



Enhancing rare-earth recovery from lamp phosphor waste

Lourdes Yurramendi^{a,*}, Lukas Gijsemans^b, Federica Forte^b, Jose Luis Aldana^a, Carmen del Río^a, Koen Binnemans^b

^a Energy and Environment Division, TECNALIA, Mikeletegi Pasealekua 2, E-20009 Donostia-San Sebastián, Gipuzkoa, Spain

^b Department of Chemistry, KU Leuven, Celestijnenlaan 200F, PO box 2404, 3001 Leuven (Heverlee), Belgium



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ABSTRACT

In the present work rare-earth recovery was performed from a residue of a hydrometallurgical process based on sulphuric acid leaching of lamp phosphor waste by which the red phosphor $Y_2O_3:Eu^{3+}$ was removed for further recovery. The undissolved residue is rich in lanthanum, cerium and the valuable terbium, present as phosphates and aluminates in the green and blue phosphors. The process here proposed is based on an integrated pyro-hydrometallurgical approach involving a thermal treatment (roasting in the presence of sodium carbonate) aimed at converting rare-earth phosphates into oxides, which can be more easily leached by mineral acids (HCl and H_2SO_4) in a further leaching step. Rare-earth recovery from the leachate was then performed by solvent extraction with the extractant di-(2-ethylhexyl)phosphoric acid, D2EHPA, followed by precipitation with oxalic acid and calcination. 82% Ce, 75% La and 82% Tb were recovered as mixed $La_2O_3 + CeO_2$ oxide (99% purity) and Tb_4O_7 (64% purity).

1. Introduction

Fluorescent lamps represent an interesting source of rare-earth elements (REEs). They consist of a glass tube coated by a fluorescent powder constituted by a blend of red ($Y_2O_3:Eu^{3+}$, YOX), green ($LaPO_4:Ce^{3+}$, Tb^{3+} , LAP; $(Ce,Tb)MgAl_{11}O_{19}$, CAT; $(Gd,Mg)B_5O_{10}:Ce^{3+}$, Tb^{3+} , CBT) and blue ($BaMgAl_{10}O_{17}:Eu^{2+}$, BAM) phosphors. About 40–50% of the powder is composed of the halophosphate (HALO) phosphor, which emits cold white light and does not contain any valuable rare earths (Binnemans et al., 2013). Processes for the recovery of rare earths from spent fluorescent lamps usually involve a sequence of treatment steps which include mercury removal, the recovery of the metallic and glass fractions by crushing and sieving and the isolation of the fluorescent phosphor powder (Binnemans et al., 2013). The high rare-earth content makes the phosphor fraction an interesting source of critical raw materials (CRMs). The European Association of Lighting reported a collection of 37,000 t of lighting products in 2015 by its members (EucoLight, 2017). This amount represents 80% of the total lighting waste electrical and electronic equipment (WEEE) in the 18 countries where they operate. Ambilamp announced the collection of 2627 t of lamps in Spain, obtaining 79.2 t of fluorescent powder after the recycling treatment (Ambilamp, 2017). Considering a similar distribution for the fluorescent lamp phosphors in Europe, this waste fraction will provide up to 87 t of yttrium, 12 t of

lanthanum, 10 t of cerium, 6 t of europium, 4.4 t of terbium and 1.9 t of gadolinium.

Rare-earth recovery from spent fluorescent lamps has been extensively reported in the literature (Belardi et al., 2014; Dupont and Binnemans, 2015; Tunsu et al., 2014; Tunsu et al., 2015; Innocenzi et al., 2016; Innocenzi et al., 2017; Innocenzi et al., 2018; Ippolito et al., 2017). Most of these studies focus on the recovery of yttrium and europium from the red phosphor, whilst a comprehensive approach for the valorisation of the whole waste fraction is still a challenge. Yttrium and europium are present in the red phosphor (YOX) in oxide form so their leaching at mild acidic solutions is easy even at room temperature as reported in the literature (Tunsu et al., 2016a, 2016b). In contrast, lanthanum, cerium and the highly valuable element terbium are present in the lamp phosphor waste as phosphates and aluminates which are very resistant to chemical attack (Binnemans and Jones, 2014). The dissolution of the LAP phosphor can be enhanced by a mechanochemical pretreatment step (Van Loy et al., 2017). Recently a solvo-metallurgical process was developed for terbium, lanthanum and cerium recovery from the LAP phosphor which makes use of concentrated methanesulphonic acid as leaching agent (Gijsemans et al., 2018).

In this paper, we propose an integrated pyro-hydrometallurgical approach for the recovery of lanthanum, cerium and terbium from spent fluorescent lamps. A thermal treatment, based on roasting in the

* Corresponding author.

E-mail address: lourdes.yurramendi@tecnalia.com (L. Yurramendi).

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presence of sodium carbonate (Na_2CO_3), was applied to the residue obtained from the HydroWEEE process (Innocenzi et al., 2016). This residue is of particular interest due to the presence of the valuable element terbium, which is mainly present in the LAP phosphor and which is not dissolved by sulphuric acid leaching in the above-mentioned hydrometallurgical process. By roasting, the rare-earth phosphates in the leaching residue are converted into the corresponding oxides, thus improving the extraction in a further leaching step with mineral acids. Rare-earth recovery from the leachate was then done by solvent extraction with di-(2-ethylhexyl)phosphoric acid (D2EHPA), followed by precipitation with oxalic acid and calcination to the pure oxide.

2. Materials and methods

2.1. Materials and chemicals

The lamp phosphor waste powder was supplied by Relight srl, while the leaching residue was obtained at lab scale using the operating conditions of the HydroWEEE process (Innocenzi et al., 2016). Sodium carbonate ($\geq 98\%$ purity) and hydrochloric acid (37%) were provided by Panreac and sulphuric acid (98% and 96%) by both Panreac and Acros Organics. Xylene (mixture of isomers, $\geq 98.5\%$ purity) and Triton X-100 were purchased from Acros Organics, and D2EHPA (95% purity) from Sigma-Aldrich. Oxalic acid ($\geq 99.9\%$) and the standard solutions ($1000 \mu\text{g mL}^{-1}$ Ga, Dy and Pr) were obtained from Merck. The silicone solution in isopropanol was purchased from SERVA Electrophoresis GmbH. Water was always of ultrapure quality, deionized to a resistivity of $18.2 \text{ M}\Omega \text{ cm}$ with a Sartorius Arium Pro ultrapure water system. All chemicals were used as received without any further purification.

2.2. Analytical techniques

Chemical characterization of the lamp phosphor waste was performed by acid digestion according to the 3052 EPA method (US EPA, 1996), followed by the analysis of the obtained solution by Inductively Coupled Plasma/Optical Emission Spectrometry (ICP-OES) using an axial Agilent VISTA-MPX. X-ray Diffraction (XRD) analyses were carried out on a Bruker D8 advance X-ray diffractometer with a $\text{CuK}\alpha$ source and a scintillation detector from 15° to $90^\circ 2\theta$ using a step width of 0.030° and 1 s per step. Phase identification was performed with EVA software. A Jeol SM-5910LV apparatus was used for Scanning Electron Microscopy (SEM) analysis. The images were taken in high vacuum mode with 20 kV voltage and a solid-state backscatter detector (SSD-BSD). Oxford Instruments INCAx-act Energy Dispersive X-ray detector (EDS) was used for chemical semi-quantitative analysis. The sample was embedded under vacuum conditions in epoxy resin, pre-polished with abrasive powder and coated with a thin layer of graphite.

Metal concentration in solution was determined by total reflection X-ray fluorescence spectroscopy (TXRF) with a Bruker S2 Picofox TXRF spectrometer equipped with a molybdenum source (Riaño et al., 2016). Polypropylene microtubes were filled with a certain amount of the sample. An appropriate internal standard was added in order to reduce the effects caused by secondary X-rays absorption. This means the internal standard has an X-ray fluorescence energy as close as possible but, at the same time, not overlapping with the element to be determined. Samples were afterwards diluted to 1 mL with Triton-X 100 solution (5 vol%) (Regadío et al., 2017). After shaking the samples on a vibrating plate (IKA MS 3 basic), a small droplet ($1.5 \mu\text{L}$) was put on a quartz carrier, previously treated with a silicone-isopropanol solution to avoid spreading of the droplet. The quartz carriers were then dried for 30 min at 60°C prior to analysis. Each sample was measured for 500 s (at 50 kV voltage and $600 \mu\text{A}$ current).

2.3. Leaching of lamp phosphor waste

A first leaching step was performed on the lamp phosphor waste to produce a residue with a considerable amount of residual rare earths in the form of phosphates, to be used as the starting material for the experiments of the present research. Leaching tests were performed in 0.5 L and 2 L jacketed reactors (Scharlab) equipped with a heating system (PolyScience SD07R-20R) using H_2SO_4 2.65 mol L^{-1} at 70°C for 2 h with a solid-to-liquid ratio (S/L) of 155 g L^{-1} . A hand vacuum pump and a lab filtration system were used to filter the solutions from both processes. Both the leachates and the residues were analysed by ICP-OES, after digestion based on the EPA 3052 method (US EPA, 1996).

2.4. Roasting and leaching of the roasted residue

The roasting tests were performed in a muffle furnace using 60 mL alumina crucibles and 25 g of sample and by varying the reaction time (1–3 h), the temperature ($200\text{--}900^\circ\text{C}$) and the waste-to-sodium-carbonate weight ratio ($R = 1:0.5, 1:1$ and $1:3$). The mass change occurring before and after roasting was calculated according to Eq. (1):

$$\text{Mass loss (\%)} = \frac{W(\text{sample before roasting}) - W(\text{sample after roasting})}{W(\text{sample before roasting})} \times 100 \quad (1)$$

The roasted products were first milled below $250 \mu\text{m}$ by an Ultra Centrifugal Mill ZM 200 and then washed with distilled water. The washing step was carried out at room temperature for 2 h, 200 rpm stirring and $S/L = 15/100$. The same amount of water was used for washing the filter cake. The filtrate was analysed by ICP-OES to verify the absence of rare earths.

The residue, once roasted and washed, was leached with mineral acids (HCl and H_2SO_4). Water washing and leaching processes were performed in a jacketed reactor, as described above.

2.5. Solvent extraction and precipitation

Rare-earth recovery from the leachate obtained in the pyro-hydrometallurgical process was investigated by solvent extraction with D2EHPA. Extraction tests were performed in glass vials placed in a mechanical shaker (TMS-200 Turbo Thermoshaker). Several operating parameters were tested, such as the dilution of the leachate in water, the extractant concentration (50–100 vol% D2EHPA in xylene) and the organic-to-aqueous volume ratio ($O/A = 0.2\text{--}1$). The contact time and temperature were set at 1 h and 25°C , respectively. The organic phase was separated from the leachate by centrifugation and the metal concentration in the raffinate was analysed by TXRF spectroscopy in order to calculate the percentage extraction % E which can be expressed, for phase ratio equal to 1, according to Eq. (2):

$$\%E = \frac{[M]_{\text{org}}}{[M]_i} \times 100 = \frac{[M]_i - [M]_f}{[M]_i} \times 100 \quad (2)$$

where $[M]_i$ is the metal concentration in the feed, $[M]_{\text{org}}$ is the metal concentration in the organic phase and $[M]_f$ is the metal concentration in the aqueous phase after extraction.

REs recovery from the loaded organic phase was then performed by precipitation with oxalic acid. The loaded organic phase was contacted with a water solution of oxalic acid (1.5 mol L^{-1}) in glass vials on a mechanical shaker for 40 min. After centrifugation, the precipitation efficiency was determined by measuring the metal concentration in the organic phase by TXRF spectroscopy. The obtained mixed oxalates were then converted into the corresponding oxides by calcination ($T = 700^\circ\text{C}$, $t = 4 \text{ h}$).

Table 1
REEs content of the lamp phosphor waste.

	Concentration, wt%
Y	6.29
La	0.90
Ce	0.74
Eu	0.43
Tb	0.32
Gd	0.14

3. Results and discussion

3.1. Characterization

The rare-earth content of the lamp phosphor waste is reported in Table 1. XRD and SEM-EDS analysis (not reported here) allowed identifying the rare earths as yttrium europium oxide, magnesium cerium terbium aluminium oxide, magnesium cerium gadolinium aluminium oxide and lanthanum terbium cerium phosphate. Other compounds such as glass and fluorapatite were identified as major components. This composition is in accordance to that described in the literature (Binnemans and Jones, 2014; Innocenzi et al., 2018).

3.2. Recovery process flow sheet

Fig. 1 shows the proposed flowsheet for enhancing the recovery of the rare earths contained in the lamp phosphor waste. The treatment was applied to the residue (sample B) obtained from a first leaching (step 1) of the lamp phosphor waste (sample A). A roasting step was then applied (step 2), aimed at converting the REE-phosphates into oxides, thus increasing their leachability (step 4). REEs recovery from the leachate was then performed through solvent extraction (steps 5 and 7), followed by precipitation with oxalic acid (steps 8 and 10) and calcination (steps 9 and 11). The flow sheet includes extra steps such as washing of the roasted residue (step 3) and dilution of the raffinate coming from the first solvent extraction step (step 6). Each of these steps will be discussed in detail in the next paragraphs.

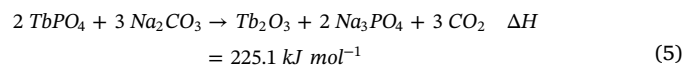
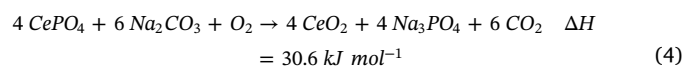
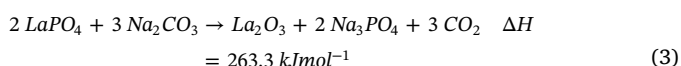
The figure also includes the mass balance of La, Ce and Tb for the main outputs (Ce–La mixed oxides and Tb oxide) in the optimised experimental conditions cited in the conclusions.

3.3. Leaching of lamp phosphor waste

A first leaching step using sulphuric acid performed on sample A produced a residue (sample B) which composition is reported in Table 2. The residue still contained REEs showing concentrations similar to those of the initial lamp phosphor waste for Ce, La and Tb. The other REEs (Y, Eu and Gd) were only present at trace level. This indicates that the first leaching is very effective for recovery of the elements present in YOX phosphor, but not for those present as phosphate or complex oxide forms. These results were confirmed by ICP-OES analysis of the leachate produced in the first leaching step (sample C, step 1), as shown in Table 2:

3.4. Roasting

In order to maximize the REEs recovery (mainly La, Ce and Tb) from the waste, sample B was roasted and leached again. A roasting process with sodium carbonate was proposed in order to convert the REE-phosphates into REE-oxides, based on the following reactions:



The values of enthalpies indicate that the three reactions are endothermic and need energy to take place. To select the temperature range for the roasting tests, the thermodynamic HSC 9 software was used as starting point. Fig. 2 shows the equilibrium phase diagram of the REE-phosphates at experimental conditions (sodium carbonate excess and air) when the temperature is increased from 200 °C up to 1200 °C.

The equilibrium phase diagram shows that, under the experimental conditions, the conversion of TbPO₄ into phosphate starts at 300 °C and that the reaction is completed towards the formation of terbium (III,IV) oxide above 500 °C. Respect to LaPO₄ behaviour, La₂O₃ begins its formation at 550 °C and the transformation is completed at 900 °C. In the case of CePO₄, the equilibrium is displaced towards the oxide over the entire temperature range evaluated. Then, 200 °C, 600 °C and 900 °C were selected as reference temperatures to carry out the roasting tests.

The transformation of REE-phosphates into the corresponding REE oxides during the roasting process is difficult to confirm by XRD analysis of the roasted product due to the low intensity of the REE-oxides characteristic peaks. However, when roasting occurs, carbon dioxide is released, giving a mass loss which increases as the reactions take place. Consequently, this mass loss (cfr. Eq. (1)) can be used as a measurement of the feasibility of the reactions. Several tests varying the reaction time and the roasting temperature were carried out while sample-B-to-sodium-carbonate mass ratio (R) was kept constant (1,1). Table 3 shows the results obtained for sample B mass loss in each experiment.

The mass of the samples treated at 900 °C was reduced drastically, while the mass of the samples treated at lower temperatures did not decrease so significantly, as predicted by the equilibrium phase diagram. A residence time of 1 h was sufficient to complete the roasting reactions at the studied temperatures. Consequently, the sample roasted at 900 °C during 1 h (sample D) was selected for further research. If reaction occurs, leachability of the REEs in a subsequent leaching step with mineral acids should clearly be improved. Thus, analysis of the leached products was established as an indirect method to evaluate the performance of the roasting process. The chosen sample was washed with water (step 3) to extract the sodium phosphate formed and the excess of sodium carbonate used in the roasting step. The analyses carried out on the washing filtrate (sample E) indicated that no REEs were leached out during the washing: concentrations of Ce, La and Tb in the filtrate were < 0.1 mg L⁻¹ (< 0.02% regarding the Ce + La + Tb content in leaching residue sample B). Therefore, the REEs remained in the roasted product (sample F).

Sodium carbonate addition was investigated at ratios from 0.5 up to 3 regarding the leaching residue (sample B) at the selected temperature. Ce, La and Tb recovery were obtained after sulphuric acid leaching of sample F (the roasted and washed residue). The leaching conditions were: H₂SO₄ 2.65 mol L⁻¹, T = 70 °C, t = 2 h, S/L = 155 g L⁻¹. Table 4 shows the concentration of REEs in the leachates and the residues as well as the calculated recovery efficiency for these REEs.

Higher REEs concentration values in the leachate H, and thus higher recovery yields, are an indication of a better roasting performance. The results show that the efficiency of the roasting decreased when the amount of sodium carbonate used for the roasting increased. The La and Tb recovery was near 60% for the optimum mass ratio studied (R = 1:0.5), while Ce recovery was poor for all the tests. Based on those experiments it was concluded that the best roasting results were found for the following process parameters: R = 1:0.5, 900 °C and 1 h residence time.

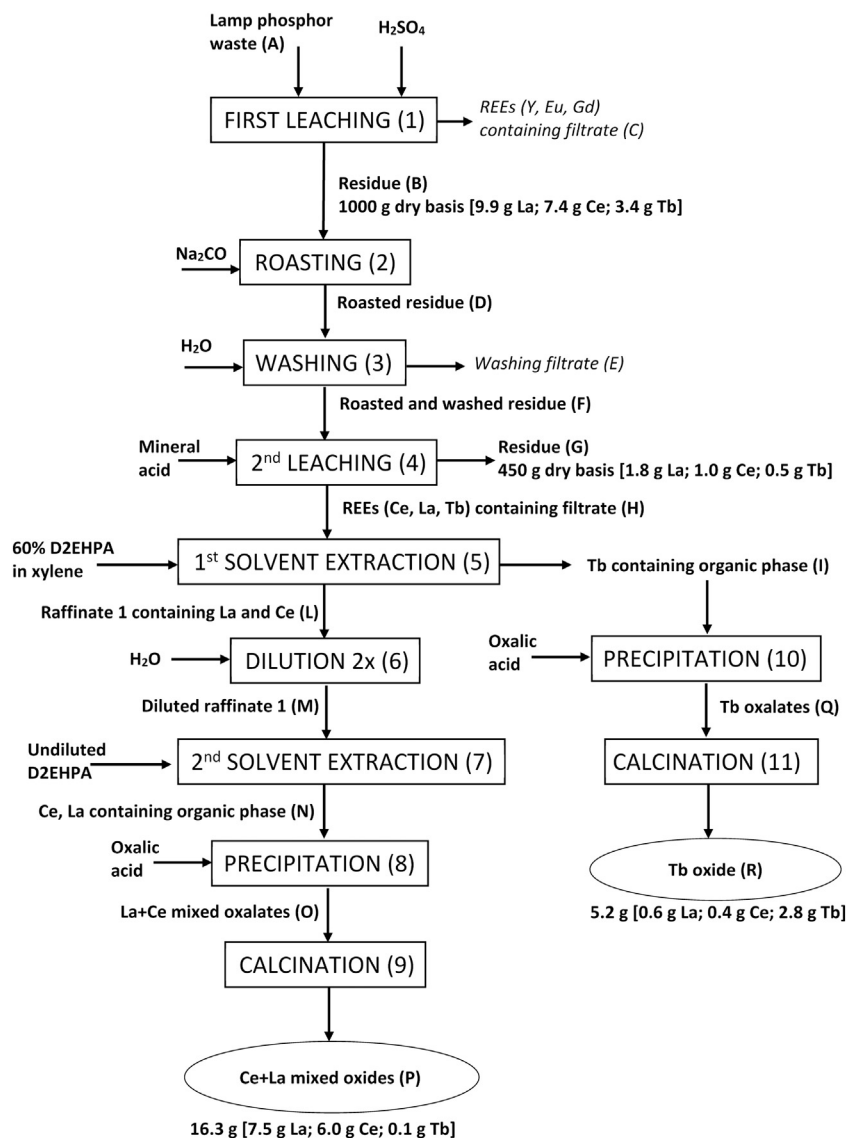


Fig. 1. Pyro-hydro process proposed to improve the REEs recovery from lamp phosphor waste.

Table 2

REEs content of the leaching residue and leaching efficiency for the first leaching step (step 1) performed on sample A.

	Sample B content, wt%	Leaching efficiency, %
Y	0.05	99.3
La	0.99	0.3
Ce	0.74	5.7
Eu	0.05	91.0
Tb	0.34	9.0
Gd	0.04	76.8

3.5. Leaching of the roasted residue

After the roasting process, the next objective was to enhance the Ce, La and Tb leaching from the roasted residue by leaching with two mineral acids, namely HCl and H₂SO₄ at three different experimental conditions reported in Table 5. In test (c), the S/L ratio was reduced to 10 g L⁻¹ and the temperature and residence time were increased when comparing with test (a), both involving leaching with H₂SO₄. This solid-to-liquid ratio is too small to be industrially feasible, but it was used to determine the maximum recovery for Ce, La and Tb that could be obtained by leaching with sulphuric acid, which is a more economic

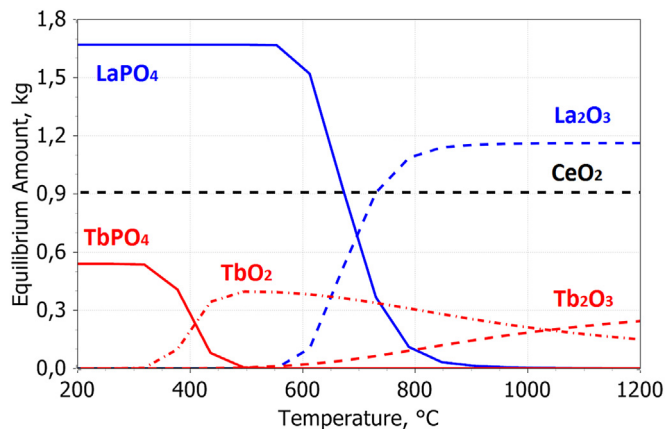


Fig. 2. Equilibrium phase diagram for the conversion of REE phosphate into REE oxide upon roasting with Na₂CO₃ in air atmosphere.

leaching agent than hydrochloric acid.

Table 6 shows the leachate and residue compositions obtained at the selected conditions for both leaching agents. Analysis of the leachates

Table 3
Mass loss of sample B (wt%) when roasting at a mass ratio $R = 1:1$.

T (°C)	Time (h)	Mass loss (wt%)
200	1	4.0
200	3	4.2
600	1	5.6
600	3	6.1
900	1	35.8
900	3	38.1

shows a significant improvement for Ce, La and Tb recovery when leaching is carried out with 6 mol L^{-1} HCl (Table 6, b) compared to H_2SO_4 (Table 6, a). The analyses of the residues (sample G) confirm the result obtained for the leachates, namely that HCl leaching results in the lowest concentration for Ce, La and Tb in the residue (Table 6, b). The results did not improve if more aggressive leaching conditions (*i.e.* higher temperature) were used (Table 6, c).

The leaching percentages for Ce, La and Tb were calculated based on the experimental results from the leachate in Table 6 and are presented in Fig. 3. HCl leaching percentages efficiency of 86%, 81% and 85% for Ce, La and Tb respectively (red), while only 14% Ce, 55% La and 63% Tb were recovered by H_2SO_4 leaching (black) at the same solid to liquid ratio. The recoveries for H_2SO_4 leaching increased to 81% for both La and Tb when the S/L ratio was reduced from 150 to 10 g L^{-1} (blue). Ce remained difficult to dissolve: the maximum recovery yield (53%), obtained with working conditions that are not industrially feasible (S/L 10 g L^{-1}), was even lower than those obtained for leaching with HCl at much higher S/L. As reported in Table 7, besides the elements of interest (Ce, La and Tb), both leachates showed the presence of Y and Eu impurities. This is due to the fact that during the HydroWEEE process, the HALO phosphor is dissolved together with the red phosphor YOX; phosphate ions are brought into solutions and react with Y (III) and Eu(III) ions released upon dissolution of the YOX, giving insoluble yttrium and europium phosphates, which are, thus, found in the leaching residue (sample B).

3.6. Solvent extraction

Filtrates (sample H) from sulphuric and hydrochloric acid leaching carried out at S/L 150 g L^{-1} (conditions (a) and (b) from Table 5) were selected to be further treated in the solvent extraction step (step 5). Solvent extraction was performed in order to separate the valuable element terbium from lanthanum and cerium. To this aim, the acidic extractant di-(2-ethylhexyl)phosphoric acid (D2EHPA) was selected, which was tested both in its undiluted form and diluted in xylene (Batchu and Binnemans, 2018; Gergoric et al., 2017; Zhang et al., 2016; Sato, 1989). The use of undiluted D2EHPA is normally avoided due to gel formation in the organic phase. Gel formation can be explained by the aggregation of metal-ligand complexes and subsequent polymerisation. Therefore, D2EHPA is often diluted in aromatic, aliphatic or mixed aliphatic-aromatic diluents. It was reported that aromatic diluents suppress the formation of emulsions or gels. It was also reported that high loadings of the organic phase are responsible for gel formation (Yurtov and Murashova, 2007). In our case, due to the relatively low concentrations of La, Ce and Tb in the leachates (Table 6), the use of

Table 4
Influence of the product-(sample F)-to- Na_2CO_3 mass ratio (R) on the concentrations of Ce, La and Tb in the H_2SO_4 leachate after roasting (at 900°C , 1 h).

Element	Leachate (mg L^{-1})			Residue (wt%)			Recovery (%)		
	R 1:0.5	R 1:1	R 1:3	R 1:0.5	R 1:1	R 1:3	R 1:0.5	R 1:1	R 1:3
Ce	46	10	6	1.10	1.34	1.23	14	3	2
La	234	210	125	0.77	0.79	1.01	55	51	31
Tb	95	78	53	0.23	0.26	0.36	63	54	35

Table 5
Leaching tests carried out on the roasted residue for three different operating conditions (a), (b) and (c).

Parameter	Leaching test		
	(a)	(b)	(c)
Temperature (°C)	70	70	85
Residence time (h)	2	2	3
Stirring speed (rpm)	200	200	200
Leaching agent	2.65 mol L^{-1} H_2SO_4	6 mol L^{-1} HCl	2.65 mol L^{-1} H_2SO_4
S/L (g L^{-1})	150	150	10

Table 6
Concentrations for Ce, La and Tb in the leachates (mg L^{-1}) and the residues (wt %) obtained for leaching tests carried out with operating conditions (a) H_2SO_4 2.65 mol L^{-1} , S/L 150 g L^{-1} , 70°C (b) 6 mol L^{-1} HCl, S/L 150 g L^{-1} , 70°C and (c) H_2SO_4 2.65 mol L^{-1} , S/L 10 g L^{-1} , 85°C .

Element	Leachate (mg L^{-1})			Residue (wt%)		
	(a) H_2SO_4	(b) HCl	(c) H_2SO_4	(a) H_2SO_4	(b) HCl	(c) H_2SO_4
Ce	46	264	15	1.10	0.23	1.39
La	234	331	28	0.77	0.39	0.64
Tb	95	129	11	0.23	0.12	0.26

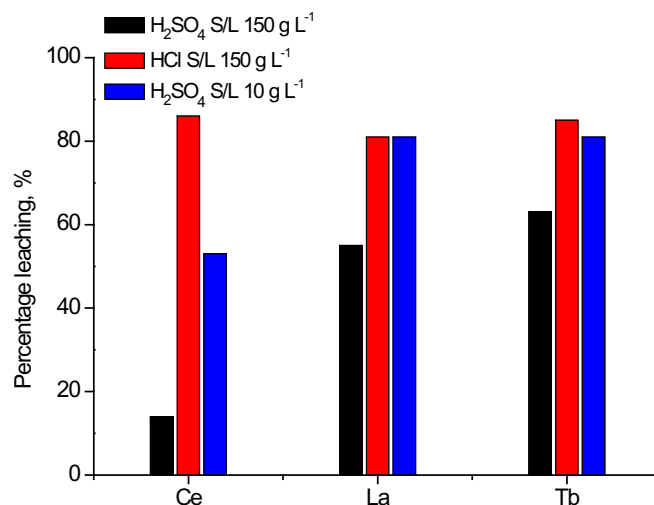


Fig. 3. Percentage leaching for Ce, La and Tb from the roasted and washed residue (sample F). Leaching tests carried out with operating conditions (a), (b) and (c) from Table 5.

undiluted D2EHPA was considered a viable option, since the system is far away from saturation. Table 8 shows the results of the solvent extraction tests (step 5) from the HCl and H_2SO_4 leachate with D2EHPA as a function of the leachate dilution. Due to the leachate dilution, chloride and sulphate concentrations as well as the initial pH were not constant in the above mentioned tests. The dilution was performed in order to lower the acidity of the aqueous phase, thus improving the

Table 7

Impurities (in mg L⁻¹) in the leachate obtained after leaching at 70 °C temperature, 2 h residence time and 200 rpm stirring using (a) 2.65 mol L⁻¹ H₂SO₄ and S/L 150 g L⁻¹, (b) 6 mol L⁻¹ HCl and S/L 150 g L⁻¹.

Impurity (mg L ⁻¹)	(a) H ₂ SO ₄	(b) HCl
Y	26	23
Eu	15	13
Gd	10	9

Table 8

Percentage extraction from the HCl and H₂SO₄ leachate with undiluted D2EHPA as a function of the leachate dilution (O/A = 1/1, T = 25 °C, t = 1 h).

Leachate	Dilution factor	Percentage extraction (%)					
		La	Ce	Eu	Gd	Tb	Y
HCl							
	1	20	44	94	100	100	100
	2	83	93	69	100	100	100
	4	98	99	74	100	100	100
H ₂ SO ₄							
	1	47	92	87	100	100	100
	2	84	100	83	100	100	100
	4	97	100	86	100	100	100

extraction performance: since D2EHPA is an acidic extractant, an increase in the pH by dilution of the acid in the leachate, leads to an increase of metal extraction (Gijsemans et al., 2018).

It was found that the selectivity of Tb over Ce/La is very low for extraction from the H₂SO₄ leachate. More promising results were, however, obtained for extraction from the HCl leachate. It is known from the literature that differences in extraction occur for feed solutions containing different anions and different concentrations due to differences in extraction mechanism (cation exchange *versus* solvating), speciation in the aqueous phase and speciation in the organic phase (Sato, 1975; Sato and Ueda, 1973). In particular, it was found that the highest selectivity was obtained by using the undiluted leachate as feed (pH = -0.8, [Cl⁻] = 6 mol L⁻¹). These conditions were further optimised for the selective extraction of Tb over Ce/La. The concentration of D2EHPA was varied by using xylene as a diluent, as shown in Fig. 4. The selectivity of Tb over Ce/La significantly increased by lowering the extractant concentration. However, a small co-extraction of Ce/La did occur. Y, Gd and Eu were co-extracted even at the lowest D2EHPA

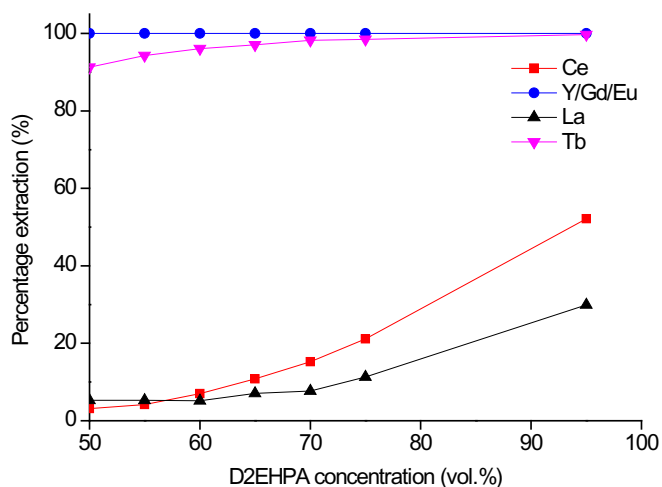


Fig. 4. Percentage extraction from the undiluted HCl leachate as a function of the D2EHPA concentration (O/A = 1/1, T = 25 °C, t = 1 h, D2EHPA diluted in xylene).

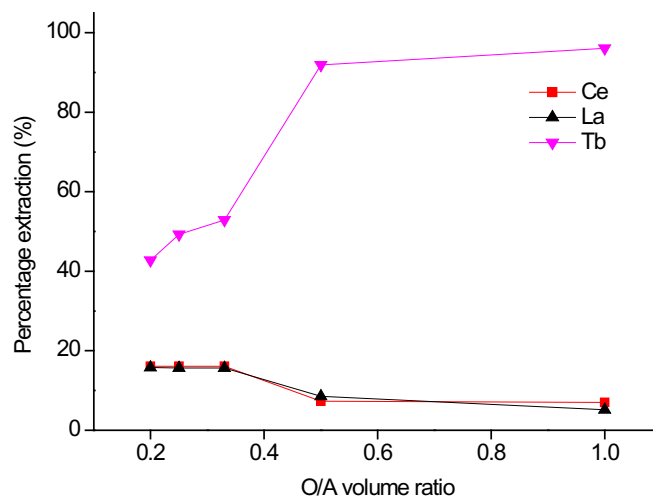


Fig. 5. Percentage extraction from the undiluted HCl leachate as a function of the O/A volume ratio (T = 25 °C, t = 1 h, 60 vol% D2EHPA in xylene).

concentration (50 vol%). To avoid co-extraction of these elements, the concentration of D2EHPA was further decreased, which resulted in a significant loss of Tb. The optimal concentration for Tb extraction was, thus, set at 60 vol% D2EHPA, where the selectivity of Tb over Ce/La was the highest.

Fig. 5 shows the results of the solvent extraction tests as a function of the aqueous-to-organic volume ratio. A phase ratio of 1 was found to be optimal since this resulted in the highest purity and percentage extraction of Tb. Complete co-extraction of Y/Gd/Eu occurred for all extraction results shown in Fig. 4. A single stage extraction was chosen because already 96.1% of Tb was extracted and extra stages would result in a higher concentration of impurities. After Tb extraction, only Ce, La and a small impurity of Tb were present in the raffinate. From Table 8, it can be seen that already a high percentage extraction of Ce/La can be obtained by diluting the leachate two times (pH = -0.5, [Cl⁻] = 3 mol L⁻¹) with ultrapure water and using undiluted D2EHPA as extractant. Further dilution of the leachate did not increase the percentage extraction significantly. For further optimisation of this second extraction step, the O/A ratio was varied and multiple extraction stages were tested. The O/A ratio was varied from 0.2 to 1.0, but using a phase ratio of 0.5 already resulted in a decrease in the percentage extraction of La and Ce from 83% and 93% to 37% and 40% respectively. Therefore, a two-stage extraction using undiluted D2EHPA and an O/A = 1 appeared to be the best condition for La/Ce extraction. The total percentage extraction of La and Ce after two stages resulted to be 93% and 95%, respectively. Alternatively, to improve the percentage extraction, the equilibrium pH can be optimised by addition of NaOH to the leachate prior to extraction, or by using partially saponified D2EHPA (Na-D2EHPA).

In conclusion, after solvent extraction, two different extracts are obtained: a 60 vol% D2EHPA extract containing Tb, Y, Eu and Gd plus a small amount of Ce and La and an undiluted D2EHPA extract containing mainly Ce and La with a small Tb impurity.

3.7. REEs recovery by precipitation

REEs recovery from these two organic phases was performed by precipitation with an oxalic acid solution (steps 8 and 10). Due to the high acidity of D2EHPA, to ensure quantitative REEs precipitation an excess of oxalic acid with a high concentration was necessary. For this step, a solution of 1.5 mol L⁻¹ oxalic acid was chosen and the phase ratio was optimised. The minimal organic-to-aqueous phase ratio to obtain quantitative precipitation was found to be 20. Quantitative precipitation of La and Ce was achieved, whilst the Tb precipitation

Table 9
Composition of the calcined terbium oxide.

Element	wt%
Tb	63.7
Y	10.8
Ce	8.6
La	7.7
Eu	5.4
Gd	3.8

yield was 94%. Both oxalates $(\text{La}_2(\text{C}_2\text{O}_4)_3 + \text{Ce}_2(\text{C}_2\text{O}_4)_3)$ and $\text{Tb}_2(\text{C}_2\text{O}_4)_3$ were then calcined for 4 h at 700 °C (step 9 and 11). The composition of terbium oxide (Tb_4O_7), calculated by measuring the extract concentration before and after precipitation, is given in Table 9. Due to the fact that the initial content of cerium and lanthanum in the HCl was quite high compared to the terbium content (Table 9) and a small percentage of lanthanum and cerium were co-extracted, the final purity of the obtained terbium oxide was only 64%. The purity of the obtained product could be improved by a multi-step solvent extraction process; however this investigation is beyond the scope of this paper. The purity of the mixed lanthanum and cerium oxide ($\text{La}_2\text{O}_3 + \text{CeO}_2$) was, instead, much higher (lanthanum, cerium and terbium content resulted to be equal to 55.5%, 43.5% and 1%, respectively). The mixed ($\text{La}_2\text{O}_3 + \text{CeO}_2$) had a purity of 99%.

4. Conclusions

If the leaching step is performed on the residue as such or on the starting fluorescent lamp powder, very long leaching times with concentrated acids are normally required to dissolve the REE-phosphates. The proposed process allows the recovery of Tb, La and Ce from a fluorescent lamps leaching residue by a combination of pyro- and hydrometallurgical technologies. Roasting with sodium carbonate ($T = 900$ °C) improved the REEs percentage leaching by converting the rare-earth phosphates into oxides. Leaching with HCl was more efficient than leaching with H_2SO_4 , reaching recovery yields of 86% for Ce, 81% for La and 85% for Tb. Due to its high economic value, terbium is the main element to be recovered and the use of HCl as lixiviant improves its recovery. However, the leaching step is cheaper when H_2SO_4 is used and also technical and environmental issues must be taken into account (such as corrosion problems when HCl is used as leaching agent and the higher environmental impacts during its production). Recovery of REEs from the HCl leachate was investigated by solvent extraction with D2EHPA in xylene. 96% of Tb was extracted in a single stage with 60% D2EHPA, with limited co-extraction of Ce and La. In the second extraction step, 93% La and 95% Ce were extracted in two stages with undiluted D2EHPA. Finally, the REEs were recovered from the loaded organic phases by precipitation with oxalic acid, followed by calcination to the corresponding oxides. The global recovery efficiencies achieved with the proposed process were 82%, 75% and 82% for Ce, La and Tb, respectively. The main advantages of the integrated process are represented by the mild conditions that can be used during the leaching step (2 h, 70 °C) to achieve a high leaching efficiency.

Declarations of interest

None.

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