



Full length article

Exploiting end-of-life lamps fluorescent powder e-waste as a secondary resource for critical rare earth metals

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ABSTRACT

The consensus is growing for the UN sustainable development goals regarding responsible consumption, production, and climate actions. Because of growth towards a digital society (“industry 4.0 revolution”), it is needed to have our resources and economies to be circular. The success also depends on appropriate management of critical raw materials, such as Rare Earth Elements (REEs). Here, a cost-effective recycling method for the recovery of single REEs from fluorescent powder (FP) with end-of-life lamp e-waste is presented with the additional benefit of having a much less environmental impact than mining. The recycling method involves a carefully designed sequential digestion of two phosphor components (YOX and LAP) and treating their leachates separately under specific hydrometallurgical conditions. The phosphors were targeted for Yttrium (Y), Europium (Eu), Terbium (Tb), Lanthanum (La), Cerium (Ce), and Gadolinium (Gd). On trace REEs basis, the leaching process with the FP showed >95% recovery for Eu, La, Ce, Y and Tb. The effective recycling was achieved to >99% purity for Y, Eu, and Tb in 1, 25, and 55 liquid-liquid extraction stages, respectively. To our knowledge, this is one of the first methods to leach and separate Tb from FP e-waste with near quantitative leaching efficiency and >99% purity.

1. Introduction

Digitalisation and use of electronic equipment and gadgets have triggered a substantial increase in e-waste with an astonishing 10% growth rate per year (Balde, 2014). Therefore, it is essential to establish economically viable recycling and treatment technologies to complement United Nations Sustainable Development Goals (SDGs), targeting sustainability and a circular economy for our resources, including sustainable cities and communities, responsible consumption and production, and climate action (Oberle et al., 2019).

Referred as industrial vitamins and the key to the “Industry 4.0 revolution”, Rare Earth Elements (REEs) are vital for our futuristic technologies for high tech applications in electronics, cleantech, energy, mobility, aviation, space, healthcare and futuristic digital and computing applications and personal wearables. These are a group of 17 elements (Sc, Y, La-Lu) characterised by extraordinary optical, chemical, magnetic, and physical properties due to their special 4f-electron configuration. The lanthanide contraction effect makes their sizes and properties very similar and their separation from one another very difficult as well as that as they tend to co-exist in ores (Dupont and

Binnemans, 2015; Gschneidner et al., 2004; Tan et al., 2016; Venkatesan et al., 2018; Yin et al., 2017). Their mining, separation and processing need special techniques and elaborate processes. Current mining-based resources and processes for REEs have a large impact on the environment and techno-economic issues (Lima, 2016). On the other hand, a large amount of REEs is also lost due to marginal (20%) recycling rates for end-of-life e-wastes (Machacek et al., 2015; Patil et al., 2019a; Patil et al., 2019b; Tunsu et al., 2014; Tunsu 2016). Moreover, some REEs are already identified as critical raw materials (CRMs) by the European Union and the US department of energy and defence (Achzet et al., 2011; Zhou et al., 2017). A way to resolve the environmental and recycling shortcomings is to integrate the e-waste supply chains back into the economy by recycling their critical or precious REEs by urban mining (Jha et al., 2016; Kim et al., 2016; Tan et al., 2015; Wu et al., 2014; Yurramendi et al., 2019; Zhou et al., 2017). However, recycling technologies for FP e-waste are often restricted by different boundary conditions, such as in-homogeneity of feedstock, immature technologies and processes that are often designed for front-end productions, high recycling costs, and low commercial-valued impure recycled products. Moreover, these recycled products

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still need to compete with the front-end mining supply (Achzet et al., 2011; Jha et al., 2016; Tan et al., 2015). Currently available processes are based on pyrometallurgy, hydrometallurgy, ionic liquid-based separations, and resin-based separations (Bogart et al., 2016; Maât et al., 2016; Maroufi et al., 2018; Tan et al., 2016; Venkatesan et al., 2018; Yin et al., 2017; Yurramendi et al., 2019). Recently, the metal-organic framework (MOF) based separations are emerging as a green alternative. However, its high cost and incompatibility in high acidity conditions make its use difficult (Bogart et al., 2016; Cheisson et al., 2019; Sun et al., 2018).

Therefore, new approaches fulfilling the criteria for economic feasibility, environmental impact and technological ease with assured qualities are needed. FP waste contains almost more than 50 metal and non-metal components and filler materials due to combined manufacturing or shredding. Economic boundary conditions make liquid-liquid extraction more favourable than chromatography in recycling (Patil et al., 2015; Patil et al., 2019; Tan et al., 2015). Because recovering or separating concentrations in huge scale can not be achieved by chromatography. Different phosphorus-based ionic and amide ligands can be exploited for the separation of REEs due to their hard nature and f-element chemistry (Patil et al., 2015). Therefore, finding the right combination of wet, cheap, regenerable, and environmentally friendly chemistry components, selective ligands, and mild processing conditions were our aims.

The present paper deals with the development of the recycling process for REEs from end-of-life lamp fluorescent powder (FP) e-waste. Near quantitative digestion has been achieved using the sequential approach. Using the leachate, the element-specific chemistry for liquid-liquid extraction has been developed using the selective ligands to separate the REEs in economically acceptable purities of >99%. Process flowsheet has been developed to arrive at pure REEs such as Y, Eu and Tb. The real FP e-waste has been thoroughly characterised by elemental analysis and used for process development after removal of toxic Hg content. The process components such as acids and organics can be reused within the system multiple times and causing minimal secondary waste generation. The exploitation of the e-waste resource for the pure metals recycling and reuse of the benign process component makes our approach environment-friendly. The developed process for real FP e-waste has the possibility to scale up, high throughput using liquid-liquid extraction, cheaper process economics as compared to conventional operations.

2. Experimental

FP pretreatment: FP from end-of-life lamps was provided by the BLUBOX Trading AG, Switzerland after segregation and mechanical shredding of the lamps. The BLUBOX process operated by the hazardous waste recycler Sovag Veolia, Rubigen, Switzerland, involves shredding of the lamps under reduced pressure, binding of the mercury vapour in carbon filters and collecting the powder, plus some small size fractions of glass (Patil et al., 2019a). The IR camera- and magnetic separation-enabled shredding machinery also pre-sorts components, such as plastics, ferrous, and nonferrous materials (see Figure S1 with the Supporting Information (SI)). These material residues are then handed over to an independent recycling process. Due to legislation, the Hg-containing FP ends up in landfills because there are no cheap, reliable industrial processes available.

Here, Hg was removed from the FP to below 10 mg/L at the BATREC AG, Seon, Switzerland, using a high-temperature furnace under inert gas conditions and a closed gas pipe system for the exhaust gas over carbon filters. During treatment, the air nearby the furnace was also analysed for Hg content using a VM-3000 Mercury vapor Monitor (Mercury Instruments), and the FP digestion solutions were also analysed for Hg at PSI using ICP-OES (Spectro Genesis and Spectro Arcos spectrometers, Spectro Analytical, Germany).

FP elemental composition: To determine its elemental composition,

the FP was first digested using the Multiwave 3000 microwave digestion unit (Anton Paar) at high temperature and pressure conditions (details are given in section S2 with the SI). The elemental analysis of the microwave-digested FP, as well as, the control and purity assessment of solutions during the development of our process was done using ICP-OES. For high purity fraction and residual impurity profiling, an inductively coupled plasma mass spectrometry (ICP-MS, 7700x, Agilent) was used. The quantification of REEs was done using REE mix standard solutions (from Fluka) and by their dilution using 1% HNO₃ in ultrapure MilliQ water, to render solutions with concentrations ranging from 0 to 10 µg/mL (mg/L) for ICP-OES, and from 0 to 100 ng/mL (ppb) for ICP-MS analysis. For each experimental condition, duplicate experiments were performed, and each was analysed unless stated otherwise.

Leaching process: Digestion of the FP was done in a 1 litre pyrex glass vessel mounted with an overhead stirrer from IKA. For the hydrometallurgical operations and separations of selected REEs, we first leached the FP in batches with a dilute mineral acid, such as 0.001 M HCl, for 30 min each. The concentration of the solid-liquid system equalled 100 g FP/litre of the leaching solution. After separating the FP from the solid-liquid suspension system using Whatman filter papers No. 41, with every FP batch, the leaching was repeated using a stepwise increased stronger HCl solution than used in the leaching run preceding it. The sequential digestion process involved 9 steps with increasing HCl concentration (0 M, 0.001 M, 0.01 M, 0.1 M, 0.5 M, 1 M, 5 M, 8 M, and 10 M). The nine steps were performed at room temperature. After this, a final leach was performed with hot 10 M HCl. With each leach batch, the solid-liquid ratio equalled 1:10, and each system was stirred to warrant homogeneous digestion reactions between all FP particles and the HCl solution. Each leachate was collected for elemental analysis with ICP-OES to evaluate its use for further processing. Leachates comprising sufficiently high amounts of a specific phosphor component were combined into one solution, and its elemental components were precipitated as hydroxides, dried, and stored before further processing.

Extraction process: With each phosphor-specific precipitate of interest prepared at the end of the leaching process, 50 g precipitate was dissolved per litre aqueous phase for subjection to liquid-liquid extraction (LLE) cycles. 1 M HNO₃ or 0.5 M HCl solutions were used to dissolve these phosphor precipitate depending on the required extraction conditions. Tricapryl methyl ammonium chloride (Al336), hydrochloric acid, bis (2-ethylhexyl) phosphate (HDEHP), oxalic acid and nitric acid were purchased from Aldrich (Details of materials and instruments are given in section S1 with the SI). The extractant solutions were prepared by dissolving the required amount of selective ligand (Al336 or HDEHP) in the nonpolar diluent. In the case of Al336, a phase modifier was also added to avoid the formation of a third phase from the splitting of the organic phase in higher diluent rich and lower extractant and metal-rich phase after high loading of the metal ions (Patil et al., 2015). The organic-aqueous phase ratio in the liquid-liquid extraction runs equalled 1:1 unless stated otherwise. Al336 was pre-equilibrated with 3 M NH₄NO₃ solution to convert it from the chloride into a nitrate derivative of Al336 for use in nitrate-containing extraction media. For extraction, 15 ml Cellstar-Centrifuge tubes (polypropylene, graduated, conical bottom, sterile) were used. After extraction, centrifugation was performed with a Hettich Universal 1200 instrument at >3000 rpm, and a 100 µl aliquot was taken from the aqueous phase to monitor the extraction stage by ICP-OES analysis after appropriate dilution of the subsample in 1% HNO₃. Acidity measurements were done by titrating against a standardised NaOH solution and using phenolphthalein as the indicator. For the filtrations of precipitates during media interconversion steps, Whatmann filter papers No. 41 were used. Eqs. (1) and (2) were used for the determination of the distribution ratio (D_M) and the separation factor (SF).

$$D_M = \frac{[REE]_{org}}{[REE]_{Aq}} \quad (1)$$

$$SF = \frac{D_{MREE1}}{D_{MREE2}} \quad (2)$$

Where $[REE]_{Org}$ denotes the REE concentration in the organic phase, $[REE]_{Aq}$ is the REE concentration in the aqueous phase, and SF designates the quotient of distribution ratios for two REEs separated from each other.

3. Results and discussions

3.1. Removal of mercury from FP waste and characterisation of the samples

The FP waste was thermally treated in a furnace at $T = 540\text{ }^{\circ}\text{C}$ for 4–5 h in order to remove the volatile Hg content. The thermally treated FP waste was then characterised by using microwave digestion and subsequent ICP-OES analysis. With the SI, Table S1 shows the Hg content in different shredding and pre-sorting stages of lamp FP e-waste. With the BLUBOX shredding process, lamps are broken down and crushed to smaller particles. Although the BLUBOX shredding process removes about 90% of the Hg from the broken and crushed lamps, the thermal treatment was necessary to reduce the Hg traces present in lamp powder captured by BLUBOX's exhaust gas system further to less than 10 mg/L. The detailed elemental characterisation process and composition are listed in Table S2 and S3, respectively, with the SI.

The thermally treated FP samples also comprised a ~35 Wt.-% fine glass fraction, being ~10–50 μm large and with a density of ~0.7 kg/L. The overall content for 6 REEs (Y 67.41 ± 1.95 g/kg, Eu 4.01 ± 0.02 g/kg, Tb 2.96 ± 0.16 g/kg, Gd 2.90 ± 0.08 g/kg, La 7.47 ± 0.21 g/kg, and Ce 6.19 ± 0.28 g/kg) was 90.94 ± 2.7 g per kg FP e-waste. Besides these, also 27 other elements were detected in the FP e-waste, such as alkali metals, Fe, Sb, and Zn, which has to be removed as well to purify REEs.

3.2. REE leaching from FP

To facilitate recovery processing, the FP was leached using mineral acids, such as HCl and HNO_3 . Instead of a one-step, complete, leaching of the FP in a concentrated acid at high temperatures and resolving its inherently more complex elemental composition, we used a sequential digestion method by taking advantage of the different solubilities of the phosphor components present in the FP waste (Dupont and Binnemans, 2015; Van Loy et al., 2017). For each leaching stage, the powder was in contact with the acid for 30 min. Fig. 1 shows the optimised conditions for the leaching of REEs from FP according to the tailor-made sequential approach developed here to minimise the complexity of each phosphor-specific leachate of interest. The decreasing solubility of the phosphors in dilute acid conditions was in the order: HALO ($\text{Ca}_{10}(\text{PO}_4)_6\text{FCl}:\text{Sb}^{3+}, \text{Mn}^{2+}$) > YOX ($\text{Y}_2\text{O}_3:\text{Eu}^{3+}$) > LAP ($\text{LaPO}_4:\text{Tb}^{3+}, \text{Ce}^{3+}$). Due to the sequential approach, the overall leaching efficiency of the targeted REEs (Y, Eu, Tb) was >95% (Table 1). We

Table 1

Concentration of the REEs and calcium after leaching following the digestion scheme shown in Fig. 1.

Metal (g/L)	Concentration in FP waste	Concentration in leachate	Leaching efficiency (in%)
Y	67.41 ± 1.95	64.85 ± 2.02	96.2
Eu	4.01 ± 0.02	3.97 ± 0.07	>99.0
Gd	2.90 ± 0.08	1.60 ± 0.09	55.1
Tb	2.96 ± 0.16	2.83 ± 0.12	95.6
La	7.47 ± 0.21	7.40 ± 0.19	>99.0
Ce	6.19 ± 0.28	6.13 ± 0.22	>99.0
Ca	99.02 ± 0.03	96.15 ± 0.09	97.1

have heated the solution to leach the LAP phosphor for $60\text{ }^{\circ}\text{C}$ for 30 min, and this is the only heating and energy-consuming step in overall process flow sheet developed by us. It is accounting for 162 kJ energy to be used to heat the solution from room temperature to the required temperature. Noteworthy is also that we achieved very satisfactory leaching also of the Tb from the LAP phosphor using a cheap mineral acid (HCl), whereas, in the literature, very harsh conditions are usually reported using high-temperature oxidation in the presence of concentrated acids (such as H_2SO_4 and H_2O_2) or by a strong base (alkali fusion) (Innocenzi et al., 2017; V. 2016, 2013; Ippolito et al., 2017; Machacek et al., 2015; Van Loy et al., 2017; Wu et al., 2014).

3.3. Processing of different phosphors for individual REEs recovery

3.3.1. Processing of YOX phosphor for Y and Eu recovery

The initial process development was done using single pure metal oxides at 0.01 M metal concentration to establish the extraction conditions with high separation factors, SF. For the optimised conditions, the SF and D_M values were determined using Eqs. (1) and (2), and they are shown in Table 2.

With the FP, leachate fractions from the sequential digestion sequence rich in YOX ($\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, red phosphor) were combined into one solution. In the literature, Al336 or HDEHP based processes for the separation of Y and Eu had been employed in nitrate, as well as, in ammonium nitrate medium. Such extraction conditions would require the interconversion of acidities via alkali-based neutralisation using the ammonium hydroxide and dissolutions in respective acid (HNO_3 or HCl) solutions as per the extraction conditions requirement between the digestion and the extractive separation steps (Jha et al., 2016; Tan et al., 2015). To avoid additional chemical steps with the extractant, we simplified the process by only adjusting the YOX phosphor-rich leachate solution arriving from the sequential acid digestion to the 0.5 M HCl medium as the feed-in solution with the liquid-liquid extraction trials (during the processing of leached YOX fraction). The concentration of the YOX-rich feed-in solution was adjusted to 50 g/L. The extraction in chloride medium avoided additional chemical steps. For efficient and selective Y extraction, less extractant inventory of 0.5 M HDEHP in toluene was used.

It is worth to note that toluene has been used as the diluent in this system instead of benzene or kerosene as a greener alternative and cost-

Table 2

Extraction system optimised for the Y/Eu separations. Feed: 0.5 M HCl; Strip: 2 M HCl; Organic phase: 0.5 M HDEHP in toluene. [M]: 0.01 M (pure REE salts); T: $25\text{ }^{\circ}\text{C}$; O:A = 1:1.

M	D_M	SF (Y/M)
La	0.02 ± 0.003	139
Ce	0.01 ± 0.001	289
Eu	0.08 ± 0.001	35
Gd	0.11 ± 0.003	25
Y	2.68 ± 0.069	1
Tb	0.45 ± 0.003	6



Fig. 1. Digestion scheme for the FP e-waste (each digestion stage lasted 30 min).

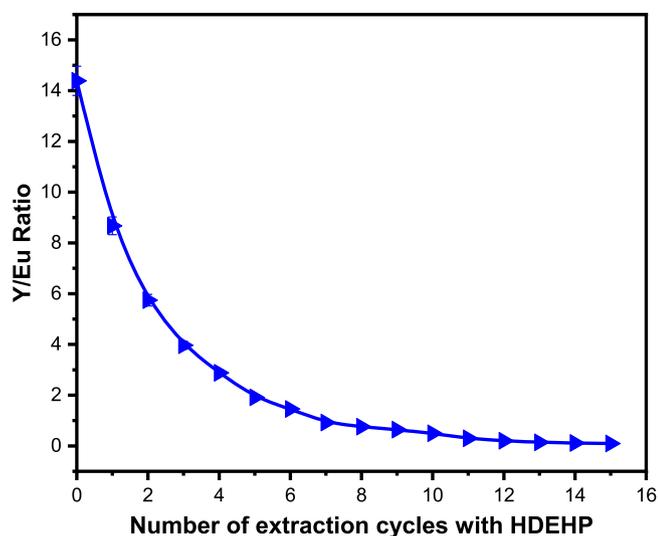


Fig. 2. Removal of excess Y from YOX containing solution (ratio of % REE content on trace metals basis). Extractant phase: 0.5 M HDEHP in toluene; feed aqueous phase: 0.5 M HCl; strip aqueous phase: 2 M HCl; [feed M]: 50 g/L; T: 25 °C; O:A = 1:1 (organic:aqueous).

effective option due to less volatility with the possibility to reuse the organic phase number of times (Cheisson et al., 2019; Patil et al., 2019a). The Eu metal was purified with the aqueous phase in further 15 extraction steps using 0.5 M HDEHP in toluene, because of the preferential transfer of the Y in the organic phase. After treatment, of the same YOX feed solution Y/Eu ratio from 14 ± 0.6 before the start (stage 0) to 0.1 ± 0.004 after the 15th extraction run (Fig. 2).

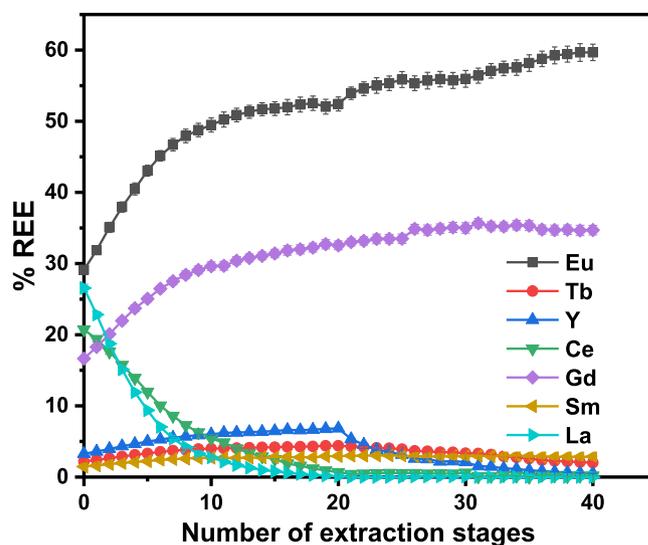
The Y was then stripped out from the extracted organic phase using the 2 M HCl stripping conditions. After the first extraction stage, the purity of the Y with the aqueous stripping solution was >99%. So, only a single diluent medium and only half the amount of extractant were used. In contrast, earlier methods reported more (10–20) liquid-liquid extraction stages and additional modifier chemicals to avoid gel or third phase formation to achieve similarly high Y purity and Eu-enrichment (Jha et al., 2016; Tunsu et al., 2016; Wu et al., 2014).

After 15 Eu-enrichment steps with HDEHP in toluene (Fig. 2), other REEs such as La and Ce were then removed from the Eu-enriched YOX solution by converting the solution first from the chloride to the nitrate anion condition via neutralisation using equimolar quantities of ammonium hydroxide and dissolving the precipitate in 1 M HNO₃ to render again a 50 g/L concentrated extraction feed-in conditions. Supported by the single REE extraction results (Table 3), the removal of the La and Ce from the Eu-enriched YOX nitrate solution was achieved by using a nitrate derivative of Tetra-alkyl ammonium ionic extractant, e.g., Methyltrioctylammonium chloride (Al336). 20 wt% of Al336 was dissolved in a 70:30 Toluene:Kerosene solution and treated with 3 M NH₄NO₃ solution for converting it to nitrate medium (pre-equilibration of Al336 to convert chloride to nitrate anionic form). Again the enriched YOX nitrate was dissolved in 1 M HNO₃ 50 g/L and extracted

Table 3

Extraction system optimised for the La and Ce removal. Feed: 1 M HNO₃; Strip: 0.001 M HNO₃; Organic phase: 20% Al336 in Toluene:Kerosene (70:30); [M]: 0.01 M (pure REE salts); T: 25 °C; O:A = 1:1, SF: separation factor.

	D _M	SF La/M
La	0.203 ± 0.009	1
Ce	0.141 ± 0.017	1.44
Eu	0.018 ± 0.002	11.3
Gd	0.006 ± 0.001	35.2
Y	0.005 ± 0.001	42.9
Tb	0.005 ± 0.001	38.6



Stage 1-20 (Al336 in nitrate); Stage 21-40 (HDEHP in sulphate)

Fig. 3. Pre-concentration of Eu from YOX containing solution, Stage 1–20: Feed: 1 M HNO₃, Strip: 0.001 M HNO₃, Organic phase: 20% Al336 in Toluene:Kerosene (70:30); Stage 21–40: Extractant phase: 1 M HDEHP in toluene, Feed aqueous phase: 1.5 M H₂SO₄, Strip aqueous phase: 2.5 M H₂SO₄, [feed M]: 50 g/L, T: 25 °C; O:A = 1:1.

using Al336 in controlled and H⁺ competing conditions (Table 3).

These conditions helped us to achieve the very high separation factors for La and Ce over other heavy REEs such as Tb and Y. The addition of 70% toluene and limited use of kerosene helped us to increase the reusability of the solvent system along with avoiding the third phase formation under high loading conditions used in present work. The LLE conditions applied allowed to remove the La and Ce almost completely in only 20 successive extraction stages (Fig. 3). The strip solution used for the REEs-loaded organic phase was 0.001 M HNO₃.

After the 20 extraction stages with Al336, the more Eu-enriched YOX fraction still contains a Tb impurity (Fig. 3). To remove the latter, the YOX was converted from nitrate to sulphate again using hydroxide and dissolving the deposit in 1.5 M H₂SO₄ to a 50 g/L concentration as a new loading phase in other extraction conditions. The extractant with the altered organic phase was 1 M alkyl phosphate, i.e. HDEHP, in toluene, and the aqueous strip solution was 2.5 M H₂SO₄ (Alstad and Farbu, 1977). The new loading phase removed the Tb and Y almost completely in several repeated stages to arrive at a nearly pure 60:40 molar Eu:Gd composition (Fig. 3) that is similar to that found with mining ores (Gschneidner et al., 2004). Unfortunately, after 20 stages with HDEHP in sulphate medium (“HDEHP II”), the Eu:Gd system could not be separated any further by extractive methods. It is noteworthy that earlier reports of FP e-waste processing did not focus on the separation of Gd, although it is co-present with the FP e-waste in substantial amounts (~3% of the FP weight) and it has good commercial value with critical technological applications. In the following, a process is presented to separate Eu from Gd successfully.

The effective inseparable Eu/Gd mixture was then subjected to optimised reduction conditions in acetic acid or HCl medium at dilute acid conditions (McCoy, 1935; Preston and Du Preez, 1996; Sayed et al., 2005). The conventional Eu reduction method in zinc chloride medium was not found suitable. Although the Zn reduction method applied here is well-established in the literature; however, it was not possible to achieve more than 99% Eu purity from FP e-waste (Lorenz and Bertau, 2017). We have modified the process using acetic acid to achieve higher Eu and Gd purities. The fact that Eu and Gd are immediate neighbours in the lanthanide series with the periodic table render their separation very difficult. In this work, the Eu/Gd mixture

Table 4

Eu purity after Zn reduction from pre-concentrated feedstock (Purity on trace REE basis) Control: feed solution before reduction.

M	Acetic Acid Feed (Control)	Product Precipitate after reduction	Product Precipitate after reduction duplicate	HCl Feed (Control)	Product Precipitate after reduction	Product Precipitate after reduction duplicate
% Eu	60.92	99.73	99.60	61.13	96.46	95.84
% Gd	38.36	0.25	0.28	38.62	3.51	4.06

was dissolved in acid, and the acid solution was purged with 4% H₂ in argon. The reduction was carried out using Zn metal powder added to the solution. The reduced Eu was precipitated using 1 M H₂SO₄ and washed with 0.001 M H₂SO₄ three times to remove possibly co-adsorbed Gd impurity. In one reduction run, the procedure rendered 99% pure Eu and 97% pure Gd purity with the washed precipitate and the supernatant, respectively in a single reduction cycle (Table 4). The fine Zn powder has a high surface area, allowing an efficient reduction, and it does not need sophisticated equipment to process. The acetic acid used here is being employed for the first time to recover pure REEs from FP e-waste as a cheaper option, whereas the use of HCl showed somewhat less satisfying results and would, therefore, need more than one reduction and precipitation cycle to achieve 99% pure Eu (Table 4 and Figure S2 with the SI).

3.3.2. Processing of LAP phosphor for Tb, La and Ce recovery

The LAP leachate fraction of green phosphor was processed independently for the recovery of La, Ce, and Tb. The LAP in chloride medium emanating from the acid digestion was converted to a nitrate solution via hydroxide precipitation and dissolving the deposit in 1 M HNO₃. The conversion avoids the use of oxalate precipitation and cost-intensive calcination (at T~1000 °C), as well as using more rigorous precipitation and ion exchange methods reported in earlier studies (Tan et al., 2015). As can be seen from Table 5, nearly 14% of Tb was present in the HCl leachate LAP fraction. By converting it to a nitrate solution, the Tb content increased from about 14% to 18%, Ce decreased from 35% to 21%, but La increased somewhat from 49% to 54%. The 1 M HNO₃ solution feedstock was subjected to liquid-liquid extraction (LLE) using 20% Al336 in a 70:30 (v/v) Toluene-Kerosene diluent as the extractant organic phase. The feed with Tb containing LAP fraction was maintained at nitrate conditions to selectively remove lighter lanthanides or REEs, e.g. La at 1 M HNO₃ conditions (Table 5).

As seen from Table 5, nearly 14% (trace REE basis wt% in feed) of Tb was present in leachate LAP fraction. However, by converting it to nitrate fraction using 1 M HNO₃, we can enrich the Tb to nearly 23–26% by limiting the Ce content up to 20% only, as depicted in Fig. 4.

This feed was then subjected to the LLE using 20% Al336 in Toluene-Kerosene (70:30) diluent. Such an efficient and fast decontamination of La and Ce was essential to get the targeted higher REE purity for the Tb. After each extraction stage, the metal loaded organic phase was stripped using 0.001 M HNO₃ and analysed for its elemental content using ICP-OES. The La and Ce purity achieved during the stripping process with 0.001 M HNO₃ was 79% and 59% (trace REE metals basis), respectively.

After the removal of La and Ce, the hardly affected, thus, subsequently higher concentrated Y impurity was removed using 1 M HDEHP in toluene as the extractant organic solution with a 1.5 M H₂SO₄

Table 5

Optimisation of LAP phosphor after leaching.

REE metal% (trace REE basis)	After HCl digestion	A clear solution in dilute nitrate medium	Precipitate in dilute nitrate medium	(After drying) Clear solution
Tb	13.7 ± 0.41	17.2 ± 0.52	8.0 ± 0.24	18.8 ± 0.56
La	49.2 ± 1.66	55.3 ± 0.79	26.3 ± 1.6	53.4 ± 1.48
Ce	34.5 ± 1.04	21.3 ± 1.79	59.6 ± 0.62	20.8 ± 0.81
Y	2.3 ± 0.10	3.2 ± 0.07	1.5 ± 0.05	3.3 ± 0.93

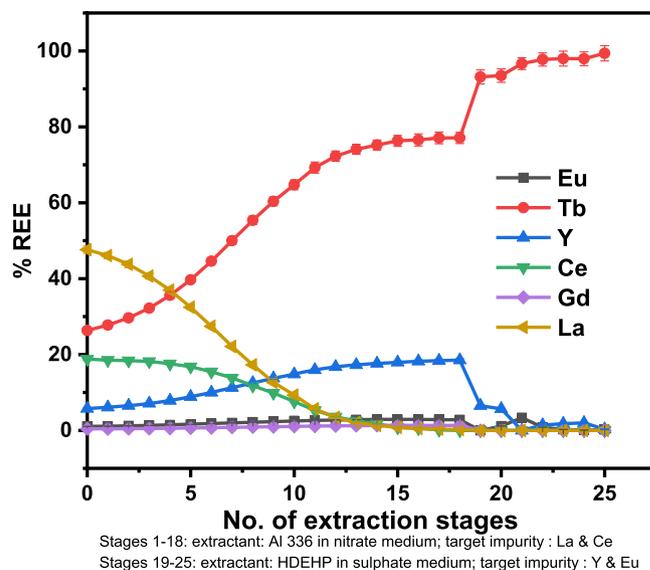


Fig. 4. Pre-concentration of Tb from LAP containing solution. Stage 1–18: Feed: 1 M HNO₃, Strip: 0.001 M HNO₃, Organic phase: 20% Al336 in Toluene:Kerosene (70:30); Stage 19–25: Extractant phase: 1 M HDEHP in toluene, Feed aqueous phase: 1.5 M H₂SO₄, Strip aqueous phase: 2.5 M H₂SO₄, [feed M]: 50 g/L, T: 25 °C; O:A = 1:1.

aqueous medium solution adjusted to 50 g/L of the hydroxide precipitated feed-out solution afforded by the LLE using 20% Al336 in a 70:30 (v/v) Toluene-Kerosene (earlier enriched to 77% Tb content). The new strip solution was now 2.5 M H₂SO₄. The HDEHP extractions gave >99% pure Tb as a product in 7 extraction cycles (Fig. 4). Summarising the above: Starting from the acid digested FP feedstock, highly pure Tb in >99% purity was achieved in overall 25 extraction stages (Figure S3 in the SI). The same type of organic extractants (Al336, HDEHP) and diluents (kerosene, toluene) was used here to treat the different phosphor fractions independently. The recycling of used acids and organic fractions within the process keeps costs further down and is another benefit for the usually conservatively approached field of waste recycling.

3.3.3. Process flowsheet for the recycling of pure REEs from FP e-waste

The overall process developed aimed at simple, minimum approaches for digestion, wet chemical transformations, and the liquid-liquid extractions cycles. In conventional processes, the FP e-waste would have been digested entirely, thus, comprising the contents of the YOX, LAP and the HALO phosphor fractions. The complete digestion leads to a very complex mixture with all REEs and non-REE (transition) metals present with the FP e-waste. Some of these elements are also

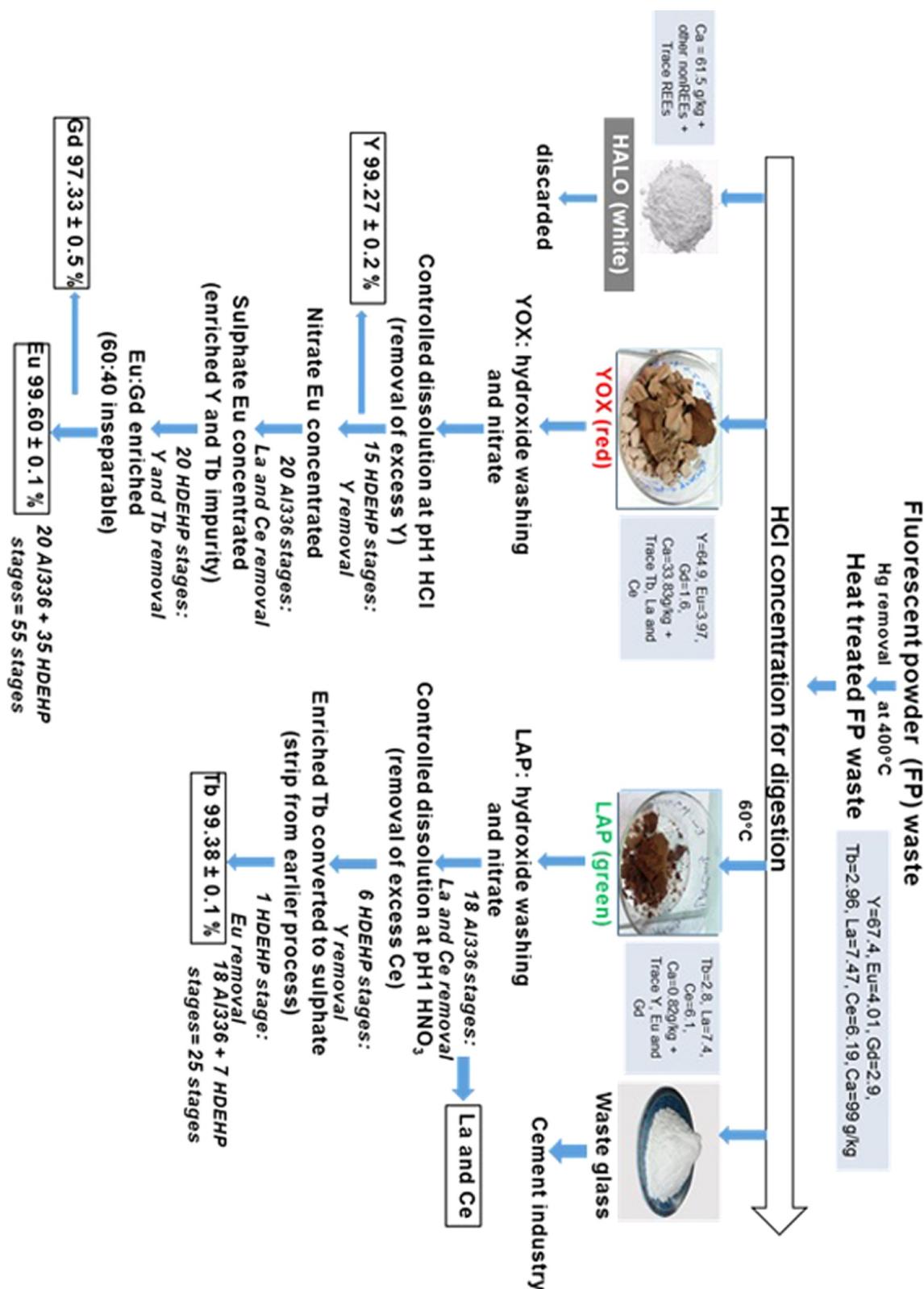


Fig. 5. Process flow sheet for recycling of REEs from end-of-life FP e-waste.

redox-active and do therefore interfere strongly with the further chemical transformations, as well as, with the extractive separations. Therefore, we have chosen the approach of sequential instead of one complete digestion. It offers the advantage of pre-concentration of the REE-containing YOX and LAP phosphors individually and thus also avoiding impurities from the HALO phosphor fraction. It also allowed

nearly complete leaching of the Tb metal from the FP e-waste. The YOX and LAP phosphor leachates were subjected individually, and therefore directly, to extractive steps and wet chemical transformations. The results are shown in Fig. 1, Table 1 and the solid phase in Fig. 5 on top are the output of the leaching process after neutralisation and precipitation. These are separate phosphors such as HALO, YOX and LAP. These

fractions were then used for the extraction procedure to purify the individual REEs as final products. The use of HDEHP in nitrate and sulphate medium for Y selective extraction conditions and that of Al336 in nitrate medium for La and Ce selective conditions allowed a quick (fewer LLE-stages demanding) decontamination of the metal impurities targeted here. With the LLE developments, also practically inseparable mixtures of REEs were encountered, such as Eu and Gd reduction chemistry with appropriate optimisations suitable to the real waste feed. With the process developed here, extra attention was put as far as possible on using commonly available, cheap, environmentally benign chemical ingredients that can also be recycled and reused within the process for achieving lower costs. The process has high scalability using mixer settlers affording great solution processing capacities. Fig. 5 shows the process flowsheet of the process developed here to produce >99% pure Y, Eu, and Tb from end-of-life lamp FP e-waste using simple chemical transformations and extractions. High purity REE output, ease of scaling up and the possibility to recycle the toluene-based solvent systems several times make our process commercially promising.

3.3.4. Comparative cost-benefit analysis of proposed flow sheet

With the digestion process, the sequential leaching steps and contact times were optimised such that the concentrated acid solutions used for the digestion are not completely saturated with the dissolved materials and still have a substantial acidity after that. Therefore, we propose here that they can be used for other FP batches within the same digestion step after adjustment of its acidity by adding a very small, fresh acid quantity. Another approach would be to collect and distil each differently concentrated acid solution and to use it again after appropriate acidity adjustment. However, the latter option would be more expensive and energy-consuming.

The purification approach adopted by us is targeting major impurities emerging along the respective extraction stages specifically. We used the same type of extractant ligand solutions, such as HDEHP and Aliquat 336 in toluene medium, to facilitate its reuse to reduce the cost substantially by using it also for the processing of different metals with both phosphor fractions of interest. We also avoided the neutralisation from the initial YOX leachate and its interconversion of the chloride ions by choosing same anion type for the subsequently performed extraction. However, other interconversion steps are likely inevitable in the pursuit of the purity of the final recycled products. In further R&D, we will try to reduce such neutralisation stages.

The high recovery rates for leaching are replicable, as shown in Table 1. The performance in the extraction system is also replicable based on our results shown in Tables 2 and 3. After removing, the pure REE fraction from extraction loops there is still concentrated mixture remains in feed output solutions (raffinate). However, this does not result in mass losses because such concentrated mixture could be reused in the next processing of the mixture in the same extraction stage with similar REE content. The processing based on heavier or lighter lanthanides could be easily tackled by our extraction system in loops and metal-specific extraction conditions, as shown in the flowsheet without considerable losses. There are excellent Tb leaching methods reported with literature with good economic feasibility (Innocenzi et al., 2016; Van Loy et al., 2017). However, our approach also relies on reduced calcination or high-temperature processing and high purity for Tb to get higher economic incentives from the sales of pure REEs.

4. Conclusions

The sequential leaching approach and process developed here allowed effective (>95%) leaching of Y, Eu, Tb, Ce, and La, at ambient temperatures. To our knowledge, this is one of the first approaches to leach Tb nearly quantitatively without using harsh oxidative acid digestion or alkali fusion methods. The combination of wet chemistry and REE-specific liquid-liquid extraction (LLE) loops developed here

allowed recovering single critical (and other) REEs from fluorescent powder (FP) afforded from end-of-life lamps. The REEs targeted here (Y, Eu and Tb) were achieved in >99% purity with each. (Purities on trace REE basis were derived from experimental, analytical data.) Also, Gd, La, and Ce were recovered in purities of >97%, 80%, and 60%, respectively. The initial sorting of different phosphor fractions by our sequential digestion method also yielded the Tb-rich LAP fraction without much contamination by other metals. Both benefits make our process very efficient. Recycling of Tb as high-value metal would help to make FP recycling process economic and much more viable than before. Notwithstanding these, the presented process is being improved further in terms of overall throughput of pure REEs and minimising the use of acids for digestion and further scale-up trials. The process proposed here would also be a step forward towards a circular economy of REEs.

CRediT authorship contribution statement

Ajay B. Patil: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Validation, Visualization, Writing - original draft, Writing - review & editing. **Mohamed Tarik:** Data curation, Formal analysis, Validation, Writing - review & editing. **Rudolf P.W.J. Struis:** Conceptualization, Data curation, Funding acquisition, Investigation, Project administration, Supervision, Validation, Visualization, Writing - review & editing. **Christian Ludwig:** Conceptualization, Funding acquisition, Supervision, Validation, 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.

The technology described in this article is covered by intellectual property in Patent Application No. WO2019201582A1.

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Supplementary materials

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