Environmental Technology & Innovation 27 (2022) 102481

Contents lists available at ScienceDirect

Environmental Technology & Innovation

journal homepage: www.elsevier.com/locate/eti

Characterization of industrially pre-treated waste printed circuit boards for the potential recovery of rare earth elements

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ARTICLE INFO

Article history:
Received 28 September 2021
Received in revised form 10 February 2022
Accepted 12 March 2022
Available online 23 March 2022

Keywords:
Critical raw material
Metal recovery
Printed circuit boards
Rare earth elements
Recycling
WEEE

ABSTRACT

Rare earth elements (REE) are classified as critical raw materials and the environmental impact of mining them is of growing concern. The recovery of REE from electronic waste (e-waste) could offer a more sustainable practice. Waste printed circuit boards (WPCBs) are an important resource in the e-waste stream due to their content of valuable materials. However, data regarding the concentration and distribution of REE in WPCBs is very limited. The aims of this research were: (a) to analyse the chemical composition of comminuted WPCBs prior to processing (industrially pre-treated) with emphasis on REE, and (b) to determine the distribution of REE and other metals in different size fractions of the pre-treated WPCBs. The samples were supplied by commercial e-waste recycling companies, which makes them representative of the e-waste processing industry in the UK. Correlation between elemental concentrations and particle size was analysed using Spearman's rank correlation. Most REE concentrations were inversely correlated to the particle size. Concentrations of Y, La and Gd were found up to a thousand times higher in the smaller particle size compared with coarser particles. However, most of base metals including Cu, Sn, Pb and Zn did not show this trend. The present study highlights the occurrence of REE in comminuted WPCBs, and fine fractions as potential sources of these critical elements, currently not recovered during recycling process. A cost-effective sieving step is proposed to enrich the REE content for further recovery, prevent the possible loss of REE and maximize the total material recovered from WPCBs.

1. Introduction

Waste printed circuit boards (WPCBs) constitute approximately 4% to 7% of the total mass of waste electrical and electronic equipment (WEEE). However, the value is higher in some equipment such as televisions (10%), computers (20%) and mobile phones (30%) (Wang et al., 2017). WPCBs contain more than 40 different elements, almost 30% metals, around 20% plastics and the remaining as glass fibre and ceramics (Zhou and Qiu, 2010). Hazardous materials found in WPCBs such as brominated flame-retardants and heavy metals represent a threat to the environment and human health when sent to conventional landfill or incineration treatments. Nonetheless, the presence of valuable and critical metals in WPCBs such as copper, gold, silver, palladium and the less explored rare earth elements (REE), makes this e-waste economically attractive for recycling (Ghosh et al., 2015).

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https://doi.org/10.1016/j.eti.2022.102481

Recovering REE from e-waste is gaining attention, as these elements are essential for modern hardware and green energy technologies. Additionally, mining REE from mineral ores is particularly difficult due to their geographical distribution and their combination with radioactive materials. For each tonne of processed REE, 2000 t of toxic waste and 1000 t of contaminated wastewater are generated (Dutta et al., 2016). The global annual demand of REE has increased from 75,000 t of rare earth oxides (REO) in 2000 to 123,000 t in 2016, and it is expected to grow to over 190,000 t per year by 2026 (Wang et al., 2020). Extracting REE from secondary resources such as electronic waste, is therefore, an important approach and a more sustainable way to help tackle future shortage.

Different hydrometallurgical processes are being researched in the recovery of REE from end-of-life products, including permanent magnets (NdFeB) (Yang et al., 2020), spent fluorescent and LED lamps (Rebello et al., 2020) and nickel metal hydride (NiMH) batteries (Ahn et al., 2020). However, the REE content in WPCBs and their potential as a secondary source for this group of elements have not been extensively addressed. The recovery of base metals like Cu, Ni, Zn, and precious metals including Au, Ag and Pd from WPCBs is the key focus of a number of research (Li et al., 2018; Lu and Xu, 2016). The recycling of non-metallic fractions in WPCBs, has also received increasing interest (Zhu et al., 2022). In the e-waste recycling sector, WPCBs are collected from different end-of-life equipment and processed to recover base and precious metals. Fig. 1 describes a traditional route of the WPCBs recycling process. Pyrometallurgy is the most common industrial practice. However, hydrometallurgical methods are becoming more accepted, including bioleaching which is a less developed but greener technology (Hsu et al., 2019).

Research on the recycling of REE from different end-of-life products is constantly growing, however knowledge on the content of REE in industrially comminuted WPCBs and their potential recovery were limited. REE are not considered in the metal recovery process in current industrial recycling practice, therefore, these elements are usually overlooked in the analysis of WPCBs samples. The present study aims to address the low yield of REE in e-waste and overcome the drawback of their recycling. The metals contents (REE, base and precious metals) and their distribution in different fractions of e-waste in industrially pre-processed (comminuted) WPCBs were analysed. These samples were obtained directly from three local e-waste recycling companies, where the particle size separation and analysis served to identify potentially REE-enriched fractions. Additionally, the challenges and prospective of REE recovery from this specific e-waste stream are discussed and a low-cost size separation step was proposed to enrich the REE content for further recovery steps, prevent potential losses and enhance the valorization of comminuted WPCBs as an untapped resource for REE recovery.

2. Materials and methods

2.1. Waste PCBs

The WPCBs material was provided by three companies from the e-waste recycling sector in the UK, referred in this document as Company I, II and III. According to the UK regulations defining company size (annual turnover and average number of employees), the three companies are classified as small. The origin of the WPCBs is defined as information technology (IT) and telecommunication equipment, also referred as Information and Communications Technology (ICT) (e.g., computers, modems, mobile phones, etc.), for all three companies. The WPCBs processed by Companies I and III were originated from a mixture of devices in this category, whilst the sample from Company II was specific from network switches PCBs. The material provided by all three companies was treated in their facilities as follows: Company I, shredding followed by crushing (hammer milling) into particle size ranges $\leq$ 4 mm; Company II and III, shredding into sizes $\leq$ 6 mm. No components were removed from the WPCBs prior to the size reduction process, other than hazardous parts such as batteries, if present. The target particle size is usually selected for an economically viable processing, as fine shredding increases costing of the mechanical pre-treatment process. Although having same size particles would better facilitate comparison between samples, this study aimed to analyse real samples as they occur in the e-waste recycling industry, hence, different mechanical treatments and particle sizes would be expected.

2.2. Sample preparation

Since e-waste is such a complex and heterogeneous matrix, a first dry sieving step was necessary to fully characterize the material. The comminuted WPCBs samples were passed through woven wire sieves with 2 mm, 1 mm, 0.5 mm and 0.25 mm apertures, using a Minor 200 vibratory sieve shaker (Endecotts UK). The largest size range (>2 mm) was selected based on conventional practices reported in the literature and in the e-waste recycling industry (Islam et al., 2020). The 0.25 mm aperture was defined as the minimum particle size range as further sieving substantially increased material loss. Particle size characterization is an important parameter as different components in the WPCBs fragment into different size ranges according to their mechanical properties, and therefore, affecting the liberation of metals and critical materials in this e-waste matrix.

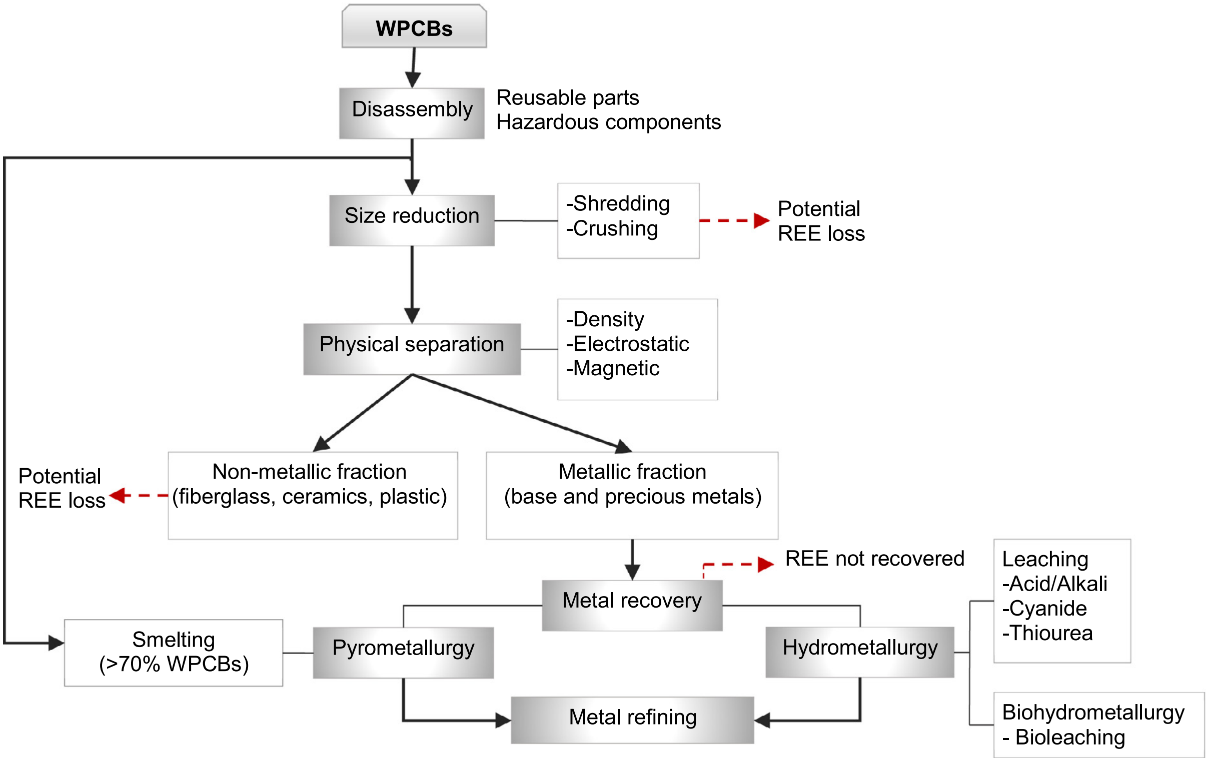


Fig. 1. Industrial and emerging recycling processes of WPCBs for metal recovery.
Source: Adapted (Li et al., 2018).

2.3. Analytical methods

2.3.1. Acid digestion and ICP-MS/ OES

To analyse the metal content of each size fraction of comminuted WPCBs, microwave-assisted acid digestion was carried out using aqua regia extraction with addition of H_2O_2 (Serpe et al., 2015). A subsample of 0.5 g was introduced in PTFE vessels, followed by the addition of 65% HNO_3(3 mL), 37% HCl (9 mL) and 30% H_2O_2(1 mL). Digestion was performed in triplicates. The microwave settings consisted of two steps; first 10 min to reach 200 ± 5 °C, then the temperature was hold for another 20 min, at 1000 W maximum power in a CEM MARS Xpress microwave. All reagents for digestion were purchased from Fisher Scientific, trace metal analysis grade. To ascertain incomplete extraction of REE, a second digestion was done on the undigested residues of the whole sample, for fine (<0.25 mm), mid-size (0.5–1.0 mm) and coarse (>2.0 mm) fractions. The material from Company II was selected for this analysis due to its higher content of REE (results available in supplementary material).

The metal characterization of all samples was performed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, X Series 2, Thermo Scientific), with the use of collision cell technology (CCT, H_2/He) for REE and precious metals. Optical Emission Spectroscopy (ICP-OES, iCAP 6000 series, Thermo Scientific), was used for all other metals. ICP element standards stock solutions were acquired from Sigma and Fisher Scientific.

2.3.2. Quality control

The metal recovery rates of the process were calculated using different certified reference materials. Calcerous soil ERM-CC690 was used for REE analysis, and soil SQC001 was used for all other elements, recovery rates ranged from 56% to 89% for REE and between 88% to 100% for all other elements. It must be noted that at the time these experiments were performed, there were no certified reference materials available for e-waste, especially for WPCBs. Currently, the certified reference material BAM-M505a Electronic Scrap has been developed by the Federal Institute for Materials Research and Testing, Germany. However, such material was produced from electronic scrap shredded and melted with pyrite, resulting in a different matrix from the purely comminuted e-waste. Furthermore, the BAM-M505a reference material certifies several commercially important metals (e.g., Cu, Au), but no critical metals such as REE are assessed. The development of reference materials that are representative of current e-waste matrixes (e.g., following comminution) and the inclusion of critical materials would be useful for the validity of the metal characterization process, not only in research, but also in the e-waste recycling sector overall.

2.3.3. SEM-EDS

The finest particle size range (< 0.25 mm) was analysed using a Phenom Pharos, Field-emission Scanning Electron Microscope (FEG-SEM), 15 kV accelerating voltage and backscattered electron detector (BSD). The fine particles were transferred to aluminium stubs using double-sided carbon adhesive tabs (Ted Pella). The elemental composition of single particles was analysed through Energy-Dispersive Spectroscopy (EDS) with silicon drift detector (SDD), 30 s analysis time. The material was not coated to avoid interferences with the metal content of the samples, as gold and other precious metals were also part of the analysis. Furthermore, no charging effects were observed and the SEM-EDS analysis was possible without the need of coating.

2.4. Statistical analysis

To analyse the differences in the elemental composition of comminuted WPCBs at different size fractions, one-way analysis of variance (ANOVA) and Tukey's honestly significant difference (HSD) test were used, at 95% confidence level ($p < 0.05$) for statistical significance. Minitab statistical software version 18 was used.

Following the elemental analysis of different size fractions, preliminary observations indicated a trend in the concentrations of REE, therefore, a correlation analysis was done to determine the relationship between the concentration of metals and the different particle size ranges. Spearman's rank correlation test was performed using the statistical software Minitab18. The Spearman's correlation coefficient (r_s) is a non-parametric measure that determines the strength and direction of this association (Gautheir, 2001). This test is specific for the detection of monotonic relationships rather than purely linear relationships. A monotonic relationship occurs as one of the variables increases and the other variable either increases or decreases, not necessarily at the same rate. Size fractions were ranked as: rank 1 (<0.25 mm), rank 2 (0.25–0.5 mm), rank 3 (0.5–1.0 mm), rank 4 (1.0–2.0 mm), and rank 5 (>2 mm). The test was run with statistical significance at a level of 95% (p value < 0.05).

3. Results and discussion

3.1. Morphology and mass distribution of comminuted WPCBs

The physical composition of each size fraction is presented in Fig. 2a. The morphology of the particles showed that fractions between 0.25 mm and 1.0 mm (for all three companies) contain few rods and flake-shaped particles, which are likely to be originated from the non-metallic material such as resins, ceramics and fibreglass, as a result of the tearing of the epoxy resin laminates constituting the PCB substrate. It was observed that the material from Company I contained more round-shaped particles in the fraction above 2.0 mm, compared to the other two companies. This reveals not only some differences in the nature of the processed WPCBs material but also the effect of the comminution process on the morphologies of the final output.

Company I comminution process was effective at reducing the material to particle sizes below 2.0 mm, 75% of the total mass was found below this size range. The opposite was observed for Company II and III samples, where particles larger than 2.0 mm in size constitute 70% and 77% of the total mass, respectively (Fig. 2b). The mechanical pre-treatment of WPCBs, such as size reduction is particularly important for the liberation and segregation of metals from this complex waste matrix, facilitating further physical separation steps of metallic and non-metallic material, as well as their compositional analysis.

The samples obtained in the present study followed a much coarser comminution (>2 mm), compared with those typically reported in studies using laboratory scale grinding (<0.5 mm) (Guo et al., 2011; Ribeiro et al., 2019). However, this study aimed to contribute data from the current e-waste recycling sector. In fact, the size reduction process in the recycling industry often aims at 2 mm to 50 mm particle size (Islam et al., 2020). Although it has been reported that comminution of WPCBs into very fine particles (< 0.1 mm) can increase liberation of metals (Ghosh et al., 2015), the main limitations of such fine comminution include high energy requirements, equipment cost and formation of dust fractions, which increases the challenges of handling the material and also its potential loss.

3.2. Elemental composition of size fractions

3.2.1. Rare earth elements

Several studies have compared the metal content of WPCBs from different sources, however, only few have investigated the occurrence of REE (Arshadi and Mousavi, 2015; Priya and Hait, 2018). The difference in the concentrations of REE for each company sample is evident, as reported in Fig. 3. However, one common finding among all three company samples was the concentration distribution of REE in the size fractions, as the finest particles showed higher concentrations. In the sample from Company I, the concentrations of some REE were a thousand times higher in the finest fraction (<0.25 mm), compared with the coarser fraction (>2 mm). In both Company II and III samples, the difference was around one to two orders of magnitude. The analysis of undigested residues served to establish that the low concentrations of REE found in the coarser particles was not due to incomplete extraction of these elements (results available in supplementary material Fig. S1). To date, there are no standard methods for the analysis of the metal content in complex e-waste matrices. Hence,

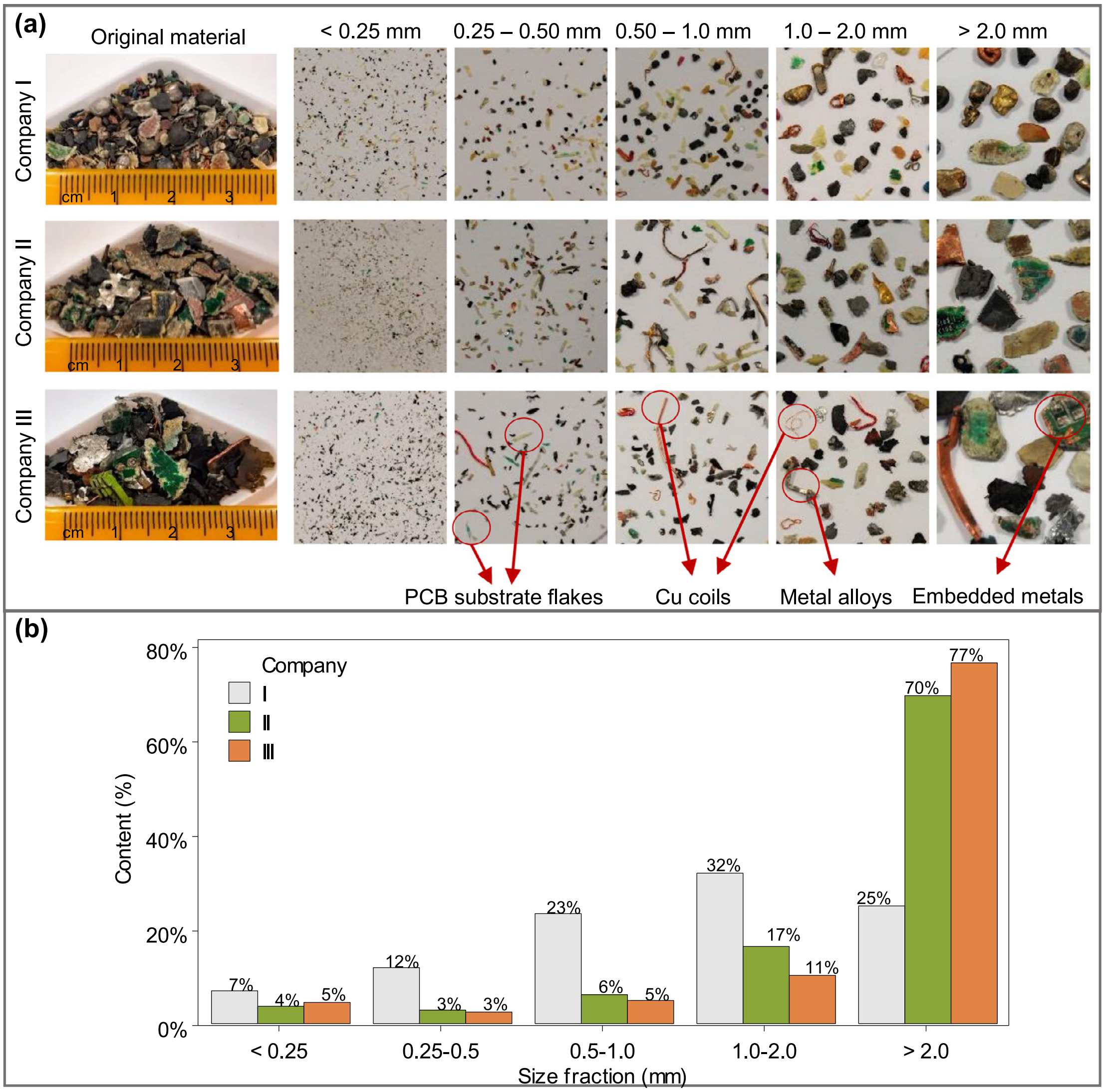


Fig. 2. WPCBs separation by size fractions after dry sieving of comminuted WPCBs from Company I, Company II and Company III samples. Morphological examination (a) and Mass distribution of size fractions (b).

there is increasing interest in the scientific community to establish accurate and reproducible procedures to determine the chemical composition of mechanically pre-treated WPCBs. However, challenges related to the variable distribution of metals in WPCBs samples (Touze et al., 2020) and limitations around the characterization of specific elements are still prevalent (Korf et al., 2019).

The highest concentrations of REE were found in the size range below 0.25 mm. The most abundant REE were La with a concentration above to 2000 g/ton in Company I, Nd over 4000 g/ton in Company II, and Y above 300 g/ton in Company III. The content of Nd, Pr and Dy in Company II sample was notably higher than the other two companies. This may be attributed to the specific WPCBs processed by Company II. Neodymium is most commonly used in permanent magnets in electronic devices, which are made from an alloy of Nd, Fe and B ($Nd_2Fe_{14}B$). Praseodymium is often used as an additive in permanent magnets to improve some of the magnetic properties, and Dy is also frequently added to preserve such properties at high temperatures (Shewane et al., 2014). In fact, SEM results showed that samples from all three companies contained NdFe alloys (the element B is not detected in our EDS set up) that were likely to come from permanent magnets, as seen in Fig. 4. Amongst REE, Nd was the only element identified by the SEM-EDS analysis. The detection limits of this technique range from 0.05wt% to 1.0wt%, depending on the matrix of the sample. Hence, one of the limitations of this approach is that elements found in very small amounts, such as most of REE, are not easily, if possible, identified.

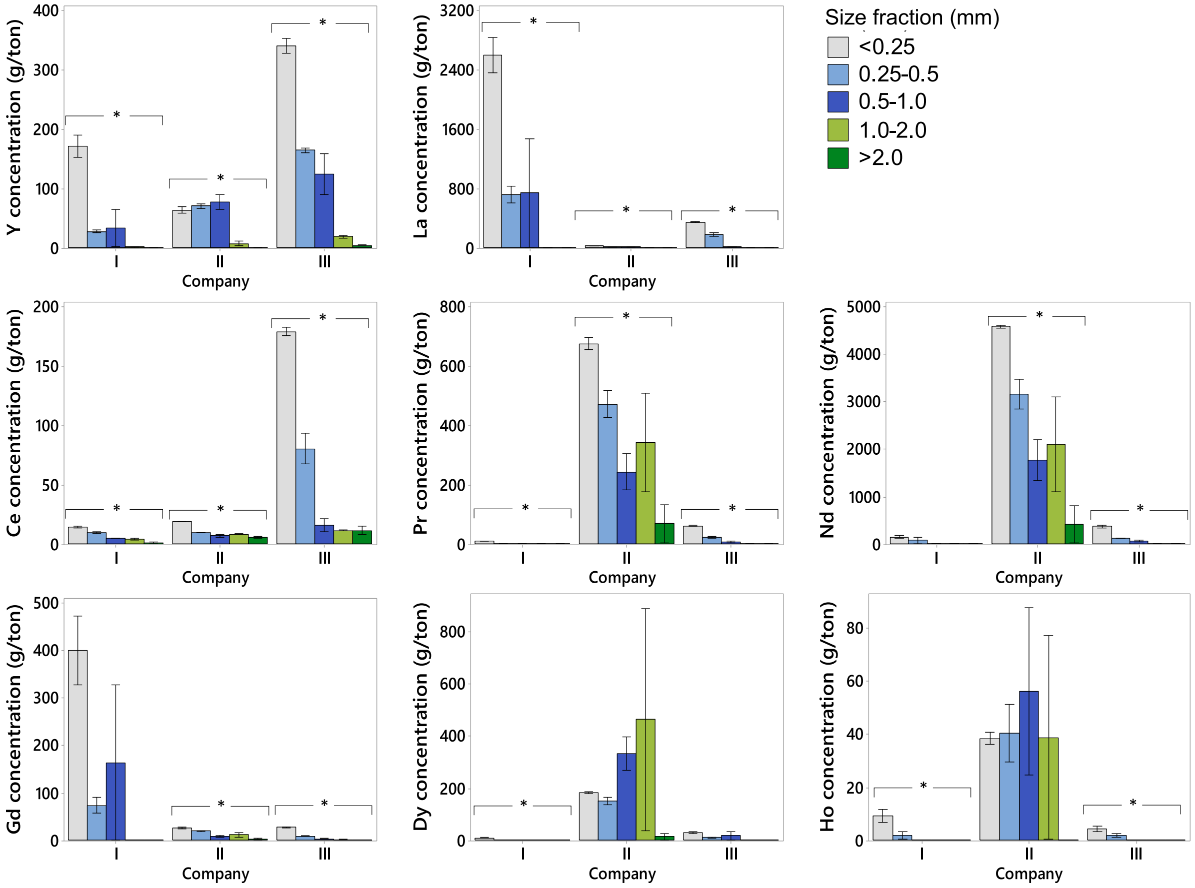


Fig. 3. Concentrations (g/ton) of REE in WPCBs. Companies I, II and III, in different particle size ranges, <0.25 mm, 0.25–0.5 mm, 0.5–1.0 mm, 1.0–2.0 mm and >2 mm. Most abundant REE are displayed for graphical comparison. $n = 3$, Means + SE.
* Significant difference between means in each company ($p<0.05$). ANOVA (Tukey).

Other REE including Sc, Er and Yb were considerably low in all samples, with levels below or close to 10 g/ton (results not shown). For the complete list of REE analysed in this study refer to Supplementary material Table S1. The concentrations of REE in WPCBs, if reported, appear very scattered in the scientific literature. For example, in a comprehensive characterization of IT and telecommunication equipment, elements such as Y, La and Nd were reported in ranges only between 0.5 to 2 g/ton, 0.3 to 5 g/ton, and 0.5 to 2.5 g/ton respectively (Priya and Hait, 2018). Similarly, Arshadi and Mousavi (2015) reported levels of REE below 10 g/ton in personal computer PCBs. Overall, the concentrations of REE found in the present study are the highest values reported for WPCBs from IT and telecommunication equipment so far. This could be explained by the particle size separation carried out, and therefore, the enrichment of certain fractions. These findings are important to determine and design further recovery steps of these critical materials.

3.2.2. Base, precious and other metals

The analysis of base and precious metals is presented in Fig. 5. Copper was the most dominant base metal in samples from all three companies. In Company I, Cu made up to 40% of the particle size range above 2.0 mm, the concentration in Company II and III ranged from 20% to almost 30% in the size fractions between 0.5 mm and 1.0 mm. The content of Zn in Company I sample was considerably higher than the other two companies, with the highest concentration (over 30%) found in the coarser particles (>2.0 mm), compared to less than 10% of Zn found in Company II and III. The SEM-EDS analysis confirmed the presence of several Zn-containing and Fe-containing particles, as shown in Fig. 6a–c. Manganese ferrite ($MnFe_2O_4$) fine particles, a common ceramic compound used in electronics for its electrically insulating and ferromagnetic properties, was often identified. Although Br was not included in the elemental analysis, the presence of brominated flame retardants was evidenced by the occurrence of few Br-containing particles (Fig. 6b).

The contents of Ni and Pb were the lowest amongst base metals for all samples, with levels below or around 4%. The use of Pb in electronic devices has been restricted following the implementation of the EU directives 2002/95/EC and 2011/65/EU (Işıldar et al., 2018). Therefore, some electronic devices would contain lower amounts of Pb, depending on the year of manufacture. The SEM-EDS analysis showed also the occurrence of lead crystal glass particles (Pb–Si)(Fig. 6f).

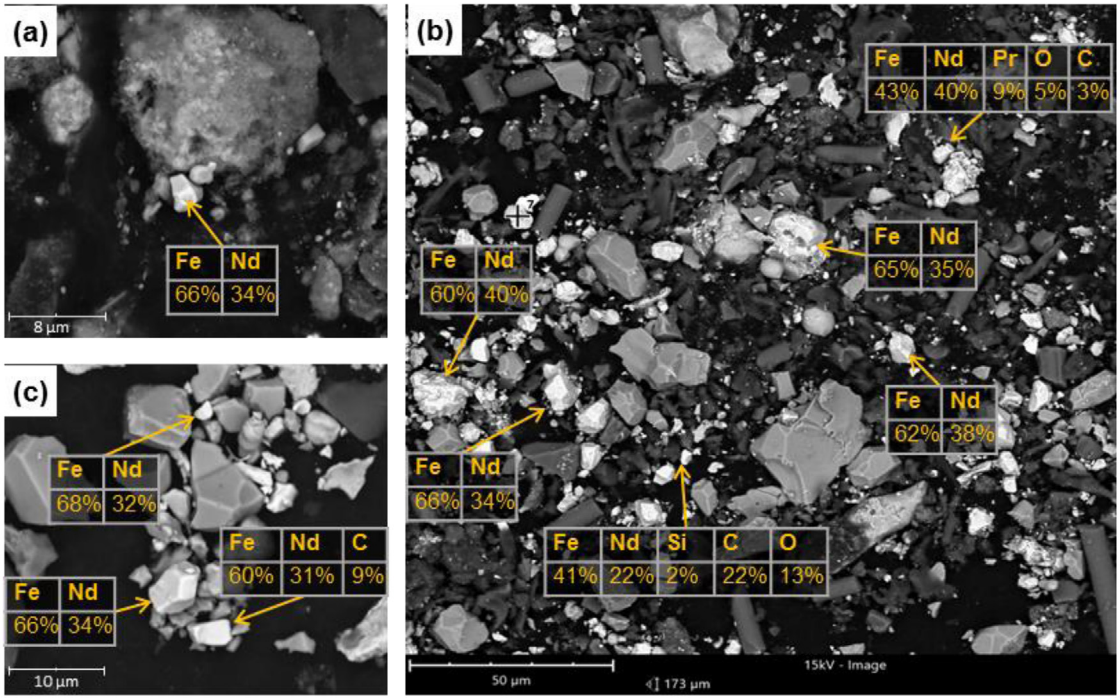


Fig. 4. Scanning electron microscopy (SEM) with Energy-Dispersive Spectroscopy (EDS) images of Rare Earth elements analysis of samples from Company I (a), Company II (b), Company III (c).

For the precious metals group, Ag and Au showed the highest values in samples from all three companies. Company II presented the highest concentration of Au, with particles between 1.0 mm–2.0 mm having over 500 g/ton. The platinum group metals Pd and Pt significantly differed in concentration. Pd was found up to 100 g/ton in particle range 0.5 mm–1.0 mm (Company II), whilst Pt was only less than 1 g/ton in the finest particles (results not shown). The results from the overall elemental analysis in this study are in agreement with other values reported in the literature for base and precious metals content in WPCBs from IT and telecommunication equipment. The base metals Al, Fe and Cu have been reported in concentrations up to 6%, 10% and 35% respectively in PCBs from mobile phones, computers and modems, whilst precious metals like Ag and Au are usually found in the range between 100 to 2000 g/ton (Guo et al., 2011; Kumar et al., 2015; Priya and Hait, 2018).

Unlike REE, base metals showed relatively higher concentrations in the coarser fractions. Whilst Ag, Au and Pd showed high values in different size fractions, including the finest and mid-sized range (0.5 mm to 1 mm). Other studies have demonstrated some enrichment of REE and precious metals in fine and dust fractions of various WEEE following shredding, while base metals seem to be more dominant in coarser fractions (Guo et al., 2011; Marra et al., 2018a). However, a correlation study has not been reported in the scientific literature so far.

3.3. Concentration of metals and size fractions correlation analysis

The relationships between the element concentration and the size fractions are presented in Table 1, where the Spearman's rank correlation coefficient indicates the strength of this relationship. Results showed that the strongest correlations occurred for REE, for all three companies. The negative correlation confirms the fine particle fractions contain the higher concentrations of REE, as the size increases the concentration is reduced. The REE correlations can also be visualized in the scatterplots in Fig. S3.

The trend was not consistent among the three companies for all other metals analysed. Copper was the only element that showed a very strong and positive correlation with the particle size, but this only occurred in Company I sample. This indicates that the specific crushing process employed by this company was effective at concentrating Cu in the coarser particles. Overall, the concentrations of base metals (e.g., Pb, Sn, Zn), and Cr did not show statistically significant correlations with the particle sizes in any of the companies' samples. Precious metals showed a similar trend to REE. However, this was not consistent for all samples, as Company II did not present statistically significant correlations.

The concentration distribution in different particle size ranges can be explained by the physical and chemical form in which these elements are found in the PCBs. During shredding or crushing processes, brittle materials would shatter sharply with very little, if any, plastic deformation, whilst ductile materials would experience more plastic deformation

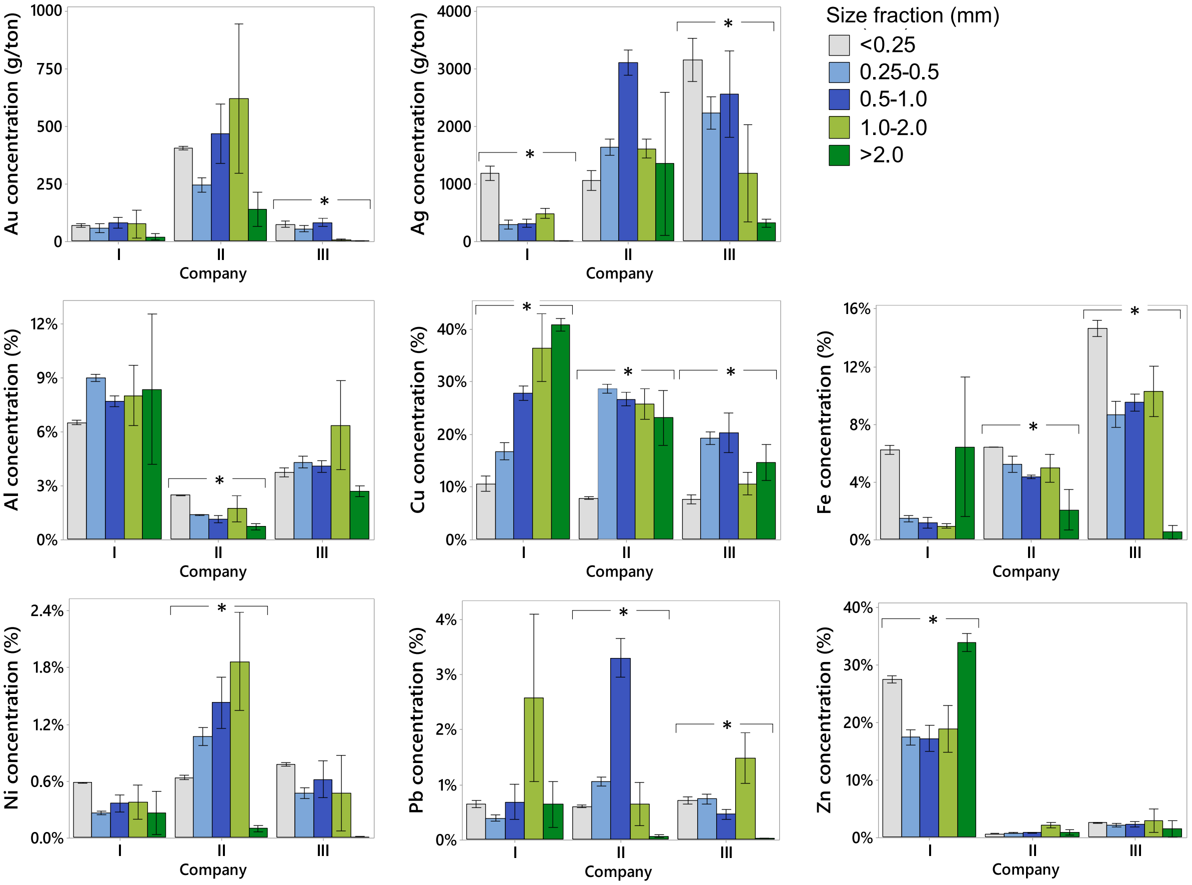
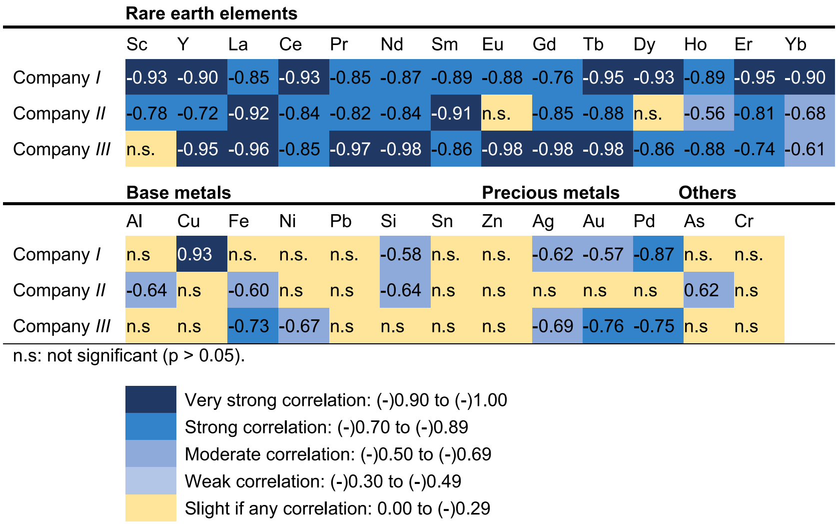


Fig. 5. Concentrations (g/ton) of base and precious metals in WPCBs. Companies I, II and III, in different particle size ranges, <0.25 mm, 0.25–0.5 mm, 0.5–1.0 mm, 1.0–2.0 mm and >2 mm. Most abundant metals are displayed for graphical comparison. $n = 3$, Means + SE.
[*] Significant difference between means in each company ($p < 0.05$). ANOVA (Tukey).

Table 1
Spearman correlation coefficients (r_s, significance level $p < 0.05$) between elemental content and size fractions of WPCBs by company.



	Rare earth elements													
	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb
Company *I*	-0.93	-0.90	-0.85	-0.93	-0.85	-0.87	-0.89	-0.88	-0.76	-0.95	-0.93	-0.89	-0.95	-0.90
Company *II*	-0.78	-0.72	-0.92	-0.84	-0.82	-0.84	-0.91	n.s.	-0.85	-0.88	n.s.	-0.56	-0.81	-0.68
Company *III*	n.s.	-0.95	-0.96	-0.85	-0.97	-0.98	-0.86	-0.98	-0.98	-0.98	-0.86	-0.88	-0.74	-0.61

	Base metals							Precious metals				Others	
	Al	Cu	Fe	Ni	Pb	Si	Sn	Zn	Ag	Au	Pd	As	Cr
Company *I*	n.s	0.93	n.s.	n.s.	n.s.	-0.58	n.s.	n.s.	-0.62	-0.57	-0.87	n.s.	n.s.
Company *II*	-0.64	n.s	-0.60	n.s	n.s	-0.64	n.s	n.s	n.s	n.s	n.s	0.62	n.s
Company *III*	n.s	n.s	-0.73	-0.67	n.s	n.s	n.s	n.s	-0.69	-0.76	-0.75	n.s	n.s

n.s: not significant (p > 0.05).

■ Very strong correlation: (-)0.90 to (-)1.00
■ Strong correlation: (-)0.70 to (-)0.89
■ Moderate correlation: (-)0.50 to (-)0.69
■ Weak correlation: (-)0.30 to (-)0.49
■ Slight if any correlation: 0.00 to (-)0.29

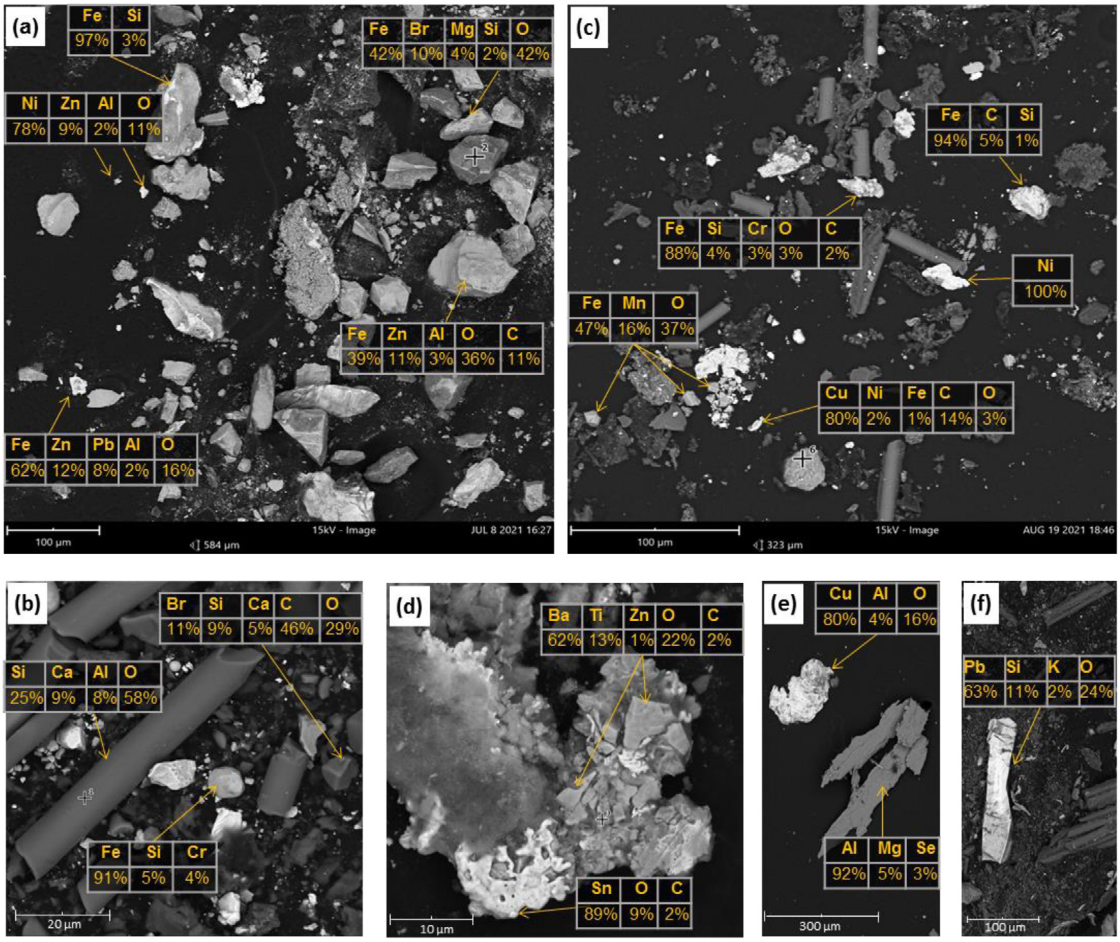


Fig. 6. Scanning electron microscopy (SEM) with Energy-Dispersive Spectroscopy (EDS) images of elemental analysis of samples from Company I (a), Company II (b), Company III (c), and single particles (d,e,f).

(malleability) before breaking. Hence, mechanical properties of the metals, alloys and components found in the PCBs would have an important effect on the particle size output. The mechanical properties of metals analysed in this study were collated from the literature and presented in Fig. 7a. Some common materials/components found in PCBs are also presented in Fig. 7b. Tensile properties such as tensile strength (force before fracture), yield strength (force before plastic deformation) and percentage of elongation, are frequently used to describe the mechanical behaviour of metals, including ductility or brittleness. Percentage of elongation in tension is one of the most conventional measurements of ductility, the percentage increases as the materials are more ductile.

As seen in Fig. 7a, the percentage of elongation is the main difference between REE and other metals. Overall, REE have lower elongation values, indicating less ductility than other metals like Cu, Ni, Pb, Sn, Zn, Ag and Au, that present elongation values above 40%. The REE La and Ce, have often been used in Pb-free solders, as an additive to improve their strength and wettability. However, when the amount of REE added increases, the elongation to failure of the solder alloys decreases, therefore, becoming less ductile (Wu et al., 2004) as presented in Fig. 7b. Another application of REE includes their use in the form of oxides in the electronic components (ECs) mounted on PCBs, such as multilayer ceramic capacitors (MLCCs), resistors, transistors and integrated circuits (ICs). Rare earth oxides (REO) like Y_2O_3, Nd_2O_3, Dy_2O_3, and Ho_2O_3 are frequently used in dielectric ceramics to improve reliability and electrical properties of such components (Alam et al., 2012; Leskelä and Ritala, 2003). Therefore, fine particles are likely to contain high concentrations of REE due to their presence in ECs mainly in the form of oxides embedded in ceramics. No data was found regarding the elongation factor (ductility) of permanent magnets. However, such magnets are mainly manufactured from powders through sintering, hence, their inherent brittleness at fracture (Jha, 2014).

In contrast to REE, metals like Cu, Al, Pb, Sn and Zn are mainly present in their elemental form and/or as alloys in PCBs, and their mechanical properties show very high ductility. Cu is mainly found in the form of coils and thin films, usually coated with Al, Sn or Ni, laminated onto PCBs that serve as signal traces to connect the electronic components (Ghosh et al.,

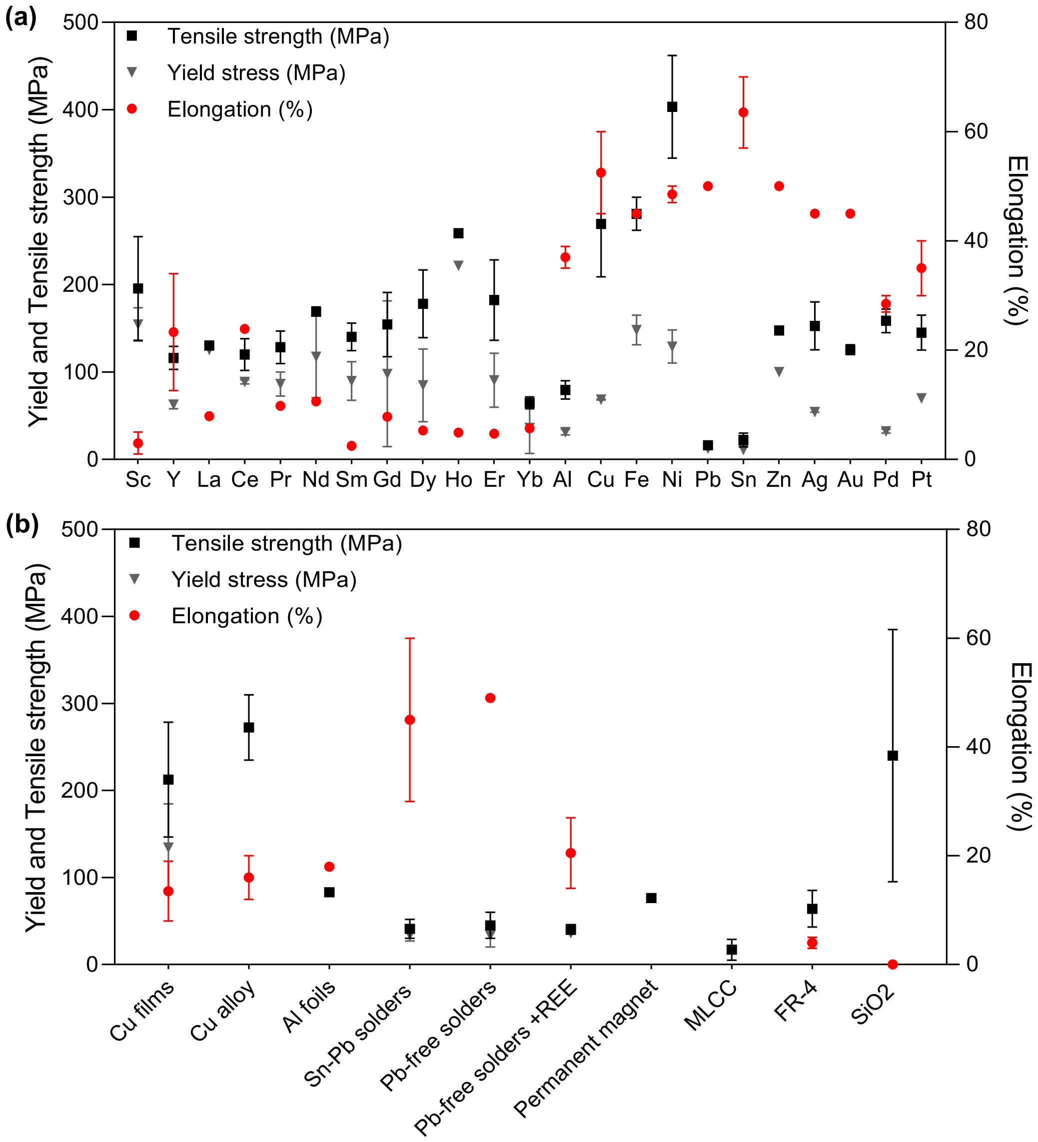


Fig. 7. Mechanical properties of metals (a) and PCBs components (b). Tensile strength given as Ultimate Tensile Strength (UTS). Yield stress given as 0.2% offset yield stress in tension. Data collated from literature included only annealed metals, and materials tested at room temperature. Median with range. (Bray, 1990; Chen et al., 2019; Hutapea and Grenestedt, 2003; Jha, 2014; Sadiq et al., 2013; Scott, 1978; Shewane et al., 2014; Zhang et al., 2011).

2015). Although metals like Fe and Al exhibit also ductile properties, these elements can be found in the form of oxides as main components of the fibreglass reinforcing material used in PCBs (Longobardo, 2010), which exhibit very brittle characteristics. Precious metals are known for their high ductility properties. However, similar to REE, precious metals are often used in small ECs mount on the PCBs, and frequently used to interconnect semiconductors and ICs. Palladium is also used in MLCCs (Korf et al., 2019). Such ECs can be easily broken into smaller particles, which can explain the enrichment in the finest fractions (negative correlation) of samples from Company I and III.

3.4. Recovery potential of REE from comminuted WPCBs

The fine fractions, found to contain the highest concentrations of REE, are likely to be overlooked and lost during conventional WPCBs recycling schemes. For instance, in the first size reduction process, REE can be lost in the form of fine and dust particles. Furthermore, during physical separation steps, REE can be trapped in both non-metallic fractions (e.g., ceramics) and metallic fractions, not destined for REE recovery. Under current smelting process, which is the most common industrial practice for e-waste, many critical materials, including REE, are lost in the sludge produced by this

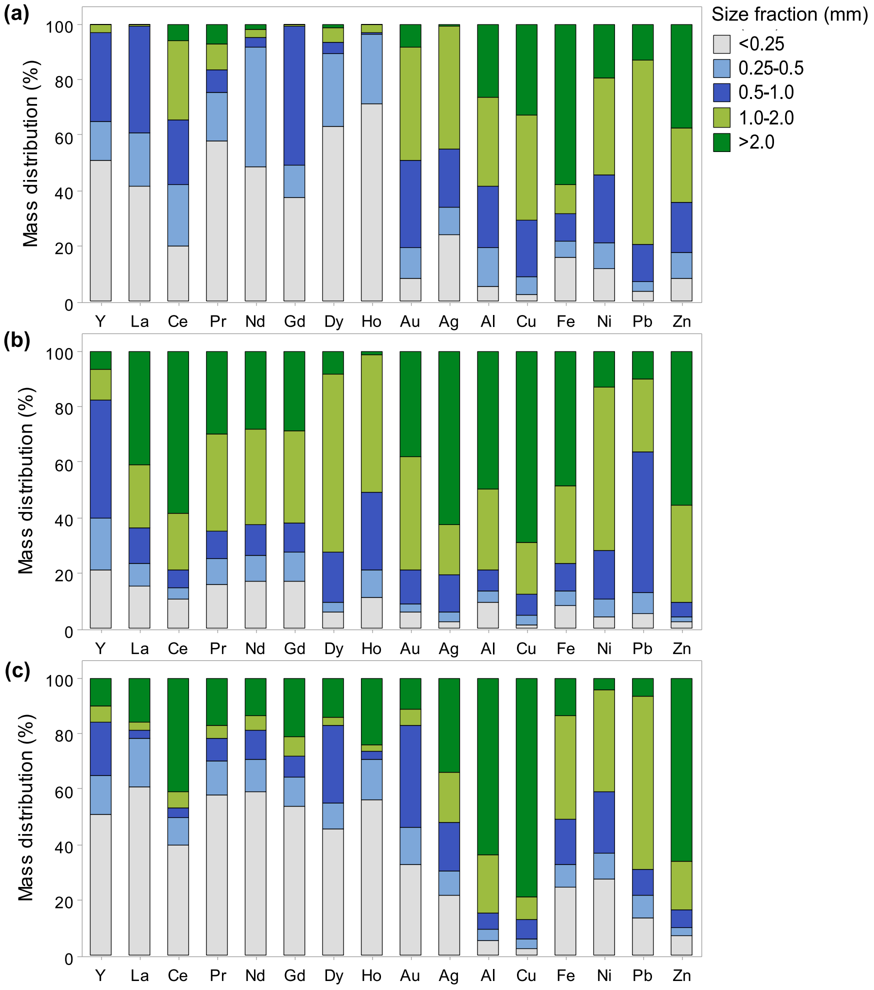


Fig. 8. Mass distribution of REE and other metals in different particle size ranges, <0.25 mm, 0.25–0.5 mm, 0.5–1.0 mm, 1.0–2.0 mm and >2 mm of comminuted WPCBs. Company I (a), Company II (b) and Company III (c). Average values are displayed. The sum of all size fractions represents the total mass (100%).

process (Hsu et al., 2019). This sludge forms a complex matrix that is not often treated, and therefore, the selective extraction of REE from this sludge becomes extremely difficult and not economically viable. Therefore, current recycling practices could benefit from alternative initial separation steps focused on critical materials, such as REE.

In order to evaluate the potential recovery of REE from this type of e-waste, it is also important to understand the total mass distribution of these elements after the comminution step, and therefore, the actual yield. Fig. 8 presents the average mass distribution of REE and other metals for each company. The sum of all size fractions represents the total mass (100%). Results from Company I and III showed similar trends, most of REE mass was found in the finer size fractions (< 0.5 mm), ranging from almost 40% up to 80%. However, the trend was different for Company II, finer particles accounted for less than or around 30% of REE mass (e.g., Pr, Nd, Gd). Most of base metals including Ni, Cu and Al, were mostly found in particles larger than 0.5 mm, from 60% up to 90%, for all three companies' samples. The accumulation of precious metals was slightly different amongst the three companies. Less than 10% of Au and Ag was found in the fractions smaller than 0.5 mm for Company II, whilst Company I and III samples contained over 30% of Ag in the same fraction range.

The present study found that particle size < 0.5 mm is an ideal cut-off point, as it could benefit the concentration of REE and yet preserve the segregation of most base metals like Fe, Cu, Al above this point. In this order, at least 40% and up to 80% of REE mass (Company I and III) could be retrieved by a simple and cost-effective sieving step, following conventional comminution process and before any other physical separation method. Although the yield for Company II ranges from only 20% up to 40%, the sieving step would still generate fractions with high REE concentrations that can be recovered and avoid their loss going into fractions that are destined for other metals recovery. Furthermore, the advantage of this fine size range is the clear separation of other commercially important metals like Cu above this size.

This study considered only samples from three e-waste recycling companies following either crushing, shredding, or both processes. However, the mechanical pre-treatments of WPCBs can differ notably in the e-waste recycling industry. Therefore, the sector could benefit from more research on the fate of critical materials, like REE, during such widely used treatments, especially because only ∼1% of REE is currently recycled from e-waste, compared to rates over 50% for base and precious metals (World Economic Forum, 2019).

The presence and combination of other metals still present a challenge for selective recovery of REE. Even though more efforts have been directed to cost-effective methods of extraction of REE from secondary sources, specifically from end-of-life magnets (Deshmane et al., 2019; Liu et al., 2020), there are still very limited, if any, data on comminuted WPCBs. Overall, the process remains at low technology readiness level (TRL) and is not yet consolidated for industrial applications. In this regard, continuous research is essential to develop sustainable and economically viable methods for REE recovery, extending this also to other sources like WPCBs. Furthermore, the use of more sustainable approaches can enhance the green credentials of WPCBs recycling. For instance, biohydrometallurgy, specifically bioleaching, is a greener recovery solution with several economic advantages (e.g., reduced capital investment and operational costs), where microorganisms are used to perform the leaching of metals. While bioleaching is still under development, researchers have accomplished high leaching efficiency making use of different microbial strains; over 80% of REE have been recovered from e-waste shredding dust (Marra et al., 2018b), and up to 100% from spent magnets (Auerbach et al., 2019). Bioleaching is being investigated along this research in order to recover REE from the fine particle fractions but is beyond the scope of the current paper.

4. Conclusions

The challenges of recovering REE from secondary sources, like e-waste, are related to the low concentrations found in the final output, mainly because such elements are used in very small quantities and are likely to be lost during conventional e-waste treatments. This study demonstrated that REE can be enriched in the finest particles of WPCBs following comminution. A correlation analysis confirmed the strong correlation between the particle size and concentration distribution of REE. For the most abundant REE like Y, La, Nd, Gd, Pr and Dy, concentrations were found to be from two to three orders of magnitude higher in the fine particles (<0.25 mm) compared with the coarser fraction (>2 mm). This trend was found for all three companies, despite the variability in the source of WPCBs and mechanical treatments. A simple and low-cost sieving step, after conventional comminution process and before any other physical separation method, is therefore, recommended to generate REE-rich fractions. However, the yield of REE would differ according to the nature of the material. For some material (e.g., Company I and III), the yield of REE was up to 80% in finer factions (<0.5 mm), whilst only around 20% and up to 40% was obtained in Company II sample. Further study is therefore needed to understand the effects of mechanical pre-treatments in the mass distribution of REE from this heterogeneous e-waste stream. Nevertheless, a cost-effective sieving could still avoid the loss of some REE going into fractions that are destined for other metals recovery.

WPCBs should be regarded as a potential source for REE beneficiation. Although there are still techno-economic challenges in recovering REE from e-waste, the environmental detriment of mining primary sources and the increasing demand of such critical materials, make WPCBs recycling an attractive alternative.

CRediT authorship contribution statement

Alejandra Gonzalez Baez: Conceptualization, Data curation, Investigation, Methodology, Resources, Writing – original draft, Writing – review & editing. **Leonardo Pantoja Muñoz:** Conceptualization, Data curation, Methodology, Resources, Writing – review & editing. **Hemda Garelick:** Conceptualization, Methodology, Resources, Writing – review & editing. **Diane Purchase:** Conceptualization, Data curation, Methodology, Resources, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors would like to thank *iNet Group, PSW Metals Ltd* and *E3 Recycling Ltd* for supplying the WPCBs material.

Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.eti.2022.102481.

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