and 70 °C.	More than 98% of Co was leached	He, Sun, Mu, Song, and Yu (2016)
Lithium ion batteries	Co - 57.94%	Succinic acid + H <sub>2</sub> O <sub>2</sub>	1.5 M C <sub>4</sub> H <sub>6</sub> O <sub>4</sub> + 4% H <sub>2</sub> O <sub>2</sub> , 1.5:100 solid to liquid ratio, 40 min and 90 °C.	More than 99% of Co was leached	Li et al. (2015)
Lithium ion batteries	-	Glycine + ascorbic acid	0.5 M C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub> + 0.02 C <sub>6</sub> H <sub>8</sub> O <sub>6</sub> , 1:500 solid to liquid ratio, 6 h and 80 °C.	More than 95% of Co was leached	Nayaka, Pai, Santhosh, and Manjanna (2016)
Ga-As waste scraps	Ga - 48.6%	HNO <sub>3</sub>	2 M HNO <sub>3</sub> , 500 rpm, 2 h and 60 °C.	Maximum 99% of Ga was leached	Lee and Nam (1998)
Ga-As waste scraps	-	HNO <sub>3</sub>	4 M HNO <sub>3</sub> , 0.3:100 solid to liquid ratio, 500 rpm, 1 h and room temperature.	Maximum 98% of Ga was leached	Chen, Tsai, Tsai, and Shu (2012)
Ga-As waste scraps	-	H <sub>2</sub> SO <sub>4</sub>	5 M H <sub>2</sub> SO <sub>4</sub> , 0.3:100 solid to liquid ratio, 500 rpm, 1 h and room temperature.	Maximum 30% of Ga was leached	Chen, Tsai, Tsai, and Shu (2012)
Ga-As waste scraps	Ga - 50.8%	HNO <sub>3</sub>	1.5 M HNO <sub>3</sub> , 2.5:100 solid to liquid ratio, 200 rpm, 1.5 h and 40 °C.	Maximum 99% of Ga was leached	Hu, Xie, Hsieh, Liou, and Chen (2015)

lixiviants were proposed. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is the commonly used reducing agent, that can reduce Co(III) to Co(II) which is more susceptible to leaching than Co(III). Inorganic acids (such as sulfuric ( $\text{H}_2\text{SO}_4$ ), nitric ( $\text{HNO}_3$ ) and hydrochloric (HCl) acids) along with  $\text{H}_2\text{O}_2$  were commonly used lixiviants to solubilize Co from spent batteries. HCl was found to be a better leachant than sulfuric and nitric acid (Sakultung, Pruksathorn, & Hunsom, 2007). The higher Co leaching efficiency by HCl could be attributed by the dissociation constants ( $K_a$ ) of the acids. For instance, the dissociation constant of HCl is  $10^6$ , which is higher than that of  $\text{H}_2\text{SO}_4$  ( $10^3$ ) and  $\text{HNO}_3$  (28) (Sakultung, Pruksathorn, & Hunsom, 2007). The leaching of Co from lithium-cobalt oxide (present in the spent batteries) by HCl and  $\text{H}_2\text{SO}_4$  is illustrated by equations 2–5:

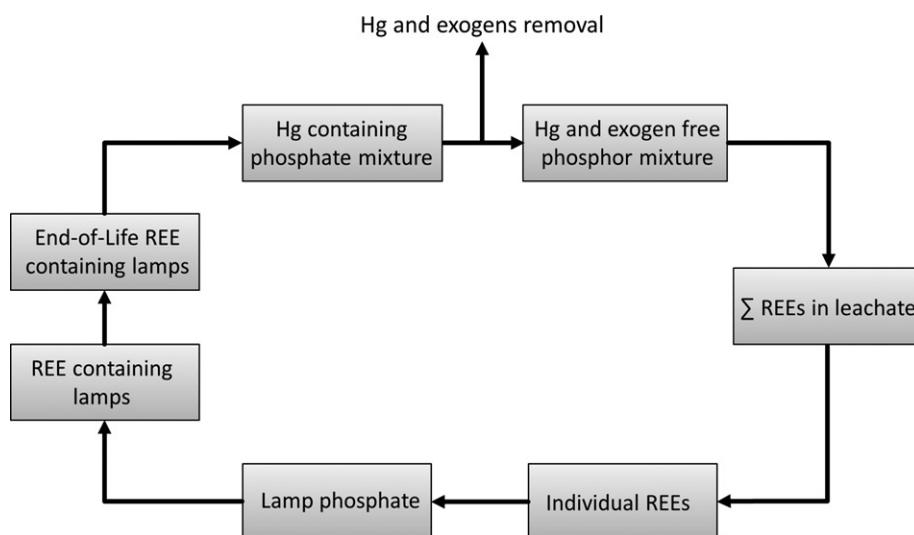


Apart from the type of acid, other factors such as acid concentration, temperature and solid to liquid phase ratio could also affect the leaching of Co from LiBs. Leaching kinetics studies reveal that increase in acid concentration and temperature increase the leaching of Co, while the increase in solid to liquid ratio decrease the leaching efficiency. An increase in acid concentration leads to an increase of protons in the system which in turn leach more Co. However, if the acid concentration exceeds 6 M, then the increase in leaching efficiency is negligible (Sakultung, Pruksathorn, & Hunsom, 2007). The cobalt leaching by HCl ( $+\text{H}_2\text{O}_2$ ),  $\text{H}_2\text{SO}_4$  ( $+\text{H}_2\text{O}_2$ ), and  $\text{HNO}_3$  ( $+\text{H}_2\text{O}_2$ ) follows shrinking core kinetics model while the reaction rate was controlled by surface chemical reaction (Lee & Rhee, 2003; Shuva & Kurny, 2013; Nayl, Elkhatab, Badawy, & El-Khateeb, 2014). The activation energy required to leach Co from spent batteries were estimated to be  $28.33 \text{ kJ}\cdot\text{mol}^{-1}$  (by HCl),  $30.1\text{--}41.4 \text{ kJ}\cdot\text{mol}^{-1}$  (by  $\text{H}_2\text{SO}_4$ ) and  $52.3 \text{ kJ}\cdot\text{mol}^{-1}$  (by  $\text{HNO}_3$ ) (Lee & Rhee, 2003; Shuva & Kurny, 2013; Nayl, Elkhatab, Badawy, & El-Khateeb, 2014). The high activation energy required confirms that the Co leaching (from spent batteries) by inorganic acids is temperature dependent.

Even though the Co leaching by inorganic acids proved efficient, toxic and hazardous  $\text{Cl}_2$ , Sox, and  $\text{NO}_x$  will also be co-generated as by-products. In order to overcome this problem, several other organic lixiviants such as

glycine (Nayaka, Pai, Santhosh, & Manjanna, 2016), malic acid (Li et al., 2010), oxalic acid (Sun & Qiu, 2012), citric acid (Zheng et al., 2016), acetic acid (Golmohammadzadeh, Rashchi, & Vahidi, 2017), succinic acid (Li et al., 2015) and tartaric acid (He, Sun, Mu, Song, & Yu, 2016) were also proposed to leach out Co from spent LiBs. Similar to inorganic acids, the leaching efficiency of Co from LiBs is increasing with increase in organic acids concentration and temperature. The apparent activation energy required to leach cobalt by citric acid was found to be  $45.72 \text{ kJ}\cdot\text{mol}^{-1}$ . The leaching efficiency decreases with increase in solid to liquid ratio as like the case of inorganic leachants (Li et al., 2010; Zheng et al., 2016). Co leaching by organic leachants follow shrinking core model, while the reaction rate is controlled by chemical reaction.

**4.1.1.3. Gallium leaching from spent LEDs and Ga/As scraps.** Lee and Nam (1998) studied the Ga leachability from the Ga-As waste scraps, which contain 47% of Ga and 51% of As. Nitric acid (2 M) was observed to leach out 99% of Ga within 2 hours at a relatively high temperature ( $60^\circ\text{C}$ ). Increase in the solid to liquid ratio (in nitric acid medium) increases the leachability of Ga, which could be influenced by the generation of  $\text{NO}_2$  gas which was due to an exothermic self-catalytic reaction. Similarly, increase in temperature and acid concentration also increases the Ga solubilisation. Chen, Tsai, Tsai, and Shu (2012) investigated the leaching of Ga from Ga-As scraps using sulfuric and nitric acids and reported that leaching efficiency of nitric acid (>95%) was higher than that of sulfuric acid (<30%). In contrast to Lee and Nam (1998), Chen, Tsai, Tsai, and Shu (2012) observed that increase in Ga-As/nitric acid ratio decrease the leaching efficiency of Ga.



**Figure 11.** Recycling routes for SFLs (Binnemans et al., 2013).

**Table 4.** Different hydrometallurgical approaches proposed for the leaching of rare earth elements from WEEE.

WEEE type	Metal content (w/w %)	Leachant	Optimum conditions	Leaching yield	Reference
Fluorescent lamps	Eu - 1.39% Y - 1.29%	Pressure acid leaching with HNO <sub>3</sub> + H <sub>2</sub> SO <sub>4</sub>	4 M acid (HNO <sub>3</sub> + H <sub>2</sub> SO <sub>4</sub> ) mixture, 4 h, 125 °C and 5 MPa	96.4% of Y and 92.8% of Eu	Rabah (2008)
Fluorescent lamps	Y - 7.2%	H <sub>2</sub> SO <sub>4</sub>	4 M H <sub>2</sub> SO <sub>4</sub> , 20% pulp density, 90 °C, 24 h and 200 rpm	85% of Y	De Michelis, Ferella, Varelli, and Vegliò (2011)
Fluorescent lamps	Y - 4.57%	H <sub>2</sub> SO <sub>4</sub>	2 M H <sub>2</sub> SO <sub>4</sub> , 20% pulp density, 70 °C, 24 h and 100 rpm	99% of Y	Innocenzi & Vegliò, 2012
Fluorescent lamps	YOX (Y <sub>2</sub> O <sub>3</sub> :Eu <sup>3+</sup> ) - 20%	Ionic liquids	2 g of [Hbet][Tf <sub>2</sub> N], 5% H <sub>2</sub> O (wt%), 10 mg g <sup>-1</sup> (SFL solid per gram of ionic liquid), 90 °C, 24 h and 600 rpm	99% of YOX	Dupont and Binnemans (2015a)
NdFeB magnets	Nd - 35.10% Dy - 1.10%	HNO <sub>3</sub>	1 M HNO <sub>3</sub> +0.3 M H <sub>2</sub> O <sub>2</sub> , 83.3 g L <sup>-1</sup> pulp density, 20 min at 80 °C.	98 % Nd and 81 % Dy	Rabatho, Tongamp, Takasaki, Haga, and Shibayama (2013)
NdFeB magnets	Nd - 31.27%	H <sub>2</sub> SO <sub>4</sub>	3 M H <sub>2</sub> SO <sub>4</sub> , 1:50 solid to liquid ratio, 27 °C and 15 min.	95% of Nd	Lee et al. (2013)
NdFeB magnets	Nd - 19.10%	H <sub>2</sub> SO <sub>4</sub>	Roasting at 600 °C, 5 h 3 M H <sub>2</sub> SO <sub>4</sub> , 110.8 g L <sup>-1</sup> pulp density, 70 °C and 4 h.	99% of Nd	Yoon et al. (2014)
NdFeB magnets	Nd - 23.00% Dy - 6.26% Pr - 6.52% Gd - 2.25%	Water	1) Mixed with 14.5 M H <sub>2</sub> SO <sub>4</sub> and drying at 110 °C, 24 h 2) Roasting at 750 °C, 1 h 3) H <sub>2</sub> O, 1:50 solid to liquid ratio, 25 °C, 1 h at 225 rpm	98% of REE mixture	Önal, Borra, Guo, Blanpain, and Van Gerven (2015)
NdFeB magnets	Nd - 25.95% Dy - 4.22%	Ionic liquids	Roasting at 950 °C, 3-15 h 1:1 wt/wt [Hbet][Tf <sub>2</sub> N]-H <sub>2</sub> O mixture, 10 mg g <sup>-1</sup> (magnets solid per gram of ionic liquid), 80 °C, 48 h and 600 rpm	99% of REE mixture	Dupont and Binnemans (2015b)
NiMH batteries	REE total (La + Ce) - 5%	H <sub>2</sub> SO <sub>4</sub>	2 M H <sub>2</sub> SO <sub>4</sub> , 80 °C, 3 h	35% La and 35% Ce were leached	Innocenzi & Vegliò (2012)
NiMH batteries	La - 2.7% Nd - 4.5% Sm - 6.2% Pr - 2.29% Ce - 2.58%	Baking followed by H <sub>2</sub> O and H <sub>2</sub> SO <sub>4</sub> leaching	Pre-treatment - Baking with 2 mL H <sub>2</sub> SO <sub>4</sub> at 300 °C Leaching - H <sub>2</sub> O, at 75 °C in 1 h, 500 rpm, 1:50 solid to liquid ratio	80.4% La, 98.8% Ce, 98.2% Nd, 98.5% Pr, 99.2% Sm were leached	Marra, Cesaro, and Belgiojorno (2017)

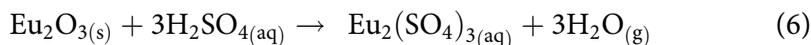
But this could be explained by the usage of low temperature (room temperature) in case of Chen, Tsai, Tsai, and Shu (2012). An apparently low activation energy of  $39.9 \text{ kJ}\cdot\text{mol}^{-1}$  was required to leach 99% of Ga by nitric acid (2 M), also suggest that Ga leaching from Ga-As scraps is a temperature dependent reaction. Hu, Xie, Hsieh, Liou, and Chen (2015) also reported similar findings on the nitric acid leaching of Ga from Ga-As scraps.

#### 4.1.2. Leaching of rare earth elements (REE) from WEEE

##### 4.1.2.1. Yttrium and europium leaching from spent fluorescent lamps.

Phosphors from spent fluorescent lamps (SFLs) is a potential source of REEs, which can be recovered (Porob, Srivastava, Nammalwar, Ramachandran, & Comanzo, 2012). Binnemans et al. (2013) illustrated the recycling routes for REEs from SFLs in Figure 11.

Over the recent years, several researchers have used all common mineral acids to recover REEs from SFLs powders (Table 4) and they could not figure out what is the most effective mineral acid for reaching the maximal leaching yields of the target elements (Virolainen, 2013). There are some reasons for this issue: first selectivity over matrix component and second suitability of the leachate to downstream processing (Virolainen, 2013). Rabah (2008) proposed that more than 90% of Y and Eu could be leached from SFLs by pressure acid ( $\text{HNO}_3 + \text{H}_2\text{SO}_4$ ) leaching. De Michelis, Ferella, Varelli, and Vegliò (2011) reported that temperature plays a significant role in the leaching of from SFLs. Hot acidic leaching (4 M  $\text{H}_2\text{SO}_4$  at  $90^\circ\text{C}$ ) could leach more than 95% of Y could from SFLs (De Michelis, Ferella, Varelli, & Vegliò, 2011). The leaching of Eu and Y from their respective oxide (present in the spent fluorescent lamps) by  $\text{H}_2\text{SO}_4$  is illustrated by the equations 6 and 7:



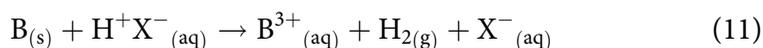
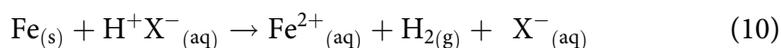
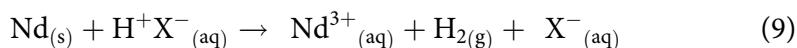
Dupont and Binnemans (2015a) studied and proposed that thermomorphic properties of carboxyl-functionalized ionic liquid: betainium bis(trifluoromethylsulfonyl)imide, [Hbet][Tf<sub>2</sub>N] can be exploited for the leaching and extraction of Y and Eu from waste fluorescent lamp phosphors. Thermomorphic properties of the [Hbet][NTf<sub>2</sub>) (betainium bis(trifluoromethylsulfonyl)imide) (thermomorphism means that the solubility of the IL with water can be thermally changed even becoming immiscible inducing a separation that can be tuned while varying the weight fraction in water) benefit the selective leaching of T and Eu from the waste lamp phosphors. The ionic liquid used in this study has protonated carboxyl-

functionalized and it showed the ability to selectively dissolve REE oxides ( $\text{Y}_2\text{O}_3$  and  $\text{Eu}_2\text{O}_3$ ) as shown in [equation 8](#) (Dupont & Binnemans, 2015b),



High water content in ionic liquid (5 wt %) and high temperature (90 °C) was found to positively influence the leaching of REE by ionic liquids. This is because, high water content and temperature decreases viscosity and improves the diffusion of the lixiviant and consequently increases the leaching efficiency.

*4.1.2.2. REE leaching from spent magnet scraps.* Various hydrometallurgical solubilization of REE (especially neodymium and dysprosium) from magnets were reported (Lee et al., 2013; Rabatho, Tongamp, Takasaki, Haga, & Shibayama, 2013; Yoon et al., 2014; Önal, Borra, Guo, Blanpain, & Van Gerven, 2015) (Table 4). Lee et al. (2013) studied the leaching of Nd from magnetic scrap using various lixivants (such as HCl,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and NaOH). NdFeB compounds in the magnets dissolve as shown in the [equations 9–11](#), in the acidic medium. Neodymium readily dissolves in the acidic pH and forms hydrogen gas. Similarly, iron and boron also dissolve in presence of acids and generate hydrogen gas.



Various factors (leachant concentration, solid to liquid ratio, temperature and leaching time) affecting the leaching of REE from magnet wastes were also investigated. The leaching efficiency of NaOH was lower when compared to that of the mineral acids. Temperature affects the leaching of REE significantly. Increase in temperature leads to the decrease in the REE leaching efficiency. Linear relationship between temperature and leaching efficiency suggests that the REE leaching rate by acids is controlled by shrinking core kinetics (Yoon et al., 2014). Similarly, increase in solid to liquid ratio decrease the leaching yield. This is because the increase in pulp density leads to lower availability of reagent per unit weight of WEEE than that of lower pulp density. On the other hand, increase in the acid concentration increases the solubilisation of REE from magnet scraps. Increasing acid concentration leads to increase in protons that attack and dissolve more REE than in the case lower acid concentration (Lee et al., 2013; Rabatho, Tongamp, Takasaki, Haga, & Shibayama, 2013; Yoon et al., 2014). Acid concentration (3 N), 2% (w/v) pulp density, temperature (27 °C) and

15 min of leaching time were found to be the optimum conditions to leach out more than 95% of Nd from the waste NdFeB magnet.

Rabatho, Tongamp, Takasaki, Haga, and Shibayama (2013) studied the effects of  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{HNO}_3$  and HCl acid solutions on the leaching Nd and Dy from waste magnetic sludge. The leaching efficiency of Nd and Dy by using  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  was lesser (less than 5% Nd and 40% Dy) when compared to that of HCl and  $\text{HNO}_3$  (more than 80% of Nd and Dy). Rabatho, Tongamp, Takasaki, Haga, and Shibayama (2013) also revealed that addition of oxidizing agent ( $\text{H}_2\text{O}_2$ ) could enhance the leaching efficiency of REE from the magnetic sludge. Both HCl and  $\text{HNO}_3$  (in presence of  $\text{H}_2\text{O}_2$ ) could leach out more than 95% of REE, however  $\text{HNO}_3$  seems to be a better leachant because of its poor leaching capacity on Fe. Higher Fe leaching and Fe concentration in the leachate impede the further selective recovery of REE from the leachates.

Yoon et al. (2014) investigated the kinetics of sulfuric acid mediated Nd leaching from waste NdFeB magnets. The waste magnets were first roasted for 5 h at 600 °C prior leaching with sulfuric acid. The results obtained in this study is comparable with data reported by Lee et al. (2013), except for the effect of temperature. Yoon et al. (2014) states that increase in temperature in turn increases the Nd leaching efficiency from waste magnets in contrast to the results of Lee et al. (2013). However, Yoon et al. (2014) claims that the effect of temperature could be influenced by the inclusion of ash layer formation due to the roasting. The leaching kinetics of Nd from the magnets follow shrinking core model, while the reaction rate is controlled by ash layer diffusion. The activation energy required to leach Nd from the magnets was found to be  $2.26 \text{ kJ}\cdot\text{mol}^{-1}$  (for 2.5 M  $\text{H}_2\text{SO}_4$ ) and  $2.77 \text{ kJ}\cdot\text{mol}^{-1}$  (for 3.5 M  $\text{H}_2\text{SO}_4$ ).

Önal, Borra, Guo, Blanpain, and Van Gerven (2015) proposed a combination of roasting followed by water leaching for the solubilization of REE from scrap magnets. Firstly, crushed magnet waste was treated with sulfuric acid and roasted to convert all the impurities to their oxides while the REE remain as sulfates. Later, the roasted sludge was water leached to solubilize more than 98% of REE (Nd, Dy, Pr and Gd).

Dupont and Binnemans (2015b) proposed a functionalized ionic liquid betainium bis(trifluoromethylsulfonyl)imide, [Hbet][Tf<sub>2</sub>N] for the effective leaching and separation of Nd and Dy from the waste FeNdB magnets.

*4.1.2.3. REE leaching from spent Ni-MH batteries.* Various hydrometallurgical processes were proposed for the leaching of REE from Ni-MH battery wastes (Pietrelli, Bellomo, Fontana, & Montereali, 2005; Innocenzi & Vegliò, 2012; Meshram, Somani, Pandey, Mankhand, & Deveci, 2017)

(Table 4). Individual or combination of mineral acids (HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>) were widely used for the extraction of REEs from Ni-MH batteries (Pietrelli, Bellomo, Fontana, & Montereali, 2005; Larsson, Ekberg, & Ødegaard-Jensen, 2013; Petranikova, Herdzik-Koniecko, Steenari, & Ekberg, 2017). In some cases, oxidants (like H<sub>2</sub>O<sub>2</sub>) were also added along with mineral acids to improve the REE leaching efficiency. Larsson, Ekberg, and Ødegaard-Jensen (2013) proposed that the anodic parts of the batteries could be completely dissolved with 1 M hydrochloric, sulfuric and nitric acids (at pH 1.0 and temperature 30 °C) within 6 hours. 2 M H<sub>2</sub>SO<sub>4</sub> was found to be efficient to dissolve the black mass within 2 hours of leaching, however it is not sufficiently effective reagent for metallic nickel (Pietrelli, Bellomo, Fontana, & Montereali, 2005). Petranikova, Herdzik-Koniecko, Steenari, and Ekberg (2017) reported that 8 M HCl was optimum for the leaching of REE from cathode and anode mixture.

Innocenzi and Vegliò (2012) proposed a two-step leaching process for the efficient leaching of lanthanum and cerium from Ni-MH scraps. In the first step, the electrode material was leached with 3 M H<sub>2</sub>SO<sub>4</sub> at high temperature (80–85 °C) for 3 hours. In the second step, the leaching was conducted with 1 M H<sub>2</sub>SO<sub>4</sub> at room temperature (20 °C) for 1 hour. The objective of the second stage was to increase the yield of REEs leaching. Prior leaching with H<sub>2</sub>SO<sub>4</sub>, washing with water was suggested to remove the electrolyte residues (KOH) present (Innocenzi & Vegliò, 2012). Becker et al. (2016) reported another two-step leaching process for the leaching Co and REEs from NiMH batteries. First step was to wash with hot water (95 °C, 1 h) followed by roasting at high temperature for 4 hours. Second step was leaching the roasted calcine with H<sub>2</sub>SO<sub>4</sub> solution at high temperature (90 °C) for 6 hours which resulted in more than 98% leaching of Co and REEs.

Meshram, Somani, Pandey, Mankhand, and Deveci (2017) proposed a different two-step leaching process for the leaching of REEs (La, Ce, Nd, Pr and Sm) from spent Ni-MH batteries. Baking with 2 mL H<sub>2</sub>SO<sub>4</sub> at 300 °C, for 90 min was as a pre-treatment in-order-to transform nickel, zinc and REEs into sulfate form. After baking, the first step leaching was carried out using water (at 75 °C) leached out 91% of Ni, 94% of Zn and 91% of REEs. In the first step, low concentration (20–30%) of Co, Fe and Mn were also leached out. The second step (reductive leaching) was carried out using NaHSO<sub>3</sub> in H<sub>2</sub>SO<sub>4</sub> (at 95 °C) to leach out the residual Co and Mn.

#### **4.1.3. Leaching of precious metals from waste printed circuit boards**

Numerous hydrometallurgical processes have been described in the literature for recovering PMs from waste PCBs (Table 5). Because PCBs contain a high content of Cu, which can increase the consumption of reagents and

**Table 5.** Different hydrometallurgical approaches proposed for the leaching of precious metals from WEEE.

Metal content in PCBs	Leachant	Conditions	Leached metal (%)	Reference
Au - 0.02% Ag - 0.07%	H <sub>2</sub> SO <sub>4</sub>	2 M H <sub>2</sub> SO <sub>4</sub> , 5% H <sub>2</sub> O <sub>2</sub> , 25 °C, 10% (w/v) pulp density, 200 rpm	Ag (60.76%); Au (0%)	Birloaga, Coman, Kopacek, and Veglio (2014)
Au - 0.01% Ag - 0.07% Pd - 0.01%	H <sub>2</sub> SO <sub>4</sub>	0.81 M H <sub>2</sub> SO <sub>4</sub> , 0.41 M Fe(III), 2 h, 80 °C and 1% (w/v) pulp density	Ag (21.4%); Au (0%); Pd (69.4%)	Yazici and Deveci (2014)
Au - 0.03% Ag - 0.09% Pd - 0.01%	HNO <sub>3</sub>	4 M HNO <sub>3</sub> , 72 min, 65 °C, 20% (w/v) pulp density	Ag (87%)	Joda and Rashchi (2012)
Au - 0.05% Ag - 0.04%	HNO <sub>3</sub>	2 M HNO <sub>3</sub> , 3.5 h, 50 °C, 10% (w/v) pulp density, 150 rpm	Ag (97%); Au (0%)	Neto, Sousa, Brito, Futuro, and Soares (2016)
Ag - 0.02% Pd - 0.03%	NaCl- CuSO <sub>4</sub>	$V_{NaCl}/m_{CuSO_4} = 6$ , 0.5 h, 60 °C	Ag (93.9%); Pd (95.3%)	Zhang and Zhang (2013)
Au - 0.01% Ag - 0.08% Pd - 0.003%	Thiosulfate	0.5 M (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>3</sub> + 0.2 M CuSO <sub>4</sub> ·5H <sub>2</sub> O + 1 M NH <sub>3</sub> , 48 h, 40 °C	Ag (93%); Au (98%); Pd (90%)	Ficerova, Balaz, and Gock (2011)
Au - 0.1%	Thiosulfate	0.1 M Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> + 0.2 M NH <sub>3</sub> OH + 0.015-0.03 M Cu <sup>2+</sup>	Au (15%)	Petter, Veit, and Bernardes (2014)
Au - 0.005% Ag - 0.008% Pd - 0.002%	Thiosulfate	0.2 M (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>3</sub> + 0.02 M CuSO <sub>4</sub> + 0.4 M NH <sub>4</sub> OH, 48 h, 40 °C	Ag (100%); Au (95%)	Oh, Lee, Yang, Ha, and Kim (2003)
Au - 0.02%	Thiosulfate	0.13 M (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>3</sub> + 20 mM Cu <sup>2+</sup> , 2 h, 20 °C	Au (70%)	Camelino, Rao, Padilla, and Lucci (2015)
Au - 0.004% Ag - 0.05%	Thiourea	24 g L <sup>-1</sup> Thiourea + 0.6% Fe(III), 2 h, 25 °C	Ag (50%); Au (90%)	Jing-Ying, Xiu-Li, and Wen-Quan (2012)
Au - 0.01% Ag - 0.07% Pd - 0.003%	Thiourea	20 g L <sup>-1</sup> Thiourea + 6 g L <sup>-1</sup> Fe(III) + 10 g L <sup>-1</sup> H <sub>2</sub> SO <sub>4</sub> , 10% (w/v), 3 h, 25 °C, 200 rpm	Ag (71%); Au (84%)	Behnamfard, Salarirad, and Veglio (2013)
Au - 0.01% Ag - 0.07%	Thiourea	20 g L <sup>-1</sup> Thiourea + 6 g L <sup>-1</sup> Fe(III) + 0.1 M H <sub>2</sub> SO <sub>4</sub> , 1 h, 25 °C, 200 rpm	Ag (75%); Au (90%)	Birloaga & Veglio (2016)
Au - 0.06% Ag - 0.52% Pd - 0.04%	Chloride	2 M HCl + 20.5 kg t <sup>-1</sup> H <sub>2</sub> O <sub>2</sub> , 33% (w/v), 3 h, 75 °C	Ag (3.9%); Au (12.9%); Pd (93.1%)	Quinet, Proost, and Van Lierde (2005)
Au - 0.01% Ag - 0.07% Pd - 0.003%	Chloride	5 M HCl + 1% H <sub>2</sub> O <sub>2</sub> + 10% NaClO, 10% (w/v) pulp density, 3 h, 55 °C, 300 rpm	Ag (16%); Au (6%); Pd (98%)	Behnamfard, Salarirad, and Veglio (2013)
Au - 0.01% Ag - 0.07% Pd - 0.01%	Chloride	4 g L <sup>-1</sup> Cu <sup>2+</sup> + 46.6 g L <sup>-1</sup> Cl <sup>-</sup> , 80 °C	Ag (92%); Pd (58%)	Yazici and Deveci (2013)

(continued)

**Table 5.** Continued.

Metal content in PCBs	Leachant	Conditions	Leached metal (%)	Reference
Au - 0.28%	Chloride	5 M HCl + H <sub>2</sub> O <sub>2</sub> 5 M, 4h	Au (30%)	Imre-Lucaci, Nagy, Imre-Lucaci, and Fogarasi (2017)
Au - 0.07%	Chloride	17 g L <sup>-1</sup> NaClO <sub>3</sub> , 80 min, 50 °C, Eh = 1.1 V	Au (93%)	Lu, Song, and Xu (2017)
Au - 1.18% Ag - 4.68% Pd - 0.46%	Chloride	1/20 g·mL <sup>-1</sup> aqua regia, 3 h	Ag (98%); Au (97%); Pd (93%)	Park and Fray, (2009)
Au - 0.01%	Iodide	2.7 mM KI + 0.51 mM I <sub>2</sub> in 10 mL iodine/iodide mole ratio of 1:5,	Au (>99%)	Serpe et al. (2015)
Au - 0.03% Ag - 0.54% Pd - 0.02%	Iodide	120 min, 10% (w/v) pulp density, pH 9	Ag (98%); Au (98%); Pd (96%)	Xiu, Qi, and Zhang (2015)

decrease PMs recoveries (Montero, Guevara, & dela Torre, 2012; Camelino, Rao, Padilla, & Lucci, 2015), leaching of PMs is usually carried out after a previous mild oxidative acid leaching of Cu and other base metals. This strategy improves the selectivity of the PMs and minimizes the impurities (Sheng & Etsell, 2007).

An important point to be considered in the leaching of PMs is related with the selection of the lixivants and fraction size of PCBs. Various lixivants are proposed for the dissolution of precious metals from WEEE. Different lixivants (such as cyanides, mineral acids, thiourea, thiosulfate and halides) exhibit different leaching mechanisms and each of them have their own merits and demerits (Syed, 2012; Lee & Srivastava, 2016). It is evident that fractions with a smaller particle size results in a better dissolution of PMs. This is due to the high surface area of the smallest particles and, thus, a higher proportion of metals exposed to the lixiviant (Sheng & Etsell, 2007; Birloaga, De Michelis, Ferella, Buzatu, & Veglio, 2013; Gurung et al., 2013).

#### *4.1.3.1. Silver, gold and palladium leaching from PCBs by mineral acids.*

Despite most common leaching agents are not selective for a specific PM, there are some alternative leaching systems, mostly inorganic acids, that can leach Ag selectively (relatively to other PMs) from PCBs residues (Table 5). This selective leaching can be carried out taking into account the redox potentials of the aqueous phase. At lower redox potentials, Au and other PMs are not solubilized while Ag is, and it can form stable complexes with halides (Lister, Wang, & Anderko, 2014). By this way, it is possible to perform a preliminary leaching of Ag together with other base metals presents in the PCBs.

Nitric ( $\text{HNO}_3$ ) and sulfuric ( $\text{H}_2\text{SO}_4$ ) acids as well as cuprous chloride or ammonium sulfate systems, at suitable oxidant conditions, are potential leaching agents described in the literature to perform a selective Ag leaching (Table 5). If  $\text{H}_2\text{SO}_4$  is used as the lixiviant, an additional oxidant is necessary to increase the redox potential of the medium. Several oxidants were suggested in the literature like hydrogen peroxide (Birloaga, Coman, Kopacek, & Veglio, 2014; Quinet, Proost, & Van Lierde, 2005), metallic cations ( $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$ ), oxygen (Quinet, Proost, & Van Lierde, 2005; Yazici & Deveci, 2014) and aqueous ozone (Vinals, Juan, Roca, Cruells, & Casado, 2005).

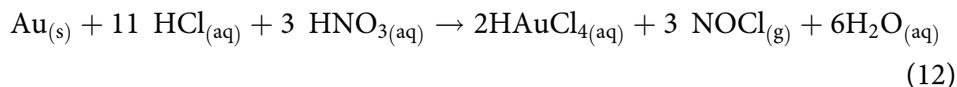
Joda and Rashchi (2012) and Neto, Sousa, Brito, Futuro, and Soares (2016) studied the ability of  $\text{HNO}_3$  to leach Ag. Joda and Rashchi (2012) achieved a leaching efficiency of 82.7% for Ag (along with 94% for Cu) using 4 M  $\text{HNO}_3$  at 65 °C within 72 min. On the other hand, Neto, Sousa, Brito, Futuro, and Soares (2016) reached a leaching of 97% of Ag (and 78% of Cu) along with less than 3% of Au using 2 M  $\text{HNO}_3$  at 50 °C within 210 min.

Serpe et al. (2015) studied the use of  $\text{NH}_3$  in combination with an  $\text{IO}_3^-/\text{I}^-$  mixture, which allows oxidizing Ag and Cu and separating them by selective AgI precipitation. Base metals were previously dissolved using citric acid. Serpe et al. (2015) approach is of particular interest because it allows the selective leaching of Ag and still insures the posterior leaching of Au using an iodine mediated leaching system.

Yazici and Deveci (2013) tested the extraction of Ag and Pd from PCBs with  $\text{H}_2\text{SO}_4\text{-CuSO}_4\text{-NaCl}$  solutions. Over a leaching period of 120 min, at a  $\text{Cl}^-/\text{Cu}^{2+}$  ratio of 21 and  $80^\circ\text{C}$ , the complete extraction of Cu as well as  $>90\%$  Ag together with 58% of Pd was reached. However, the extraction of Au was very limited when a cupric chloride leaching system was used (Yazici & Deveci, 2015). Lister, Wang, and Anderko (2014) reported that the use of  $\text{Fe}^{3+}$  in acidic sulfate allowed recovering more than 95% of Ag and Cu while Au and Pd remained intact in the residue.

Zhang and Zhang (2013) developed a process for cuprous chloride synthesis and simultaneous extraction of Ag and Pd from waste PCBs without using aggressive acids or strong oxidants.

The traditional medium for dissolving Au, as well as the platinum group metals, is aqua-regia, a mixture of three parts of concentrated HCl to one part of concentrated  $\text{HNO}_3$  (Cui & Zhang, 2008). Aqua-regia is known to be the best reagent to dissolve Au and it is used for refining Au with highest quality. However, due to the reaction between  $\text{HNO}_3$  and HCl that results in its decomposition, aqua-regia quickly loses its effectiveness and cannot be reused. Moreover, aqua-regia is highly corrosive, which is a major disadvantage that implies the necessity for the construction of suitable reactor for these extreme conditions and thus limiting its industrial feasibility. Precious metals (e.g. Au) leaching by aqua-regia is shown in Eq. (12).

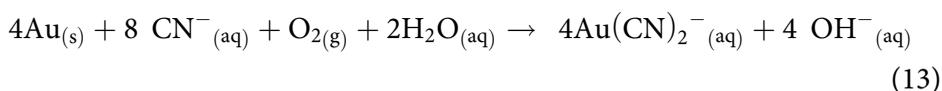


Sheng and Etsell (2007) found a quicker leaching of Au from PCBs using aqua-regia through the implementation of a sequential three-stage leaching process, which combined two first steps with  $\text{HNO}_3$  and the last one using aqua-regia. The third step increases Au and Ag extraction. Park and Fray (2009) also tested the ability of aqua-regia for leaching PMs from PCBs. The authors reported that aqua-regia was very effective because it was possible to leach out Ag, Pd and Au simultaneously. Ag was relatively stable in aqua-regia and remained unreacted. On the other hand, a quantitative recovery of Pd (93%) and Au (97%) was achieved after leaching and subsequent separation processes as a precipitate of  $\text{Pd}(\text{NH}_4)_2\text{Cl}_6$  and as

nanoparticles of gold (after liquid-liquid extraction followed by reduction), respectively.

Other than mineral acids, there are also various other lixivants like cyanides, thio-compounds and halides were proposed for the leaching of PMs, which are discussed below in detail.

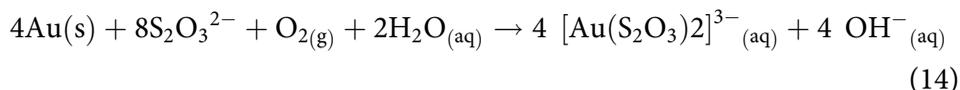
*4.1.3.2. Silver, gold and palladium leaching from PCBs by cyanides.* Cyanide is the most used reagent for Au extraction from ores and secondary sources. More than 90% of Au and Ag extracted from the natural ores are extracted using cyanide lixiviant systems. The mechanism of PMs dissolution in cyanide solution is essentially an electrochemical process. The order of activity for PMs is: Au > Ag > Pd > Pt. A generalized equation of Au leaching by cyanides is illustrated in Eq. (13).



Maximum dissolution of these metals in cyanide solution can be obtained at pH 10–10.5. At this pH, the cyanidation process is safe and economically and environmentally more friendly because most of the free cyanide present in solution is in the form of the cyanide anion, which avoids its volatilization as HCN that is highly toxic. Aqueous solutions of cyanide degrade rapidly in sunlight, but, the less-toxic products, such as cyanates and thiocyanates, may persist for some years (Yarar, 2002). However, a series of environmental accidents at various Au mines that caused severe contamination of rivers and groundwater occurred in the last years. These facts hinder the implementation of future applications of cyanide.

In last three decades, numerous potential non-cyanide leaching systems have been studied for extracting PMs (in particular Au) from PCBs (Cui & Zhang, 2008; Syed, 2012, Zhang, Li, Xie, Zeng, & Li, 2012) (Table 5). Among them, thiosulfate, thiourea and halides have been intensively investigated and will be reviewed below in detail.

*4.1.3.3. Silver, gold and palladium leaching from PCBs by thiosulfates.* Thiosulfate can be considered a good candidate for replacement of cyanide for the PMs extraction due to its lower environmental impact and low cost. However, leaching efficiencies from thiosulfate leaching was comparatively lesser than cyanides (Zhang, Chen, & Fang, 2009). Au leaching by thiosulfates is shown in Eq. (14).



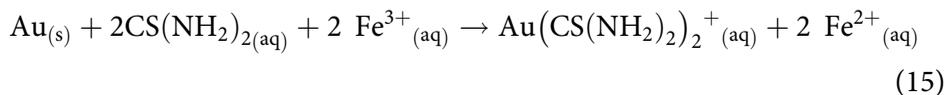
The principal problems with thiosulfate leaching are related with the high consumption of reagent and the slower reaction kinetics than cyanides. However, the leaching rates can be improved in the presence of ammonia and using  $\text{Cu}^{2+}$  as an oxidant (Cui & Zhang, 2008). The dissolution of PMs in thiosulfate solution is an electrochemical reaction catalyzed by the presence of  $\text{Cu}^{2+}$ . This cation acts as an oxidant and at suitable concentrations can significantly improve the leaching rate. However, the presence of ammonia is essential to stabilize  $\text{Cu}^{2+}$ , since  $\text{Cu}^{2+}$  as well as other metals can increase the decomposition of thiosulfate (Arslan & Sayiner, 2008). Moreover, it is important to emphasize that, in the case of direct thiosulfate leaching of PCBs, the Cu dissolved from PCBs may adversely affect the leaching process through decomposition of thiosulfate.

The biggest disadvantage of thiosulfate leaching is the low chemical stability of this compound. The stability of thiosulfate decreases at high temperature and low pH values. Alkaline conditions are necessary to prevent thiosulfate decomposition, which is quickly degraded under acidic conditions. The pH range is dictated by the ammonia/ammonium buffer point ( $\text{pK}_a = 9.25$  at  $25^\circ\text{C}$ ). A pH range of 9–10 is generally preferred at ambient temperature because thiosulfate appears to be less prone to degradation in this region and  $\text{Cu}^{2+}$ -ammonia complex is also stable.

Ficeriova, Balaz, and Gock (2011) reported a successful leaching of Au (98%) and Ag (93%) from waste PCBs using ammonium thiosulfate during 48h after a pre-treatment step to reduce the particle size ( $<0.80$  mm). Petter, Veit, and Bernardes (2014) found that the leaching process using sodium thiosulfate was more efficient when an elevated concentration of  $\text{CuSO}_4$  (between 0.015 and 0.030 M) was added. Oh, Lee, Yang, Ha, and Kim (2003) and more recently Camelino, Rao, Padilla, and Lucci (2015) developed a two-step leaching process for recovering metals from PCBs. In a first step, base metals were leached from PCBs using  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$ . In the second step, a thiosulfate leaching solution was used. Higher Au leaching yields were obtained by Oh, Lee, Yang, Ha, and Kim (2003) when a higher thiosulfate concentration was used (0.2 M) and a longer leaching time (48 hours). Işıldar, van de Vossenbergh, Rene, van Hullebusch, and Lens (2017) demonstrated Au leaching of more than 90% within 6.73 hours using 0.038 M copper sulfate, 0.3 M 0.38 M ammonium hydroxide at 10.76% pulp density (w/v).

**4.1.3.4. Silver, gold and palladium leaching from PCBs by thiourea.** Thiourea is also a potential non-cyanide lixiviant that reacts selectively with PMs to produce stable cationic complexes (Birloaga, De Michelis, Ferella, Buzatu, & Veglio, 2013). Leaching studies using thiourea suggested that the lone pairs of electrons on nitrogen and sulfur atoms of thiourea have a better

potential for a coordination bond between Au and Ag compared to cyanide (Gurung et al., 2013; Akcil et al., 2015). A generalized equation of Au leaching thiourea is depicted in Eq. (15).



Thiourea leaching process has a fast kinetic reaction with Au and Ag as well as a low impact on the environment compared to cyanide. Leaching of PMs with thiourea can result in a leaching efficiency more than 90% in a short leaching time but the reagent consumption is higher when compared to cyanide; as consequence, the process is more expensive (Tanriverdi, Mordogan, & Ipekoglu, 2005). However, when compared with thiosulfate leaching, it involves lower operating costs because it consumes a smaller amount of leaching reagent.

Thiourea should be used under relatively restricted conditions as it is fairly stable in acidic and neutral mediums but it decomposes rapidly in basic solution. The leaching is usually carried out in the pH range between 1.0 and 2.0. Thiourea leaching requires the presence of an external oxidant in order to accelerate the leaching rate. Gurung et al. (2013) revealed that addition of  $\text{Fe}^{3+}$  maximizes Au and Ag leaching.

Lee, Tang, and Popuri (2011) obtained complete extraction of Au and Ag from WEEE with a two steps leaching with thiourea,  $\text{H}_2\text{SO}_4$ , and ferric sulfate at ambient temperature. Jing-Ying, Xiu-Li, and Wen-Quan (2012) observed that the leaching rate of Au was highly affected by the thiourea concentration. The leaching rate of Au increased with the thiourea mass concentration but decreased for values higher than  $24 \text{ g L}^{-1}$ . When the content of thiourea is too high, thiourea is easily oxidized by ferric ion in acidic solution and formamidine disulfide is produced. With a lixiviant containing  $24 \text{ g} \cdot \text{L}^{-1}$  thiourea and  $\text{Fe}^{3+}$  concentration of 0.6% at room temperature, a leaching of 90% of Au and 50% of Ag from PCBs of waste mobile phones was achieved. In many instances, a two-step leaching was proposed, in which Cu was leached completely in the first step and more than 80% of Au and 70% of Ag was leached in the second step with acidic thiourea (Lee, Tang, & Popuri, 2011; Birloaga, De Michelis, Ferella, Buzatu, & Veglio, 2013; Behnamfard, Salarirad, & Veglio, 2013; Birloaga & Veglio, 2016).

High capital costs and easy oxidation of thiourea are major drawbacks for the commercial application of PMs leaching by thiourea.

**4.1.3.5. Silver, gold and palladium leaching from PCBs by chlorides.** Chlorine was extensively used as a leaching reagent for Au extraction from ores and concentrates, even at industrial scale (Cui & Zhang, 2008; Syed, 2012). Chlorination is a practicable alternative for Au leaching due to its high

dissolution rate that is achieved by controlling the redox potential. The use of chloride to leach PMs requires the presence of a strong oxidant, such as  $\text{H}_2\text{O}_2$  or  $\text{NaClO}_3$ . Under these conditions,  $\text{Cl}_2$  is produced, which is extremely toxic and corrosive and should be manipulated only at specific conditions and with resistant equipment. Due to these facts, chloride leaching is more difficult to apply than cyanide leaching because special stainless steel and rubber-lined equipment are required to resist to the highly corrosive acidic and oxidizing conditions. Moreover, the chlorine gas is highly poisonous and must be controlled to avoid any health risk (Syed, 2012).

Quinet, Proost, and Van Lierde (2005) applied chloride leaching (HCl and NaCl) to recover Pd from WEEE using two oxidants:  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$ . Both oxidants ( $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$ ) achieved a similar (93–95%) recoveries of Pd when HCl was used as the lixiviant. Zhou, Zheng, and Tie (2005) patented a process for recovering PMs from WEEE containing plastics. A leaching of 92% of Au and Pd content was obtained using HCl and  $\text{NaClO}_3$ . Behnamfard, Salarirad, and Veglio (2013) obtained an almost total (98%) leaching of Pd using the chlorination (HCl 5 M and NaClO 10% (w/v)) after three previous subsequent extraction steps, already described above. Yazici and Deveci (2013) tested  $\text{Cu}^{2+}$  and  $\text{Cl}^-$  as oxidant and ligand, respectively, to recover Ag from PCBs. The extent of Ag extraction was dependent of the amount of  $\text{Cl}^-$  concentration. At low  $\text{Cl}^-$  concentrations, Ag precipitated as AgCl. The increase of  $\text{Cl}^-$  concentration enhanced the Ag extraction due to the formation of silver chloride complexes, being the highest (92%) extraction of Ag achieved when  $4\text{ g L}^{-1} \text{ Cu}^{2+}$  and  $46.6\text{ g L}^{-1} \text{ Cl}^-$  were used at  $80^\circ\text{C}$ . He and Xu (2015) studied a chlorination process to recycle Au from PCBs. Results showed that the process was efficient and less-pollutant. Moreover, more than 90% of Au could be recovered by controlling the redox potential (above 1100 mV) of the leaching solution.

Xing and Lee (2017) studied the mixtures of HCl and several oxidizing agents, such as  $\text{H}_2\text{O}_2$ , NaClO and  $\text{HNO}_3$ , to dissolve Au and Ag from anode slime resultant from the treatment of copper sludge. The authors reported a complete dissolution of Au from the anode slime after addition of the oxidizing agent to the HCl solution. While a complete dissolution of Cu, Zn, Ni, and Sn was achieved with a mixture of HCl with either  $\text{H}_2\text{O}_2$  or NaClO, a low leaching of Ag (less than 10%) was verified. Imre-Lucaci, Nagy, Imre-Lucaci, and Fogarasi (2017) studied the Au extraction from PCBs using a  $\text{H}_2\text{O}_2$ -HCl leaching system followed by electrowinning. A high efficient Au dissolution took place when a mixture of 1 M  $\text{H}_2\text{O}_2$  and 5 M HCl was used. Lu, Song, and Xu (2017) described a two-stage chlorination leaching process for extracting selectively Cu and Au from waste memory modules from PCBs by controlling the redox potential of the solution using  $\text{NaClO}_3$ . Under optimal experimental conditions, an almost total

extraction of Cu (96.5%) and Au (93%) was obtained at redox potentials of 0.4 and 1.1V, respectively.

**4.1.3.6. Silver, gold and palladium leaching from PCBs by iodides.** Besides being less reactive than chloride, iodide allows achieving a faster dissolution of PMs. The use of iodine-iodide system to leach Au and other PMs is extremely advantageous because iodide leaching is considered to be non-toxic, noncorrosive and very selective to Au (Konyratbekova, Baikonurova, & Akcil, 2015). Moreover, both iodine and iodide can be recovered and reused. Under general conditions, iodine dissolves in the presence of iodide to form triiodide ion, which acts as oxidant for elemental Au originating the Au-iodide complex (Konyratbekova, Baikonurova, & Akcil, 2015). The Au-iodide complex is the most stable compound formed by Au and a halogen (Zhang, Chen, & Fang, 2009). However, high rate of reagent consumption during the leaching and high reagent cost limits its industrial application (Syed, 2012; Ghosh, Ghosh, Parhi, Mukherjee, & Mishra, 2015).

Addition of oxidants to iodine leaching systems enhances the Au extraction and decreases the iodine consumption resulting in a more economical and cheaper process (Xu, Chen, Chen, & Huang, 2009; Xu, Chen, Chen, & Huang, 2010). Xu, Chen, Chen, and Huang (2009 and 2010) studied the utilization of  $H_2O_2$ , as oxidant, in iodine leaching of Au from fine particle size fractions of PCBs. It was observed that 0.2% iodine resulted in low Au leaching rate but increasing the iodine concentration to 1–2% with 1% of  $H_2O_2$ , 95% of Au was leached. Sahin et al. (2015) investigated a two-step leaching of Au from waste PCBs. Firstly, Cu and other base metals were removed (2 M  $H_2SO_4$ , 0.2 M  $H_2O_2$  for 120 min, at 80 °C). In a second step, 93% of Au was obtained when iodine leaching tests were performed in the presence (2% of  $H_2O_2$ ) of oxidant.

Serpe et al. (2015) described an iodine-iodide leaching process where the vast majority (>99%) of Au was dissolved from the waste PCBs under optimized leaching. Xiu, Qi, and Zhang (2015) studied the possibility of using iodine (oxidant)-iodide (complexing agents) system for leaching Au, Ag and Pd from a pre-treated (with supercritical water + hydrochloric acid) waste PCBs. Previously, the organic matter of the PCBs was removed using super critical water oxidation and the base metals were leached using HCl 1 M. The iodine/iodide ratio was crucial for leaching Au, Ag, and Pd with high yield; a maximum leaching of Au and Pd was obtained when the iodine/iodide molar ratio was 1:5 (1:6 for Ag).

## **4.2. Recovery of critical elements from leachates**

Researchers recently focused on the recovery of critical elements from secondary sources because of increasing demand for high-purity critical

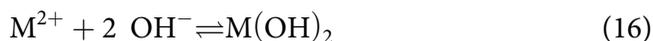
elements. Since it has been observed that the WEEE leachates contain substantial quantities of multi metals with potentially high economic values, it is important to develop proper selective recovery strategies. Leachates from WEEE, and other domestic and industrial metallic waste materials, often contain a large number of different soluble metals, and a major challenge is how to recover these metals as separate entities, for example using selective technologies (Johnson & Du Plessis, 2015). There are a lot of methods for the recovery of metal ions from aqueous solution, such as precipitation, liquid-liquid extraction, electrowinning, cementation and adsorption (Fujiwara, Ramesh, Maki, Hasegawa, & Ueda, 2007; Zhu, Zheng, & Wang, 2015; Anastopoulos, Bhatnagar, & Lima, 2016, Kucuker, 2018).

#### **4.2.1. Critical and precious metals and REE recovery by chemical precipitation**

Precipitation is a well-established metal recovery techniques to recover metals from multi metallic leachates. Certain chemicals like sulfides, hydroxides and carbonates when added to a polymetallic solution, could change the ionic equilibrium of the system and precipitate the metals as respective salts (e.g. metal-sulfides or metal-carbonate or metal-hydroxide) (Sethurajan, Lens, Horn, Figueiredo & van Hullebusch, 2017). Precipitation is widely used to remove metals from contaminated wastewater or acid mine drainage.

Metal precipitation reaction follows three important phases like (1) nucleation, (2) growth of nucleus, and (3) aggregation and crystallization (Lewis, 2010). pH and concentration of the metals are two important factors that affect the metal precipitation. Sludge generation and high requirements of chemicals to adjust the pH are the major draw backs of the metal precipitation technique.

**4.2.1.1. Hydroxide precipitation.** Strong bases like sodium hydroxide (NaOH), and lime or hydrated lime (Ca(OH)<sub>2</sub>) are the commonly applied chemicals the precipitation of metal hydroxides. Weak bases (e.g. ammonia solution) can also be used to precipitate metal hydroxides, however at higher pH it can form stable complexes because of the dissolution of metal hydroxides (Contestabile, Panero, & Scrosati, 2001). A generalized equation for the metal hydroxide precipitation can be written as follows,



where M is a divalent metal ion.

Metal removal by hydroxide are widely used because of its relatively simple operation and low capital cost (Huisman, Boks, & Stevels, 2003). A major disadvantage of this process is the high solubilities of the metal hydroxide complexes precipitated, when the pH is not optimum. A soluble metal complex

$M(OH)^+$  will be formed with respect to the change in the pH. Contestabile, Panero, and Scrosati (2001) demonstrated a selective recovery of Co from spent batteries as  $Co(OH)_2$  using NaOH. They observed that the pH was increased from initial pH 6.0 to 8.0 during the precipitation reaction. Silveira, Fuchs, Pinheiro, Tanabe, and Bertuol (2015) demonstrated a selective recovery of In (as  $In(OH)_3$ ) using  $NH_4OH$ . They investigated the indium hydroxide precipitation in the pH range 5.0 - 9.0 and found out that more than 90% of In can be precipitated in the pH range 6.0–9.0. However, at pH 7.4, a maximum of 99.8% of In was precipitated (Silveira, Fuchs, Pinheiro, Tanabe, & Bertuol, 2015). Lee et al. (2013) proposed selective recovery of REE (Nd in particular) from NdFeB magnet scrap leachate by altering the system pH. The pH of the leachate was highly acidic ( $-0.13 < pH < 0.02$ ) and it was adjusted using sodium hydroxide. It was found that at pH 0.6, more than 95% of Nd can be selectively recovered as Nd-hydroxide precipitates, from the sulfuric acid leached NdFeB magnet wastes. However it is worth to note that the selective recovery of Nd from HCl leached NdFeB magnet wastes was not successful as  $H_2SO_4$  leachate.

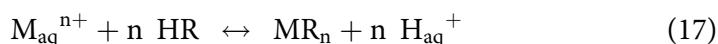
**4.2.1.2. Sulfide precipitation.** Ferrous sulfide (FeS), calcium sulfide (CaS), sodium sulfide ( $Na_2S$ ), sodium hydrosulfide (NaHS), ammonium sulfide ( $(NH_4)_2S$ ), hydrogen sulfide ( $H_2S$ ) are the major chemicals used for the metals sulfides precipitation (MSP). MSP has various advantages over other methods including the metal sulfide precipitates are less soluble, selective metal precipitation can be done, reaction rates are fast, settling properties are far better and sulfide precipitates can be reused (Lewis, 2010). In addition to that, MSP also offers selective metal precipitation and can successfully be applied to extremely low concentration (ppb) of metals (Kim, Kim, Lee, & Pandey, 2011). Operating pH plays an important role in the precipitation of metal sulfide and also various metal sulfides has the tendency of solubility with respect to pH (Lewis, 2010; Sethurajan, Lens, Horn, Figueiredo & van Hullebusch, 2017). Concentration of the sulfide is the key factor in the MSP, if it exceeds or depletes either sulfides or metals will remain in the solution (Veeken, Akoto, Pol, & Weijma, 2003). Also, metal removal by MSP has other various barriers (Lewis & Van Hille, 2006) to overcome such as (1) formation of poly sulfides due to the localization of supplied sulfides, which results in excessive consumption of sulfide and low metal removal and (2) low solubility of metal sulfides and higher supersaturation which resulted in the formation of fine particles with unfavorable solid-liquid separation difficulties. Optimization of sulfide dosage is the limiting parameter for its less known commercial applications, as the metal sulfides have very less solubility which will have an impact in the process sensitivity (Veeken, Akoto, Pol, & Weijma, 2003; Lewis, 2010). Lewis and Van Hille (2006) proposed that the gaseous

hydrogen sulfide source could decrease the level of supersaturation and in turn the formation of fine particles was controlled. Li, Liu, Li, Liu, and Zeng (2011) demonstrated a selective recovery of In from In/Sn leachate. Sn was firstly removed by H<sub>2</sub>S (gas) as tin sulfide (SnS). Ga-sulfide precipitation of WEEE leachate was investigated and reported (Chen, Tsai, Tsai, & Shu, 2012; Hu, Xie, Hsieh, Liou, & Chen, 2015). Chen, Tsai, Tsai, and Shu (2012) observed that 49% of Ga could be precipitated from nitric acid medium, using Na<sub>2</sub>S at initial pH 3.0. However, 49% of precipitation is relatively a low recovery and to overcome this Hu, Xie, Hsieh, Liou, and Chen (2015) proposed drop-wise addition of sulfide to the leachate. Drop wise addition (5 L·min<sup>-1</sup>) of Na<sub>2</sub>S to Ga and As containing leachate, resulted in 98% selective recovery of Ga-precipitates (Hu, Xie, Hsieh, Liou, & Chen, 2015).

**4.2.1.3. Other precipitation techniques.** Carbonates precipitation is also used to precipitate the metals as metal carbonates, in which straight precipitation by chemicals such as calcium carbonate is used or conversion of hydroxides to carbonates is applied for the precipitation of metals (Wang, yung-tse, & Shammas, 2005). Carbonates precipitation can also be applied in combination with hydroxide precipitations. Operation at low pH, faster settling and good metal removal were some of the merits of carbonates precipitation. Sometimes oxalate precipitation was also used to precipitate REE from leachates. De Michelis, Ferella, Varelli, and Vegliò (2011) illustrated oxalate precipitation of Y from spent fl. lamp waste leachate. Rabatho, Tongamp, Takasaki, Haga, and Shibayama (2013) investigated the selective recovery of REE from spent magnetic sludge. Nitric acid mediated magnetic sludge leachate contain 28 g·L<sup>-1</sup> of Nd, 0.7–0.8 g·L<sup>-1</sup> of Dy, 4.0–6.6 g·L<sup>-1</sup> of Fe and 0.4–0.5 g·L<sup>-1</sup> of B. Firstly, Fe was removed as Fe(OH)<sub>3</sub> using sodium hydroxide at pH 2.0–3.0. However 20–25% of REE (Nd and Dy) was co-precipitated or trapped with Fe-precipitate. Finally, oxalic acid was used to precipitate REE as their oxalate salts from the Fe-depleted leachate. More than 70% of Nd could be recovered as Nd<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·10H<sub>2</sub>O (neodymium oxalate hydrate) using 1.1 M oxalic acid. Double sulfate precipitation is another form of metal recovery by chemical precipitation. For instance, REEs were precipitated as Na(REE)(SO<sub>4</sub>)<sub>2</sub> by using concentrated NaOH (5 M) (Nan, Han, Yang, Cui, & Hou, 2006; Li et al., 2010; Innocenzi & Vegliò, 2012; Becker et al., 2016).

#### **4.2.2. Critical and precious metals and REE recovery by solvent extraction**

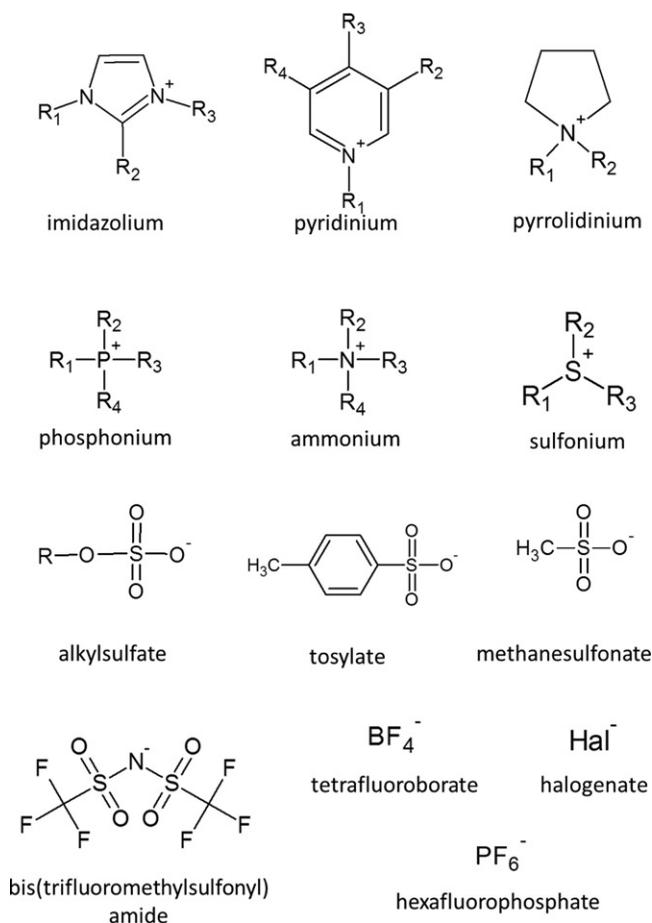
Solvent extraction (SX) or otherwise referred as liquid-liquid distribution which requires two liquid phases which are completely immiscible with each other. Liquid-liquid distribution is an equilibrium process and can be explained by the following equation (Bertuol, Tanabe, Meili, & Veit, 2015),



where HR - organic solvent,  $\text{MR}_n$  - metal-organic species (extracted),  $\text{H}^+$  - proton released by the organic solvent in exchange for the cationic metal species  $\text{M}^{n+}$ . Various factors such as (1) selection of suitable organic extractant (2) selection of proper diluent and (3) pH can affect the solvent extraction efficiency. Also, lixiviant (e.g., Cl) used to leach, could also play an important role in the SX recovery efficiency of CRMs. For instance, In recovery from mild acidic HCl leachate was found to be better than mild acidic  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$  leachate (Křištofová, Rudnik, & Miškufová, 2017). It is known that the extraction efficiency of aliphatic diluents (such as hexane, octane, and Solvent 70), is higher than the polar diluents (such as cyclohexanone, 1-octanol, and chloroform) (Mohammadi, Forsberg, Kloo, De La Cruz, & Rasmuson, 2015). In recent times, solvent extraction is applied to many electronic waste materials like spent LCDs (Yang, Kubota, Baba, Kamiya, & Goto, 2013) and spent NdFeB magnets (Gergoric, Ekberg, Steenari, & Retegan, 2017). Bis(2-ethylhexyl) phosphoric acid D2EHPA (or DEHPA), tributyl phosphate TBP, bis(2,4,4-trimethylpentyl) phosphinic acid Cyanex 272, or a mixture of different phosphine oxides known as Cyanex 923 are some of the common extractants used to recover critical metals (Křištofová, Rudnik, & Miškufová, 2017). Yang, Kubota, Baba, Kamiya, and Goto (2013) investigated the separation of In from the LCD waste by using di-2-ethylhexyl phosphoric acid (D2EHPA). Indium and other metals concentration in sample feed were selected based on 10 gram of LCD waste per 100 mL of lixiviant (HCl or  $\text{H}_2\text{SO}_4$ ) and contains In 2 mM, Sn 0.2 mM, Zn 2.5 mM, Cu 2.5 mM, Fe 3 mM and Al 6 mM. It was observed that, 0.25 M was the optimal D2EHPA concentration that can selectively recover maximum In from acidic leachate (pH < 1.0).

Temperature was also found to influence the extraction of In from the leachate. When the temperature is lower (<20 °C), In extraction efficiency is higher than In extraction obtained at higher temperature (>20 °C) (Yang, Kubota, Baba, Kamiya, & Goto, 2013). This is due the exothermic nature of the D2EHPA mediated In extraction from the leachate. Riaño and Binnemans (2015) demonstrated the separation of Nd and Dy by using ionic liquids in the solvent extraction process. Gergoric, Ekberg, Steenari, and Retegan (2017) studied the recovery of REE by solvent extraction from the waste NdFeB magnets leachate by using D2EHPA. The NdFeB magnets were first sulfated, roasted and leached with water to solubilize the REEs. The leach liquor contain Nd 9.1 mM, Dy 2.7 mM, Pr 3.2 mM, Gd 0.69 mM, Co 0.17 mM and B 0.55 mM. Iron concentration was below detectable. D2EHPA was used as the organic extractant, with a wide range of concentrations (0.3, 0.6, 0.9, and 1.2 M). Different diluents such as Solvent 70, hexane, octane, toluene, 1-octanol, cyclohexanone and chloroform were

used in order to see the effects of diluents. All the REE (Nd, Dy, Gd and Pr) were separated as a group and it was also observed that aliphatic diluents illustrate more extraction efficiency than polar diluents. 0.3 M D2EHPA in hexane was found to be the best operating condition for maximum extraction and separation between heavy REEs (Nd, Dy and Pr) and light REE (Gd) and 100% stripping was achieved with 2 M or higher HCl. Petranikova, Herdzik-Koniecko, Steenari, and Ekberg (2017) reported multi-stage solvent extraction for the recovery of REEs using TBP and Cyanex 923 dissolved in kerosene, from Ni-MH battery scraps. In the first step, an extractant consisting of 8% Cyanex 923, 10% TBP, 82% kerosene was used in order to remove Zn and Fe (with 99.9% efficiency). It was followed by three-stages of washing and four stages of stripping. Finally, Al and REEs were extracted using a mixture of 70% Cyanex 923, 10% TBP, 10% kerosene, 10% 1-Decanol. The final raffinate was characterised by high purity (>99.9% Ni). Co-extracted Co, Mn and Ni were removed from organic phase using 0.9 M  $\text{NaNO}_3$  and 0.1 M  $\text{HNO}_3$  mixture.



**Figure 12.** Some common cations and anions constituents of ionic liquids.

#### **4.2.3. Critical and precious metals and REE recovery by adsorption**

Adsorption is one of the most effective methods among the metal recovery strategies due to its simplicity and wide-range availability (Fujiwara, Ramesh, Maki, Hasegawa, & Ueda, 2007; Anastopoulos, Bhatnagar, & Lima, 2016). Adsorption is an alternative process, if the metal concentration in the leachate is sufficiently low (Cunha et al., 2015; Zazycki, Tanabe, Bertuol, & Dotto, 2017; Kucuker, 2018).

Adsorption studies have mainly been focusing on the removal of heavy metal ions from industrial effluents, being the detoxification of these solutions prior to disposal as the primary goal (Volesky, 2007). On the other hand, adsorption technique has been using for the recovery of precious metal from aqueous solution since 1951 (McQuiston & Chapman, 1951; Syed, 2012). Until now, there has been a growing tendency to introduce new developments to this process for metal recovery from primary and secondary solutions (Syed, 2012). However, limited research has been carried out on the metal recovery from secondary sources using adsorption process. Mechanism and kinetic of adsorption of PMs and REEs from leachate have been investigated by researchers in batch mode using a number of parameters that can potentially influence the efficiency of the adsorption process: namely, pH, temperature, initial metal concentration, time and agitation rate (Syed, 2012; Kucuker, Nadal, & Kuchta, 2016). Syed (2012), Das and Das (2013), Jha et al. (2016) and Anastopoulos, Bhatnagar, and Lima (2016) summarized the published literature (1995–2016) on the use of sorbents for REEs and PMs adsorption. According to the literature survey, recovery of precious metals and rare earth elements from leachates through adsorption is a promising approach. However, further research should also focus on the development of adsorption aspect to generate operational and cost data with the ultimate aim of commercialization.

#### **4.2.4. Critical and precious metals and REE recovery by ionic liquids**

A fascinating development in the hydrometallurgy of metals is the use of ionic liquids (IL) to perform or enhance that extraction. Some of the more common cations and anions used are presented in Figure 12.

Ionic liquids are environmentally friendly solvents with favourable properties such as extremely low vapour pressure, low combustibility, excellent thermal stability, and a wide temperature range in its liquid state. The low volatility and combustibility of ionic liquids (ILs) together with the high extractability presented in many cases make its use in extraction methods a promising approach (Sun, Luo, & Dai, 2013; Park et al., 2014).

In many instances IL were used as mere solvents trying to improve the conditions of which can be called classical extractants. A comprehensive, but not exhaustive, list of these studies follows. They used N,N-

dioctyldiglycol amic acid (DODGAA) as extractant and 1-octyl-3-methylimidazolium bis(trifluoromethyl sulfonyl) imide,  $[C_8mim][NTf_2]$  as solvent (Yang et al., 2012); triphosphine trioxide as extractant and  $[EBPip][NTf_2]$  or  $[EOPip][NTf_2]$  as solvents (Turgis et al., 2016); octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide (CMPO) as an extractant and  $[Bmim][PF_6]$  or  $[Bmim][NTf_2]$  as solvents (Nakashima, Kubota, Maruyama, & Goto, 2005); choline hexafluoroacetylacetonate as extractant and choline bis(trifluoromethylsulfonyl)imide as solvent (Onghena, Jacobs, Van Meervelt, & Binnemans, 2014); di(2-ethylhexyl)phosphoric acid (HDEHP) as an extractant and various imidazolium ILs or one pyrrolidinium as solvents for the separation among lanthanides (Sun, Bell, Luo, & Dai, 2011). The selective recovery of metals by ionic liquids depend on different extraction parameters like the metal loading in the feed phase, percentage of water in the feed solution, equilibration time, and type of hydrated melt (Rout, Kotlarska, Dehaen, & Binnemans, 2013).

Yang, Kubota, Baba, Kamiya, and Goto (2013) studied the use of DODGAA as an extractant and  $[C_4mim][NTf_2]$  as a solvent for the separation of REE from other metals in fluorescent lamps phosphors leachate (Yang, Kubota, Baba, Kamiya, & Goto, 2013). Another hydrometallurgical process using the undiluted ionic liquid trihexyl(tetradecyl)phosphonium chloride for the separation of the transition metals iron, cobalt, copper, manganese and zinc from the rare earths neodymium and samarium was studied (van der Hoogerstraete, Wellens, Verachtert, & Binnemans, 2013). Dialkylphosphate ionic liquids were also proposed to separate Nd from nitric acid leached magnet leachate (Rout, Kotlarska, Dehaen, & Binnemans, 2013). Riaño and Binnemans (2015) investigated the selective recovery of Nd and Dy (from waste magnets) by using a combination of the ionic liquid trihexyl(tetradecyl)phosphonium nitrate and a selective complexing agent ethylenediaminetetraacetic acid (EDTA).

Also the recovery of REEs from metal hydride batteries was addressed in few instances (Larsson & Binnemans, 2014; van der Hoogerstraete & Binnemans, 2014). By using trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101) or tricaprilmethylammonium chloride (Aliquat 336) ionic liquids (Larsson & Binnemans, 2014), it is possible to separate cobalt, manganese, iron and zinc from REE's. By using trihexyl(tetradecyl)phosphonium nitrate, it was demonstrated to achieve good separations between Co/Sm and Ni/La (van der Hoogerstraete & Binnemans, 2014).

A more recent approach is the use of bifunctional ionic liquid extractants. Cations and anions of well-known extractants were modified in order to enhance the ionic liquid properties of those extractants. Yang et al. (2012) proposed that bifunctional ionic liquid Aliquat336 could extract more than 95% of REE from a very acidic solution. Modification of other

industrial extractants like di(2-ethylhexyl)phosphoric acid (HDEHP) and 2-ethyl(hexyl) phosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) could produce a typical acid-base coupling bifunctionalized IL's which provide a good separation between early and late REEs (Sun & Waters, 2014). Bifunctional ionic liquid extractant (bif-ILE) [A336][P507] was also proposed for the extraction of mid-heavy rare earths elements (REEs) (Shen et al., 2016).

#### **4.2.5. Critical and precious metals and REE recovery by electrowinning**

Electrowinning (EW) is also one of the efficient technologies that helps to recover metals from the metal containing solutions or leachates. Selective recovery of the target metal is one of the main advantages of electrowinning. EW has some other merits such as (1) less or no secondary waste generation, (2) no hazardous chemical usage and (3) comparatively lesser investment cost. EW technology was successfully applied to electronic scraps for the selective recovery of base metals such as Cu and Pb (Mecucci & Scott, 2002; Madenoğlu, 2005). However, EW technology application on the selective recovery of critical and precious metals is still in its early stages. Selective separation of precious metals (Au) by EW is challenging especially in presence of Cu (Grosse, Dicoski, Shaw, & Haddad, 2003). However, Chehade et al. (2012) demonstrated on the selective separation of pure Cu, Ag, Au and Pd from the PCBs (containing (wt %) Cu 18.49%, Au 0.04%, Ag 0.16%, Pd 0.01%, Cu  $0.06 \text{ g}\cdot\text{L}^{-1}$ , Cd  $0.04 \text{ g}\cdot\text{L}^{-1}$ ). The PCBs were first digested using aqua-regia and then electrowinning was applied to the leachate. Four sequential EW chambers were used and in each chambers one metal was electro deposited on the cathode. Copper was the first to selectively recover by this technology, followed by gold, palladium and finally silver. A maximum of 0.04 kg of Au, 0.18 kg of Ag, 0.01 kg of Pd and 21.00 kg of Cu was recovered from 125 kg of PCBs (Chehade et al., 2012).

### **5. Techno-economic feasibility of hydrometallurgy of WEEE**

Pyro-metallurgical recycling of WEEE were demonstrated and integrated at commercial level (Ebin & Isik, 2017). Mobile plant for WEEE treatment by a full hydro-metallurgical process exists as well, but it has not been implemented on an industrial scale yet (Zeng, Li, & Singh, 2014; Innocenzi, De Michelis, & Vegliò, 2017). Innovative development of a sustainable hydrometallurgical process requires the application of knowledge and experience gained in a variety of chemical processing steps and economic and environmental evaluation of many parameters. Current recycling technologies adopted by mobile recycling plants do

not permit to reach an economic advantage for all the valuable materials coming from WEEEs, especially if recycling plants are focused on a particular waste stream or product (Innocenzi, De Michelis, & Vegliò, 2017; De Michelis & Kopacek, 2018). Nevertheless as already stated, the main driving force for WEEE recycling is the recovery of metals. Unfortunately this may not be feasible due to economic reasons and technological limitations.

The recyclability of a metal can be determined by the “contribution score” of the individual metal which is related to weight content, environmental hazards associated with the metal, energy consumption, natural resources depletion, etc. The most widely used assessment index is the resource recovery efficiency (RRE) (Legarth et al., 1995) which compares different metals based on their weight content, recycling efficiency and world reserves and is expressed as:

$$\text{RRE} = \sum_i (E_i F_i / P_i) \times (C_i / R_i) \sim \sum_i E_i F_i / R_i \quad (18)$$

Where E is the recovery percentage, F is the amount of resource/ton of scrap, P and C are the annual production and consumption of the primary resource respectively, R is the world reserve of the resource, and i counts the type of the resources in the scrap.

In order to determine the environmental performance, Huisman developed the QWERTY index (Quotes for environmentally Weighted Recyclability) (Huisman, Boks, & Stevels, 2003) for calculating product recyclability defined in equation (14):

$$\text{QWERTY}_i = \sum_i \left[ \frac{(\text{EVW}_{\text{actual},i} - \text{EVW}_{\text{max},i})}{(\text{EVW}_{\text{min}} - \text{EVW}_{\text{max}})} \right] \quad (19)$$

Where,  $\text{EVW}_{\text{actual},i}$  is the actual environmental impact for the weight of material i,  $\text{EVW}_{\text{max},i}$  is the maximum environmental impact for the weight of material i,  $\text{EVW}_{\text{min}}$  and  $\text{EVW}_{\text{max}}$  are the total defined minimum and maximum environmental impact for the complete product, respectively.

Based on the above mentioned two approaches, Le, Yamasue, Okumura, and Ishihara (2013) developed the Model for Evaluating Metal Recycling Efficiency from Complex Scraps (MEMRECS) for prioritizing the selection of target metals. This approach not only includes the weight of each metal fraction but also comprises two critical aspects associated with sustainable issue: natural resources conservation and environmental impact reduction.

According to these models, the recovery priority should be on precious metals such as Au, Ag and Pd along with some base metals such as Cu, Sn, and Ni.

In the light of these considerations, an economic evaluation of hydrometallurgical processing routes and the techno-economical assessment has to be reached through the development of gold amount variation models,

present in waste material, as a crucial economical component of PCBs. Other parameters to be evaluated are the total capital cost and operating cost, involving all economic factors in final executive summary, regarding total plant direct costs, total plant indirect costs, labor, utilities and raw material costs. In this way, using proper algorithms it is possible to assess the operational time, needed to achieve economical sustainability of the hypothetical hydrometallurgical plant.

This set of considerations are fundamental in setting the benchmark for metal recycling strategy, and it is also helpful in technological selection or technological improvement for metal recycling from waste PCBs in particular and scraps containing various metal fractions in general.

The future of the WEEE treatment industry will require manufacturing firms to be highly agile enterprises, capable of exploiting rapid market changes by increasing flexibility in their physical infrastructures and production processes.

In this field, noteworthy is the PCRec project ([www.pcrec-network.eu](http://www.pcrec-network.eu)), funded by the European Institute of Technologies and currently in progress in Europe: it has been built a network of infrastructures conceived as a response to the present necessity to overcome the limited capacity of any single research groups to face small to medium enterprises (SME's) complex innovation needs and to maximize synergetic collaboration between research infrastructures and enterprises. The goal is to strengthen the overall capacity and to respond to the present and upcoming innovation needs and improve the exploitation of European secondary resources from Hi-tech EoL products. Also, in the European FP7 framework HydroWEEE-demo project, a mobile plant was designed and demonstrated for the recovery of metals from WEEE (Innocenzi, De Michelis, & Vegliò, 2017). The results showed the process could be commercially feasible for PCBs. And for REEs, net gain could be positive only when the market price of RE concentrate increase from 14 €/kg (price in 2017) to 20 €/kg or more and also the plant works at its highest capacity (Innocenzi, De Michelis, & Vegliò, 2017).

## 6. Conclusions and research needs

Huge loads of electronic wastes are generated and discarded in the environment. There are different types of WEEE (spent PCBs, spent LCDs, spent LEDs, spent batteries, spent magnets and spent fluorescent lamps) that contain different REE, critical and precious metals in significant concentrations. Apart from metal values, WEEE also contain toxic elements and harmful pollutants. Leaching and selective recovery of the heavy metals is the best solution to meet the growing critical raw materials demands and

also to reduce the environmental impacts caused by the WEEEs in the environment. There are a number of leaching processes suggested by various researchers for distinctly different WEEE and also different metal recovery techniques that have been demonstrated to be successful for the recovery of REE, critical and precious metals from the WEEE leachates.

Elemental composition of the WEEE and the metals targeted plays an important role in the selection of appropriate hydrometallurgical processes. Good understanding on the bulk chemical composition of the WEEE, knowledge on the leaching strategies and the understanding of the metal recovery process will help to use the end of life WEEEs as alternative for critical raw materials. WEEE is not only heterogeneous in nature, but also significantly changed in the elemental composition (due to update and cost cutting in manufacturing techniques). Pre-treatment is the foremost step to recycle the WEEE and care must be taken not to lose much of the valuable CRMs and to remove as much as possible hazardous and non-economic parts of WEEE. For instance, Hg removal in case of waste LCDs and plastic and filter dusts removal in case of waste PCBs. This impedes the recovery of metals by conventional metallurgical operations and compel for an updating of the existing technologies.

The most common leaching agents for dissolution of critical metals REE from WEEE including mineral acids and organic acids and cyanide, aqua-regia, thiosulfate and thiourea were proposed for precious metals. Sulfuric acid was found to be the best leachant for REE and critical metals. Selection of lixiviant also plays a role in the recovery efficiency of REE from the leachates. For instance, solvent extraction of critical metals from HCl system is better than  $\text{H}_2\text{SO}_4/\text{HNO}_3$  systems, while selective precipitation of REE is better in  $\text{H}_2\text{SO}_4$  than in HCl system. Optimization of leaching parameters such as lixiviant concentration, temperature, pulp density, agitation and particle size are very important to achieve maximum leaching efficiency. In some cases, (1) mixture of lixiviants, (2) addition of oxidising/reducing agents and (3) multi-step leaching could increase the leaching efficiency.

In the case of precious metals, aqua regia allows the highest gold dissolution rate among different leaching agents, but it is applied usually at laboratory scale because of the strong oxidation and high-corrosion power which limits its industrial applications. Furthermore, management of the highly acidic wastewaters is very difficult. Over the last century, cyanide leaching has been widely used to recover gold from gold minerals and secondary sources its high efficiency and relatively low cost. The main drawback of this method is the production of a huge amount of cyanide contaminated wastewaters, which can lead to a serious damage to people and the environment: for this reason, this method is being gradually replaced by other methods.

Another important issue to address is the upscaling of the new leaching systems at industrial scale. For instance, stability of the leaching system and PM-complexes are determinant for its implementation at large scale. The presence of Fe(III) and Cu(II) catalysts during PM leaching using thiourea and thiosulfate, respectively, provokes a rapid oxidation of the ligands and, thus, an increase of the reagent consumption. Therefore, despite the intense research, which occurred in the last three decades on the study of non-cyanide lixivants (including mainly thiourea, thiosulfate and halides) for extracting Au and other PMs, unless halides, all other alternatives are clearly more complex to operate at industrial scale than cyanide. Thus, further development is needed before they can be considered as real alternatives when thinking in a future commercial implementation.

In the last step, various methodologies are available for the recovery of the metals from the leachate such as precipitation, adsorption, solvent extraction, electrowinning and ionic liquids. Selective recovery is one of the important aspects to consider and techniques such as precipitation, ionic liquids can offer such advantage. While precipitation could generate secondary sludge production, adsorption and electro-winning can be used to overcome this issue. Single stage operation still has some limitations and might not solve all problems because WEEE is a complex matrix. Some combined and integrated recovery technologies have begun to be put forward.

In conclusion, the reason for preferring hydrometallurgy over pyrometallurgy is because of reduced gas emission compared to pyro process which releases toxic gases (dioxins/furans) and volatile metals, dust, Cl<sub>2</sub>, Br<sub>2</sub>, SO<sub>2</sub> and CO<sub>2</sub> together with Pb, Hg, Cr<sup>6+</sup>, Cd and flame retardants. Moreover lower dust emissions are generated and energy consumption is reduced. Other advantages are the high recovery rate, no slag generation and easy working condition. In hydrometallurgical processes, a large amount of liquid wastes and sludge are produced and must be disposed carefully. Another drawback is represented by the slow leaching kinetics.

Earliest cost benefit analysis show encouraging results on the prices and the net gain (for instance, REE from spent fluorescent lamps), however rigorous techno-economic feasibility studies and demonstration are needed prior the commercial implementation.

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