Rare earth elements recovery from E-wastes by solvent extraction and supported liquid membrane processes

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“Life is not easy for any of us. But what of that? We must have perseverance and above all confidence in ourselves. We must believe that we are gifted for something and that this thing must be attained”

Marie Curie
Acknowledgments

It seems like yesterday, when I had the possibility to take part as a researcher in an investigation group in Vilanova i la Geltrú. After three years doing the PhD, writing the acknowledgments is a real proof that everything is possible if you never give up. I remember each moment, since the satisfaction when I received the first journal editor email accepting a manuscript to every meeting done in these years.

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I sincerely think that this thesis would not be the same without everybody’s support.
Abstract

Nowadays, rare earth elements (REEs) have gained importance due to their indispensable and critical use in many high-tech industries like hybrid cars, fluorescent lamps, flat screen televisions, mobile phones, disc drives and wind turbines. Since these metals are needed to supply the required functionality in advanced technologies development and the lack of alternative materials, the REEs recovery from urban mining seems to be promising. Moreover, being the ores mines and their strip mining to REEs production placed in a few specific countries such as China, United States and Australia, the stable supply of such metals is becoming a concern. The absence of economical and operational primary deposits in other territories is making many countries consider the REEs recycling from pre-consumer scrap, industrial residues and end-of-life products. However, about only 12.5% of e-waste is currently being recycled for all metals due to technological problems, inefficient collection and a lack of incentives and pilot-scale feasible testing to be industrially implemented.

In this thesis, different routes to recover and separate these elements from end-of-life products like NdFeB magnets and fluorescent lamps have been developed considering the relevance of these applications in the REEs field and the feasibility of the complete industrial implementation.

Regarding NdFeB magnet, it was demonstrated that Nd, the most REE representative component found in magnet wastes, was separated from an Nd/Tb/Dy mixture by using solvent extraction process and intensified processes like liquid membranes in flat sheet configuration. To avoid the inter-step pH conditioning in a continuous industrial process when cationic extractants are used, an ionic liquid such as Primene 81R·Cyanex 572 was proposed in an industrial counter-current extraction process. The results disclosed that two stages were required to separate Nd from the mixture with a purity of 99.7% removing ≥99% of the initial Tb and Dy. Although both cationic extractants, Cyanex 272 and Cyanex 572, were able to separate the Nd, the transport through the liquid membrane using the former is about 35% slower than using Cyanex 572. Hence, to obtain similar results to those got with Cyanex 572, the membrane area or the working time should be increased when Cyanex 272 is used.

REEs from fluorescent lamp wastes were recovered and selectively separated with purities ≥99.9% by using a process that can be industrially implemented and combines acidic leaching treatments, liquid membranes and cross-flow solvent extraction process. Two successive acidic leachings were needed: (L1) to remove the Ca avoiding its precipitation in following stages of the process and (L2) to recover the REEs present in the waste. Unfortunately, a REEs amount, mainly Y and Eu, was also dragged in the liquid fraction from L1 and these REEs were recovered using Cyanex 923 as carrier by a hollow fibre renewal liquid membrane module. Furthermore, a transport modelling was developed to foresee the permeability
coefficient values for Y and Eu depending on the organic solution viscosity and the membrane characteristic parameters. A mathematical modelling was developed using D2EHPA to predict the Y/Eu/Ce mixture extraction behaviour to investigate the optimal separation conditions of the REEs found in the leachate coming from the L2. Once the REEs behaviour was studied in the extraction modelling, the recovery and separation of the REEs were experimentally achieved obtaining purities ≥99% by four stages cross-flow solvent extraction process using two ionic liquids, Primene 81R-D2EHPA and Primene 81R-Cyanex 572.

In this sense, REEs recycling processes of both wastes promote potential circular economy based on solutions where a waste is turned into a resource.
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Glossary

AIMCo | Aluminium-Nickel-Coalt
BLM | Bulk liquid membranes
CRT | Cathode ray tube
Cyanex 272 | Bis(2,4,4-trimethylpentyl)phosphinic acid
Cyanex 572 | Mixture of phosphinic and phosphonic acids
Cyanex 923 | Mixture of four trialkylphosphine oxides
D2EHPA | Bis(2-ethylhexyl)phosphoric acid
$E$ | Solvation extractant
ELM | Emulsion liquid membranes
FSSLM | Flat sheet supported liquid membrane
$HA$ | Extractant acid
HFRLM | Hollow fibre renewal liquid membrane
HFSLM | Hollow fibre supported liquid membrane
$HR$ | Chelating extractant
HREEs | Heavy rare earth elements
IL | Ionic liquid
IUPAC | International Union of Applied and Pure Chemistry
L1 | First leaching stage
L2 | Second leaching stage
LM | Liquid membranes
LREEs | Light rare earths elements
Me$^{3+}$ | Any rare earth metal
MP-AES | Microwave plasma atomic emission spectroscopy
NdFeB | Neodymium-Iron-Boron
Primene 81R | Trimethyloctyl amine
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluorethylene</td>
</tr>
<tr>
<td>REEs</td>
<td>Rare earth elements</td>
</tr>
<tr>
<td>REMs</td>
<td>Rare earth metals</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SLM</td>
<td>Supported liquid membrane</td>
</tr>
<tr>
<td>SmCo</td>
<td>Samarium-Cobalt</td>
</tr>
<tr>
<td>SSC</td>
<td>Solid-state-chlorination</td>
</tr>
<tr>
<td>SX</td>
<td>Solvent extraction</td>
</tr>
<tr>
<td>TBP</td>
<td>Tributylphosphate</td>
</tr>
<tr>
<td>USGS</td>
<td>U.S. Geological Survey</td>
</tr>
<tr>
<td>VOCs</td>
<td>Volatile organic compounds</td>
</tr>
<tr>
<td>WEEE</td>
<td>Electrical and electronic waste equipment</td>
</tr>
<tr>
<td>W/O</td>
<td>Water in oil emulsion</td>
</tr>
</tbody>
</table>
Rare earth elements recovery from E-wastes by solvent extraction and supported liquid membrane processes

1. INTRODUCTION
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1. Introduction

1.1. Rare earth elements

Rare earth elements (REEs) or rare earth metals (REMs), as defined by the International Union of Applied and Pure Chemistry (IUPAC), are a group of 17 elements from the periodic table, specifically the 15 lanthanides plus scandium and yttrium [1]. REEs are typically divided into two categories by atomic numbers, light rare earth elements (LREEs) and heavy rare earth elements (HREEs) on the basis of their electronic configuration [2]. According to U.S. Geological Survey (USGS), the REEs with atomic numbers from 57 to 61 such as lanthanum, scandium, cerium, praseodymium, neodymium, promethium, samarium and gadolinium are classified as LREEs while terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium with atomic numbers greater than 62 are classified as HREEs. Moreover, yttrium is grouped as HREEs and europium as LREEs due to chemical similarities [3].

The first REE discovered was yttrium by the Swedish chemist Carl Axel Arrhenius in 1887 from the ytterbite, a mineral which nowadays is known as gadolinite. Until the 1940s the REEs were almost exclusively of scientific interest. However, they acquired notoriety with the nuclear technology, since the REEs were produced as uranium fission products and they could influence the nuclear reaction as a neutron receptor [4,5]. The relevance of the REEs was increasing to reach a peak in recent years since these metals play an important role in the emerging clean technologies because of their excellent electronic optic, magnetic and catalytic properties [6–8].

Although the REEs are relatively abundant in the Earth’s crust, they are not found as native element minerals in nature. Therefore, the recovery of the REEs must be succeeded through complex processing methods to chemically break down the minerals containing these metals. However, they are typically dispersed and rarely found in concentrated media and economically exploitable mineral deposits. Despite the abundance of more than 200 known REE-bearing minerals, bastnasite, \((\text{La, Ce})\text{FCO}_3\), monazite, \((\text{Ce, La, Y, Th})\text{PO}_4\) and xenotime, \(\text{YPO}_4\), are the most feasible REE mineral ores for the extraction [9,10]. Due to the lanthanide contraction, the LREEs are more incompatible than HREEs in rock-forming minerals while HREEs may prefer to remain in the crystalline residue. Thus, the LREEs tend to occupy larger coordination sites with 8-10 of coordination numbers in minerals based on carbonate and phosphate. However, the HREEs tend to concentrate in oxide and phosphate minerals with 6-8 as coordination numbers. Hence, monazite and bastnasite are mainly composed by LREEs instead of xenotime whose principal component is the HREEs [11].
INTRODUCTION

They began to be exploitable in the 1950s in South Africa, India and Brazil mines, yet, from the 1960s to the 1980s the largest global producer was a mine in Mountain Pass (California). Despite the fact that Mountain Pass is in the USA, China is currently the world’s largest producer of REEs, providing more than 95% of the world total supply from its mines in Inner Mongolia [12]. REEs world reserves and production are summarised by countries in Table 1.1.

Table 1.1. World mine production and reserves of REEs* [13].

<table>
<thead>
<tr>
<th></th>
<th>Mine production</th>
<th>Reserves</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2017</td>
<td>2018</td>
</tr>
<tr>
<td>United States</td>
<td>-</td>
<td>15.000</td>
</tr>
<tr>
<td>Australia</td>
<td>19.000</td>
<td>20.000</td>
</tr>
<tr>
<td>Brazil</td>
<td>1.700</td>
<td>1.000</td>
</tr>
<tr>
<td>Burma (Myanmar)</td>
<td>Not available</td>
<td>5.000</td>
</tr>
<tr>
<td>Burundi</td>
<td>-</td>
<td>1.000</td>
</tr>
<tr>
<td>China</td>
<td>105.000</td>
<td>120.000</td>
</tr>
<tr>
<td>India</td>
<td>1.800</td>
<td>1.800</td>
</tr>
<tr>
<td>Malaysia</td>
<td>180</td>
<td>200</td>
</tr>
<tr>
<td>Russia</td>
<td>2.600</td>
<td>2.600</td>
</tr>
<tr>
<td>Thailand</td>
<td>1.300</td>
<td>1.000</td>
</tr>
<tr>
<td>Vietnam</td>
<td>200</td>
<td>400</td>
</tr>
<tr>
<td>Other countries</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>World total (rounded)</strong></td>
<td><strong>132.000</strong></td>
<td><strong>170.000</strong></td>
</tr>
</tbody>
</table>

* data in metric tons of REEs oxide

The global REEs production and consumption have had a significant increase in the following decades due to their uses in our daily life, such as television screens, petroleum industry and computer systems. As shown in Fig. 1.1, the 2000s was the most important period where achieved the highest raise of demand and production because the REEs are especially indispensable in emerging clean and advance technologies, such as wind power turbines, electric vehicles, energy-efficient lighting, and catalytic converters [14–16].

![Fig. 1.1. Global REEs production and demand](image-url)
Even though China has the highest production and reserves of these metals, the production was remained mostly constant in 2016-2017 [3] due to economic and political decisions. The environmental problems caused by the no regulation of the mining in different producer companies and the reduction of the REEs exportations due to the taxes are being increased since 2010 by China, bringing an uncertain supply of these metals. The prices of REEs were raising in the last years until reaching the highest level in 2011, especially; neodymium, dysprosium, terbium and europium were notably affected, concurring with the critical REEs consideration based on the importance of clean energy and supply risk (Fig. 1.2).

**Fig. 1.2.** Critical matrix (2015-2025) term, data obtained from [17].

Furthermore, there are not alternative materials for most of the REEs applications, only the batteries and the Al and Mg alloys are easy and completely substitutable at no additional cost. Five REEs, europium, dysprosium, neodymium, terbium and yttrium, were found to be critical in between 2015-2025 based on two factors: the importance of clean energy and supply risk (Fig. 1.2). As a result, in spite of just 12.5% of metals are currently being recycled from e-waste [18], so it is indispensable and promising to find effective mechanisms and techniques to recover and separate REEs from urban mining to contribute a circular economy.

The end uses of the REEs can be divided into two broad categories: (1) process enablers and (2) product enablers. In the former category, the REEs are used in the production process but they are not actually contained in the end product. However, the REEs act as “product enablers” giving advanced materials unique properties that play a key role in the performance of high-tech products. In Fig. 1.3, the estimated REEs consumption by sector is shown, so the REEs used in each sector too. These applications rely on individual rare earths to different extents, creating a unique demand profile for each element.
Fig. 1.3. Breakdown of estimated rare earth consumption by sector with the REEs utilized in each application, the data obtained from [19].

Nowadays, 59% of the total worldwide consumption of the REEs is on the mature markets such as catalysts, glass marketing and metallurgy, and the other 41% represents the total worldwide consumption in battery alloys, ceramics and permanent magnets as high-growth markets. However, taking into account the continuous increase of the new and greener technologies, the use of the REEs in modern and clean technologies seems to be the centre of attention in the next years, as it can be seen in Table 1.2.

Table 1.2. Progression global clean technologies demand overview [8].

<table>
<thead>
<tr>
<th>Year</th>
<th>Wind Power (MW)</th>
<th>Lighting LED (Million Cps)</th>
<th>Electric Vehicles (Million Cars)</th>
<th>NiMH Batteries (Million Batteries)</th>
<th>Catalytic Converter (Million Cars)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2016</td>
<td>63350</td>
<td>2675</td>
<td>35.7</td>
<td>0.6</td>
<td>95</td>
</tr>
<tr>
<td>2020</td>
<td>79005</td>
<td>4828</td>
<td>37.6</td>
<td>1.3</td>
<td>100</td>
</tr>
<tr>
<td>2025</td>
<td>76810</td>
<td>5874</td>
<td>44.2</td>
<td>0.7</td>
<td>111</td>
</tr>
<tr>
<td>2030</td>
<td>107488</td>
<td>7146</td>
<td>66.5</td>
<td>2.7</td>
<td>117</td>
</tr>
</tbody>
</table>

1.1.1. Recycling from urban mining

The electrical and electronic waste equipment (WEEE) amount has been grown at 3-5% per year reaching in the European Union about 10.1 million ton in 2016 [20]. Considering that a high quantity of REEs is found in WEEE in different devices such as neodymium-iron-boron (NdFeB) permanent magnets, fluorescent lamps and NiMH batteries, to recover them from
discarded products cannot only protect the environment, but also promote the sustainable development of rare earth resources. Currently the mechanical separation is used for the aluminium, plastics, circuit boards and glass recovery. Further processing such as dense medium centrifugation, flotation, acid and non-acid treatments followed by the solvent extraction (SX) and membrane technologies of the waste is required to recover all of the valuable metals. Table 1.3 summarizes the main results and references dealing with the REEs recovery and separation by various separation techniques.

Table 1.3. State of the art of recovery and separation of REEs using different techniques.

<table>
<thead>
<tr>
<th>REEs</th>
<th>Raw material</th>
<th>Technique</th>
<th>Extractant</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy, Nd</td>
<td>Magnet scrap</td>
<td>Flat sheet supported liquid membranes</td>
<td>C₆mim-Tf₂N IL + DODGAA</td>
<td>[21]</td>
</tr>
<tr>
<td>Nd, Dy</td>
<td>NdFeB magnets</td>
<td>Solid-state chlorination</td>
<td>-</td>
<td>[22]</td>
</tr>
<tr>
<td>Dy, Nd, HREEs and LREEs</td>
<td>Permanent magnet scraps leach liquors</td>
<td>Solvent extraction</td>
<td>D2EHPA</td>
<td>[23]</td>
</tr>
<tr>
<td>NdFeB magnet leachate</td>
<td>Neodymium magnet leachate</td>
<td>Solvent extraction</td>
<td>D2EHPA</td>
<td>[24]</td>
</tr>
<tr>
<td>Pr, Nd</td>
<td>NdFeB magnet leachates</td>
<td>Solvent extraction</td>
<td>Cyanex 272-Alamine 336 IL</td>
<td>[25]</td>
</tr>
<tr>
<td>Pr, Nd, Dy, Y</td>
<td>Nickel metal hydride battery</td>
<td>Solvent extraction</td>
<td>Cyanex 923 + Aliquat 336</td>
<td>[26]</td>
</tr>
<tr>
<td>Y, Eu, Ce</td>
<td>Fluorescent lamp wastes</td>
<td>Cross-flow solvent extraction process</td>
<td>Primene 81R-Cyanex 572</td>
<td>[14]</td>
</tr>
<tr>
<td>Y, Eu</td>
<td>Fluorescent lamp wastes</td>
<td>Solvent extraction</td>
<td>Cyanex 572</td>
<td>[27]</td>
</tr>
<tr>
<td>Nd</td>
<td>Nitrate solution from monazite processing</td>
<td>Hollow fibre supported liquid membranes</td>
<td>PC88A</td>
<td>[28]</td>
</tr>
<tr>
<td>La, Ce, Nd, Y</td>
<td>REEs synthetic mixture</td>
<td>Emulsion liquid membranes</td>
<td>Aniline</td>
<td>[29]</td>
</tr>
<tr>
<td>Dy, Eu</td>
<td>Dy/Eu synthetic mixture</td>
<td>Flat sheet supported liquid membranes</td>
<td>D2EHPA+Cyanex 272</td>
<td>[23]</td>
</tr>
<tr>
<td>REEs</td>
<td>REEs synthetic mixture</td>
<td>Solvent extraction</td>
<td>USTB-2</td>
<td>[30]</td>
</tr>
<tr>
<td>Nd</td>
<td>Nd/Tb/Dy synthetic mixture</td>
<td>Counter-current solvent extraction process</td>
<td>Primene 81R-Cyanex 572 IL</td>
<td>[31]</td>
</tr>
</tbody>
</table>

Pyrometallurgical or hydrometallurgical processes can be used for the REEs separation and purification. However, hydrometallurgical processes are more widespread and developed by industry compared to the pyrometallurgical ones due to its advantages like its applicability for
both high and low-grade ores, its ability to oxidize and non-oxidize alloys, its low requirement of energy and low generation of air pollution, the ease of leaching processes and nonrequirement of additional processing for the obtained products [2].

Since the REEs recovery and separation investigated in this PhD thesis have been carried out fluorescent lamp wastes and synthetic mixtures of the most representatives REEs in NdFeB magnets, a brief description of both applications has been done.

**Permanent magnets**

Efficient permanent magnet consists of a material with high residual induction, square magnetization loop, large coercive field and a high saturation magnetization. Due to their ability to transform attractive or repelling force into mechanical work, to turn mechanical energy into electrical one and to transmit and distribute electric power, their interest and necessity have been increased the last years.

Commercial permanent magnets are divided into four categories: (1) NdFeB, (2) Samarium-Cobalt (SmCo), (3) Ferrite and (4) Aluminium-Nickel-Cobalt (AlNiCo). NdFeB and SmCo magnets are more appropriate for large applications because they have higher residual induction, larger coercive field and their sizes are not restricted due to brittleness problems [31]. Furthermore, the NdFeB magnets are commonly used in the REEs field since its market is higher and its annual consumption increased from 20 thousand tons in 2006 to nearly 55 thousand tons in 2017 [32]. Regarding these NdFeB magnets would become electric waste with the end-of-life and their content in REEs is high (about 30%) [33], it is a kind of promising resource with more refined value than natural rare earths. Thus, NdFeB magnets have been chosen in this PhD thesis as end-of-life products to research the most suitable recovery of REEs from them. Although neodymium is the most representative REE in these magnets, terbium, dysprosium and praseodymium can be found on them too. However, the amount of dysprosium in magnet applications is being reduced [34], since it is being replaced by terbium, which is a cheap element for the decreasing terbium demands in lighting [35].

The challenge of cleaning energy technologies has caused a massive spread of the products and applications that use NdFeB since 2000s. Nowadays, these magnets can be found in hard disk drives, DVD and CD players, automotive applications, motors in industrial applications (motors from robotics), loudspeakers, air conditioning compressors, magnetic separators, mixed electronics, electric bicycles and wind turbines.
Many electric goods are shredded to break the products into pieces which can be separated by magnetism and electrostatics. However, recovering the powder that contains the REEs, becomes very difficult after shredded step. Thus, it is advantageous to remove the REE-containing components prior to crush. Despite that, these separation processes often would require manual labour and it would pose both technical and economic challenges. Once the powder rich in REEs is obtained, different hydrometallurgical and pyrometallurgical processes are used to recover and separate REEs with high purity [7,36–39].

**Phosphors**

A phosphor is a solid material that emits visible light when exposed to radiation from ultra-violet, deep blue, or electron beam source. The phosphors are widely used in the lighting and electronic industry why the spectral content of the emitted light can be tailored to meet certain performance criteria changing the phosphor composition.

REE phosphors are currently used in cathode ray tube (CRT) screens, plasma screens, LCD backlighting, fluorescent lamps and white LEDs. However, the REE recovery priority is focused on the fluorescent lamps since they offer the largest potential in terms of mass of the waste fraction. A market for collecting and physically sorting the metal, glass and mercury components of the lamps are already in place. Furthermore, the fluorescent lamps contain significant amount of more critical HREEs such as europium, terbium and yttrium. Thus, the selling price can compensate for the recycling processes costs.

Modern fluorescent lamps, known as tri-band lamps, use a mix of red, blue and green phosphors to generate white light (Table 1.4) [27]. Although up to six different REEs can be found in fluorescent lamps, yttrium and europium are the REEs present in largest amounts due to the prevalence of the red phosphors, as well as the relatively high REEs content in this type of phosphor when compared to blue and green phosphors.

**Table 1.4.** REE-based phosphors used in fluorescent lamps [14,27,40].

<table>
<thead>
<tr>
<th>Phosphor type</th>
<th>Possible compounds</th>
<th>Typical amount in tri-band lamps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red</td>
<td>(Y_2O_3:Eu^{3+})</td>
<td>55% (contains mostly yttrium; 4-10% europium)</td>
</tr>
<tr>
<td>Blue</td>
<td>(\text{BaMgAl}<em>{10}\text{O}</em>{17}:\text{Eu}^{2+})((\text{Sr,Ca,Ba})_3(\text{PO}_4)_5\text{Cl:Eu}^{2+})</td>
<td>10% (contains &lt;5% europium)</td>
</tr>
<tr>
<td>Green</td>
<td>(\text{CeMgAl}<em>{10}\text{O}</em>{17}:\text{Tb}^{3+})(\text{LaPO}<em>4:\text{Ce}^{3+},\text{Tb}^{3+})((\text{Ce,Tb})\text{MgAl}</em>{11}\text{O}_{19})((\text{Ce,Gd,Tb})\text{MgB}<em>5\text{O}</em>{10})</td>
<td>35% (contains approx. 10% terbium)</td>
</tr>
</tbody>
</table>
An overview of the schematic fluorescent lamp recycling is depicted in Fig. 1.4. Crushing, shredding and sieving processes are required to facilitate the collection of phosphors fractions obtaining macro-fractions such as aluminium end caps, glass, electronics, etc. Although these methods are fast and applicable to large batches of lamps, the material can still contain impurities, so it increases the difficulty to collect phosphors without them [7,14]. Hence, the chemical separation processes are often directed towards a group recovery of all REEs found in products and not in an individual separation.

![Fig. 1.4. Schematic overview of fluorescent lamps recycle stages, data obtained from [19].](image)

1.2. Separation techniques

1.2.1. Solvent extraction

SX, also known as liquid-liquid extraction, is a mass transfer process in which a component called solute, is transferred from an aqueous to an organic phase, which is immiscible into the aqueous phase. So, the solute of the aqueous phase is chemically bonded to the extractant of the organic phase forming a complex and it is obtained a refining with less concentration of solute than the initial aqueous phase. Then, an extract composed by organic stream containing the extracted metal is also obtained.

- **Aqueous phase**
  The solute extracted is in this phase. Different factors can modify the extraction process such as the pH, the effect of salts concentration in the medium and the solute concentration.
Organic phase

The extractant agent is not the only one in the organic phase. In order to minimize the viscosity of this phase and favour the extraction process, the extractant is diluted in an organic dissolvent. A phase modifier can be also added in the organic phase to improve its proprieties as the extraction process, the extractant solubility to the dissolvent, the phases separation and the solubility of the complex formed with the solute.

The extraction process (Fig. 1.5) is divided into two stages called extraction and stripping. In the first stage, the aqueous phase is in contact with the organic phase obtaining a solute less concentrated called raffinate and the organic flow which contains the extracted solute, extract. In the second stage, a new aqueous phase is introduced to be in contact with the extract so the extractant can be reused in multistage extractions.

![Fig. 1.5. Scheme of the solvent extraction process.](image)

The extraction efficiency is due to the extractant affinity with the solute to be extracted, the composition of both phases and the volume ratio. Although the SX is the most common technique used by hydrometallurgical processes in the industry using a wide range of extractants and it was firstly used to separate nuclear and rare earths elements in 1940’s, the selective REEs liquid-liquid extraction is a complex operation because of the similarity of the physical and chemical properties of these elements [41].

1.2.2. Liquid membranes

Although the solvent extraction is the most common technique to recover and separate REEs, comparing it to the membrane separation technique, this one is more efficient for the metal ions separation and pre-concentration due to the small extractant amount needed and its large mass transfer interfacial areas [42].
The liquid membranes (LM) are one of the membrane technologies with high selectivity which consists in a liquid solution supported or unsupported which serves as a barrier between two aqueous solutions. It is remarkable that this barrier is immiscible into these solutions and thanks for the physical state of these membranes, mass transfer phenomena are usually faster, since liquid membranes facilitate the processes of permeability, dissolution and diffusion. However, one of the problems of this kind of membrane is its stability which means the pore of the liquid membrane is completely full with the carrier and its concentration remains constant throughout the LM.

From the point of view of the configuration of liquid membranes applied to the extraction with solvents, three fundamental groups of LM are usually considered:

(1) **Bulk liquid membranes (BLM)**

BLM is the simplest form of LM without support which consists of an aqueous bulk feed and receiving solution separated by an organic bulk, water-immiscible liquid solution (Fig. 1.6). The membrane phase is usually mixed so the diffusion path is limited to the distance of the boundary layer. Although it is one of the simplest types of liquid membranes that shows superior membrane stability, inferior solute fluxes, low selectivity and high operating costs are obtained [43]. Thus, this LM configuration is mostly used in laboratory measurements for evaluation of the metal mass transfer but this membrane configuration has not relevance for large-scale separation processes due to their large thickness [44–46].

![Fig. 1.6. BLM configuration.](image)

(2) **Emulsion liquid membranes (ELM)**

ELM is obtained by adding an extractant into the organic solution to stabilize water in oil emulsion (W/O). Then, this emulsion is dispersed in the feed so the organic solution becomes the membrane (Fig. 1.7). ELM process consists of (1) emulsion preparation, (2) solute permeation through membrane solution from feed to the receiving solution through emulsion and continuous solution consisting in metal waste interfacial contact and (3) emulsion and external solutions settled and demulsification to recover the membrane solution. Many studies have been carried out using ELM for metal ions recovery [47–49], organic acids [50,51] and ammines [52] in spite of its high fluxes and high selectivity [53]. Nevertheless, the major problems with the ELMs is emulsion
Rare earth elements recovery from E-wastes by solvent extraction and supported liquid membrane processes

stability and the fact of being easily broken to recover the internal solution [54]. So, the speed of the stirring in the feed has to be slow to avoid the emulsion’s destruction. In addition, the metal transport using the ELM is slower compared to other LM configurations.

![Fig. 1.7. ELM configuration.](image)

(3) Supported liquid membranes (SLM)

A SLM is one of the LM systems in which the liquid membrane is held by a microporous, inert and hydrophobic support which provides the mechanical resistance. The LM is placed between both aqueous solutions (feed and receiving phase) (Fig. 1.8).

![Fig. 1.8. SLM configuration [54].](image)

The suitable transported solute in the feed phase and it has to be transported through the hydrophobic membrane phase and diffused through it to enter the aqueous stripping solution by chemical bond. The basic principle of the transport of the LM supported is the gradient of concentrations which is generated between both internal sides of the membrane by the extraction and stripping processes [55]. The whole transport process studied in this PhD consists of seven steps and the concentration profile in the SLM system is schematically shown in Fig. 1.9.

1. Metal convection in the feed solution.
2. Metal diffusion across the boundary layer in the feed solution.
3. Extraction process in the interphase feed/membrane solutions.
4. Metal diffusion through the membrane.
5. Stripping process in the interphase membrane/receiving solutions.
6. Metal diffusion across the boundary layer in the receiving solution.
7. Metal convection in the receiving solution.
Although every diffusion stage has a specific resistance to transport, as a first approach, the resistance in the feed and stripping sides can be ignored since the position of the agitators in the cells are very close to the membrane, thus the thickness of the boundary layer is minimized. Moreover, the chemical reaction is instantaneous (extraction and stripping process) so these both temporal resistances can be considered also negligible. Given these facts, it has been considered that the diffusion through the liquid membrane is the metal transport process limiting step.

This membrane technique has a lot of salient features such as simultaneous extraction and stripping, low solvent inventory, process economy and operating costs, high efficiency and less carrier consumption [56–58]. Hence, it is one of the best alternate and promising technologies for the ion metals separation from solutions over other hydrometallurgical separation processes [55,59–61].

Although there are many SLM configurations, like flat sheet supported liquid membrane (FSSLM), hollow fibre supported liquid membrane (HFSLM), hollow fibre renewal liquid membrane (HFRLM), etc. only some of them are suitable to be scaled-up because of the membrane stability problems [62].

**Flat sheet supported liquid membranes**

The FSSLM uses a microporous solid support impregnated with the carrier and this configuration is the simplest form of the LM. It takes place between two halves cells using gaskets thus forming two compartments: one for the feed solution and another...
for the receiving solution (Fig. 1.10). Both phases are stirred by mechanical stirrers. Thus, it is used to investigate if the metal recovery and separation is succeeded and to find the optimal conditions for achieving it saving major amount of reagents. Once it is demonstrated, the liquid membranes set-up is changed by using hollow fibre modules to increase the low area/volume ratio obtained using FSSLM [63].

**Fig. 1.10.** Scheme of the flat sheet supported liquid membrane.

**Hollow fibre supported liquid membranes**

To increase the area/volume ratio and to maximize the efficiency of the process, the HFSLM is one of the best choices. The extraction and stripping processes can be carried out simultaneously with only one HFLM module which contains a set of hydrophobic microporous fibres packed and contained inside a shell (Fig. 1.11). The outer cell of the module is a single nonporous material through which the solution present inside cannot be transported. Inside the shell, many thin fibres are packed in nice and neat rows. The basic principle of the HFSLM is the immobilization of the extractant into the pores of hydrophobic membranes using the wetting characteristics of membrane.

**Fig. 1.11.** Representation of the interior of a hollow fibre module [64].

The most common applications of HFSLM are the sea water desalination and the medical fields. However, the use of this SLM as for real REEs leachate samples is increasing in the recent years by using different configurations such as hollow fibre renewal supported liquid membrane to improve, even more, the membrane stability.
Hollow fibre renewal liquid membranes

The renewal configuration has been chosen in the hollow fibre experiments due to the improvement of the LM stability. The renewal effect of the liquid membrane, the high membrane surface area and the long-time stability of the liquid membrane are the causes of that improvement [65–67].

The feed flowed along the shell side of the module and to prevent membrane stability problems losing organic solution from the membrane pores, a pseudo-emulsion containing the stripping solution and carrier are flowed along the lumen side. Thus, the organic solution, which is in contact with the aqueous solution, extracts the metal and transports by diffusion to the other hollow fibre pore side where the Me-loaded is stripped [67–69].

1.3. Extraction mechanisms

Extractants could be classified depending on the reaction mechanisms as (1) cation exchangers or acidic extractants, (2) solvation extractants or neutral extractants and (3) anion exchangers. Although these three major classes have been mostly utilized for REEs separation, some (4) chelating extractants have been suggested to the REEs separation too.

Furthermore, the aqueous medium conditions determine the type of extractant to be used to extract the metal. For instance, in nitrate medium the neutral species predominate while cationic species predominate in chloride and sulphate medium. Hence, the solvating extractants are used when the aqueous system is in nitrate media [70,71] and the cation exchangers for the chloride and sulphate ones. Table 1.5 summarizes the most common extractants reported in the rare earths literature.

(1) Cation exchangers

The cationic extractants are usually expressed as $HA$ and the extraction mechanism as a more simplifier form [72]:

$$Me^{n+} + nHA \leftrightarrow Me_{n}A + nH^+ \quad (1.1)$$

where $Me^{n+}$ denotes any metal overscroing means species present in the organic phase. As it is shown, the extraction is strongly pH dependent. So, three protons are involved in the extraction mechanism reducing the $pH_{eq}$ on the aqueous phase, thus, requiring a pH conditioning for the reuse of the extractant in a continuous industrial process.
Carboxylic and organophosphorus acids are two different classes of cation exchangers used in the REEs separation. Since the last group is usually in dimeric form, \((HA)_2\) [27,73,74], the mechanism is commonly expressed as [73,75,76]:

\[
Me^{n+} + n(\overline{HA})_2 \leftrightarrow Me_{n}(\overline{HA}) + nH^+ \tag{1.2}
\]

(2) **Solvating extractants**

In an extraction by solvation, the extractant replaces some or all of the coordinated water molecules from the aqueous metal ion to form a species which is soluble in the organic phase. The mechanism can be represented by the general reaction:

\[
MeB_n + x\overline{E} \leftrightarrow MeB_{n}\overline{E}_x \tag{1.3}
\]

where \(MeB_n\) refers to a neutral species and \(\overline{E}\) denotes any solvation extractant.

(3) **Anion exchangers**

Anion exchangers extract metal ions as anionic complexes and are only effective in presence of strong anionic ligands. Although the four types of amines are able to recover and separate REEs, the quaternary amines are more utilized in the REEs field. Considering a quaternary amine as the extractant, the extraction mechanism can be written as follows:

\[
(MeA)^{n-} + n\overline{R_4NX} \leftrightarrow \overline{n(R_4N)}^+_n (MeA)^{n-} + nX^- \tag{1.4}
\]

Moreover, this extraction mechanism is the most common for extractants called ionic liquids (ILs) or quaternary ammonium salt. Both names are accepted but the last one is more commonly used when the IL is diluted with a solvent. Unlike molecular extractants, ILs are salts composed of ionic species with low melting points, which many of them are liquids at room temperature. They are considered non-volatile solvents since they have a very low vapor pressure, thermal stability and high conductivity. ILs have a great interest from a chemical perspective because of their use for replacing the VOCs (volatile organic compounds) as solvent in chemical reactions. Since a large number of combinations can be achieved choosing the anion and cation, the ILs properties can be tuned, therefore, can be designed to a specified use and their applications are extended to different fields: media for green synthesis [77,78], CO\(_2\) capture [79,80], removal of fermentation products [81] and as solvents or extractants for liquid-liquid extraction [14,82–85] and hence, for supported liquid membrane processes [61,86–88]. According to an industrial liquid-liquid extraction application, the chemical stability of the ILs has to be insured. Some problems like the solubility in the aqueous phase or its decomposition at acidic media have been avoided.
(4) Chelating extractants
Chelating extractants extract metals by a cation exchange mechanism and they are characterized by having two bond sites forming chelate complexes. Thus, these extractants are considered a combination between cation and solvating exchangers [89].

1.4. Solid-state chlorination
Although the hydrometallurgical processes used for extracting REEs from primary and secondary sources commonly involve an acid digestion step, the solid-state chlorination (SSC) process proposes a more sustainable method to recover these metals. As it is known, the economic efficiency dictates if a new process can be implemented industrially or not. Hence, the SSC aspire to fulfill both industrial requirements: being economic and environmentally friendly.

Nevertheless, once the acid leaching process is done, the stream obtained is highly acidic. For recovery of the REEs by precipitation or solvent extraction process the pH of the solution needs to be increased, generating a chemical consumption due to this neutralization stage. Thus, an unconventional method such as SSC has been evaluated in this thesis to optimize the REEs recovery from fluorescent lamp wastes. The aim of this process is to replace the acid digestion reducing the chemical consumption and the acidity of the stream after the leaching step. Through mixing \( \text{NH}_4\text{Cl}(s) \) with end-of-life fluorescent lamp wastes at high temperature, the metals are chlorinated by \( \text{HCl(g)} \), which is formed by the thermal decomposition of ammonium chloride (Eqs. 1.5-1.6). The produced \( \text{NH}_3(g) \) excess can be collected and sold as a by-product.

\[
\text{NH}_4\text{Cl}(s) \xrightarrow{\Delta} \text{HCl(g)} + \text{NH}_3(g) \tag{1.5}
\]

\[
\text{REE}_2\text{O}_3(s) + 6 \text{NH}_4\text{Cl}(s) \rightarrow 2 \text{REECl}_3 + 3 \text{H}_2\text{O} + 6 \text{NH}_3(g) \tag{1.6}
\]

Comparing the SSC to the acid leaching process, several advantages of the former are described: (1) Reducing chemical consumption for the digestion medium by up to 50%, because \( \text{NH}_4\text{Cl}(s) \) contains almost twice as much HCl as \( \text{HCl(aq)} \). Moreover, the unreacted \( \text{HCl(g)} \) and \( \text{NH}_3(g) \) can be cooled to reuse the \( \text{NH}_4\text{Cl}(s) \) in subsequent SSC runs. (2) Reducing chemical costs, because \( \text{NH}_4\text{Cl}(s) \) is cheaper than \( \text{HCl(aq)} \) according to its higher \( \text{HCl(aq)} \) content and lower demand [22]. The excess of \( \text{NH}_3(g) \) in the exhaust gas can be sold; and (3) Reducing the steps in the REEs recovery process because the neutralization stage is not required since the pH of the aqueous phase obtained after the leaching process is around 4.
Table 1.5. Summarizes the most common extractants reported in the rare earth elements solvent extraction literature.

<table>
<thead>
<tr>
<th>Reagents class</th>
<th>Structure</th>
<th>Extractants</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxylic acids</td>
<td><img src="image" alt="Structure" /></td>
<td>Versatic acids: $R_1 + R_2 = C_6-C_8$, Versatic 10, Versatic 911</td>
<td>[90,91]</td>
</tr>
<tr>
<td>Phosphorous acids</td>
<td><img src="image" alt="Structure" /></td>
<td>Phosphoric acids: $R_1 = R_2 = C_4H_9$CH(C_2H_5)CH_2O-, bis(2-ethylhexyl)phosphoric acid (D2EHPA)</td>
<td>[92–94]</td>
</tr>
<tr>
<td>(3) Anion exchangers</td>
<td><img src="image" alt="Structure" /></td>
<td>Phosphinic acids: $R_1 = C_6H_13$, $R_2 = C_6H_13$, bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272)</td>
<td>[96,97]</td>
</tr>
<tr>
<td>Molecular extractant</td>
<td>RNH$_2$</td>
<td>Primary amines: $R = (C_6H_13)C(CH_3)(C_2H_5)_2$</td>
<td>[101]</td>
</tr>
<tr>
<td>(4) Chelating exchangers</td>
<td><img src="image" alt="Structure" /></td>
<td>β-diketones: $R_1 = R_2 = C_6H_13$, $R_3 = CH_3(CH_2)_2$, R:unknown side alkyl (LIX54)</td>
<td>[102]</td>
</tr>
<tr>
<td>(2) Solvating extractants</td>
<td><img src="image" alt="Structure" /></td>
<td>Phosphorous ester: $R_1 = R_2 = R_3 = CH_3(CH_2)CH_2O-$, tri-n-butyl phosphate (TBP)</td>
<td>[98]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Phosphine oxides: $R_1 = R_2 = R_3 = C_8-C_{10}$ mixture (Aliquat 336)</td>
<td>[102]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Quaternary amines: $R_1 = R_2 = R_3 = C_9-C_{12}$ mixture (Aliquat 336)</td>
<td>[102]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tetradecyl(trihexyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos IL 104)</td>
<td>[102]</td>
</tr>
</tbody>
</table>
1.5. References


Rare earth elements recovery from E-wastes by solvent extraction and supported liquid membrane processes


1. INTRODUCTION


Rare earth elements recovery from E-wastes by solvent extraction and supported liquid membrane processes


1. INTRODUCTION


1. INTRODUCTION


1. INTRODUCTION

2. OBJECTIVE
2. Objective

Nowadays, our society has suffered significant changes due to the development of high-technologies. Apparently, today's daily life seems impossible without these devices, but it is essential to consider the overuse and depletion of natural resources, as well as climate changes associated with their development. Hence, it has been placed a lot of emphasis on clean energy production, improving the efficiency of electricity and the circular economy implementation.

It can be seen in Fig. 2.12, different metals, especially the REEs which can be recovered from wastes of different technology devices and thus contributing to a circular economy minimizing the mining processes and favouring the recycling ones to reuse these metals in other applications. From all applications described above, permanent magnets and phosphors were chosen as raw materials to recover and separate REEs since they represent 68% of these metals use in terms of economic value.

![Fig. 2.12. Schema of the circular economy for the rare earth elements.](image)

Thus, the main aim of the current PhD thesis was to develop processes the recovery and separation of the REEs from the NdFeB magnets and fluorescent lamps wastes by using solvent extraction processes supported liquid membranes with flat sheet and hollow fibre configuration.

2.1. Specific objectives

The specific purposes were to characterize the raw material sample, to find the optimal working conditions of the recovery and separation processes and to design a process dissolving the end-of-life products and achieving the REEs separation. Although to achieve those purposes are not wieldy, in this research a complete process was developed. It can be industrially implemented to recover and separate the REEs from an end-of-life fluorescent lamp waste in
powder form. Table 2.6 summarizes the specific objectives depending on the end-of-life product studied.

**Table 2.6. Specific objectives depending on the end-of-life product.**

<table>
<thead>
<tr>
<th>End-of-life product</th>
<th>Specific objectives</th>
</tr>
</thead>
</table>
| NdFeB magnets             | ➢ To determine the optimal conditions for REEs separation using two cationic extractants by FSSLM.  
                               ➢ To design a SX process using a synthetized ionic liquid REEs selective.                                                                      |
| Fluorescent lamps scraps | ➢ To characterize the waste.  
                               ➢ To study the REEs behaviour using different kinds of SX molecular extractants.  
                               ➢ To model the SX process to summarize its behaviour.  
                               ➢ To develop a SX process, using synthetized ILs REEs selective.  
                               ➢ To determine the optimal conditions to recover and to separate REEs using FSSLM and HFRLM.  
                               ➢ To optimize the REEs recovery via solid-state chlorination instead of acid leaching process. |

**2.2. Thesis overview**

In this work, solvent extraction and liquid membrane technologies were assessed for the REEs recovery and separation from NdFeB magnet wastes and fluorescent lamp wastes using different molecular and IL extractants. Main contributions of this PhD thesis are summarized in Figs. 2.13-2.14.

![Fig. 2.13. Schema of thesis overview related to NdFeB magnets.](image-url)
Since real NdFeB magnet wastes could not be obtained, a synthetic leaching solution containing the representative REEs present in magnet wastes was prepared. Although the SX is usually used to find the optimal REEs separation conditions, a flat sheet supported liquid membrane was utilized comparing the metals transport using two cationic extractants, since these extractants have already been tested by the company who produces them. Therefore, it was already known that they would be useful for the REEs separation aim (Publication 1). Besides, a multistep counter-current solvent extraction separation process was developed using a synthetized IL. The use of the IL as extractant has the advantage of avoiding the inter-step pH control needed when cationic extractants are used in a continuous process (Publication 2).

![Schema of thesis overview related to fluorescent lamp wastes.](Image)

As far as the fluorescent lamp scraps concerned, a complete process was developed. Since more than one leaching step is required due to the high impurity level, two leaching steps were proposed. In this sense, the preliminary leaching (L1) was used to separate most of the base metals, but, some REEs were also dragged. In order to recover these lost metals a membrane step working in flat sheet configuration was added to the process. The solid obtained from the L1 stage was undergone to a second leaching (L2) to obtain a REEs rich liquor which was mixed with the permeate fraction coming from the membrane stage (Publication 3). Then, a
Ce/Eu/Y solvent extraction model in chloride media using D2EHPA as extractant was developed to minimize the efforts on the optimization of the REEs recovery and separation processes (Publication 4). Finally, once the REEs behaviour was studied by modelling, a multistep cross-flow solvent extraction process, synthetizing a Ce/Eu/Y mixture with the same ratio as in the liquor from L2. It was developed using two ILs as extractants in order to achieve the complete separation of each REEs reaching purities higher than 99% (Publication 5). Thinking about a possible industrial implementation of the process, the flat sheet supported liquid membranes are not feasible, so the membrane stage was improved using hollow fibre modules working with the renewal liquid membrane configuration (Publication 6, submitted). Finally, an unconventional process as solid-state chlorination was evaluated to optimize the REEs recovery replacing the acid leaching stage to develop a more sustainable method (Chapter 10).

Publications

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DOI: 10.1016/j.seppur.2019.05.015

DOI: 10.1002/aic.16627

DOI: 10.1016/j.wasman.2018.10.027

Publication 6: S. Pavón, A. Fortuny, M.T. Coll, M. Bertau, A.M. Sastre. *Permeability dependencies on the carrier concentration and medium viscosity for Y(III) and Eu(III) transport by using liquid membranes*. Separation and Purification Technology. Submitted
3. MATERIAL AND METHODS
3. Material and methods

3.1. End-of-life products

3.1.1 NdFeB magnets
NdFeB magnets are chiefly composed by Fe, Nd (main REE), Dy and B with traces of Ni, Tb, Pr, among others [1,2], so the synthetic leaching solution contained Nd, Dy and Tb. It was introduced the last metal because the NdFeB-alloys may be doped with Tb to increase thermal stability [3].

The aqueous solution was firstly a mixture containing the same amount, 1 g/L, of the three chosen REEs in chloride medium. Once the behaviour of these metals was known, a synthetic mixture of 9, 0.5 and 2.5 g/L of Nd/Tb/Dy, respectively was used to find the optimal separation conditions. These concentrations correspond to the representative ratio of these metals on the NdFeB magnets [1,4,5].

3.1.2. Fluorescent lamps
End-of-life fluorescent lamp waste was supplied by Recyberica Ambiental S.L (Spain). The sample received had already been treated to eliminate the Hg. For this reason, in the analyses carried out for the waste characterisation it is not found.

Although the high amount of yttrium and europium suggests that the Y₂O₃:Eu³⁺ is the main phosphor of the waste, the presence of calcium ion suggests that the sample is formed by a mixture of different halophosphors rich in YOX containing 93 gₐₗₐₚₑ₃/kgₜₐₚₑ [6].

3.2. Extractants
Different kinds of extractants were used for the extraction and membrane experiments. All of them were employed as received. As expected, the extractants had not been used in pure form, but they have been mainly diluted in kerosene.

Cationic extractants
Bis-(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), a mixture of phosphinic and phosphonic acids (Cyanex 572) and di-(2-ethylhexyl)phosphoric acid (D2EHPA) were used as extractants. Both Cyanex were supplied by Cytec Canada Industries (Canada) and D2EHPA was provided by Sigma-Aldrich (Ref. 237825, Missouri, USA).

Neutral extractant
Cyanex 923 (mixture of four trialkylphosphine oxides) was chosen in membrane experiments and was provided by Solvay Cytec Industries Incorporated (New Jersey, USA).
Ionic Liquid extractants
Primene 81R-Cyanex 572 and Primene 81R-D2EHPA ILs were synthesized following the procedure reported Coll et al. [7]. As it is shown in Eq. 3.7, stoichiometric quantities of the primary amine were mixed with an organic acid using kerosene as diluent to prepare both ILs. Primene 81R was supplied by Dow Chemical (Michigan, USA).

\[ \text{2RNH}_2 + (\text{HA})_2 \leftrightarrow \text{2RNH}_3^+ \text{A}^- \] (3.7)

Phase modifiers
Tributylphosphate (Ref. 240494) and 2,6-Dimethyl-4-heptanone (Ref. 02-L16015) from Sigma Aldrich (Missouri, USA) and Alfa Aesar (Massachusetts, USA), respectively were utilized as phase modifiers in the membrane experiments to reduce the organic phase viscosity and thus, to increase the REEs transport.

3.3. Stripping solutions
Hydrochloric acid (Ref. 131020) and Disodium ethylenediaminetetraacetate, Na₂EDTA (Ref. 131669) supplied by PanReac AppliChem (Barcelona, Spain) and citric acid (Ref. 251275) by Sigma Aldrich (Missouri, USA) were used as stripping solutions.

3.4. Separation techniques

3.4.1. Solvent extraction
SX experiments were carried out by shaking equal volumes, 10 mL, of the aqueous and organic solutions in a separatory funnel at room temperature (20 ± 2°C) by using a horizontal mechanical shaker (SBS Mechanical Shaker, Spain) at 140 rpm. As in previous kinetic experiments, the extraction equilibrium was achieved after 5 min. However, the shaking time for all the experiments was prolonged until 10 min to guarantee complete equilibration. The aqueous phase came from the synthetic Nd/Tb/Dy mixture in chloride medium or the nitric or hydrochloric acid leaching to the fluorescent lamp wastes.

Once both phases were separated, the aqueous phase was taken out and put aside for the analysis of the metal concentration. After the concentration of the metal was measured, the metal concentration in the organic phase was determined from the mass balance. Then, the metal loaded was recuperated by contacting with stripping agents and analysed to check whether the mass balance calculated previously after the extraction stage was balanced. The procedure followed in the stripping experiments was the same as in the extraction stage: shaking 10 mL of the stripping and organic solutions in the separatory funnel at 20 ± 2°C by the horizontal mechanical shaker at 140 rpm for 10 min. The metal concentration in the stripping phase was measured and the concentration in the organic phase was determined
from the mass balance. Metal concentrations in the aqueous phases were determined by atomic emission spectrometry using a 4100 MP AES System (Agilent Technologies, California, USA) with an analytical error ≤ 5%. The dilutions of the samples were prepared using HNO₃ 0.5% and the REEs were measured in the following wavelengths (nm): 342.247 Gd, 350.917 Tb, 353.171 Dy, 371.029 Y, 381.967 Eu, 401.225 Nd, 408.672 La and 446.021 Ce.

Extraction efficiency (%E), stripping efficiency (%S), distribution ratio (D) and separation factor (β) were the parameters used to analyse the obtained results. Since the volumes of the both phases were equal, they were defined in Eqs. (3.8)-(3.11) as:

\[
\%E = \frac{[Me]_{\text{org}}}{[Me]_0} \cdot 100
\]  
\[
\%S = \frac{[Me]_{\text{str}}}{[Me]_{\text{org}}} \cdot 100
\]  
\[
D_{Me} = \frac{[Me]_{\text{org}}}{[Me]_{\text{aq}}}
\]  
\[
\beta_{1,2} = \frac{D_{Me1}}{D_{Me2}}
\]

where \([Me]_0\) and \([Me]_{\text{aq}}\) refer to the initial and equilibrium metal concentration in the aqueous phase, \([Me]_{\text{org}}\) is the metal concentration in the loaded organic phase obtained by mass balance and \([Me]_{\text{str}}\) refers to the equilibrium metal concentration in the stripping phase.

### 3.4.2. Supported liquid membranes

**Flat sheet supported liquid membranes**

FSSLM experiments were carried out in an experimental set-up depicted in Fig. 3.15. Two cylindrical compartments were connected by a lateral window where the impregnated support of the carrier was placed. The feed and receiving cells were filled with 210 mL of the corresponding aqueous solutions and mechanically stirred at 1000 rpm at room temperature (20 ± 2°C). Samples from both cells were withdrawn at regular time intervals, up to 8 h; a final sample was taken after 24 h to have a first approach of the membrane stability. The metal concentrations in every sample was determined by using the procedure mentioned above in 3.4.1 section.

![Fig. 3.15. Scheme of FSSLM experimental set-up [8].](image)
Combining the mass balance in the feed solution and the 1st Fick’s law, the simplified Eq. 3.12 is obtained [8–12]. This equation has been used in the membrane experiments to determine the metal permeability coefficient whose value is related to the rate with which the metal is transported from the feed to the stripping solution.

\[
\ln \frac{[Me]_f}{[Me]_{0,f}} = -P \cdot \frac{A}{V} \cdot t 
\]  

(3.12)

where \([Me]_f\) and \([Me]_{0,f}\) are the metal concentration in the feed cell at time \(t\) and initial time, respectively; \(A\) is the membrane area; \(V\) is the volume of the feed solution in the cell; \(t\) is the time and \(P\) refers to the permeability coefficient.

**Hollow fibre renewal liquid membranes**

The transport experiments were carried out using the experimental set-up depicted in Fig. 3.16. The lab-scale plant worked with 4 L of the feed solution and a pseudo-emulsion containing stripping/organic which was made up of 400 mL of the stripping agent and 50 mL of the organic solution. The feed and stripping/organic streams flow at 50 L·h\(^{-1}\) and a low transmembrane pressure (\(P_f - P_s = 0.2\) bar) between shell and lumen side was applied to avoid the organic solution of the strip dispersion passing through the pores to arrive at feed solution side.

![Fig. 3.16. Scheme of HFRLM experimental set-up.](image)

Samples from the feed and the receiving solutions were withdrawn at regular time intervals and the metal concentrations in all aqueous samples were measured using the procedure mentioned in 3.4.1 section.

Before doing a new experiment using another extractant concentration, the extractant used in the previous experiment which was inside the pores was removed. To do it, the transmembrane pressure was changed to -1 bar in order to force the organic solution to cross
the fibre pores. Since the total volume of the pores was about 50 mL, the pore liquid was completely renewed when 150 mL of the organic solution appeared in the feed tank. Then, both membrane sides were cleaned. The percentage of the transported metal and the permeability coefficients of each REE were obtained using the Eqs. (3.8) and (3.11).

### 3.5. Support membranes

Two different support membrane types were used in flat sheet and hollow renewal configuration, Fluoropore™ FHLP04700 provided by Merck Millipore (Darmstadt, Germany) and a hollow fibre G-502 module supplied by 3M™ Liqui-Cel™ (New Jersey, USA). The characteristics of both membranes are summarized in Table 3.7.

<table>
<thead>
<tr>
<th>Membrane/plotting material</th>
<th>Fluoropore™ FHLP04700</th>
<th>G-502 module</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (cm)</td>
<td>4.7</td>
<td>-</td>
</tr>
<tr>
<td>Pore diameter (μm)</td>
<td>0.45</td>
<td>0.03</td>
</tr>
<tr>
<td>Fibre OD/ID (μm)</td>
<td>-</td>
<td>300/200²</td>
</tr>
<tr>
<td>Thickness (μm)</td>
<td>150¹</td>
<td>40</td>
</tr>
<tr>
<td>Area (m²)</td>
<td>11.4·10⁻⁴</td>
<td>1.4</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>85</td>
<td>40</td>
</tr>
<tr>
<td>Hold-up volume shell side (cm³)</td>
<td>-</td>
<td>400</td>
</tr>
<tr>
<td>Hold-up volume tube side (cm³)</td>
<td>-</td>
<td>150</td>
</tr>
<tr>
<td>Module diameter (cm)</td>
<td>-</td>
<td>7.7</td>
</tr>
<tr>
<td>Module length (cm)</td>
<td>-</td>
<td>27.7</td>
</tr>
<tr>
<td>Cartridge configuration</td>
<td>-</td>
<td>Extra-glow with centre baffle</td>
</tr>
</tbody>
</table>

¹including 100 μm of the polyethylene grid
²OD/ID

### 3.6. Solid-state chlorination

#### 3.6.1. Experimental set-up

The rotary kiln used for the solid-state chlorination experiments is described by Lorenz and Bertau [3]. This reactor consists of a glass tube, which contains the sample to be chlorinated. It is placed into a quartz rotary kiln and hold at both ends by gears that facilitate rotation. The excess of NH₃(g) produced during the NH₄Cl decomposition, was firstly introduced to a bottle with glass wool and then, absorbed in a second bottle containing deionised water.

#### 3.6.2. Chlorination process

The sample introduced in the centre of the glass tube was composed by 1 g of the unreacted solid residue (g_{solidL1}) obtained after the first leaching with HNO₃ [6] and a specified amount of NH₄Cl depending on the g_{NH₄Cl}/g_{solidL1} ratio in each experiment. Flushing N₂(g) at 350 mL/min for
3. MATERIAL AND METHODS

30 min at 120 rpm, the O$_{2(g)}$ was removed. Then the rotary kiln was heated 10 K/min to a specified temperature depending on each experiment. The leaching process started once the reactor was cooled back to room temperature and the chlorinate sample was transferred to a beaker by rinsing the tube with the organic solution.

3.6.3. Leaching solution

The organic solution used in the leaching process was prepared by diluting 10% of 2,4-pentanedione (99%, Ref. A14117, Alfa Aesar) in ethanol (ACS grade, Ref. 100983, Sigma-Aldrich) in a total volume of 50 mL. The chlorinated residue in the organic leaching was stirred at room temperature for 30 min. Then, the suspension was filtered using a PTFE membrane (0.2 µm, Filtrak, Germany) under 200 mbar. The organic/ethanol mixture had to be replaced by nitrate medium adding HNO$_3$ and evaporating the organic mixture to have the same conditions as the REEs liquor obtained in the liquid membrane step, process depicted by Pavón et al. [6]. Finally, this organic/ethanol mixture was collected by distillation to reuse it in further leaching processes. Metal concentrations were measured by atomic emission spectrometry (ICP-AES, Optima 4,300DV by Perkin Elmer, USA).

3.7. References


4. PUBLICATION 1
Comparison of Cyanex 272 and Cyanex 572 for the separation of Neodymium from a Nd/Tb/Dy mixture by pertraction

Sandra Pavon, a* Merve Kutucu, a M Teresa Coll, a Agustin Fortunya a and Ana M Sastre b

Abstract

BACKGROUND: Recovering Nd(III) from waste magnets is an alternative method to satisfy the increasing demand for this metal. For this reason, the separation of Nd from a mixture containing Nd/Tb/Dy in chloride media using Cyanex 272 and Cyanex 572 has been evaluated.

RESULTS: Using Cyanex 272 and Cyanex 572, the metals are transported in the order Dy(III) > Tb(III) > Nd(III) in all conditions studied. The optimum feed conditions to achieve Nd(III) separation are: Cyanex 272: pH 2 and Cyanex 572: pH 1.5 with 1.2 mol L⁻¹ HCl as a receiving agent for both carriers.

CONCLUSION: The results obtained suggest that Cyanex 572 is a better carrier than Cyanex 272 for separating Nd(III) from a mixture containing Nd/Tb/Dy.

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Supporting information may be found in the online version of this article.

Keywords: membranes; separation; waste treatment and waste minimisation; liquid–liquid extraction; supported liquid membrane; pertraction
Rare earth elements recovery from E-wastes by solvent extraction and supported liquid membrane processes

5. PUBLICATION 2
Neodymium recovery from NdFeB magnet wastes using Primene 81R·Cyanex 572 IL by solvent extraction

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Agri-Food Engineering and Biotechnology Department, ESAB, Universitat Politècnica de Catalunya, Esteve Terrades 8, 08860 Castelldefels, Spain

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ARTICLE INFO

Keywords:
Neodymium recovery
Counter-current process
Ionic liquid
Solvent extraction
Primene 81R·Cyanex 572 IL

ABSTRACT

The necessity of Rare Earth Elements (REEs) recycling is crucial to minimizing their supply risk and provide an alternative to greener technologies. Hence, the REEs recovery from NdFeB magnet wastes using cationic extractants by solvent extraction technique has been investigated in this research. Due to the difficulty in maintaining the aqueous pH in the industrial counter-current devices when extractants like Cyanex 272 or Cyanex 572 are used, the Primene 81R·Cyanex 572 ionic liquid has been synthesised to overcome this. 99.99% Nd(III) recovery with a purity of 99.7% from an aqueous mixture of Nd/Tb/Dy in chloride medium, the three representative REEs present in the NdFeB magnets wastes, has been achieved after two stages counter-current extraction process using 0.30 M of Primene 81R·Cyanex 572 ionic liquid (1:4 A/O ratio) diluted in Solvesso 100, without any aqueous pH conditioning.

1. Introduction

Rare earth permanent magnets are increasingly playing a relevant role in clean energy applications.

In fact, this sector holds first place in the priority of recycling taking into account the difficulty in finding substitutes, the critical use of REEs in magnets which are neodymium, praseodymium, dysprosium, terbium and samarium and the potential value of the waste stream (European Commission, 2014; U.S. Department of Energy, 2012). Therefore, the magnets growing tendency does not seem to be changing in the near future, because nowadays, there is a high dependence on the REEs from different sectors and applications, like the motor industry, automation, technology devices, e-mobility, renewable energies and wind power. Although prices and demand are high, only a small fraction of REEs are being recycled. In 2011, just 1% was recycled (Tsamis and Coyne, 2015).

Nevertheless, recycling and recovering these metals from urban mines is economically and environmentally beneficial because these wastes are reduced and it brings some independence from REEs producing countries.

Permanent magnets are divided into four categories: (1) Neodymium-Iron-Boron (NdFeB), (2) Samarium-Cobalt (SmCo), (3) Ferrite and (4) Aluminium-Nickel-Cobalt (AlNiCo). The formers are stronger than the other ones and their sizes are not restricted due to brittleness problems. Thus they are more appropriate for large applications (Smith Stegen, 2015). Therefore, the NdFeB magnets are used more than the SmCo ones, and approximately 26,000 tons per year of REEs are used in the manufacture of NdFeB permanent magnets (Rare et al., 2015). Although NdFeB magnets are more expensive than ferrite and AlNiCo magnets, which are commonly used in wind turbine generators (WTGs), they can produce a higher magneto-motive force in smaller magnet sizes (Rao et al., 2017). Due to the advantages of permanent magnet generators (PMG) based on the REEs use, the average annual demand growth rate forecast for NdFeB in WTGs will increase by 10% in the 2020–2030 period (Schulze and Buchert, 2016). For this reason, it is necessary to study these magnets and find efficient separation and recovery processes.

Up to now, there are many separation and recovery processes for REEs. Among them, the solvent extraction is the most common technique using a wide range of extractants. Cyanex 272 (bis(2,4,4-trimethylpentyl)phosphinic acid, Cy272) (Liu et al., 2014), DEHPA (di(2-ethylhexyl)phosphoric acid) and EHEHPA (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester, PC88A, P507) (Mohammadi et al., 2015), Cyanex 923 (mixture of trialklyphosphine oxides) (Batchu et al., 2017), TBP (tributyl phosphate) (Chen et al., 2016) and the ionic liquids (Larsson and Binnemans, 2015; Chen et al., 2017) are but a few examples. Liu et al. suggest that by adding TBP into the binary mixture of Cyanex 272 and Alamine 336 a better Nd/Pr separation factor is obtained (Liu et al., 2015). The extraction of neodymium and
praseodymium abilities in using different ionic liquid were investigated by Padhan and Sarangi and they proposed the Cyaxen 272Aamine 336 IL > DEHPA·Aamine 336 IL > Cyaxen 272 > DEHPA > Aliquat 336 extraction order (Padhan and Sarangi, 2017). Cyaxen 572 (Cy572) is a commercial extractant that has been specially developed for the extraction and purification of REEs (CYTEC Industries Inc., 2013). It is a mixture of Cy272 and PC88A and it allows the stripping of REE using lower acid concentrations rather than using phosphonic acids due to the complex strength formed by the REEs (CYTEC Industries Inc., 2013; Quinn et al., 2015; Wang et al., 2015). Tunsu et al. reported that the separation of Yttrium and Europium from solutions of fluorescent lamp waste was successfully achieved using Cy572 (Tunsu et al., 2016). Th was recovered using Cy572 with two different processes depending on its concentration. 95% and 99.9% purity of Th were respectively obtained by Wang et al. recovering from low and high Th concentrations using different extraction, scrubbing and stripping stages (Wang et al., 2017). The extraction and separation of Heavy Rare Earth Elements (HREEs) from ion-adsorbed deposits using Cy572 was more effective than using P507; considering the stripping efficiency, the lower acid requirements and also from an environmental point of view (Wang et al., 2015).

Taking into account that 30% of the NdFeB magnets are REEs (Tunsu et al., 2015; Binnenmann et al., 2013) and Nd, Dy and Tb, are critical REEs according to their supply risk and importance in clean energy markets (Tunsu et al., 2015), the current research has been focused on how to recover and separate these REEs from magnet wastes.

In order to evaluate the selectivity to separate the REEs from a mixture containing neodymium, terbium and dysprosium in chloride media, extractants such as Cyanex 272 and Cyanex 572 have been studied using the solvent extraction technique. However, extrapolating the results obtained in this study to set up an industrial separation process, it appears the dimeric form of the extractant involved in the extraction process is shown (Tunsu et al., 2016). Although there are many industrial processes, where the pH is controlled when cation extractants are used, this research suggests an alternative to avoid the necessity of the inter-step pH control using an ionic liquid as an extractant.

\[
Me^{3+} + 3(\text{HA})_2 \overset{K}{\leftrightarrow} Me(\text{HA})_3^{+} + 3 H^+ \tag{1}
\]

For this reason, the investigation of Primene 81R·Cyanex IL behaviour as the extractant to selectively recover REEs from magnet wastes is promising. As shown in Eq. (2), there is no proton exchange to the aqueous phase when rare earths are extracted with this IL, and consequently, the aqueous phase pH is not modified after extraction.

\[
3 \text{RNH}_{2}A^{+} + Me^{3+} + 3 Cl^- \overset{K}{\leftrightarrow} MeA_3 - 3 \text{RNH}_3^+Cl^- \tag{2}
\]

According to this, the first part of the study was focused on the Cyanex choice (C272 or C572) to form the ionic liquid taking into account its selectivity HREEs/neodymium and its behaviour on the neodymium separation. When the Primene 81R-Cyanex IL was synthesized, different parameters were studied, such as contact time, pH, ratio of IL, IL concentration and diluent used, to achieve the Nd(III) separation from a mixture of Nd/Tb/Dy using an aqueous phase concentration coincident with the real concentration of these REEs in the magnet wastes by a counter-current extraction process.

2. Experimental

2.1. Reagents

The aqueous phase solutions were prepared by dissolving Nd₂O₃ (Sigma Aldrich Ref. 228656, 99.9%), Tb₂O₃ (Sigma Aldrich Ref. 590509, 99.99%) and Dy₂O₃ (Sigma Aldrich Ref. 289264, 99.9%) in hydrochloric acid. NaCl, NaOH or HCl were added to adjust the pH and the chloride concentration. Citric acid (Sigma Aldrich Ref. 251275, 99.5%) and hydrochloric acid were used as stripping agents. Cy272, Cy572 and Primene 81R·Cyanex 572 IL (P81R·Cy572 IL) were used as extractants. Both Cyanex extractants and P81R were kindly supplied by Cytec Canada Industries and Dow Chemical, respectively, and they were used as received. Detailed specifications of these extractants are summarized in Table 1. Kerosene, from Sigma-Aldrich, was used mainly in the majority of the experiments as a diluent. Toluene (methylbenzene), Cumene (isopropylbenzene), Solvesso 100 (a mixture of alkyl(C₃)-benzenes) and Solvesso 200 (a mixture of alkyl(C₅-C₇)-benzenes) were also used to investigate the effects of the diluent on the extraction. ExxonMobil supplied both Solvesso diluents and they were used as received.

2.2. Primene 81R-Cyanax 572 IL preparation

P81R·Cy572 IL is a home-made ionic liquid that was produced by mixing these two commercial extractants, Primene 81R (primary t-alkyl amine, P81R) and Cy572. In order to prepare the P81R·Cy572 IL, stoichiometric quantities of P81R and Cy572 were mixed in kerosene as can be seen in Eq. (3) below.

\[
2 \text{RNH}_2A^+ + (\text{HA})_3^+ \leftrightarrow 2 \text{RNH}_3^+A^- \tag{3}
\]

2.3. Solvent extraction procedure

For the extraction experiments, the concentration of Nd(III), Tb(III) and Dy(III) in the aqueous phase was 1 g dm⁻³ of each metal (or specified concentration) in 4 M Cl⁻. 10 cm³ of this aqueous phase were equilibrated at room temperature (20 ± 2 °C) with an equal volume of organic phase in a separatory funnel using a horizontal mechanical shaker (SBS Mechanical Shaker) at 140 rpm for 10 min, until the equilibrium was achieved. In order to evaluate the effect of the citric acid and HCl as stripping agents, 5 cm³ aliquots of the organic phase were placed in two new separatory funnels to make the stripping process using citric acid 1 M and HCl 1.2 M. After the separation phases, the concentration of the REEs in the aqueous phase was determined by atomic emission spectrometry using a 4100 MP AES System (Agilent Technologies) with an analytical error ≤ 5%. A triplicate test was made.

Extraction efficiency (%E), stripping efficiency (%S), distribution ratio (D) and separation factor (β) are defined in Eqs. (4)–(7) to

---

Table 1

<p>| Physical properties of Cy272, Cy572 and P81R. |</p>
<table>
<thead>
<tr>
<th>Commercial name</th>
<th>Content %</th>
<th>Density kg m⁻³</th>
<th>Viscosity (25 °C) mPa s</th>
<th>Av. Mol. Weight g mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyanex 272 (CYTEC Industries Inc, 2008)</td>
<td>85</td>
<td>920</td>
<td>14.2</td>
<td>290⁸</td>
</tr>
<tr>
<td>Cyanex 572 (CYTEC Industries Inc, 2013)</td>
<td>100</td>
<td>933</td>
<td>&lt; 50</td>
<td>310⁸</td>
</tr>
<tr>
<td>Primene 81R</td>
<td>100</td>
<td>860</td>
<td>2.58</td>
<td>191⁸</td>
</tr>
</tbody>
</table>

⁸ As a monomer.

---

Appendix

Table 1

<p>| Physical properties of Cy272, Cy572 and P81R. |
|-----------------|-----------|----------------|----------------------|----------------------|</p>
<table>
<thead>
<tr>
<th>Commercial name</th>
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<th>Density kg m⁻³</th>
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</tr>
<tr>
<td>Primene 81R</td>
<td>100</td>
<td>860</td>
<td>2.58</td>
<td>191⁸</td>
</tr>
</tbody>
</table>

⁸ As a monomer.
evaluate the results.

$$\%E = \frac{[Me]_{aq,0} - [Me]_{aq,eq}}{[Me]_{aq,0}} \times 100$$  (4)

$$\%S = \frac{[Me]_{org,eq}}{[Me]_{aq,eq}} \times 100$$  (5)

$$D_{Me} = \frac{[Me]_{aq,eq}}{[Me]_{aq}}$$  (6)

$$\beta_{1,2} = \frac{D_{Me}}{D_{Me,0}}$$  (7)

where $[Me]_{aq,0}$ and $[Me]_{aq,eq}$ refer to the initial and equilibrium concentration of rare earth in the aqueous phase, $[Me]_{org,eq}$ is the equilibrium concentration of REE in the stripping phase and $[Me]_{aq}$ is the concentration of REE in the loaded organic phase.

### 2.4. Extraction mechanism

The metal extraction mechanism was investigated taking into account Eq. (1) using Cy272 or Cy572, Eq. (2) in the case of P81R·Cy572 IL and irrespective of the REEs speciation. In this extraction mechanism investigation, the equilibrium constants can be written as follows in Eq. (1) using Cy272 or Cy572, Eq. (2) in the case of P81R·Cy572 IL and irrespective of the REEs speciation.

The metal-ligand complexes, $[L_{THA}], [L_{THA}]^{-}, [L_{THA}^{2-}], [L_{THA}^{3-}]$, according to the equilibrium equations, respectively:

$$K_i = \frac{[Me][L_{THA}]}{[Me^{2+}][L_{THA}]}$$  (8)

$$K_i = \frac{[Me^{3+}, 3RNH_2Cl^-]}{[Me^{2+}, 3RNH_2Cl^-]^{-}}$$  (9)

Replacing the distribution ratio D (Eq. (6)) on Eq. (8) and Eq. (9):

$$K_i = \frac{D[H^+]^{3+}}{[THA]_{aq}}$$  (10)

$$K_i = \frac{D}{[RNH_2Cl^-]^{-}}$$  (11)

Applying logarithms on Eq. (10) and Eq. (11), the linearized Eq. (12) and Eq. (13) were obtained.

$$\log D = \log K_i + 3 \log [THA]_{aq} - 3 \log [H^+]$$  (12)

$$\log D = \log K_i + 3 \log [RNH_2A^-] + 3 \log [Cl^-]$$  (13)

According to these equations, plotting $\log D + 3 \log [H^+]$ vs. $\log [THA]_{aq}$ and $\log D - 3 \log [Cl^-]$ vs. $\log [RNH_2A^-]$, a slope equal to 3 should be obtained if the stoichiometry metal-ligand matches with the proposed mechanism. Additionally, a slope of 3 should be obtained plotting $\log D - 3 \log [THA]_{aq}$ vs. $-\log [H^+]$, meaning that three protons are involved in the suggested extraction process.

The equations have been written in terms of hydrogen ion concentration, since the pH measurements are not accurate under the highly acidic conditions studied.

### 2.5. Counter-current extraction procedure

The counter-current process was carried out using separatory funnels in which 5 cm$^3$ of the aqueous phase and 20 cm$^3$ of the organic phase were introduced. The metal concentrations in the feed solution corresponded to the representative REE concentrations on magnet wastes. Therefore, the aqueous phase was a mixture containing 9.00, 0.50 and 2.55 g dm$^{-3}$ of Nd(III), Tb(III) and Dy(III), respectively (Binnemans et al., 2013; Sasai and Shimamura, 2016; Yang et al., 2017) at an initial pH 0.10 and 4 M Cl$^-$ medium. The organic phase was 0.30 M of P81R·Cy572 IL. The process separation started with 2 separatory funnels, named funnel 1 and funnel 2, with an aqueous to organic (A/O) phase ratio 1:4, then shaken for 10 min. When both phases were separated, the steps described below were followed:

1. Take a new separatory funnel, the number 2', and a fresh organic phase is introduced.
2. Remove the aqueous phase from the separatory funnel number 2 as a sample.
3. Put the raffinate from the funnel 1 into funnel 2'.
4. A fresh aqueous phase in the separatory funnel 2 is introduced.
5. Take out the funnel 1 and the other two funnels (funnel 2 and 2') will be relabelled as 1 and 2, respectively) are shaken for 10 min.

This procedure was repeated (11 times) until the REE concentrations were constant, meaning that the process was stabilized. In order to check the process stabilization, the remaining organic phases were stripped. Then, Nd(III), Tb(III) and Dy(III) concentrations in the aqueous phases were determined.

### 3. Results and discussion

#### 3.1. Cyanex 272 and Cyanex 572

#### 3.1.1. Effect of the contact time

The extraction of Nd/Tb/Dy by Cy272 and Cy572 and the stripping of these REEs by HCl 1.2 M and citric acid 1 M were investigated at specific contact times. The results showed that the equilibrium was achieved within 5 min and the extraction and stripping percentages were unchanged while extending the mixing time. Consequently, a fixed mixing time of 10 min was used in all the subsequent experiments to ensure complete equilibrium.

#### 3.1.2. Effect of pH

The pH is a critical parameter to separate REEs using cationic extractants. As is seen in Fig. 1a and Fig. 1b, the extraction of Nd(III), Tb(III) and Dy(III) increased due to the increasing equilibrium pH. The

![Fig. 1. Effect of the equilibrium pH on the extraction of 1 g dm$^{-3}$ REEs in 4 M Cl$^-$ (triplicate test). a) Cy272 10% (v/v) in kerosene b) Cy572 10% (v/v) in kerosene.](image-url)
appropriate pH ranges to achieve the REEs separation are from 1.4 to 1.8 using Cy272 (Fig. 1a) and from 0.4 to 1.3 using Cy572 (Fig. 1b); because, in these ranges, the bigger selectivity values of HREEs/neodymium were obtained (Pavon et al., 2017).

The contrasting plots of log $D$ = $3 \log [HA]$ vs. $- \log [H^+]$ (see Fig. S1.a and b in the supplementary material) allow us to determine the slope values for each metal using both Cyanex. The obtained results are consistent with the proposed extraction mechanism in Eq. (1). Although the values of the Nd(III) slopes for both extractants are less than 2.50, the slope values of terbium and dysprosium indicate that the extraction process result obtained is three protons are involved in the extraction process within our experimental ranges (Eq. (1)). The extraction process result obtained is also in accordance with references (Tunsu et al., 2016) and Huang and Tanaka, (2010).

3.1.3. Effect of the extractant concentration

The effect of the extractant concentration was investigated in the range 5%–20% range (v/v) using Cy272 (0.14–0.54 M) and Cy572 (0.15–0.60 M) as extractants (Fig. 2a and Fig. 2b) and kerosene as diluent. The concentration of each REE in the mixture was 1 g dm$^{-3}$ in 4 M Cl$^-$ medium. The initial pH was set to 3.50 for both extractants and the stripping agent used was HCl 1.2 M.

Although the results showed that the percentages of REEs extraction increases when the extractant concentration increases, the rise in the extracted Nd(III) was less than the other two REEs. Even though the equilibrium pHs decreased when the concentration of the extractants increased in all the cases, the equilibrium pH values using Cy572 was less than when Cy272 was used, being in agreement to the obtained extraction percentages (Fig. 2a and b). This fact accords with the extraction mechanism for cationic extractants depicted previously in Eq. (1).

Because the neodymium was not extracted using Cy272 throughout the studied range, 0.54 M was chosen since the HREEs extraction rate was the highest. This Nd(III) behaviour was also observed using the lowest (0.15 M) Cy572 concentration. In order to separate Nd(III) from the mixture, 0.30 M was decided using Cy572 due to their highest selectivity values in Table 2.

With the aim of investigating the extraction reaction stoichiometry of both Cyanex, the log $D + 3 \log [H^+]$ vs. log $[HA]$ (see Fig. S2. a and b in the supplementary material) presented in (Fig. S2. a and b in the supplementary material). In these plots, Cy272 and Cy572 are considered as dimers according to Eq. (1) and both plots show linear tendencies using both Cyanex. Due to the non-extraction of the neodymium using Cy272, the $D_{Nd}$ cannot be calculated and therefore no slope is presented. The slope values were 2.76 and 2.85 for Tb (III) and Dy(III), respectively. In the same way, the obtained slope values using Cy572 were 3.37, 3.36 and 3.30. This accords with the extraction mechanism depicted in Eq. (1).

3.1.4. Effect of the chloride concentration in the aqueous feed

In order to compare the chloride concentration effect using both extractants, this was investigated in the 0.10–4 M concentration range. The aqueous phase contained 1 g dm$^{-3}$ of each metal at initial pH 3.50. The extractant concentrations used were 0.54 M and 0.30 M for Cy272 and Cy572, respectively.

It can be observed from the results in Fig. 3 that there is an inversely proportional relationship between the percentage of REEs extraction and the Cl$^-$ concentration. These results can be explained according to the hypothesis that the Me$^{3+}$ is the extracted species. If the MeCl$^2+$, MeCl$^3+$ or MeCl$^4+$ species were produced, consistently with Eq. (14)–(16), less Me$^{3+}$ would have been extracted and consequently, the extraction would decrease, as is depicted in Eq. (1).

\[
\begin{align*}
\text{Me}^{3+} + \text{Cl}^- & \rightarrow \text{MeCl}^2+ \\
\text{MeCl}^2+ + \text{Cl}^- & \rightarrow \text{MeCl}_3^2+ \\
\text{MeCl}_3^2+ + \text{Cl}^- & \rightarrow \text{MeCl}_4^+ 
\end{align*}
\]

The Cl$^-$ influence order on the extraction is Nd(III) > Tb (III) > and Dy(III) in the studied chloride range. This behaviour can be associated with bigger metal complex formation constants in the same order as mentioned above. Although the extraction decreasing tendency is the same using both extractants, it is more accentuated using Cy572 rather than Cy272. That is why the best optimal range to separate Nd (III) from the mixture is considered to be from 2 M up to 4 M of chlorides.

According to all the aforesaid, and with the aim of achieving a low extraction yield for neodymium and, simultaneously, achieving greater selectivity values in reference to terbium and dysprosium, 4 M Cl$^-$ concentration has been chosen (Table 3).

3.1.5. Effect of the different stripping agents

The loaded organic phases obtained in the previous experiments described in section 3.1.3 and 3.1.4 were used to investigate the effect of HCl 1.2 M and citric acid 1 M as stripping solutions. They have been chosen due to the acidic character in promoting the extraction process as is written in Eq. (1). As is shown in Fig. 4, the stripping percentage using hydrochloric acid 1.2 M as the stripping agent for Tb(III) and Dy (III) is around to 80% for both extractants. Neodymium data is not included in Fig. 4 a because the metal was not extracted using Cy272 in the whole range of extractant concentrations, and so it is not considered for stripping in this case.

![Fig. 2. Effect of extractant concentration of 1 g dm$^{-3}$ of REEs at initial pH 3.50 in 4 M Cl$^-$ (triplicate test). Diluent: kerosene a) Effect of [Cy272]. b) Effect of [Cy572].](image-url)
The main differences between Cy272 and Cy572 appear when citric acid 1 M is used as the stripping agent. In this case, metals are stripped from organic phase containing Cy272 (Fig. 4a and Fig. S3.a in the supplementary material) and not from Cy572 (Fig. S3.a and Fig. S3.b in the supplementary material). It may be due to the complexing effect of citric acid which compensates its lack of acidity. To prove it, a solution of HCl 0.01 M was prepared with the same pH as the 1 M solution of citric acid (pH 2) and no stripping of any REEs was obtained using both Cyanex. Therefore, citric acid mainly strips due to its complexing effect.

The results show that to achieve a complete stripping for both extractants using HCl 1.2 M, two stages will be required or the HCl concentration would have to be increased (Panda et al., 2015). As already noted previously, the optimum stripping agent to achieve a good stripping is HCl 1.2 M for both extractants while citric acid 1 M could be also used in the case of Cy272.

3.2. Primene 81R-Cyanex 572 IL

Even though good separation factors of Dy/Nd and Tb/Nd were obtained using both Cyanex, more than one stage is required to achieve a complete neodymium separation from the mixture of Nd/Tb/Dy in 4 M Cl\(^{-}\). From an industrial separation process scale-up point of view, this fact makes the previous conditioning of the pH in the successive extraction stages necessary.

In this sense, the use of an extractant like P81R·Cyanex IL is essential in order to avoid a proton exchange during the extraction process. Comparing the results of Cy272 and Cy572, the HREEs selectivity value is better when Cy572 is used. The amount of Cy572 necessary to achieve higher values of separation factors is also less than using Cy272. Consequently, Cy572 has been chosen to be used in the P81R·Cy572 IL, in order to maintain the pH during the extraction process.

3.2.1. Effect of the contact time

Following the procedure previously mentioned in 3.2, the extraction and the stripping using HCl 4 M were investigated at specific contact times; and within 5 min, the equilibrium was achieved. In order to make sure that equilibrium was completely achieved, a 10 min of shaking time was utilised.

3.2.2. Effect of pH

Although the IL is a mixture of P81R and Cy572, its behaviour -when combined-could be different compared to its individual components (Liu et al., 2014). To study the pH effect on the Nd/Tb/Dy extraction using the P81R-Cy572 IL diluted in kerosene, the extraction curves using 0.30 M of IL and 1 g dm\(^{-3}\) REE solution in 4 M Cl\(^{-}\) medium were carried out.

The results show that the extraction percentages of Tb(III) and Dy(III) are similar throughout the entire pH range. However, Nd(III) shows an extraction behaviour completely different which can be harnessed to separate it from the mixture (Nd/Tb/Dy). As can be seen in Fig. 5a, the greater difference in the Nd(III) extraction compared to the other two REEs is obtained in the 0.8–1.5 pH range.

In order to confirm the mechanism described in Eq. (3), the plot of pH\(_{in}\) vs. pH\(_{max}\) for the Nd/Tb/Dy metals is presented in Fig. 5b. The results indicate that there is no proton release when the REEs are extracted. As a consequence, the choice of using an ionic liquid like the P81R-Cy572 IL, in order to maintain the pH during the extraction process, is confirmed.

3.2.3. Effect of Primene 81R concentration

Being the objective to determinate the P81R/Cy572 ratio in the IL, in this section, a study has been done maintaining 0.30 M of Cy572 and varying the P81R concentration from 0.09 M up to 0.36 M. The diluent used was kerosene. The aqueous phase was 1 g dm\(^{-3}\) of each REE in 4 M Cl\(^{-}\) at an initial pH 0.10. The higher the P81R concentration is in the IL, the bigger the extraction of REEs is as shown in Fig. 6. This is because when the P81R concentration increases, more IL is formed up to 0.30 M (1:1 M ratio). However, the neodymium extraction increase is suppressed by the preferential loading of the two heavy REEs in the organic phase.

As shown in Table 4, the \(\beta_{\text{Dy/Nd}}\) values increase until achieving the maximum value, 86, using 0.30 M of both extractants (P81R and Cy572), then the separation factor decreases because the Dy(III) extraction is almost maintained, and the extraction of Nd(III) increases at

<table>
<thead>
<tr>
<th>[Cl(^{-})] (M)</th>
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<th>Cy572</th>
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<td>(d_{\text{Tb}})</td>
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</table>

Table 3

Separation studies of Nd/Tb/Dy using different Cl\(^{-}\) concentrations.

Fig. 3. Effect of medium concentration on the extraction of Nd(III), Tb(III) and Dy(III) at initial pH 3.50 (triplicate test). Aqueous phase: 1 g dm\(^{-3}\) of each metal solution. a) Cy272 in kerosene. b) Cy572 in kerosene.
Taking into account that the neutral equivalent values of P81R and Cy572 are 191 and 310 g/mol, respectively (Table 1) and regarding Table 4 results, the maximum selectivity corresponds to an equimolar mixture of Cy572 and P81R, which also accords with the IL formation stoichiometry (Eq. (2)).

3.2.4. Effect of IL concentration

In order to investigate the effect of the P81R·Cy572 IL concentration on the extraction, experiments were performed varying the IL concentration from 0.10 up to 0.60 M. Kerosene was the diluent used. The aqueous phase was 1 g dm$^{-3}$ of each REE in 4 M Cl$^{-}$ fixing the initial pH at 0.10. The extraction percentages of neodymium, terbium and dysprosium increase as the ionic liquid concentration increases (Fig. 7). The equilibrium pH is maintained in the 1.19–1.25 range. This confirms that there are no protons exchange to the aqueous phase when the REEs are extracted with P81R·Cy572 IL (Eq. (3)). Additionally, taking into account the Padhan and Sarangi investigation where Pr and Nd were stripped with an efficiency of 98.11 and 98.75%, respectively, using 1.8 M of H$_2$SO$_4$ (Padhan and Sarangi, 2017), the Nd(III), Tb(III) and Dy(III) loaded in the organic phase was completely stripped using HCl 4 M.

The aforementioned experiment by Padhan and Sarangi, also suggests that three molecules of Aliquat 336·Cyanex 272 IL are involved in the solvent extraction of one molecule of neodymium and praseodymium (Padhan and Sarangi, 2017) and our results are in consonance with this study because the slope values of $-\log D - 3 \log [\text{CT}^-]$ vs. $-\log \{\text{P81R-Cy572 IL}\}$ are 3.03, 2.74 and 2.54 for neodymium, terbium and dysprosium, respectively (Fig. S4 in the supplementary material).

Keeping in mind that the objective is to separate Nd(III) from the Nd/Tb/Dy mixture, 0.30 M of P81R·Cy572 IL is chosen, because using this IL concentration a higher selectivity is obtained (Table 5).

3.2.5. Effect of the diluent to be used in the counter-current extraction

Since kerosene is one of the most commonly utilized diluents due to its properties, it was mainly used in this investigation as a diluent. However, considering the possibility of the appearance of a third phase at a higher REEs organic phase loadings and with a higher pH$_{eq}$, it has
been considered appropriate to investigate the effect of different diluents on the REEs extraction to be used in the counter-current extraction process. Although nowadays the use of aromatic diluents is not recommended, they can be utilized to avoid the third phase formation. Because of this, apart from the kerosene, toluene, cumene, Solvesso 100 and Solvesso 200 were the different aromatic diluents studied.

As a result, different extraction experiments with 0.30 M of P81R·Cy572 IL have been carried out. The aqueous phase contained the same REE concentrations that will be used in the counter-current experiments, 9.00, 0.50 and 2.50 g dm\(^{-3}\) of Nd(III), Tb(III) and Dy(III), respectively, in 4 M Cl\(_2\). The results are shown in Table 6 where it can be observed that the diluent effect on the REEs extraction is not non-existent.

The dielectric constant was chosen as a key parameter since it allows us to get an idea of the polarity of the studied diluents. It was observed that the higher is the dielectric constant, the greater is the polarity of the diluent. Even if this parameter is different for the investigated diluents, the extraction percentages are very similar using all the used diluents. As a result, the polarity of the diluents studied has no influence on the neodymium, terbium and dysprosium extraction using P81R·Cy572 IL.

Taking into account the third phase formation restraining, Solvesso 100 was selected to be the diluent to make the counter-current extraction experiments.

3.2.6. Counter-current experiment

The REEs separation from a synthetic magnet waste solution sample which is considered equal to a real magnet waste sample, was carried out by the counter-current extraction process. The theoretical number of stages required to separate neodymium from the mixture using a counter-current system can be calculated if the extraction equilibria are known and solving the mass balance equations at all stages. Taking into account that the REE concentrations in magnet wastes are Nd(III) ≫ Dy (III) > Tb(III) and the REEs affinity using P81R·Cy572 IL is Dy (III) > Tb(III) ≫ Nd(III), the extraction isotherm study has been done referring to Dy(III).

The aqueous phase was a mixture of 9.00 g dm\(^{-3}\) of Nd(III), 0.50 g dm\(^{-3}\) of Tb(III) and a range of Dy(III) concentrations from 0.10 up to 2.55 g dm\(^{-3}\), coincident with the real concentration of these REEs in the magnet wastes (Binnemans et al., 2013; Sasai and Shimamura, 2016; Yang et al., 2017). The IL concentration was 0.30 M and Solvesso 100 was used as the diluent to avoid the third phase formation in the organic phase. The working conditions required an A/O ratio of 1:4. The McCabe-Thiele plot (Fig. 8a) indicates that at least two stages are required to obtain the total elimination of Dy(III) from the aqueous phase at A/O ratio of 1:4. Following the procedure established in Section 2.5 and as can also be seen in Fig. S5 (in the supplementary material), eleven contacts were necessary to achieve the steady-state concentrations in all the phases. The bold points shown in Fig. 8a are the Dy(III) experimental concentrations obtained in the two counter-current stages after the system stabilisation. Bold points are close to the isotherm line and the differences can be explained because the initial pH was not exactly the same that the isotherm experiment.

Fig. 8b shows the measured concentrations of Nd(III), Tb(III) and Dy(III) in each phase and for every step of the separation process in the counter-current extraction process. The equilibria pH for each stage is also shown. The Tb(III) and Dy(III) concentrations in the raffinate gradually decrease while the concentration of Nd(III) remains constant throughout the whole process, so there is no co-extraction of this LREE at these pHs. This can be explained by the HREEs preferential extraction over the LREEs. Conversely, terbium and dysprosium concentrations increase in the loaded organic solutions. Consequently, the main objective for using the P81R·Cy572 IL in the counter-current extraction experiment has been demonstrated because the pH during the extraction remained close to 1.2.

Summing up, the counter-current process allows us to recover 99.99% of the neodymium with a purity of 99.7% maintaining the pH close to 1.2 without pH conditioning.

4. Conclusions

The P81R·Cy572 IL has been proposed as the extractant to recover neodymium from synthetic magnet waste leachings and its choice to be used in an industrial counter-current process has been successfully demonstrated.

The pH dependence on REEs extraction was investigated, and the optimum range to achieve the separation goal is from 0.8 up to 1.5. The organic phase composition that allows, the separation of Nd(III) from the mixture with the highest selectivity is 0.30 M of P81R·Cy572 IL in kerosene. It is possible to strip completely the Nd(III), Tb(III) and Dy(III) completely from the loaded organic phase by using a 4 M HCl solution.

The study of the extraction mechanism of REEs using P81R·Cy572 IL by slope analysis suggests that three molecules of IL are involved in the solvent extraction of one molecule of Nd(III), Tb(III) and Dy(III).

Aromatic

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<th>Dielectric constant</th>
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<td>48.8</td>
<td>67.9</td>
<td>Yes</td>
<td></td>
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</tbody>
</table>

Fig. 7. Effect of P81R·Cy572 IL concentration on the REEs extraction at initial pH 0.10 using kerosene as diluent (triplicate test). Aqueous phase: 1 g dm\(^{-3}\) of each metal in 4 M Cl\(_2\).
working two stages without any aqueous pH conditioning. Thus, the pH remained constant around 1.2 during the extraction in the two counter-current process stages. This fact is the main claim of the current investigation in order to recover REEs using an industrial process.

Acknowledgments

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We express our gratitude to Cytec Industries Inc., Dow Chemical and ExxonMobil for providing free samples of Cyanex 272, Cyanex 572, Primene 81R, Solvesso 100 and Solvesso 200.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jenvman.2018.05.054.

References


6. PUBLICATION 3
Improved rare earth elements recovery from fluorescent lamp wastes applying supported liquid membranes to the leaching solutions

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Agri-Food Engineering and Biotechnology Department, ESAB, Universitat Politècnica de Catalunya, Castelldefels 08860, Spain
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A R T I C L E   I N F O

Keywords:
Fluorescent lamp wastes
Leaching
REEs recovery
REEs transport
Supported liquid membranes

A B S T R A C T

Due to the continuously growing demand of rare earths in advanced technologies, end-of-life fluorescent lamps may become feasible rare earth elements (REEs) raw materials, reducing thus their supply risk. Considering acid leaching as the most common method in the metal recovery from an end-of-life product real scratch resulting from the fluorescent lamps, this paper proposes an improvement of the REEs recovery from these wastes adding a supported liquid membrane (SLM) step to minimize the loss of these metals in the first leaching (L1). HNO₃ or HCl are the most appropriate acid agents in the L1 stage considering the balance between the Ca (II) impurity removal and the REEs losses minimization. These REEs lost can be entirely recovered from the L1 leachate by flat sheet supported liquid membranes (FSSLM) using Cyanex 923 as carrier and Na₂EDTA as the receiving phase. REEs, especially Y and Eu, have been recovered in quantitative yields using a L₁–FSSLM–L₂ process.

1. Introduction

Nowadays, the recovery and separation of REEs has become one of the main interest subjects in the scientific community due to their increasing consumption and supply risk. Moreover, the REEs growing consumption tendency does not seem to change in the upcoming years since their use is essential for the advanced technologies development. Neodymium, terbium, dysprosium, yttrium and europium have been considered as critical metals by several technical reports inducing the need for improved recovery pathways [1].

In order to provide a new way to recover and recycle REEs, the use of end-of-life products and the processing of their waste streams has turned into a promising alternative. According to the fact that the content of REEs in phosphors lamps can reach 27.9%, though only 10% being recovered [2], these end-of-life products have been chosen as the source material of this research. Red phosphors Y₂O₃:Eu³⁺ (YOX), blue phosphors BaMgAl₁₁O₁₉:Eu²⁺ (BAM) and green phosphors La₃PO₄Ce³⁺,Tb³⁺ (LAP), (Gd,Mg)₂O₁₂:Ce³⁺,Tb³⁺ (CBT), (Ce,Tb)MgAl₁₁O₁₉ (CAT) are the three main phosphorus compounds of the fluorescent lamps [3].

Mechanical separation is the most established way to remove components such as plastics, glass and aluminium end caps. Afterwards, acid leaching is the most common method in the metal recovery from an end-of-life product real scratch resulting from the fluorescent lamps [4,5]. Due to the REEs interest and the deficit between consumption and exploitation, taking advantage of these wastes seems to be promising.

Up to now, although there are many investigations which focus on the characterization of real fluorescent lamp wastes and the recovery of REEs from these end-of-life products, industrial-scale applications are scarce. A review regarding the yttrium recovery by leaching and SX from spent fluorescent lamps was published [6]. This review suggests a hydrometallurgical process to separate yttrium and calcium from acid leach liquor (leaching conditions 2 M of sulfuric acid, 70 °C, 15% w/v pulp density and 2 h of reaction time) using 20% v/v D2EHPA in kerosene by three-stage cross current extraction at the initial pH 0.02. Leaching using different solutions such as ammonium chloride, acetic acid, pure water, nitric and hydrochloric acid were investigated by Tunsu et al. for REEs and mercury recovery. Although hydrochloric and nitric acids are able to solubilizing most of the rare earths, the former at a concentration of 4 M showed better efficiency for mercury [7]. Apart from the leaching studies, another important point is the choice of the extractant, because it must have a high selectivity to achieve the complete REEs separation. In this sense, literature studies depict a wide range of extractants, used to separate selectively the rare earths by the SX technique. Adding TBP into the Cyanex 272/Alamine 336 IL, a better Nd/Pr separation factor was obtained [8]. The separation factors between Ce(IV), Y(III) and Yb(III) from aqueous nitrate solution were in...
the order: Cyanex 923/kerosene < TBP/kerosene < HQ (mixture of 8-hydroxyquinoline) + Cyanex 302/heptane [9]. Besides commercial extractants, ionic liquids have been also used in liquid-liquid extraction to recover and separate REEs. The Cyanex 272-Alamine 336 IL was the best extractant to recover neodymium and praseodymium [10]. The Nd (III) separation is possible using Cyanex 272 and Cyanex 572 from a mixture with Tb(III) and Dy(III) in chloride media by SLM [11]. However, using the former, less metal is transported in the same working time. 99% of Dy(III) and Nd(III) transport from a Dy/Nd/Fe mixture in nitric acid medium using [C8mim][Tf2N] containing N,N-dioctyldiglycolic acid (DODGAA) was obtained by using SLMs [12].

For delineating a complete potential hydrometallurgical process of REEs recovery and separation from fluorescent lamp waste samples, the current investigation aims on the first part of the hydrometallurgical process. That is, on the REEs recovery improvement from a YOX phosphors waste real sample to achieve the highest amount of these metals so that they can be selectively separated applying the cross-flow solvent extraction process using IL’s as extractants in chloride media depicted in the previous investigation [13].

In order to evaluate the leaching efficiency for the REEs recovery from the fluorescent lamp wastes, different acidic leaching agents such as aqua regia, acetic, gluconic, hydrochloric and nitric acids have been tested. Once a leach liquor has been obtained, selective separation techniques should be used to achieve the REEs recovery. Several studies suggest a one-step leaching to REEs recovery from the solid waste, however, the fluorescent lamp wastes contain mainly calcium as an impurity. If the chosen technique is the REEs precipitation using oxalic acid [14], calcium becomes an insurmountable problem. Consequently, as shown in Fig. 1, two leaching steps are proposed, using the former to remove the main impurities (calcium). Unfortunately, a small REE amount is also dragged in the liquid fraction. For this reason, SLM was chosen to minimize the REEs losses, because this technique is economically viable to separate the metals presents at low concentrations, as is shown in literature [11,14]. The solid obtained from the L1 stage will be undergone to a second leaching (L2) using high acid concentration to obtain a liquor rich in REEs which will be mixed with the permeate fraction coming from the SLM stage.

Our investigation is focused on the halophosphors rich in YOX phosphors because they have a high REES content, especially yttrium and europium. The characterization and leaching of a fluorescent lamp waste in powder form for the REEs recovery has been carried out in the current study. Using a real waste sample induces to the evaluation of every process-step to achieve the complete REE recovery. The removal of the high impurity level is a demanding key step. In this sense, it is necessary to carry out a preliminary leaching (L1) to separate most of the base metals, but in this stage some REEs are also lost. The innovation provided by this investigation is the use of SLMs to recover the REEs from the liquor obtained after the first leaching (L1) which contains REEs at low concentrations. To evaluate the viability of the proposed procedure and to determine the optimal experimental conditions for the metal ion transport, the SLM experiments have carried out by using flat sheet supported liquid membrane (FSSLM) previously and foremost to be able to apply a hollow fibre renewal configuration.

2. Material and methods

2.1. Reagents

The end-of-life fluorescent lamp samples were obtained from Recyberica Ambiential. The acids used as leaching solutions were: gluconic acid (50%, Ref. 8.22057, Merck), acetic acid (Ref. 131008, Panreac), nitric acid (69%, Ref. 131037, PanReac AppliChem) and hydrochloric acid (37%, Ref. 131020, PanReac AppliChem) diluted with pure water (MilliQ, Millipore, > 18 MΩ/cm).

Cyanex 572 (Cy572) and Cyanex 923 (Cy923) were used as carriers in the SLM experiments since the acidic and neutral carriers are the most used in the REEs recovery field. While Cy572 is a mixture of phosphinic and phosphonic acids, Cy923 is a mixture of four trialkylphosphate oxides, with general formula RnP(O), Rn−1R′P(O), RR′2P(O) and R′3P(O), where R′ refers to n-octyl and R denotes n-hexyl groups [16,17]. Both Cyanex carriers were kindly supplied by Cytec Canada Industries and used as received. Detailed specifications of these extractants are summarized in Table 1. Kerosene from Sigma-Aldrich was used as a diluent (Ref. 607010). HCl and Na2EDTA from PanReac AppliChem (Ref. 131669) were used as stripping agents.

2.2. Characterization of the waste

The end-of-life fluorescent lamp wastes supplied by Recyberica Ambiential was used as received, without crushing or grinding since the sample was already in the powder form.

SEM/EDX (INCA250, Oxford Instruments, Oxford, UK) and X-ray photoelectron spectroscopy (XPS) (SPES, XR-50 Dual anode source, non-monochromated “Al k-alpha, Mg k-alpha”) were applied to determine the solid sample composition. The analyses of the fluorescent lamp wastes using both techniques were measured in triplicate.

Aquag regia was used as reference to determine the maximum leachable amount of metals from the waste. The aqua regia was prepared by mixing concentrated hydrochloric and nitric acids at 3:1 v/v ratio. 10 g of waste were stirred with 0.1 L of aqua regia at 90 ± 2 °C for 2 h. After regaining standard conditions, it was filtered (Filter Paper 1001 070, Whatman International Ltd) and the volume was adjusted to 0.1 L with pure water. The concentration of the metals in the aqueous samples was determined by atomic emission spectrometry using a
4100 MP AES System (Agilent Technologies) within the typical 95% confidence interval.

Molybdenum blue method was chosen as the standard determination method for phosphor, as reported elsewhere [20,21]. The concentration of this metal was colorimetrically determined using UV–VIS spectroscopy (Agilent Technologies, Cary 60) at 660 nm.

2.3. Screening of leaching agents

Pure water, gluconic acid (HOCH2(CHOH)4COOH) 1 M, acetic acid (CH3COOH) 1 M, nitric and hydrochloric acid of various concentrations (0.5 M, 1 M, 2 M) were investigated as leaching solutions. The experiments were carried out using 10 g of end-of-life fluorescent lamps and 0.1 L of leaching solutions (10% w/v), using magnetic stirring (200 ± 10 rpm) at different contact times and room temperature (20 ± 2 °C). The non-dissolved solids were oven-dried overnight at 100 °C (Selecta, Conterm Ref. 2000209). A second leaching (L2) was done using the dry non-dissolved solids from L1 with a higher acid concentration (2 M) and the same S:L ratio. The leaching experiments were done in triplicate.

2.4. Supported liquid membranes procedure

SLM is the most appropriate technique to recover the REEs from the L1 leachates since the concentration of these metals is low and therefore it permits the process intensification. In the flat sheet supported liquid membrane configuration, a microporous polymer film placed between the feed and receiving cells is impregnated with the carrier that selectively binds to a target metal ion. A microporous polytetrafluoroethylene support (Fluoropore™ FHLP04700, Merck Millipore), 4.7 cm diameter, 85% porosity, thickness 150 µm, 0.45 µm pore size and 11.4 cm² of effective membrane area was used as the basic matrix. The transport experiments were carried out using the same experimental set-up and procedure depicted by Pavon et al. [11].

The L1 leachate is used as the feed solution, the carrier was prepared dissolving Cy572 or Cy923 in kerosene and HCl 1.2 M or Na2EDTA 0.05 M were the stripping agents chosen respectively depending on the carrier used. The feed and the receiving solutions were magnetically stirred at 1000 rpm at room temperature (20 ± 2 °C). Samples from both solutions were taken every hour, until completed treatment time of 8 h. The metal concentrations were quantified by atomic emission spectrometry.

The permeability coefficient of each metal was obtained from the Eq. (1) derived by combining metal balance in the feed cell and the Fick’s law in the membrane [22–25]:

\[
\ln \left( \frac{[Me]_0}{[Me]} \right) = -D \frac{A}{V} \cdot t
\]

Table 1

<table>
<thead>
<tr>
<th>Commercial name</th>
<th>Content %</th>
<th>Density (25 °C) kg m⁻³</th>
<th>Viscosity (25 °C) mPa s</th>
<th>Av. Mol. Weight g mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cy572 [18]</td>
<td>100</td>
<td>933</td>
<td>&lt; 50</td>
<td>310</td>
</tr>
<tr>
<td>Cy923 [19]</td>
<td>93</td>
<td>880</td>
<td>40</td>
<td>348</td>
</tr>
</tbody>
</table>

* Experimental data by potentiometric titration in water/ethanol.

Fig. 2. SEM images of the fluorescent lamp wastes. (a) 1.00 kX magnification (Signal InLens). (b) 1.00 kX magnification using light contrast applied (Signal QBSD). (c) Magnification (2.00 kX) of the largest particles in the white-framed area shown in (a). (d) Magnification (2.00 kX) of the smallest particles in the white-framed area shown in (b).
where \([\text{Me}]\) and \([\text{MeO}]\) are the metal ion concentration (g L\(^{-1}\)) in the feed cell at time \((t)\) and initial time \((t_0)\), respectively; \(P\) is the permeability coefficient (m s\(^{-1}\)), \(A\) is the membrane area (m\(^2\)); \(V\) is the volume of the feed solution in the cell (m\(^3\)) and \(t\) is the time (s).

3. Results and discussion

3.1. Waste characterization

To characterize the fluorescent lamp wastes, the sample was dried at 60 ± 1 °C until constant weight, and 0.3% weight loss was observed. The sample complexity, consequence of the particle size and the variety of metals present, requires different analytical techniques for a complete characterization of the starting material.

In this sense, SEM/EDX analysis was chosen to elucidate the heterogeneity of the sample. As can be seen in Fig. 2, the sample is heterogeneous and the size of the particles differs over a wide range (2.1–31.1 µm). Because of this, exhaustive spectra considering possible differences between small and large particles were done. Moreover, in the Fig. 2a a contrast was applied to the same region shown in the Fig. 2b and the results confirm that the bigger particles correspond to elements which are in glasses such as Al-Si and the smaller and more luminous ones are the REEs such a Y, Eu, La and Gd (Fig. 2c and d).

For acquiring further information, XPS technique for screening the metals included in the sample was applied. The relative composition of the detected metals showed a high dispersion in function of the analysed sample point. The complex composition revealed by XPS showed the existence of several strategic metals present in the waste. Especially yttrium and europium achieved high content in the waste compared to other REEs (Fig. 2d). Moreover, the total REEs relative percentage in the end-of-life fluorescent lamp wastes is 6.3 ± 0.04% (Table 2).

The chemical treatment with aqua regia has been applied for acquiring a standard reference of the elements that can be leached from the real sample. After a partial separation of impurities such as glass and plastic, the concentration of 26 metals from the waste was analysed using XPS technique. Achieving a representative waste composition, the experiment was carried out 25 times.

The REEs content average was 93.2 ± 1.2 g kg\(^{-1}\). Calcium and yttrium achieving the largest amounts with an average of 79.0 ± 3 and 84.0 ± 8 g metal kg\(^{-1}\) waste, respectively. As expected, Y and Eu are the main REEs present in this waste because they are the relevant REEs of red phosphors (Y\(_2\)O\(_3\):Eu\(^{3+}\)) [7].

Due to the similar amounts of Ca and Y the removal of the former is essential for a selective leaching to recover and separate the REEs. For this reason, a screening of different leaching agents has been carried out.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Analysed elements and their content in the dried waste using XPS technique.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>% w/w</td>
</tr>
<tr>
<td>Non-REEs</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>43.1 ± 1.0</td>
</tr>
<tr>
<td>C</td>
<td>20.0 ± 2.1</td>
</tr>
<tr>
<td>Al</td>
<td>12.3 ± 0.9</td>
</tr>
<tr>
<td>Ca</td>
<td>5.8 ± 0.1</td>
</tr>
<tr>
<td>Na</td>
<td>5.5 ± 0.1</td>
</tr>
<tr>
<td>P</td>
<td>3.7 ± 0.2</td>
</tr>
<tr>
<td>F</td>
<td>2.6 ± 0.4</td>
</tr>
<tr>
<td>Co</td>
<td>0.5 ± 0.1</td>
</tr>
<tr>
<td>Fe</td>
<td>0.3 ± 0.2</td>
</tr>
<tr>
<td>REEs</td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>5.4 ± 0.1</td>
</tr>
<tr>
<td>Eu</td>
<td>0.5 ± 0.1</td>
</tr>
<tr>
<td>La</td>
<td>0.2 ± 0.1</td>
</tr>
<tr>
<td>Gd</td>
<td>0.1 ± 0.01</td>
</tr>
<tr>
<td>Dy</td>
<td>0.01 ± 0.03</td>
</tr>
<tr>
<td>Ce</td>
<td>0.003 ± 0.001</td>
</tr>
<tr>
<td>Total REEs</td>
<td>6.3 ± 0.04</td>
</tr>
</tbody>
</table>

3.2. Screening of leaching agents

To evaluate the fluorescent lamp wastes leaching efficiency for the REEs recovery, different acidic leaching agents such as gluconic, acetic, hydrochloric and nitric acids have been compared. The studied parameters were acid concentration, contact time and different kind of acid.

3.2.1. Leaching 1 (L1)

Different kind of acids have been used to recover REEs from end-of-life products [7, 26, 27]. The most promising are the strong acids such as sulphuric, nitric and hydrochloric acid due to their strong acidic character [28, 29]. However, considering the L1 leaching stage aim of maximizing the Ca (II) elimination rate and losing the minimum amount of REEs, sulphuric acid was discarded. To avoid the CaSO\(_4\) precipitation, other weak acids were chosen and evaluated by their efficiency to achieve the designed purpose. Hence, the L1 leaching experiments were carried out using pure water, acetic acid 1 M, gluconic acid 1 M, hydrochloric and nitric acid 1 M as the leaching agents using a contact time of 10 min. As is shown in Fig. 3a, the efficacy in removing Ca was: pure water < acetic acid (pKa 4.76) < gluconic acid (pKa 3.60) < nitric acid < hydrochloric acid linked to their increased acidic character. Hydrochloric and nitric acid were the optimal leaching agents because the removed Ca was 100 and 87%, respectively. However, in order to minimize the REEs losses in this leaching step, HCl 1 M seems to be the best choice (Fig. 3a).

The HCl and HNO\(_3\) concentration and the contact time for both leaching agents were the main parameters studied. As can be seen in Fig. 3b and c, the difference of Ca eliminated using 1 M or 2 M HCl and HNO\(_3\) was not significant because in all cases, the Ca removed was higher than 87%. However, when 0.5 M was used, Ca leaching dropped to approximately 60% in contrast to 1 M or 2 M. REEs removal was higher using 2 M of HCl or HNO\(_3\) than 1 M of these leaching agents. The contact time experiments were carried out using a range from 5 to

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Average elements content in the waste. Aqua regia leaching (90 ± 2 °C, 2 h).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>r(<em>{\text{ES}}) (\text{kg}</em>{\text{ES}}) (\text{kg}^{-1})</td>
</tr>
<tr>
<td>Non-REEs</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>79.0 ± 3</td>
</tr>
<tr>
<td>P</td>
<td>43.3 ± 2</td>
</tr>
<tr>
<td>Al</td>
<td>11.0 ± 0.1</td>
</tr>
<tr>
<td>Fe</td>
<td>5.0 ± 0.01</td>
</tr>
<tr>
<td>Ba</td>
<td>4.0 ± 0.2</td>
</tr>
<tr>
<td>Sr</td>
<td>4.0 ± 0.1</td>
</tr>
<tr>
<td>Mn</td>
<td>2.0 ± 0.1</td>
</tr>
<tr>
<td>Na</td>
<td>1.7 ± 0.1</td>
</tr>
<tr>
<td>Mg</td>
<td>1.5 ± 0.01</td>
</tr>
<tr>
<td>K</td>
<td>0.9 ± 0.1</td>
</tr>
<tr>
<td>B</td>
<td>0.7 ± 0.1</td>
</tr>
<tr>
<td>Sb</td>
<td>0.4 ± 0.1</td>
</tr>
<tr>
<td>Cu</td>
<td>0.1 ± 0.1</td>
</tr>
<tr>
<td>Ni</td>
<td>0.1 ± 0.1</td>
</tr>
<tr>
<td>Si</td>
<td>0.1 ± 0.01</td>
</tr>
<tr>
<td>Co</td>
<td>Not detected</td>
</tr>
<tr>
<td>Hg</td>
<td>Not detected</td>
</tr>
<tr>
<td>REEs</td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>84.0 ± 8</td>
</tr>
<tr>
<td>Eu</td>
<td>6.0 ± 0.1</td>
</tr>
<tr>
<td>La</td>
<td>1.6 ± 0.3</td>
</tr>
<tr>
<td>Gd</td>
<td>1.1 ± 0.8</td>
</tr>
<tr>
<td>Tb</td>
<td>0.2 ± 0.1</td>
</tr>
<tr>
<td>Ce</td>
<td>0.1 ± 0.1</td>
</tr>
<tr>
<td>Dy</td>
<td>0.1 ± 0.01</td>
</tr>
<tr>
<td>Nd</td>
<td>0.1 ± 0.01</td>
</tr>
<tr>
<td>Er</td>
<td>Not detected</td>
</tr>
<tr>
<td>Yb</td>
<td>Not detected</td>
</tr>
<tr>
<td>Total REEs</td>
<td>93.2 ± 1.2</td>
</tr>
</tbody>
</table>

* Molybdenum blue method.

References
15 min. Despite of using 15 min, higher amount of Ca is leached, 10 min is the optimal contact time condition to minimize the losses of REEs trying to maximize the Ca elimination.

In conclusion, the optimal conditions for the L1 step to minimize the REEs losses and maximize the Ca separation from the fluorescent lamp wastes are: 1 M of HCl or HNO3 and a contact time of 10 min.

3.2.2. Leaching 2 (L2)

According to Tunsu et al., to recover completely REEs from fluorescent lamp wastes, acid agents with higher acidic character and severe working conditions are required [7]. Thus, HCl and HNO3 instead of weak acids were the chosen leaching agents to investigate the REEs recovery in the L2 leaching stage. The contact time was the studied parameter, maintaining the hydrochloric and nitric acid concentration at a constant level of 2 M. The metal leached percentages have been referred to the metal concentrations obtained using aqua regia. The leaching behaviours are presented in Fig. 4. For Eu and Y, the leached metal was stabilized after 48 h. However, the Gd and La were not stabilized in whole the investigated time (168 h). Moreover, the metal leaching yield was above 80% for Eu using HCl or HNO3. These results are similar to the ones reported by Tunsu et al. [7] except for the La, since the percentage of metal leached is around 25% in contrast to only 5% in our investigation.

In order to recover Y and Eu quantitatively from L1 solid waste, HCl and HNO3 2 M need to be applied for 48 h. The recovery of Gd and La could be acquired at higher extensions using more drastic conditions in a 3rd leaching (L3).

3.3. Supported liquid membranes

Cy923 and Cy572 have been chosen to study the recovering of the REEs present in the L1 leachate by SLMs. Since the obtained results in the L1 using HCl and HNO3 were similar, both extractants can be used in the membranes experiments depending on the species, cationic or neutral, present in the media. When nitric acid was used as the leaching agent, the formed species are mainly neutral, whereas cationic species are produced by using hydrochloric acid. Since Cy923 extracts neutral species and Cy572 cationic ones, nitric acid was used as the media to leach REEs when the former extractant was utilized as the carrier, whereas hydrochloric acid was chosen for Cy572, as previous studies recommend [30,31].

Considering that the complete Eu and Y recovery was achieved by solvent extraction at pH = 1.5 using Cy572 [13], the leachate pH was set to this value and used as a feed in an SLM experiment following the procedure depicted in Section 2.4. Unfortunately, at these conditions, a precipitate appeared. This fact can be explained using the MEDUSA software since REEPO₄(s) (YPO₄(s) or EuPO₄(s)) is obtained above a pH value of 0.5 (Fig. 5).

To avoid the precipitation in the feed solution, the pH was fit to 1.2. However, at this pH there had no metal transport using Cy572 0.3 M as
carrier. Cause of the tight pH range to have REEs transport and avoid the REEPO₄(s) precipitation, it seemed to be promising to change the strategy and use the Cy923 since using this extractant no pH conditioning is required to extract the REEs.

The SLM experiments using Cy923 were carried out using the leachate obtained from the L1 using 1 M of HNO₃ for 10 min. The composition of this leachate is depicted in Table 4. The pH of the feed solution was adjusted to 1.2 and four different concentrations of Cy923, 0.3, 0.6, 0.9 and 1.2 M, were investigated. Even though the use of strong acids to recover the REEs loaded has been reported in different investigations [17,33–35], one of the most common stripping agents, HNO₃, was rejected since the same neutral complex species (Y(NO₃)₃) would be formed in the receiving phase transporting it to the feed phase, thus, reducing the REEs transport through the membrane from the feed to the receiving phase. Hence, the Na₂EDTA 0.05 M was chosen as the receiving solution in the membrane experiments to avoid the neutral complex species formation encouraging the anionic species ones.

Fig. 6 shows that the transported REEs increased with the carrier concentration. Meanwhile the Ca, the most representative impurity of the sample, was not transported in any conditions. After 8 h, the percentage of Y transported was 40%, using the highest Cy923 concentration. The Eu behaviour followed the same tendency that Y. However, the transport of Y using 0.9 M is similar to 1.2 M of Cy923. Comparing the metal appeared in the receiving solution with the metals disappeared from the feed phase we can affirm that the loaded metals were wholly stripped.

From the data, where the higher impurity in Ca form is removed, it is demonstrated that in order to avoid the REEs losses after the first leaching process, to use Cy923 as carrier is a viable option.

As shown in Fig. 7, the permeability increases when the carrier concentration increases until 0.9 M of the carrier. This means that at low concentrations of Cy923 the metal transport is only controlled by the diffusion through the membrane, but at higher Cy923 concentrations, the effect of the shear stress become predominant, reducing the apparent permeability due to the increase in the viscosity.

The permeability coefficients using 0.9 M of Cy923 for Eu and Y were 4.9·10⁻⁶ and 3.6·10⁻⁶ m s⁻¹, respectively. The results indicate that the Cy923-metal complex transport increases linearly when the carrier concentration range is 0.3–0.9 M. The permeation coefficients values are similar to those obtained for Cd(II) transport through hollow fibre supported strip dispersion (HFSD) by N.S. Rathore et al. using

---

**Table 4**

<table>
<thead>
<tr>
<th>Element</th>
<th>mg L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>6820 ± 150</td>
</tr>
<tr>
<td>P⁶⁻</td>
<td>759 ± 14</td>
</tr>
<tr>
<td>Fe</td>
<td>41 ± 8.5</td>
</tr>
<tr>
<td>Ba</td>
<td>311 ± 0.1</td>
</tr>
<tr>
<td>Sr</td>
<td>236 ± 5.6</td>
</tr>
<tr>
<td>Mn</td>
<td>152 ± 3.5</td>
</tr>
<tr>
<td>Si</td>
<td>132 ± 3.1</td>
</tr>
<tr>
<td>Al</td>
<td>116 ± 2.5</td>
</tr>
<tr>
<td>Na</td>
<td>90 ± 2.1</td>
</tr>
<tr>
<td>Mg</td>
<td>64 ± 1.7</td>
</tr>
<tr>
<td>K</td>
<td>56 ± 1.4</td>
</tr>
<tr>
<td>Sb</td>
<td>20 ± 0.6</td>
</tr>
<tr>
<td>Y</td>
<td>491 ± 12</td>
</tr>
<tr>
<td>Eu</td>
<td>41 ± 0.9</td>
</tr>
<tr>
<td>La</td>
<td>16 ± 0.3</td>
</tr>
<tr>
<td>Total REEs</td>
<td>548 ± 6.6</td>
</tr>
</tbody>
</table>

* Molybdenum blue method.

---

**Fig. 4.** Eu, Gd, La and Y leached (%) over 168 h, S:L ratio of 10% w/v, magnetic stirring – 200 rpm. (a) HCl 2 M. (b) HNO₃ 2 M.

**Fig. 5.** Speciation diagram using MEDUSA software [32]. [PO₄³⁻] = 0.2 M, [Ca²⁺] = 0.2 M, [Cl⁻] = 1 M, Ionic strength: 1 M. (a) Y 6·10⁻³ M (b) Eu 3.3·10⁻⁴ M.
Cyanex 923 [36] and for Nd, Tb and Dy using Cyanex 572 and Cyanex 272 in the S. Pavón et al. [11].

To sum up, considering the scale-up industrial process using hollow fibre membrane modules, 7 h will be required to recover the 95% of REEs from 1 m³ of L1 leachate of 100 kg of the fluorescent lamp waste using a 33 m² membrane area if a permeability coefficient is 3.6 · 10⁻⁶ m s⁻¹ being this value for the Y since it is the main REE in the fluorescent lamp waste.

4. Conclusions

YOX phosphors from end-of-life fluorescent lamps were investigated to evaluate their recycling potential. The main impurities of the real scratch were iron and calcium that were removed using magnetic separation and an acidic leaching stage respectively.

Nitric acid is the most appropriate leaching agent when Cy923 is used as the carrier in the SLM to recover the REEs because their recovery is obtained using an acid feed pH = 1.2. The losses of these metals in the first leaching stage have been minimized adding a membrane stage with a flat sheet configuration. Although Cy923 is able to recover these REEs losses, the higher permeability coefficients are obtained when the concentration of Cy923 is 0.9 M. Metals transport increases when the Cy923 concentration also increases, resulting in a reduction of the membrane area or the working time needed to achieve the REEs recuperation. Finally, an L2 stage using HNO₃ or HCl 2 M for 48 h is required to recover completely the REEs, especially Y and Eu from the waste.

Based on the obtained results, the REEs can be completely recovered from their leachates optimizing the leaching process and using flat sheet supported liquid membranes.

Acknowledgments

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References


7. PUBLICATION 4
Solvent extraction modeling of Ce/Eu/Y from chloride media using D2EHPA

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Abstract
End-of-life fluorescent lamps are becoming essential in the rare earths (REEs) field and suppose a feasible secondary source for getting them, reducing thus their supply risk. Considering the proved viability of the cationic extractants, the present study aims at establishing a solvent extraction model using di-(2-ethylhexyl)phosphoric acid (D2EHPA) not only based on the individual Ce, Eu, and Y behavior in chloride media, but also bearing in mind the competitive extraction of these metals in Ce/Eu/Y mixtures, depending on the media variables. Furthermore, the model allow determining the optimal REEs separation conditions. The results disclose that Y could be separated from the mixture using 0.1 mol/L D2EHPA, acidity above of 3 mol/L of protons and chloride concentrations higher than 4 mol/L.

KEYWORDS
D2EHPA, mathematical modeling, rare earths, separation, solvent extraction

ATTENTION
Pages 83 to 92 of the thesis, containing this article are available at the editor’s web
Rare earth elements recovery from E-wastes by solvent extraction and supported liquid membrane processes

8. PUBLICATION 5
Rare earths separation from fluorescent lamp wastes using ionic liquids as extractant agents

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b Agri-Food Engineering and Biotechnology Department, ESAB, Universitat Politècnica de Catalunya, Esteve Terrades 8, 08850 Castelldefels, Spain
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Solvent extraction
Primene 81R D2EHPA IL
Primene 81R Cyanex 572 IL

A B S T R A C T

Processing of end-of-life products has become essential in the rare earth elements (REEs) recovery field because the demand for these metals has increased over the last years due to their intensive use in advanced technologies. Fluorescent lamp wastes are considered one of the most interesting end-of-life products for investigation due to their high REEs content, mainly yttrium and europium. As a result, red phosphors (Y2O3:Eu3+ – YOX) have been chosen for evaluating their REEs’ recovery potential. The REEs from a YOX reach liquor, coming from a soft leaching process have been precipitated adding oxalic acid and calcined to get the REEs in oxide form. Cyanex 572, D2EHPA and the ionic liquids, Primene 81R D2EHPA IL and Primene 81R D2EHPA IL, have been chosen to investigate the efficiency of REEs separation in chloride media. Yttrium, europium and cerium have been individually recovered by a four stages cross-flow solvent extraction process using the Primene 81R D2EHPA IL and the Primene 81R Cyanex 572 IL as extractants. Ce(III), Eu(III) and Y(III) have been obtained at high purities ≥ 99.9%. 4 mol/L HCl has been used to recover the yttrium and the europium from the organic phases.

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1. Introduction

In recent years, the REEs group has been considered crucial in advanced technologies (such as phosphors, permanent magnets, batteries, lasers, etc.) because of their chemical properties. The continuous growing interest in electric and hybrid cars, fluorescent lamps, wind turbines, technologic devices and permanent magnets leads to an exponential increasing demand for REEs. As shown in the literature, the high fluctuations price, the grown usage, especially in the clean energy markets and their supply risk are the main reasons for declaring neodymium, terbium, dysprosium, especially yttrium and europium, are concentrated in the fluorescent lamps market. Due to the eradication of the traditional incandescent bulbs, the manufacture of the fluorescent lamps containing phosphors has increased in the last few years (Ippolito et al., 2017). This substitution allows a saving up to €100 over a product’s lifetime which is around 20 years. Furthermore, fluorescent lamps, which produce an efficient use of the lighting energy, could save enough energy to power 11 million households for one year and avoid emissions of 12 million tonnes of CO2 in Europe (European Commission, 2009).

Fluorescent lamps contain mainly three different phosphors: red phosphors Y2O3:Eu3+ (YOX), blue phosphors BaMgAl10O17: Eu2+ (BAM) and green phosphors LaPO4:Ce3+, Tb3+ (LAP), (Gd, Mg) B2O3:Ce3+, Tb3+ (CBT) and (Ce, Tb)MgAl11O19 (CAT) (Song et al., 2013). The REEs amount present in these three different phosphors is about 55.35 and 10 wt%, respectively. As the most abundant representatives of REEs, the separation process of Y(III) and Eu(III) has been investigated in this study by using halophosphate phosphors, rich in YOX phosphors.

Although the cationic commercial extractants such as Cyanex 572 (Cy572) or D2EHPA (di-(2-ethylhexyl)phosphoric acid) have been studied in many investigations, they have also been evaluated in the current research as well as the ionic liquid extractants formed by Primene 81R (t-alkyl primary amine) along with them. Several reports on ionic liquids for REEs separation have appeared in recent literature (Prodjio and Mudring, 2018; Su et al., 2018). However, they usually are formed by a cation from a quaternary ammonium or phosphonium salt and a conjugated base from an acidic cation exchanger. In this investigation, an innovative...
approach is presented by using a primary amine, such as Primene 81R for the formation of the ionic liquid because of its higher basicity compared to the secondary and tertiary amines (Borai et al., 2014).

Up to now, there are many separation and recovery processes for REEs. Nevertheless, solvent extraction (SX) is the chosen technique since a lot of literature studies depict a wide range of different extractants that can be used to selectively separate the REEs (Innocenzi et al., 2017; Tunsu et al., 2014). Different separation studies using ionic liquids were reported recently. A better Nd/Pr separation factor was obtained with the addition of TBP in the binary mixture of Cyanex 272 and Alamine 336 (Liu et al., 2015). Padhan and Sarangi proposed Cyanex 272-Alamine 336 IL as the best extractant to recover neodymium and praseodymium (Padhan and Sarangi, 2017). The Mishra and Devi investigation suggested the extraction mechanism for Cyphos IL 104. They concluded that three H+ ions are involved to the aqueous phase making the solution acidic using D2EHPA, while an ion association is the extraction mechanism when Cyphos IL 104 is used. Although a higher extraction efficiency was observed in the Ce, La, Y and Eu extraction using Cyphos IL 104, the Y/Eu selectivity was higher using D2EHPA (Mishra and Devi, 2018). Belova et al. studied the REEs extraction in chloride and nitrate media using Aliquat 336-Cyanex 272 IL in toluene (Belova et al., 2009). They noted that the distribution ratio was almost constant above pH 5 and the extraction mechanism was depicted as a binary extraction by (Eq. (1)):

$$3\text{RNH}_2 + 3\text{Me}^{3+} + 3\text{Cl}^{-} \rightarrow 3\text{RNH}_3^+ \text{MeCl}_3$$  (1)

The separation of Th(IV) from several rare earths (III) such as La, Ce, Nd, Gd and Er was investigated using N1923/[C8mim][PF6] IL by Zuo et al. (2008). A four-stage counter current extraction process was carried out by Coll et al. using a bench scale mixer-settler to separate Co(II) and Ni(II) by 20% of JMT-Cy727 IL (Coll et al., 2012). Although the technique used was not SX, García-Díaz et al. investigated the In(III) transport using RNH₂HSO₄ IL by hollow fiber strip dispersion (García-Díaz et al., 2017). 80% of In(III) transport was achieved after 3 h using a feed at pH 2.0 and 0.25 mol/L of IL in Solvesso 100.

The amount of waste electrical and electronic equipment (WEEE) generated in Europe is about 12 million of tonnes per year and the forecast is expected to increase in the next years of at least 4% per annum (Tsamis and Coyne, 2015). According to data from the European Electronic Recycles Association, its 38 members and over 100 subsidiaries had a total of 2.2 million tonnes of WEEE treated per year. There are a small number of companies focusing on the refining and smelting of the rare earths and precious metals. To minimize the residuous amount and contribute to a green and circular economy, the legal framework of 2008 has been changed by the European Union introducing the following priority objectives for waste management in the EU: (1) reduce the waste generated amount, (2) maximise the recycling and the re-use, (3) limit the incineration to non-recyclable materials, (4) phase out landfilling to non-recyclable and non-recoverable waste (5) ensure the full implementation of the waste policy targets in all the EU Member States. In addition, the waste management domain represents one of the most important contributor to employment growth in the environmental economy as shown by the environmental goods and services accounts. Furthermore, banning the fluorescent lamps to LEDs (European Union, 2009) could cause an increase on the REEs wastes. The main approach of this research is the use of these waste products to overcome the overexploitation of the primary resources, which are not sustainable. The recycling of REEs from lamp phosphors can be carried out by: (1) direct re-use of these recycled lamps in new ones, (2) recycling the components of these phosphors using physicochemical separation methods to re-use in new lamps and (3) chemical attack to the fluorescent lamps to recover their REE content (Binnemans et al., 2013).

In this sense, recycling of REEs from the secondary resources like scraps or fluorescent lamp wastes should gain relevance. Considering that their main REEs content are yttrium and europium which are both critical REEs, a Ce/Eu/Y mixture has been investigated to reach the individual REEs separation. The aim of this research is to achieve their separation from leachates, using D2EHPA and Cy572 as cationic commercial extractants or Primene 81R/D2EHPA IL (P81R-D2EHPA IL) and Primene 81R-Cyanex 572 IL (P81R-Cy572 IL) as ionic liquid extractants. The first part of the study focused on the choice of the commercial cationic or ionic liquid extractants, taking into account their selectivity and their behaviour on the Ce/Eu/Y separation and the second part aims on the separation of the REEs from the Ce/Eu/Y mixture using the concentrations found in real fluorescent lamps wastes using IL’s.

2. Experimental and methods

2.1. Reagents

End-of-life fluorescent lamp waste as the main raw material in this investigation was obtained from Recyberica Ambiental S.L (Spain). Cyanex 572 and Primene 81R were supplied by Cytec Canada Industries and Dow Chemical, respectively and D2EHPA was provided by Sigma-Aldrich (Ref. 237825), and all of them were used as received. Kerosene (Ref. 607010) from Sigma-Aldrich as a diluent and hydrochloric acid as stripping agent were used. Detailed specifications of the extractants are summarized in Table 1.

A procedure similar to the reported by Coll et al. was followed to prepare both ionic liquids (Coll et al., 2012). Stoichiometric quantities of two commercially available extractants P81R and D2EHPA or P81R and Cy572 were mixed in kerosene to prepare both ionic liquids, P81R-D2EHPA IL and P81R-Cy572 IL, as is shown in Eq. (2). Cationic extractants were considered in dimeric form.

$$2\text{RNH}_2 + \text{HA}^+_2 \rightarrow 2\text{RNH}_3^+ \text{A}^-$$  (2)

<table>
<thead>
<tr>
<th>Table 1</th>
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<tr>
<td>Physical properties of Cy572, P81R and D2EHPA.</td>
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<tr>
<td>----------------------------------</td>
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<tr>
<td><strong>Commercial name</strong></td>
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<tr>
<td>----------------------------------</td>
</tr>
<tr>
<td>Cyanex 572</td>
</tr>
<tr>
<td>Primene 81R</td>
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<tr>
<td>D2EHPA</td>
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a (CYTEC Industries Inc., 2013).

b As a monomer.

c Experimental data by potentiometric titration in water/ethanol.


e (Sigma-Aldrich, 2002).
2.2. Experimental procedure

Fluorescent lamp wastes were treated in a first leaching, L1, with HCl of low concentration (1 mol/L) for 10 min to separate non-ferrous impurities, mainly calcium. Then, the solid residue obtained from L1 stage underwent a second leaching process (L2) using high HCl concentration (2 mol/L) for 2 h to obtain a liquor reaching in REEs. After the acid treatments, the REEs oxalate precipitate was obtained by addition of oxalic acid 1 M. Then, the REEs oxalate precipitate was calcined at 600 °C for 1 h (Ippolito et al., 2018) to recover the metals in oxide form. REEs oxides were dissolved with HCl 2 mol/L to obtain the work solution to carry out the YOX leachate separation process.

2.2.1. Solvent extraction

The preliminary solvent extraction experiments were carried out using an aqueous phase containing 1 g/L of yttrium, europium and cerium in 4 mol/L Cl\textsubscript{3} medium. 10 mL of this aqueous phase were equilibrated with an equal volume of organic phase into a separatory funnel at room temperature (20 ± 2 °C) using a horizontal mechanical shaker (SBS Mechanical Shaker) at 140 rpm. Like done in previous kinetic experiments (Pavón et al., 2018), after 5 min the extraction equilibrium was achieved. Nevertheless, the shaking time for all the experiments was prolonged until 10 min to guarantee complete equilibration. After both phases were separated, the aqueous phase was taken out and put aside for metal concentration measurement. The loaded organic phases were stripped using HCl 4 mol/L. The experiments were carried out three times and the REEs concentration in the aqueous phase was determined by atomic emission spectrometry using a 4100 MP AES System (Agilent Technologies) with an analytical error <5%.

Extraction efficiency (%E), stripping efficiency (%S), distribution ratio (D) and separation factor (β) were the parameters used to analyse the obtained results, and are defined in Eqs. (3)–(6):

\[
\%E = \frac{|Me|\text{ini} - |Me|\text{log}}{|Me|\text{ini}} \times 100
\]

\[
\%S = \frac{|Me|\text{str}}{|Me|\text{log}} \times 100
\]

\[
D_Me = \frac{|Me|\text{log}}{|Me|\text{ini}}
\]

\[
\beta_{1:2} = \frac{D_{Me1}}{D_{Me2}}
\]

where [Me]\text{ini} and [Me]\text{log} refer to the initial and the equilibrium REE concentration in the aqueous phase, [Me]\text{str} is the equilibrium REE concentration in the stripping phase and [Me]\text{log} is the REE concentration in the loaded organic phase obtained by mass balance.

2.3. Extraction mechanism

The metal extraction mechanism was investigated to confirm the difference between the extraction process using cationic extractants such as Cy572 or D2EHPA, mechanism proposed in Eq. (7), and the ionic liquids such as P81R-Cy572 IL or P81R-D2EHPA IL (Eq. (8)). The equilibrium constants are written and shown in Eqs. (9), (10) taking into account the distribution ratio D:

\[
Me^{3+} + 3[HA]_2 \overset{K_1}{\rightleftharpoons} Me[HA]_3 + 3H^+ \tag{7}
\]

\[
3RNH_2A^+ + Me^{3+} + 3Cl^- \overset{K_2}{\rightleftharpoons} MeA_3 \cdot 3RNH_3Cl \tag{8}
\]

Eqs. (11) and (12) were obtained by applying logarithms to Eqs. (9) and (10).

\[
\log D = \log K_1 + 3\log [HA]_2 - 3\log [H^+]
\]

\[
\log D = \log K_2 + 3\log RNH_3A^- + 3\log [Cl^-]
\]

A slope of 3 should be obtained plotting \(\log D - 3\log [HA]_2\) vs. \(\log [H^+]\), meaning that three protons are involved in the suggested cationic extraction process, according to the Eq. (7). However, protons are not involved in the proposed extraction mechanism using ionic liquids as shown in Eq. (8). Therefore, plotting pH\text{eq} vs. pH\text{initial}, a slope of 1 should be obtained.

3. Results and discussion

3.1. REEs separation/extractability investigation

3.1.1. Effect of pH

Cy572, D2EHPA, P81R-Cy572 IL and P81R-D2EHPA IL were the chosen extractants to investigate their affinities for the REEs from YOX phosphors. The effect of the equilibrium pH on the extraction of cerium, europium and yttrium was investigated using an aqueous phase containing 1 g/L of each REE in 4 mol/L Cl\textsubscript{3} medium and 0.30 mol/L of each extractant in the organic phase using a phase ratio (A:O) of 1:1. Since the pH measurements are not accurate under the highly acidic conditions studied, the equations have been written in hydrogen ion concentration terms.

As shown in Fig. 1, the REEs extraction tendency is the same regardless of each extractant used. Cy572 extracted at a higher pHs compared to D2EHPA, due to the strength of the complex formed with the REEs. Apart from this fact, the extraction yield order obtained was always Y(III) > Eu(III) > Ce(III) (Fig. 1a and b). The same behaviour is observed when P81R-Cy572 IL and P81R-D2EHPA IL were used (Fig. 1c and d). This extraction order is in accordance with the fact that the heavy rare earth elements (HREEs) are extracted before the light rare earth elements (LREEs), because of the existence of a characteristic diagonal relationship for REEs with the equilibrium pH (Swain and Otu, 2011). Moreover, the relationship between the extraction percentage and the ionic radii of the REE is inversely proportional (Mohammedi et al., 2015), so the charge density of Ce(III) is lower than that for Eu (III) and Y(III).

The Y/Eu and Y/Ce selectivities are higher when using P81R-D2EHPA IL compared to using D2EHPA. For this reason, the P81R-D2EHPA IL was chosen to separate the yttrium from the Ce/Eu/Y mixture at equilibrium pH less than 0.3. In order to separate the europium from the remnant Eu/Ce solution mixture, the P81R-Cy572 IL at an equilibrium pH range of 0.5-1.5 was chosen, taking advantage of its higher selectivity value in comparison to the Cy572.

As is shown in Fig. 2a, the results obtained plotting \(\log D - 3\log [HA]_2\) vs. \(-\log [H^+]\) using Cy572 or D2EHPA 0.30 mol/L are consistent with the suggested extraction mechanism in Eq. (7) due to the fact that the obtained slopes are about 3 for cerium,
europium and yttrium. Hence, three protons are involved in the extraction process using cationic extractants such as Cy572 and D2EHPA in accordance with Pavón et al. (2018) and Tunsu et al. (2016). However, the extraction mechanism, when ionic liquids such as P81R·C1·Cy572 IL or P81R·C1·D2EHPA IL are used, follows Eq. (8) mechanism, with no involved protons in it since there are not significant changes between the pH_initial and the pH_eq as can be seen in Fig. 2b.

3.1.2. Effect of IL concentration

To investigate the effect of the P81R·Cy572 IL and the P81R·D2EHPA IL concentration on the extraction of the Ce/Eu/Y mixture, the range of ILs concentration studied was 0.15 up to 0.60 mol/L. The aqueous phase solution contains 1 g/L of each REE in 4 mol/L Cl¯ medium and an initial H+ concentration of 0.90 mol/L.

As expected, the percentages of extraction for Ce(III), Eu(III) and Y(III) increase when the ILs concentrations also increase as is shown in Fig. 3.

Ce(III), Eu(III) and Y(III) loaded in the organic phase can be stripped using HCl 4 mol/L, as can be seen in the results presented in Table 2, similar to the Padhan and Sarangi investigation in which Alamine 336·Cyanex 272 IL is used as extractant to recover Nd and Pr from NdFeB magnets. These REEs could be completely stripped using a H2SO4 concentration higher than 2.16 mol/L (Padhan and Sarangi, 2017).

Fig. 1. Effect of equilibrium pH on the extraction of 1 g/L of each rare earth in 4 mol/L Cl¯. (a) Cy572 0.30 mol/L, (b) D2EHPA 0.30 mol/L, (c) P81R·Cy572 IL 0.30 mol/L, (d) P81R·D2EHPA IL 0.30 mol/L.

Fig. 2. Determination of the stoichiometric ratio of the extraction mechanism. (a) Plot of logD − 3log([HA]2)/2 vs. −log[H+] using Cy572 or D2EHPA 0.30 mol/L. (b) Variation of the pH during the REE extraction by using P81R·D2EHPA IL or P81R·Cy572 IL 0.30 mol/L.
are in the 0.15–0.30 mol/L range. However, when 0.30 mol/L of P81R is shown, the most appropriate IL concentrations for this purpose to the Table 3, where the separation factors defined in Eq. (6) are be used, due to the high REEs extraction yields reached. According to the Table 3, the separation factors defined in Eq. (6) are shown, the most appropriate IL concentrations for this purpose are in the 0.15–0.30 mol/L range. However, when 0.30 mol/L of P81R D2EHPA IL is used, the highest separation values are obtained, reaching 810 and 286 for $P_{\text{Y/Ce}}$ and $P_{\text{Y/Eu}}$, respectively. Although the $P_{\text{Y/Ce}}$ obtained a value of 29 with 0.45 mol/L using P81R D2EHPA IL, which could be considered a good separation value, more amount of extractant would be required to increase it. Moreover, the highest Eu/Ce selectivity value is achieved when 0.30 mol/L of P81R Cy572 IL is used.

### 3.1.3. Stripping study

The stripping study of cerium, europium and yttrium was carried out with different HCl concentrations. This acid stripping agent was chosen according to the stripping efficiency order: HCl > HNO₃ > H₂SO₄ suggested by the Kuang et al. investigation (Kuang et al., 2017). The proposed stripping mechanism is shown in Eqs. (13), (14).

The stripping study results using different concentrations of HCl are presented in Fig. 4. The REEs loaded in the organic phase, when 0.30 mol/L of P81R Cy572 IL was used, contained 0.05, 0.76 and 1 g/L of Ce(III), Eu(III) and Y(III), respectively. In the case of P81R D2EHPA IL 0.30 mol/L, 0.12, 0.28 and 0.99 g/L of Ce(III), Eu (III) and Y(III), respectively, were the concentrations loaded in the organic phase. The H⁺ initial concentration was 0.90 mol/L and the phase ratio (A:O) was 1:1. Since the amount of Ce(III) extracted using this extractant concentration (0.30 mol/L) is low (≤12%) compared to the Eu(III) and Y(III) extracted, the stripping percentages of this metal are not included in Fig. 4. Fig. 4 shows the plot of the stripping percentages of Eu(III) and Y (III) vs. the HCl concentration. As expected, their REE stripping percentages increase when the hydrochloric acid concentration also increases. However, comparing the stripping REE percentages obtained using P81R Cy572 IL and P81R D2EHPA IL, when the former is used, higher stripping REE percentages are obtained, as can be seen in Fig. 4a. In the case of P81R D2EHPA IL, a higher hydrochloric acid concentration is required to achieved the same percentage of stripping compared to P81R Cy572 IL due to the bigger acidic character of P81R D2EHPA IL. Using 4 mol/L of HCl, the stripping efficiency was 100% for both ionic liquid extractants.

#### 3.2. Cross-flow REEs separation process from a synthetic feed

Ce/Eu/Y synthetic mixture contained 1 g/L of each metal because it was the same concentration used in previous experiments. P81R D2EHPA IL and P81R Cy572 IL have been used to...
achieve the Ce(III), Eu(III) and Y(III) separation, since using a three-stage cross-flow solvent extraction scheme allows us to recover each rare earth separately. The flow-sheet of the separation process is outlined in Fig. 5.

After the previously obtained results with a REEs mixture of 1 g/L, it was concluded that the P81R-D2EHPA IL allows obtaining higher separation values of Y/Eu and Y/Ce. Once the yttrium is separated from the mixture, the europium and the cerium can be separated using P81R-Cy572 IL.

P81R-D2EHPA IL was used in the first two stages with concentrations of 0.30 mol/L and 0.15 mol/L, respectively, to obtain 98% of the yttrium in the organic phase. In the second stage the concentration is reduced by half to avoid the Ce(III) and Eu(III) extraction. Cerium and europium were separated using 0.30 mol/L of P81R-Cy572 IL in the third stage, obtaining 96% of the Eu(III) in the organic phase. Finally, Eu(III) and Y(III) were completely recovered from the organic phase using 4 mol/L of HCl and 97% of the initial Ce(III) was obtained in the raffinate flow. Obviously, higher REEs concentrations in the stripping streams could be obtained by using lesser A:O ratios.

3.3. Cross-flow REEs separation process from YOX leachate

Once the Ce/Eu/Y separation was successfully achieved using a synthetic mixture of 1 g/L of each REE, a new separation flow-sheet of these metals was proposed, adapted to the concentrations of Ce(III), Eu(III), Y(III) found in the end-of-life fluorescent lamp wastes. After acid leaching of the sample, the REEs reach liquor contains 0.2, 6.0 and 8.5 g/L of Ce(III), Eu(III), and Y(III), respectively. The concentration of these REEs are similar to the concentrations found by Tunsu et al. (Tunsu et al., 2014). However, in fluorescent lamps, more REEs such as gadolinium, terbium, dysprosium and lanthanum were identified, but their concentrations were less than 0.04 g/L (0.04, 0.03, 0.01, 0.03 g/L, respectively) and these metals were considered as trace metals.

Four stages were used to reach the REEs separation using P81R-D2EHPA IL and P81R-Cy572 IL, as shown in Fig. 6. An extra stage in the process using P81R-D2EHPA IL was required because of the high Y(III) concentration (8.5 g/L) compared to the synthetic one (1 g/L). The first three stages were necessary in order to obtain 98% of the yttrium in the organic phase using the P81R-D2EHPA IL.
This IL was used at 0.30 mol/L in the two first stages. However, 0.15 mol/L was the concentration in the third stage, to avoid the Eu/Ce extraction. Ce(III) and Eu(III) were separated using 0.30 mol/L of P81R-Cy572 IL in the last stage, obtaining 99.99% of Eu(III) in the organic phase. 4 mol/L of HCl was enough to recover the Eu(III) and the Y(III) from the organic phases and 99.99% of Ce (III) was recovered in the raffinate flow.

4. Conclusions

The separation of REEs from a reach liquor from end-of-life fluorescent lamps was investigated in order to evaluate its recycling potential. This separation process that combines the use of P81R-D2EHPA IL and P81R-Cy572 IL as extractants allow us to obtain the individual metals of Ce(III), Eu(III) and Y(III) with purity ≥ 99.9%. The loaded REEs from the organic phases were recovered using 4 mol/L of HCl.

After the systematic analysis of the effect of the parameters on the REEs extraction and successful application to a real waste stream from the fluorescent lamp waste, it can be concluded that Ce(III), Eu(III) and Y(III) can be selectively recovered from their leachates using ionic liquid extractants from chloride media by a cross-flow solvent extraction process.

Acknowledgments

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Rare earth elements recovery from E-wastes by solvent extraction and supported liquid membrane processes

9. PUBLICATION 6
Permeability dependencies on the carrier concentration and medium viscosity for Y(III) and Eu(III) transport by using liquid membranes

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\textbf{ABSTRACT}

The recovery of Y(III) and Eu(III) from fluorescent lamp leachates via supported liquid membranes using Cyanex 923 as a carrier has been studied. The results reveal that the transport process is mostly controlled by the diffusion or the viscosity of the organic phase depending on the carrier concentrations. Furthermore, this paper compares the transport model by using the flat sheet supported liquid membranes with the hollow fibre renewal liquid membranes one, for both REEs in nitrate media. The model allows foreseeing the permeability coefficients for these REEs depending on the organic phase variables. It has been also found that the permeability coefficient values difference between both membranes can be justified in terms of tortuosity, thickness and porosity.

\textbf{Keywords}

REE permeability coefficient; Supported liquid membrane; Hollow fibre renewal liquid membrane; REE recovery; Cyanex 923;

1. Introduction

Rare earths elements (REEs) have been widely used in advanced technologies due to their physical and chemical characteristics. The growing consumption tendency of these metals does not seem to change in the near future because their use is indispensable for electronic devices, electric and hybrid-electric vehicles and permanent magnets for wind turbines development [1]. Since the content of REEs in phosphors of lamps can reach 27.9\% [2], the
processing of their waste streams and the use of the end-of-life products may become feasible metal raw materials, so it provides an alternative to recover and recycle REEs.

Red phosphors \( \text{Y}_2\text{O}_3\cdot\text{Eu}^{3+} \) (YOX), blue phosphors \( \text{BaMgAl}_{10}\text{O}_{17} \cdot \text{Eu}^{2+} \) (BAM) and green phosphors \( \text{LaPO}_4\cdot\text{Ce}^{3+},\text{Tb}^{3+} \) (LAP), \( (\text{Gd,Mg})\text{B}_2\text{O}_5\cdot\text{Ce}^{3+},\text{Tb}^{3+} \) (CBT), \( (\text{Ce,Tb})\text{MgAl}_{11}\text{O}_{19} \) (CAT) are the three main different phosphors of the fluorescent lamps where, the former contains the highest amount of REEs (55%) [3]. Moreover, since yttrium and europium are the REEs with the highest content on the halophosphate phosphors rich in YOX phosphors, these metals have been the target of this investigation.

Despite the fact that there are many researches focused on the REEs recovery from the end-of-life products, industrial-scale applications are not wide spread. The solvent extraction is the most common technique to recover and separate REEs. But in comparison to the membrane separation technique solvent extraction is less efficient for the metal ions separation and pre-concentration, as membranes have the benefit of fast and selective ion transport due its large mass transfer interfacial areas [4].

There are a lot of membrane types, for instance, the liquid membranes, which have high selectively consist of a supported or unsupported liquid phase serving as a membrane barrier between two phases of aqueous solutions. Emulsion liquid membrane (ELM) and immobilized liquid membrane, also called a supported liquid membrane (SLM), are the two main types of liquid membranes. Although there are a great number of SLM, such as flat sheet supported liquid membrane (FSSLM), hollow fibre supported liquid membrane (HFSLM), hollow fibre renewal liquid membrane (HFRLM), etc. only some of them are suitable to be scaled-up because of the membrane stability problems [5].

Wannachod et al. proclaim that the 98% of neodymium (III) was transferred by HFSLM at pH 4.5 using PC88A as carrier. \( \text{H}_2\text{SO}_4 \) 1 M as the stripping solution was enough to recover 95% of the loaded Nd [6]. Using the same extractant, Pei et al. report that Dy(III) can be selectively transported from a REEs solution in HCl media by strip dispersion hollow fibre liquid membrane obtaining a better stability than traditional HFSLM [7]. Since the organic mass transfer coefficient \( (k_{om} = 0.788 \text{ cm} \cdot \text{s}^{-1}) \) was higher than the aqueous one \( (k_i = 0.0103 \text{ cm} \cdot \text{s}^{-1}) \) using Cyanex 272 as carrier by HFSLM, Wannachod et al. conclude that the diffusion of the praseodymium ions through the stagnant boundary layer between the feed solution and liquid membrane is the one which controls the process [8]. Furthermore, Ramakul et al. suggest that the percentages of extraction and stripping of yttrium increase when TBP is added to Cyanex 272 due to the synergistic effect of the extractants using nitric acid as stripping solution by HFSLM, [9]. Yadav et al. demonstrate that the separation and purification of Dy(III) from NdFeB magnets scrap using EHEHPA as the extractant by a two- cycle hollow fibre membrane operation can be successfully achieved working in non-dispersive solvent extraction mode.
Despite the amount of research using hollow fibre membranes to recover and separate REEs, there are only a few which use this technique in a complete separation process. The added value provided by this investigation is focused on the implementation of a membrane step to completely recover REEs in a process that can be industrially implemented.

In a previous article, a process to recover REEs from YOX fluorescent lamp wastes was proposed [11]. The end-of-life product was the main raw material and treated in a first leaching (L1) with nitric acid 1 M to separate non-ferrous impurities, mainly calcium. Then, the solid obtained after the L1 was undergone to a second leaching (L2) using 2 M of nitric acid for the REEs recovery. Unfortunately, a small amount of these metals was also washed-up the liquid fraction in the L1 stage. For this reason, in order to minimize these losses, a SLM step was added. The purpose of the current research is to improve and increase the efficiency of this membrane step by using hollow fibre modules so that the entire process can be implemented at industrial scale to recover and separate the REEs from the non-REEs. Consequently, the leachate obtained from the L1 stage was used as feed solution in all the experiments.

From Pavón et al. report, where Cyanex 923 (Cy923) diluted in kerosene was used as the carrier, it was observed that at high Cy923 concentrations promote a reduction in the metal transport [11]. To elucidate this fact, a modifier has been incorporated in the organic phase and a study of the effect of the dynamic viscosity on the diffusional coefficient has been carried out. Furthermore, this paper proposes a transport model for yttrium and europium using the permeability coefficient as the characteristic parameter considering three parameters: Cy923 concentration, modifier percentage (v/v) and viscosity of each mixture. The proposed model minimizes the efforts on the membrane process optimization, since determining the optimal conditions experimentally is labourious and time-consuming.

To sum up, the membrane step on the REEs recovery from the fluorescent lamp wastes has been substantially improved using hollow fibre modules working with renewal liquid membrane configuration.

2. Experimental methods

2.1. Reagents

Cyanex 923 was supplied by Cytec Canada Industries and used as received. Tributylphosphate (TBP, Ref. 240494) from Sigma Aldrich and 2,6-Dimethyl-4-heptanone (ONE, Ref. L16015) from Alfa Aesar were utilized as modifiers. Kerosene (Ref. 329460) and Na2EDTA (Ref. E4884) from Sigma-Aldrich were used as a diluent and stripping agent, respectively. Detailed specifications of the compounds are summarized in Table 1.
Table 1. Physical properties of the organic compounds.

<table>
<thead>
<tr>
<th>Commercial name</th>
<th>Content %</th>
<th>Density (25°C) kg·m⁻³</th>
<th>Viscosity (25°C) mPa·s *</th>
<th>Av. Mol. Weight g·mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyanex 923 [12]</td>
<td>93</td>
<td>880</td>
<td>38.28</td>
<td>348</td>
</tr>
<tr>
<td>Tributylphosphate [13]</td>
<td>100</td>
<td>970</td>
<td>3.28</td>
<td>266.32</td>
</tr>
<tr>
<td>2,6-Dimethyl-4-heptanone [14]</td>
<td>92.8</td>
<td>809</td>
<td>0.94</td>
<td>142.24</td>
</tr>
<tr>
<td>Kerosene</td>
<td>100</td>
<td>800</td>
<td>1.64</td>
<td></td>
</tr>
</tbody>
</table>

*Viscosity determined using an Ostwald's viscometer

The acidic leachate (L1) from fluorescent lamp wastes obtained following the procedure depicted in Pavón et al. was used as the feed solution whose composition is shown in Table 2 [11].

Table 2. Composition of the feed solution after HNO₃ 1 M leaching and contact time for 10 min [11].

<table>
<thead>
<tr>
<th>Element</th>
<th>mg·L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-REEs</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>6820±150</td>
</tr>
<tr>
<td>P*</td>
<td>759±14</td>
</tr>
<tr>
<td>Fe</td>
<td>41±8.5</td>
</tr>
<tr>
<td>Ba</td>
<td>311±0.1</td>
</tr>
<tr>
<td>Sr</td>
<td>236±5.6</td>
</tr>
<tr>
<td>Mn</td>
<td>152±3.5</td>
</tr>
<tr>
<td>Si</td>
<td>132±3.1</td>
</tr>
<tr>
<td>Al</td>
<td>116±2.5</td>
</tr>
<tr>
<td>Na</td>
<td>90±2.1</td>
</tr>
<tr>
<td>Mg</td>
<td>64±1.7</td>
</tr>
<tr>
<td>K</td>
<td>56±1.4</td>
</tr>
<tr>
<td>Sb</td>
<td>20±0.6</td>
</tr>
<tr>
<td>REEs</td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>491±12.2</td>
</tr>
<tr>
<td>Eu</td>
<td>41±0.9</td>
</tr>
<tr>
<td>La</td>
<td>16±0.3</td>
</tr>
<tr>
<td>Total REEs</td>
<td>548±6.6</td>
</tr>
</tbody>
</table>

* by molybdenum blue method [15]

2.2. FSSLM transport

The liquid membrane required a support to hold the carrier between the feed and the receiving solution. The support in this kind of membranes must be a hydrophobic and porous material with high chemical resistance against the organics utilized. It is impregnated with the carrier and placed between the feed and the receiving cells. Table 3 shows the characteristics of the polymeric support used in these experiments. They were carried out using the same experimental set-up depicted by Pavon et al. [16].
Table 3. Characteristics of the microporous polytetrafluoroethylene film (Fluoropore™ FHLP04700, Merck Millipore).

<table>
<thead>
<tr>
<th>Material</th>
<th>PTFE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (cm)</td>
<td>4.7</td>
</tr>
<tr>
<td>Pore diameter (μm)</td>
<td>0.45</td>
</tr>
<tr>
<td>Thickness (μm)</td>
<td>150*</td>
</tr>
<tr>
<td>Effective area (m²)</td>
<td>11.4</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>85</td>
</tr>
</tbody>
</table>

*including 100 μm of the polyethylene grid

The feed cell was filled with 210 mL of the L1 leachate at pH=1, Cy923 diluted in kerosene was the carrier and 210 mL of Na₂EDTA 0.05 M was used as the stripping agent in the receiving cell. Both aqueous solutions were mechanically stirred at 1000 rpm and at room temperature (20±2°C). Samples from feed and receiving cells were withdrawn every hour, up to 8 h, and the metal concentrations were quantified by atomic emission spectrometry using a 4100 MP AES System (Agilent Technologies) with an analytical error less than 5%.

Transported metal (% Me) was the parameter used to evaluate the obtained results and can be referred to the feed or the receiving cell by Eq. (1) as:

\[
\% Me = \left( \frac{[Me]_{t,f} - [Me]_{t,r}}{[Me]_{0,f}} \right) \cdot 100 = \left( \frac{[Me]_{t,r}}{[Me]_{0,f}} \right) \cdot 100
\]

where \([Me]_{0,f}\) and \([Me]_{t,f}\) refer to the initial and at time \(t\) REE concentrations in the feed solution and \([Me]_{t,r}\) is the REE concentration at time \(t\) in the receiving solution.

2.3. HFRLM transport

To overcome the low area/volume ratio obtained using FSSLM, hollow fibre module was used to recover REEs from the L1 leachate. The feed flowed along the shell side of the module and to prevent organic solution losses from the membrane pores, a pseudo-emulsion containing the stripping phase and carrier flowed along the lumen side. The transport experiment was carried out using a hollow fibre module from Liqui-Cel™ (G-502) whose characteristics are provided in Table 4.

Table 4. Details of hollow fibre membrane module (G-502 from Liqui-Cel™).

<table>
<thead>
<tr>
<th>Module diameter (cm)</th>
<th>7.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Module length (cm)</td>
<td>27.7</td>
</tr>
<tr>
<td>Cartridge configuration</td>
<td>Extra-glow with center baffle</td>
</tr>
<tr>
<td>Membrane surface area (m²)</td>
<td>1.4</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>40</td>
</tr>
<tr>
<td>OD/ID (μm)</td>
<td>300/200</td>
</tr>
<tr>
<td>Membrane/plotting material</td>
<td>PP/PE</td>
</tr>
<tr>
<td>----------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>Hold-up volume shell side (cm³)</td>
<td>400</td>
</tr>
<tr>
<td>Hold-up volume tube side (cm³)</td>
<td>150</td>
</tr>
</tbody>
</table>

The lab-scale plant worked with 4 L of the feed solution containing around 500 mg·L⁻¹ of Y(III) and 50 mg·L⁻¹ of Eu(III), from the L1 leachate. The pseudo-emulsion containing stripping/organic was made up of 400 mL of Na₂EDTA 0.05 M and 50 mL of organic phase, Cy923 diluted in kerosene. The feed and stripping/organic streams flowed at 50 L·h⁻¹ and a low transmembrane pressure (Pₐ - Pₛ = 0.2 bar) between shell and lumen side was applied to avoid the organic phase transfer to the feed phase. The transport experiments were carried out using the experimental set-up depicted in Rathore et al. research [17]. Samples from feed and receiving phases were withdrawn at regular time intervals and the metal concentrations in both aqueous phases were determined by atomic emission spectrometry. The percentage of each REE transported were obtained using the Eq. (1).

It is mandatory the total replacement of the organic phase present in the pores after each experiment, to work at the new carrier concentration. For this reason, the transmembrane pressure was changed to -1 bar in order to force the organic phase to cross the fibre pores to the feed flow. Since the total volume of the pores was about 50 mL, the pore liquid has been completely renewed and the membrane will be ready for the next run when 150 mL of the organic phase appears in the feed tank.

3. Transport model

The metal transport through the membrane includes three resistances: (1) diffusion resistance in the feed side, (2) diffusion through the liquid membrane and (3) diffusion resistance in the stripping side (Fig. (1)).

![Fig. 1. Concentration profile for the REEs transport.](image-url)
Taking into account that the stirrers in the cells are very close to the membrane, the thickness of the boundary layer is minimized. For this reason, the resistance in the feed and stripping sides can be neglected. So, assuming instantaneous extraction and stripping reactions, it has been considered that the diffusion through the liquid membrane is the limiting step of the metal transport process.

The diffusion process is controlled by the 1st Fick’s law.

\[ J = -D \cdot \frac{dC_{lm}}{dx} \]  

(2)

where \( J \) is the diffusional REEs molar flux (mol REE/s·m²), \( D \) is the diffusion coefficient (m²/s), \( C_{lm} \) is the REE concentration in a point between both internal sides of the membrane (mol/L) and \( x \) is the position (m).

Discretizing the 1st Fick’s law and applying it to the membrane, the Eq. (3) is obtained.

\[ J = -D \cdot \frac{\Delta C_{lm}}{\Delta x} = -D \cdot \frac{\Delta C_{lm}}{\delta \tau} \]  

(3)

where \( \tau \) and \( \delta \) are the tortuosity and the thickness (m), respectively.

On the other hand, the metal mass balance in the feed cell can be written as the following way:

\[ \text{Accumulation} = \text{Input} + \text{Generation} - \text{Output} - \text{Consumption} \]  

(4)

Since there are not consumption and generation, and there is not input, the mass balance is simplified to:

\[ \text{Accumulation} = -\text{Output} \]  

(5)

where the accumulation can be expressed as the REE rate of change over time in the feed cell and the output as the mass flow of transferred REEs to the receiving phase (\( N_{REE} \)) expressed in mol/s.

\[ \frac{dm_{if}}{dt} = -N_{REE} \]  

(6)

The molar flow from the feed to the receiving phase is expressed as:

\[ N_{REE} = J \cdot A_{eff} \]  

(7)

Considering the porosity (\( \varepsilon \)), the effective transference area \( A_{eff} \) (m²) can be written as:

\[ A_{eff} = A \cdot \varepsilon \]  

(8)

where \( A \) is the membrane area (m²).
Replacing Eqs. (6)-(8) in Eq. (3):

\[
\frac{dm_{if}}{dt} = V_f \cdot \frac{dC_{if}}{dt} = -D \cdot \frac{\varepsilon}{\delta \tau} \cdot (C_{imf} - C_{ims}) \cdot A
\]

where \( V_f \) is the feed phase volume.

By the equilibrium extraction constant \( (K_{eq}) \), depicted in Eq. (10), it is possible to relate the concentrations to the REE in the membrane/feed \( (C_{i,mf}/C_{if}) \) and the membrane/stripping \( (C_{ims}/C_{is}) \) interfaces.

\[
K_{eq} = \frac{C_{REE,organic}}{C_{REE,aqueous}C_{carrier}} = \frac{C_{im}}{C_{if}C_{carrier}}
\]

Being \( C_{im} \) the concentration in the membrane at the feed or the stripping side, \( C_{if} \) the concentration in the feed or the receiving phase and \( C_{carrier} \) the concentration of the carrier.

The REEs neutral species concentration in the receiving phase, \( C_{is} \), is maintained at zero because it is turned into an anionic species by EDTA complexation. Hence, considering the Eq. (10), the \( C_{ims} \) is also zero. Thus, the Eq. (9) can be rewritten as:

\[
\frac{dC_{if}}{dt} = -D \cdot \frac{\varepsilon}{\delta \tau} \cdot \frac{A}{V_f} \cdot C_{imf}
\]

Considering the extraction equilibrium (Eq. (10)):

\[
\frac{dC_{if}}{dt} = -D \cdot \frac{\varepsilon}{\delta \tau} \cdot \frac{A}{V_f} \cdot C_{if} \cdot K_{ex} \cdot C_{carrier}
\]

Eq. (13) is obtained by grouping the support membrane characteristics parameters such as thickness, tortuosity and porosity, diffusion coefficient, extraction equilibrium constant and carrier concentration in a single variable.

\[
\frac{dC_{if}}{C_{if}} = -P \cdot \frac{A}{V_f} \cdot dt
\]

Being \( P \) the permeability coefficient (m/s) whose value refers to the speed which the REE from the feed phase are transported to the stripping phase.

Eq. (14) is obtained by integration of Eq. (13), and it is used to determine the REE permeability coefficient value for each specific concentration of carrier.

\[
\ln \frac{C_{if}}{C_{i,0,f}} = -P \cdot \frac{A}{V_f} \cdot t
\]

where \( C_{i,0,f} \) is the initial concentration of the REE in the feed phase.
3.1. Mathematical model

A mathematical model that allows predicting the evolution of the yttrium and europium metal ion concentrations in nitrate media using Cy923 as carrier has been developed. The Matlab R2018a software was used to solve the equations proposed relating the permeability coefficient to the concentration of carriers (Cy923 and ONE).

It is generally accepted that the diffusion coefficient \( D \) and the viscosity \( \mu \) are the parameters which control the transport through the membranes and can be related to the Eq. (15):

\[
D \cdot \mu^\alpha = \text{constant}
\]

(15)

where \( \alpha \) is a coefficient with a value in the 0.5-1 range for this kind of aqueous media [18,19].

To sum up, the diffusional process contemplates different parameters, some of them associated to the support membrane characteristics including the thickness, the porosity and the tortuosity, and others like viscosity which depends on the liquid membrane composition. Hence, the diffusion coefficient can be written as Eq. (16), considering that the support membrane characteristics are included in the permeability coefficient.

\[
D = K \cdot \frac{P}{[\text{Cy923}]}
\]

(16)

where \( K \) incorporates the membrane characteristics parameters (tortuosity, thickness and porosity).

Thus, the equation that permits to foresee the permeability coefficient of the REEs considering the membrane characteristics and the organic phase viscosity can be described by Eq. (17) as follows:

\[
P = K' \cdot \mu^{-\alpha} \cdot [\text{carrier}]
\]

(17)

where \( K' \) is the proportionality constant.

Assuming that the interactions between the Cy923, ONE and kerosene can be neglected, the viscosity of a mixture can be calculated from the viscosities of the components by using Eq. (18) [18,20].

\[
\ln \mu_m = X_{\text{Cy923}} \cdot \ln \mu_{\text{Cy923}} + X_{\text{ONE}} \cdot \ln \mu_{\text{ONE}} + X_{\text{kerosene}} \cdot \ln \mu_{\text{kerosene}}
\]

(18)

where \( \mu_m \) is the viscosity of the mixture, \( X_{\text{Cy923}}, X_{\text{ONE}} \) and \( X_{\text{kerosene}} \) are the molar fractions and \( \mu_{\text{Cy923}}, \mu_{\text{ONE}} \) and \( \mu_{\text{kerosene}} \) are the viscosities of each component in the ternary mixture. Firstly, the viscosities of the mixtures were measured using an Ostwald’s viscometer (Type 509 04. Ref. 285404014 from Schott Geräte GmbH) and then, the Eq. (18) was validated from the
experimental viscosities of different mixtures. Thus, the Eq. (18) was useful to calculate the viscosities of any composition of the organic phase.

Considering that Cy923 and ONE, transport REEs, the permeability can be written as follows:

\[ P = (K_{Cy923} \cdot [Cy923] + K_{ONE} \cdot [ONE]) \cdot \mu^{-\alpha} \]  

(19)

The model depicted in the previous equations was used to obtain the optimized values of the proportionality constants, \( K_{Cy923} \) and \( K_{ONE} \). The purpose is to find the parameters values that fit the calculated with the experimental data minimizing the error. The applied algorithm for the resolution of the model is shown in Fig. 2.

The resolution of the system starts with a matrix of the experimental data (15 experimental points), whose rows are the system conditions: concentration of Cy923 (0.3-1.2 M), ONE (0-40 % (v/v)) and kerosene and the experimental permeability coefficient (\( P_{exp} \)) from Eq. (14).

The theoretical viscosity of each organic phase (\( \mu_m \)) was determined by using the Eq. (18). Then, the initialization of the proportionality constants (\( K_{Cy923} \) and \( K_{ONE} \)) is introduced and the \( P_{calc} \) was obtained by Eq. (19), taking into account the objective function \( F(x) \) defined as the sum of the quadratic differences between the calculated and experimental permeability coefficients (Eq. (20)). This function was undergone to minimize using the \textit{fmincon} subroutine. The standard deviation value (\( \sigma \)) was also evaluated following the Eq. (21) to quantify the dispersion of the calculated to experimental data.

\[ F(x) = \sum_{i=1}^{N} (P_{i,calc} - P_{i,exp})^2 \]  

(20)

\[ \sigma = \sqrt{\frac{\sum_{i=1}^{N} (P_{i,calc} - P_{i,exp})^2}{N-1}} \]  

(21)

where \( N \) is the number of experimental points.
4. Results and discussion

4.1. FSSLM transport

The leachate from a first leaching of the fluorescent lamp wastes was used as the feed solution for Y(III) and Eu(III) metal ions transport experiments using Cy923 as carrier by FSSLM. In a previous investigation published by Pavón et al. using the same system, it was observed that at low Cy923 concentrations, the metal ions transport is only controlled by the diffusion through the liquid membrane, but at higher Cy923 concentrations, the effect of the shear stress became
predominant reducing the permeability [11]. This decrease could be explained by the rise of the organic phase viscosity.

In order to elucidate it, two experiments using Cy923 1.2 M were carried out adding 20% of ONE or TBP as modifiers and the results are depicted in (Fig. 3).

![Graph showing the effect of ONE or TBP addition on REEs transport](image)

**Fig. 3.** Effect of the ONE or TBP addition in the organic phase on the REEs transport. [Cy923]=1.2 M. Feed: [Y(III)]=0.5 g·L\(^{-1}\). [Eu(III)]=0.04 g·L\(^{-1}\); pH=1.2. Receiving solution: 0.05 M Na\(_2\)EDTA. a) Y(III). b) Eu(III).

Comparing the obtained results, it can be asserted that the TBP has a negative effect on the transport and the permeability decreases due to the high viscosity value (Table 1). However, the REEs transport increases using the ONE as modifier obtaining permeability coefficients values depict in Table 5.

**Table 5.** Permeability coefficients of Y(III) and Eu(III) using 1.2 M of Cy923 and TBP or ONE as modifiers.

<table>
<thead>
<tr>
<th>Modifier</th>
<th>(P \cdot 10^6) (m·s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Y(III)</td>
</tr>
<tr>
<td>-</td>
<td>3.31</td>
</tr>
<tr>
<td>TBP 20% (v/v)</td>
<td>2.11</td>
</tr>
<tr>
<td>ONE 20% (v/v)</td>
<td>4.03</td>
</tr>
</tbody>
</table>

To confirm the positive effect of the ONE on the REEs transport, a set of experiments using different Cy923 concentrations in the range of 0.3-1.2 M with 20% and 40% of the modifier were carried out. As is shown in Fig. 4, the permeability coefficients increased when the modifier was added to the organic phase. The increase of these values for the yttrium were
around 18% and 33% when the percentage of the ONE was 20 and 40%, respectively, compared to the permeability values without ONE.

![Diagram](image1)

**Fig. 4.** Effect of the Cy923 concentration on the permeability of REEs using 20% or 40% of ONE as modifier. Feed: [Y(III)]=0.5 g·L⁻¹, [Eu(III)]=0.04 g·L⁻¹; pH=1.2. Receiving solution: 0.05 M Na₂EDTA. a) Y(III). b) Eu(III)

Moreover, a study of the dynamic viscosity effect on the diffusional coefficient was done following the procedure described in section 3.1. By this way, linearizing the Eq. (17) helps to obtain the results shown in (Fig. 5).

![Diagram](image2)

**Fig 5.** Effect of the dynamic viscosity on the diffusional coefficient. Feed: [Y(III)]=0.5 g·L⁻¹. [Eu(III)]=0.04 g·L⁻¹; pH=1.2. Receiving solution: 0.05 M Na₂EDTA. a) Y(III). b) Eu(III)

(Eq. (22)) proposed by Reid and Sherwood, Bird et al, Edward and Hildebrand [18,21–23] who described an inverse dependence between the diffusion coefficient and the viscosity is commonly used. However, since the viscosities of the different concentrations of solvent
studied are in a range of $1.8 \cdot 10^{-3}$ to $6.9 \cdot 10^{-3}$ kg·m$^{-1}$·s$^{-1}$, the power for Y(III) and Eu(III) is very close to the (-2/3) power (Eq. (23)) according to Hiss and Cussler [19]:

$$D \cdot \mu^{-1} = \text{constant} \quad (22)$$

$$D \cdot \mu^{-2/3} = \text{constant} \quad (23)$$

As a result, the viscosity is responsible for the fact that the permeability remains practically constant or decrease at high Cy923 concentrations. Nevertheless, the ONE can be used as modifier in the organic phase because it reduces the viscosity obtaining thus higher permeability coefficients.

4.2. FSSLM model solving

To be able to predict the permeability coefficients for any concentration of Cy923 and ONE, the algorithm depicted in Fig. 2 has been followed. Assuming that the power of the viscosity is close to 2/3, this value was used in the model. The optimized equations for yttrium and europium are:

$$P_{Y(III)} = (1.03 \cdot 10^{-5} \cdot [Cy923] + 8.06 \cdot 10^{-7} \cdot [ONE]) \cdot \mu^{-2/3} \quad (24)$$

$$P_{Eu(III)} = (1.47 \cdot 10^{-5} \cdot [Cy923] + 4.26 \cdot 10^{-6} \cdot [ONE]) \cdot \mu^{-2/3} \quad (25)$$

where $P$ is in m·s$^{-1}$, [Cy923] in M, [ONE] in % (v/v) and $\mu$ in mPa·s.

The ionic radii of the heavy rare earths elements (HREEs) are smaller than of the ones of light rare earths elements (LREEs) due to the lanthanide contraction and the higher charge density of Y(III) related to Eu(III) [24,25]. However, the permeability coefficient of europium is higher than the yttrium one, contrary to what was expected.

This fact is according to the diffusional coefficient of Eu(III) whish is higher than the one of Y(III). It was confirmed by two individual transport experiments using the same concentration for both REEs (0.5·L$^{-1}$) containing 0.60 M of Cy923 and 20% of ONE in the organic phase. The results shown in Fig. 6 demonstrate that the permeability coefficient of Eu(III) is around 1.7 times higher than Y(III) ($P_{Eu(III)} = 6.58 \cdot 10^{-6}$ and $P_{Y(III)} = 3.97 \cdot 10^{-6}$ m·s$^{-1}$).
Fig. 6. REEs linear fitting of experimental data. Feed: \([\text{Y(III)}] = [\text{Eu(III)}] = 0.5 \text{ g·L}^{-1}\). \(\text{pH} = 1.2\). Receiving solution: 0.05 M \(\text{Na}_2\text{EDTA}\). Organic phase: 0.60 M Cy923 and 20\% of ONE.

Fig. 7 shows the permeability modelling results obtained in the 0-1.2 M Cy923 concentration range and a ONE range of 0-40\%(v/v). The bold points are the experimental permeability values and the line corresponds to the local maximums. The proposed model is able to predict the permeability coefficient values for both REEs since the calculated data fit for the experimental one, obtaining standard deviation values of 0.16 and 0.39 for Y(III) and Eu(III), respectively.

Fig. 7. Permeability coefficients calculated results vs. experimental ones varying the concentrations of Cy923 and ONE. Feed: \([\text{Y(III)}] = 0.5 \text{ g·L}^{-1}\). \([\text{Eu(III)}] = 0.04 \text{ g·L}^{-1}\); \(\text{pH} = 1.2\). Receiving solution: 0.05 M \(\text{Na}_2\text{EDTA}\). a) Y(III). b) Eu(III).
The positive effect of the ONE addition to the organic phase is more significant at high concentrations of Cy923 because the viscosity is notably decreased when the ONE concentration increase. For this reason, the transport is meaningful favoured using 40%(v/v) of ONE reaching the maximum value of the permeability for both REEs. The optimal conditions for achieving the highest permeability coefficient value for Y(III) and Eu(III) are depicted in Table 6.

**Table 6.** Optimization parameters by using FSSLM.

<table>
<thead>
<tr>
<th>REE</th>
<th>[Cy923] (M)</th>
<th>%%(v/v) ONE</th>
<th>P·10^6 (m·s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y(III)</td>
<td>1.19</td>
<td>40</td>
<td>4.38</td>
</tr>
<tr>
<td>Eu(III)</td>
<td>1.18</td>
<td>40</td>
<td>7.00</td>
</tr>
</tbody>
</table>

4.3. HFRLM transport

Owing to the chemical incompatibility of the ONE with the polypropylene material of the membrane fibres [26], the experiments using HFRLM have been carried out without modifier. Additionally, due to the 95% of REEs are transported after 2 h when the 0.3 M of Cy923 was used, lower carrier concentration range (0.1-0.3 M) was studied instead of the optimal concentration range described in Table 5.

As can be seen in Fig. 8. a, 92% of Y(III) is transported after 4 h for whole range of Cy923 concentration and 98% of Eu(III) is transported too (Fig. 8. b) due to its high diffusion coefficient. A study of the dynamic viscosity effect of the diffusional coefficient was studied (Fig. 8. c) to confirm that the power is close to (-2/3). In addition, to verify that the permeability follows the same tendency obtained from the model by using FSSLM, the permeability coefficients for each experiment were determined and plotted in Fig. 8. d considering the (-2/3) power in the viscosity.
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Fig. 8. Effect of Cy923 concentration on the REEs transport. [Y(III)]=0.5 g·L⁻¹, [Eu(III)]=0.04 g·L⁻¹. a) Y(III). b) Eu(III). c) Effect of the dynamic viscosity on the diffusional coefficient: d) Effect of the Cy923 concentration on the permeability of the REEs.

As was expected, in this working range of Cy923 concentration the dependence on the permeability of the Cy923 concentration is linear because, the viscosity of the organic phase is not the parameter that restricts the REEs transport. In these conditions, the diffusion controls the transport process obtaining a linear equation which relates the permeability to the carrier concentration (Eqs. (26)-(27)):

\[
P_{Y(III)} = 8.08 \cdot 10^{-6} \cdot \text{[Cy923]} \cdot \mu^{-2/3} \quad (26)
\]

\[
P_{Eu(III)} = 1.20 \cdot 10^{-5} \cdot \text{[Cy923]} \cdot \mu^{-2/3} \quad (27)
\]

where, as Eqs. (24)-(25), \(P\) is in m·s⁻¹, [Cy923] in M and \(\mu\) in mPa·s.

4.4. FSSLM and HFRLM comparison

In order to justify the experimental permeability differences using FSSLM and HFRLM, and to confirm that these differences are due to the characteristics of the membranes [27–30], the permeability coefficient was calculated following the model depicted in Eqs. (24)-(25) and considering the (-2/3) power. Moreover, three experiments using a Cy923 concentration range of 0.1-0.3 M without ONE by using FSSLM were carried out to compare with the results obtained from HF module and also to assure that the experimental data fit with the model proposed. The linear dependence between the permeability and the carrier concentration is shown in Fig. 9 and the equations that relate to both parameters can be seen in Eqs. (28)-(29) without ONE.
Fig. 9. Effect of the Cy923 concentration (without ONE) on the permeability of REEs using FSSLM. Feed: [Y(III)]=0.5 g·L⁻¹. [Eu(III)]=0.04 g·L⁻¹; pH=1.2. Receiving solution: 0.05 M Na₂EDTA.

Although the permeability coefficient for both membranes follows the same tendency, comparing the effect of the Cy923 concentration on the permeability of both membranes per unit area, it can be affirmed that the permeability coefficients using FSSLM are around 25% higher than using HFRLM. This value has to be the same for both REE since it is not depended on the metal but only on the membrane characteristics.

\[
P_{Y(III)}_{\text{FSSLM}} = 1.27 \cdot P_{Y(III)}_{\text{HFRLM}} \quad (28)
\]

\[
P_{Eu(III)}_{\text{FSSLM}} = 1.23 \cdot P_{Eu(III)}_{\text{HFRLM}} \quad (29)
\]

The permeability coefficients of two different membranes can be related to themselves using the diffusion coefficient, the extraction equilibrium constant, the carrier concentration, the thickness, the tortuosity and the porosity (Eq. (13)). The tortuosity is the only structural parameter unknown for both membranes (Table 1 and Table 2), it was the characteristic parameter studied to correlate the permeability of both membranes. Hence, considering the linear dependence on the permeability from the Cy923 concentration, Eq. (30) was obtained.

\[
\tau_{\text{FSSLM}} = 1.28 \cdot \tau_{\text{HFRLM}} \quad (30)
\]

where \( \tau_{\text{FSSLM}} \) and \( \tau_{\text{HFRLM}} \) are the tortuosity of the support of the FSSLM and HFRLM, respectively.

To confirm this tortuosity relation when both different membranes are used, the tortuosity of both membranes was also determined using Eqs. (31)-(32) [31–33].

\[
\tau_{\text{FSSLM}} = A \cdot (1 - \varepsilon) + 1 \quad \varepsilon \in [0.5 - 1] \quad (31)
\]
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\[ \tau_{HFRLM} = B \cdot \frac{(1-\varepsilon)}{(\varepsilon-0.33)m} + 1 \quad \varepsilon \in [0.4 - 0.5] \tag{32} \]

where \( A, B \) and \( m \) are fitting parameters.

Using the \( A, B \) and \( m \) parameters shown in Table 7, the tortuosity relation between FSSLM to HFRLM is 1.29.

**Table 7.** Fitting parameters and tortuosity for both membranes.

<table>
<thead>
<tr>
<th></th>
<th>FSSLM</th>
<th>HFRLM</th>
</tr>
</thead>
<tbody>
<tr>
<td>( m )</td>
<td>-</td>
<td>0.02</td>
</tr>
<tr>
<td>( A )</td>
<td>2.00</td>
<td>-</td>
</tr>
<tr>
<td>( B )</td>
<td>-</td>
<td>0.01</td>
</tr>
<tr>
<td>( \tau )</td>
<td>1.30</td>
<td>1.01</td>
</tr>
</tbody>
</table>

To sum up, the permeability differences when the FSSLM and HFRLM are used, can be justified in terms of tortuosity, thickness and porosity differences.

**4.5. Model solving for HFRLM**

The mathematic model depicted in section 3.2 can be modified applying the 1.28 factor above mentioned in section 4.4 in the permeability equation obtained using FSSLM to have the correct modelling of the permeability when HFRLM membranes are used. The Eqs. (33)-(34) are the optimized for yttrium and europium.

\[
P_{Y(III)} = 8.24 \cdot 10^{-6} \cdot [Cy923] \cdot \mu^{-2/3} \tag{33}
\]

\[
P_{Eu(III)} = 1.18 \cdot 10^{-5} \cdot [Cy923] \cdot \mu^{-2/3} \tag{34}
\]

where \( P \) is in m-s\(^{-1} \), \([Cy923]\) in M and \( \mu \) in mPa-s.

Fig. 10 shows the permeability modelling using a Cy923 concentration range of 0-1.4 M being the bold points the maximums of the permeability values. As the calculated data fits with the experimental ones obtaining standard deviation values for Y(III) and Eu(III) of 0.04 and 0.13, respectively, the proposed models for both REEs are able to predict the permeability coefficient values. To achieve the maximum permeability value, the optimum Cy923 concentration is 1.14 (Table 8).
Fig. 10. Cy923 concentration effect on REEs permeability using HFRLM. Feed: [Y(III)]=0.5 g·L⁻¹, [Eu(III)]=0.04 g·L⁻¹; pH=1.2. Receiving solution: 0.05 M Na₂EDTA. a) Y(III). b) Eu(III).

Table 8. Optimization parameters by using HFRLM.

<table>
<thead>
<tr>
<th>REE</th>
<th>[Cy923] (M)</th>
<th>P·10⁶ (m·s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y(III)</td>
<td>1.18</td>
<td>2.80</td>
</tr>
<tr>
<td>Eu(III)</td>
<td>1.18</td>
<td>4.10</td>
</tr>
</tbody>
</table>

5. Conclusions

Membrane step from L1-SLM-L2 process was investigated to increase its efficiency to implement the entire process at industrial scale.

Based on the obtained results using both kind of membrane, the metal transport is only controlled by the diffusion through the membrane at low Cy923 concentrations. However, the effect of the shear stress become predominant at higher concentrations of the carrier reducing the apparent permeability.

The transport model for Y(III) and Eu(III) was proposed to predict the permeability coefficients for both REEs depending on the Cy923 and ONE concentration and the organic phase viscosity. The results disclosed that the optimized parameters using FSSLM are 1.19 and 1.18 M of Cy923 for Y(III) and Eu(III), respectively and 40% (v/v) of ONE to achieve permeability coefficients of 4.38·10⁻⁶ and 7.00·10⁻⁶ m·h⁻¹.

Due to the incompatibility of the ONE with the polypropylene material of the HFRLM membrane fibres, it is not possible to use this phase modifier. In this case, the highest Y(III) and Eu(III)
permeability coefficients, $2.80 \cdot 10^{-6}$ and $4.10 \cdot 10^{-6}$ m·h$^{-1}$, respectively can be achieved by using 1.18 M of Cy923.

Thus, the REEs recovery from the fluorescent lamp wastes has been considerably improved by using hollow fibre renewal liquid membranes.

**Acknowledgements**

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References


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10. RECOVERY OF RARE EARTH ELEMENTS FROM FLUORESCENT LAMP WASTES BY USING SOLID-STATE CHLORINATION
10. RECOVERY OF RARE EARTH ELEMENTS FROM FLUORESCENT LAMP WASTES BY USING SOLID-STATE CHLORINATION
Recovery of rare earth elements from fluorescent lamp wastes by using solid-state chlorination process

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10.1. Introduction

In recent years, rare earth elements (REEs) have become a critical commodity due to their growing demand, because they are essential on the advanced technologies development, and to their small and opaque market [1]. Many researchers focused their investigations on the development of the processes for the recycling of urban mining with the principle propose to recover REEs [2–4]. Most of scientific articles are focused on REEs recovery from NdFeB magnets [5–8] or fluorescent lamps [3,9–11], because they represent 68% of these metals used in terms of economic value [12]. Thus, recovering REEs from these discarded products can not only protect the environment, but also promote the sustainable development of rare earth resources. Due to the high content of REEs, mainly Y/Eu (55%) [13] in the red phosphors (YOX), they have been the starting material in the current investigation.

Despite the large number of studies, the recovery of REEs from fluorescent lamp wastes is not wide-spread at industrial scale [3]. Hydrometallurgy has traditionally been the method used for extracting REEs from primary sources [14]. The hydrometallurgical processes commonly contain an acid digestion step, which is cost-intensive and unfriendly from an environmental point of view. Moreover, once the leaching step is done, the stream is highly acidic, thus, the pH value should be increased generating a chemicals consumption for this neutralization stage. Because of that, an unconventional method such as solid-state chlorination (SSC) has been considered in the present work to recover REEs from fluorescent lamp wastes.

SSC is proposed to replace the acid leaching stage and to reduce chemical consumption and the acidity of the wastewater after the digestion step. This SSC process consists of mixing NH₄Cl(ₗ) with end-of-life products in powder form. Then, when the thermal decomposition of NH₄Cl(ₗ) starts, HCl(₉) is produced, which is required to convert the metals into soluble metal
chlorides. The excess of the NH$_3$(g) produced by the NH$_4$Cl(s) thermal decomposition is collected in a bottle which contains deionised water. Once the SSC process is finished, the solid is leached by using an organic diluted in ethanol to proceed to the leaching stage.

Hence, the SSC process and the non-acid leaching provide several advantages compared to acid leaching: (1) Reducing chemical consumption for the digestion medium by up to 50%, since NH$_4$Cl(s) contains almost twice as much HCl as HCl$_{(aq)}$. In addition, NH$_4$Cl(s) can be re-used in subsequent SSC runs as unreacted HCl$_{(g)}$ and NH$_3$(g) in the exhaust gas recombination upon cooling. (2) Reducing chemical costs, because NH$_4$Cl(s) is cheaper than HCl$_{(aq)}$ according to its lower demand and higher HCl$_{(aq)}$ content [15]. In addition, the excess of NH$_3$(g) in the exhaust gas could be a marketable by-product; and (3) the aqueous phase obtained after the leaching process does not require neutralization since the pH is around 4.

Although the SSC process has already been utilized to REEs recovery, the success of these studies published in literature is limited mostly due to two reasons: (1) Underestimation of reaction parameters which are significant to the SSC process. As a result, the temperature used is too high, thus, the volume expansion of the gas phase is considerable due to the NH$_4$Cl(s) thermal decomposition rate [16]. (2) Wrong choice of the reactor equipment, since industrial production requires reactors operating continuously [17].

However, according to Lorenz and Bertau [15], different changes can be implemented to optimize and improve the SSC process. For instance, (1) conducting the SSC in an inert-gas flushed rotary kiln which can be operated by batch wise or continuously to enable industrial implementation. (2) Collecting the excess of NH$_3$(g) in the exhaust gas to be a marketable by-product. (3) Designing properly the REEs yield optimization considering correlations among factors that influence one another to obtain higher REEs yields. Nevertheless, the current research improves the leaching stage after the SSC process because using an organic diluted in ethanol instead of a buffer leaching (such as acetic acid), the recovery of the REEs can be achieved separating them selectively in one stage from the REEs of the other metals present in the end-of-life products such as fluorescent lamps. Hence, the REEs recovery process starting with the raw material and obtaining the REEs individually with high purity is reduced because the stage of precipitation with oxalic acid is not needed.

The purpose of this research is to improve the L2 leaching stage proposed by Pavón et al. [4]. In the previous investigation, it was used acidic solution via solid-state chlorination process and, the fluorescent lamp waste was treated by two leaching stages: (L1) using HNO$_3$ 1 M to separate non-ferrous impurities, mainly calcium and (L2) the solid obtained in L1 was leached with 2 M HNO$_3$ for the REEs recovery. However, a small amount of these metals remained in the liquid fraction in the L1 stage. A SLM step was implemented to minimize the REEs losses
in this particular step. In this regard, the leachate obtained from the L1 stage was used as the feed solution in all the experiments in the current study.

Introducing the SSC, the acidity of wastewater is reduced, and the process recovering REEs from fluorescent lamp wastes becomes more effective as less stages are required to separate REEs from others metals. So, the leaching solution used after the SSC is selective, thus, the leachate is only composed of REEs. Hence, the REE liquor shown in Fig. 10.17 can be directly treated to separate the REEs individually avoiding the precipitation, for instance, with oxalic acid.

As a result, the process to recover REEs from the fluorescent lamp wastes can be substantially improved via SSC using an organic diluted in ethanol in the L2 leaching stage to separate selectively the REEs from other metals present in the real wastes.

10.2. Material and methods

10.2.1. Starting material

The fluorescent lamp waste in powder form was supplied by Recyberica Ambiental S.L. and it had already been treated to eliminate the Hg. The waste was introduced to a first leaching process using 1 M HNO\(_3\) for 10 min [4] and the solid obtained after filtration was used as the starting material in this research. The particle size was measured by laser diffraction analysis (MasterSize 3000, Malvern Pananalytical, United Kingdom).
10.2.2. Experimental set-up

The reactor employed for the solid-state chlorination is shown in Fig. 10.18. It was a rotary kiln with a tubular inert gas connection of quartz glass to prevent corrosion. The glass tube, which contains the sample for the solid-state chlorination, is placed into the quartz rotary kiln and held at both ends by gears that facilitate rotation. Each sample was placed in the centre of the glass tube between two tappers (Fig. 10.18. b). The excess of NH₃(g) produced during the NH₄Cl decomposition was firstly introduced to a bottle with glass wool and then, absorbed in a second bottle containing deionised water (Fig. 10.18. c).

![Fig. 10.18. a) Front view, b) cross section of the rotary kiln. c) scrubbing bottles for recovering the NH₃(g) excess produced during the solid-state chlorination from the gaseous phase.](image)

10.2.3. Box Behnken design

The optimization of the REE yield was carried out by varying parameters (factors) of both steps, solid-state chlorination and leaching with an organic solution. The factors studied in the 3³ Box Behnken design were the temperature, the residence time and the ratio of \( g_{\text{NH}_4\text{Cl}}/g_{\text{solid,L1}} \). The mass of the leaching solution was not considered as a factor because the organic solution is incapable of leaching metals from the unchlorinated waste material. Thus, this organic solution has no influence on REE yield.

The powdery fluorescent lamp waste was mixed with NH₄Cl in a 1:1 ratio to get thermal decomposition information of the sample and thus, to select properly the temperature values in the Box Behnken design. The chosen techniques used for that purpose were the thermogravimetric analysis (TGA) and differential thermal analysis (DTA) using the TGA/DSC 1 device from Mettler Toledo, USA.

All experiments and their respective parameters are listed in Tables 10.8 and 10.9, and the software utilized for statistical evaluation was Statgraphics v.18 (Statpoint Technologies, USA). This software allows for determining the REE model equation and the global optimum for the REE yield.
Table 10.8. Factors and levels in the $3^3$ Box-Behnken design.

<table>
<thead>
<tr>
<th>Factors</th>
<th>Factor levels</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-1</td>
</tr>
<tr>
<td>A Temperature (°C)</td>
<td>250</td>
</tr>
<tr>
<td>B Residence time (min)</td>
<td>30</td>
</tr>
<tr>
<td>C Ratio (g$_{\text{NH}<em>4\text{Cl}}$/g$</em>{\text{solid}}$)</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 10.9. $3^3$ Box-Behnken design (A: Temperature; B: Residence time; C: ratio of g$_{\text{NH}_4\text{Cl}}$/g$_{\text{solid}}$). The experiments shaded in grey correspond to the replicated central point.

<table>
<thead>
<tr>
<th>Nr.</th>
<th>A (°C)</th>
<th>B (min)</th>
<th>C (g$_{\text{NH}<em>4\text{Cl}}$/g$</em>{\text{solid}}$)</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>275</td>
<td>60</td>
<td>2</td>
<td>0</td>
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<td>2</td>
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<td>90</td>
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<td>90</td>
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<td>60</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

10.2.4. Solid-state chlorination

The mixture of 1 g of fluorescent lamp waste powder with NH$_4$Cl (according to the Table 10.8) was introduced in the quartz tube of the stationary rotary kiln. This mixture was placed in the centre of the tube (Fig. 10.18. b). Then, the O$_2$(g) was removed by flushing with N$_2$(g) at 350 mL/min for 30 min at 120 rpm. Under N$_2$(g) atmosphere the kiln was heated to the specified temperature in Table 10.8 with 10 K/min as the heating rate. When the reactor was cooled back to room temperature, the chlorinated sample was transferred to a beaker by rinsing the quartz tube with the organic leaching solution.

10.2.5. Leaching solution

The leaching solution was prepared by diluting 10% of 2,4 pentanedione (99%, Ref. A14117, Alfa Aesar) in ethanol (ACS grade, Ref. 100983, Sigma-Aldrich) in a total volume of 50 mL. The pH value of this organic solution was around 4. This leaching solution was chosen instead of water to recover the REE selectively. That means being able to separate these metals from...
other elements such as Ca\(^{2+}\) saving one more stage in the REEs recovery and separation process from fluorescent lamp wastes.

After the chlorinated residue was recovered, it was introduced into the organic leach solution and stirred at room temperature for 30 minutes. Then, the suspension was filtered using a PTFE membrane (0.2 µm, Filtrak, Germany) under reduced pressure at 200 mbar. In order to obtain the REEs liquor (Fig. 10.17) under the same aqueous medium conditions, the organic/ethanol mixture had to be replaced by nitrate medium. By addition of HNO\(_3\) and evaporation of the organic/ethanol \((T > 90^\circ\text{C})\), the nitrate medium of the leachate was obtained. Then, the organic/ethanol mixture was collected by distillation to re-use it in further leaching processes. Metal concentrations were measured by atomic emission spectrometry (ICP-AES, Optima 4,300DV by Perkin Elmer, USA).

10.3. Results and discussion

10.3.1. Starting material

The fluorescent lamp wastes had been leached employing HNO\(_3\) at room temperature \((18\pm2^\circ\text{C})\) for 10 min in a previous investigation to separate most of the base metals (mainly Ca\(^{2+}\)) [4]. The solid obtained after filtration \((\text{solid}_{L1})\) was used as the starting material in the current research. The composition of this solid is shown in Table 10.10.

<table>
<thead>
<tr>
<th>Element</th>
<th>(g) metal/(kg) waste(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-REEs</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>10.6±1</td>
</tr>
<tr>
<td>P*</td>
<td>32.1±2</td>
</tr>
<tr>
<td>Fe</td>
<td>0.1±0.1</td>
</tr>
<tr>
<td>Ba</td>
<td>1.2±0.3</td>
</tr>
<tr>
<td>Sr</td>
<td>1.6±0.5</td>
</tr>
<tr>
<td>Mn</td>
<td>0.5±0.1</td>
</tr>
<tr>
<td>Na</td>
<td>0.8±0.2</td>
</tr>
<tr>
<td>Mg</td>
<td>0.9±0.2</td>
</tr>
<tr>
<td>K</td>
<td>0.4±0.1</td>
</tr>
<tr>
<td>Sb</td>
<td>0.2±0.1</td>
</tr>
<tr>
<td>REEs</td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>79.3±3</td>
</tr>
<tr>
<td>Eu</td>
<td>4.8±0.2</td>
</tr>
<tr>
<td>Ce</td>
<td>0.9±0.1</td>
</tr>
<tr>
<td>La</td>
<td>0.6±0.01</td>
</tr>
<tr>
<td>Gd</td>
<td>0.4±0.01</td>
</tr>
</tbody>
</table>
Dy $0.3 \pm 0.01$
Tb $0.2 \pm 0.01$

**Total REEs** $86.5 \pm 0.5$

* by molybdenum blue method [18]

As shown in Table 10.10, the starting material is mainly composed by calcium, phosphor and yttrium. Since Y(III) represents 92% of the REE content and it is part of the least chemical resistance compound ($Y_2O_3$:Eu$^{3+}$, YOX) within fluorescence wastes. This metal has been chosen as representative to focus the study on recovery via SSC process. Moreover, the recovery of the Eu/La would not be cost-effective since their concentrations represent 10% of the REE content. Thus, the current investigation is focused solely on Y recovery instead of RE recovery.

The distribution of particle size is shown in Fig. 10.19. The results disclosed that 5.92 µm is the particle size with the highest volume (4.54%). Most particles are in the order of 2.75-8.70 µm (~60.76%). Particles < 2 µm made up 5.50% of the volume. The $d_{10}$-, $d_{50}$- and $d_{90}$- values were 2.42, 8.68 and 58.90 µm, respectively.

![Particle-size distribution of the starting material.](image)

**Fig. 10.19.** Particle-size distribution of the starting material.

### 10.3.2. Box Behnken design

The $3^3$ Box-Behnken design has been chosen from all the possible statistical designs (Table 10.11) since it allows modelling linear as well as non-linear dependencies with comparatively low experimental effort. Moreover, the $3^3$ Box-Behnken design allows examining cross effects. This is required in the optimization when the temperature is one of the factors because of two contrary effects on the Y yield. As expected, the more temperature increase, the faster chlorination process proceeds, thus, the higher Y yield obtained. However, the NH$_4$Cl$_{(s)}$ decomposition became faster too, and the Y yield could not benefit from higher
temperature because of the accelerated decomposition removing unreacted HCl\(_{(g)}\) from the heating zone [15].

**Table 10.11.** Comparison of different statistical designs considering three factors.

<table>
<thead>
<tr>
<th>Statistical design</th>
<th>Experiments</th>
<th>Error DF*</th>
<th>Factor levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>3(^3) Box-Behnken design</td>
<td>15</td>
<td>5</td>
<td>(-1</td>
</tr>
<tr>
<td>3(^3) Central composite design</td>
<td>16</td>
<td>6</td>
<td>(-1</td>
</tr>
<tr>
<td>3(^3) Full factorial design</td>
<td>27</td>
<td>17</td>
<td>(-1</td>
</tr>
<tr>
<td>3(^3)-1 Fractional factorial design</td>
<td>9</td>
<td>0</td>
<td>(-1</td>
</tr>
</tbody>
</table>

\* Degrees of freedom

In order to select the levels of the temperature properly, TGA and DTA were carried out mixing 1 g of powder fluorescent lamp waste with 1 g of NH\(_4\)Cl\(_{(s)}\) from 30 up to 500\(^\circ\)C at 10K/min and the results are shown in Fig. 10.20.

![TGA/DTA curve of the starting material with NH\(_4\)Cl from 30 up to 500\(^\circ\)C at 10K/min.](image)

**Fig. 10.20.** TGA/DTA curve of the starting material with NH\(_4\)Cl from 30 up to 500\(^\circ\)C at 10K/min.

There are four characteristic peaks corresponding to NH\(_4\)Cl\(_{(s)}\) decomposition and REE chlorination. At 184\(^\circ\)C, NH\(_4\)Cl\(_{(s)}\) changes its modification (Eq. (10.13)), and thermal decomposition occurs at T ≥ 220\(^\circ\)C (Eq. (10.14)) [19] and reaches its maximum at 320\(^\circ\)C (Fig. 10.20).

\[ \alpha \rightarrow NH_4Cl\(_{(s)}\) \xrightarrow{\Delta} \beta \rightarrow NH_4Cl\(_{(s)}\) \]

\[ \beta \rightarrow NH_4Cl\(_{(s)}\) \xrightarrow{\Delta} HCl\(_{(g)}\) + NH_3\(_{(g)}\) \]  

(10.13)  

(10.14)

Once HCl\(_{(g)}\) is released, REE chlorination takes place between 250 and 400\(^\circ\)C. The chlorination process for the REE proceeds in two stages [20] as depicted in Eq. (10.15) or Eq. (10.16) depending on whether the starting material is an oxide or a phosphate. Hence, the chosen levels of the temperature were 250, 275 and 300\(^\circ\)C (Table 10.8).
Rare earth element recovery from E-wastes by solvent extraction and supported liquid membrane processes

\[
Y_2O_3(s) + 6 NH_4Cl(s) \rightarrow 2 YCl_3 + 3 H_2O + 6 NH_3(g) \tag{10.15}
\]

\[
YP_2O_5(s) + 3 NH_4Cl(s) \rightarrow YCl_3 + (NH_4)_3PO_4 \tag{10.16}
\]

To select accurately the levels of the residence time, an experiment was carried out checking how much time was needed to achieve the selected temperature. For this purpose, 300°C were chosen as chlorination temperature. Since the rotary kiln heats up by \(\sim 10\) K/min (Fig. 10.21), 30 min was the lowest residence time level.

![Fig. 10.21. Verification of the rotary kiln heats up.](image)

Although 12 experiments would be expected in this type of statistical design (Fig. 10.22), 15 were performed because three central point replicas were carried out to determine the experimental error associated with the 95% confidence interval.

![Fig. 10.22. 3³ Box-Behnken experimental design.](image)

Finally, a model equation was developed using Eq. (10.17) and a multi-linear regression to achieve the Y yield optimum and to determine the significant effects evaluating all linear, squared and cross effects.

\[
y = b_0 + \sum_{i=1}^{N} b_i x_i + \sum_{1 \leq i < j}^{N} b_{ij} x_i x_j + \sum_{i=1}^{N} b_{ii} x_i^2
\]
where:

- $y$: Target value: $Y$ yield
- $x_i$: Factors: Temperature, residence time and $g_{NH4Cl/g_{powder}}$ ratio
- $N$: Number of factors (3)
- $b_0$: Ordinate section
- $b_i$, $b_{ij}$, $b_{ii}$: Regression parameters of linear, squared and cross effects

### 10.3.3. Optimization

In order to get the model equation with the optimization of the $Y$ yield, Eq. (10.17) was used to investigate the nine effects which can influence $Y$ yield: three linear ($A$, $B$, $C$), three squared effects ($AA$, $BB$, $CC$) and three binary correlations ($AB$, $BC$, $AC$). To determine which effect contributes significantly to $Y$ yield, an ANOVA was conducted using the Stratgraphics v.18 software (Table 10.12).

**Table 10.12. ANOVA results from the $3^3$ Box-Behnken design with three central points.**

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>DF*</th>
<th>Mean square</th>
<th>F-value</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A:Temperature</td>
<td>7815.63</td>
<td>1</td>
<td>7815.63</td>
<td>34.54</td>
<td>0.0020</td>
</tr>
<tr>
<td>B:Residence time</td>
<td>994.134</td>
<td>1</td>
<td>994.134</td>
<td>4.39</td>
<td>0.0902</td>
</tr>
<tr>
<td>C:Ratio</td>
<td>426.174</td>
<td>1</td>
<td>426.174</td>
<td>1.88</td>
<td>0.2283</td>
</tr>
<tr>
<td>AA</td>
<td>600.113</td>
<td>1</td>
<td>600.113</td>
<td>2.65</td>
<td>0.1643</td>
</tr>
<tr>
<td>AB</td>
<td>688.013</td>
<td>1</td>
<td>688.013</td>
<td>3.04</td>
<td>0.1417</td>
</tr>
<tr>
<td>AC</td>
<td>1423.93</td>
<td>1</td>
<td>1423.93</td>
<td>6.29</td>
<td>0.0539</td>
</tr>
<tr>
<td>BB</td>
<td>69.1069</td>
<td>1</td>
<td>69.1069</td>
<td>0.31</td>
<td>0.6043</td>
</tr>
<tr>
<td>BC</td>
<td>11.4244</td>
<td>1</td>
<td>11.4244</td>
<td>0.05</td>
<td>0.8311</td>
</tr>
<tr>
<td>CC</td>
<td>413.597</td>
<td>1</td>
<td>413.597</td>
<td>1.83</td>
<td>0.2343</td>
</tr>
<tr>
<td>Total error</td>
<td>1131.32</td>
<td>5</td>
<td>226.265</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total (corr.)</td>
<td>13459.7</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9159</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R^2$ adjusted for DF</td>
<td>0.7647</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Degrees of freedom

As is shown in the Pareto diagram in Fig. 10.23, eight of the nine effects were insignificant. Only temperature affects $Y$ yield significantly. All insignificant effects were therefore removed by the stepwise method.
Once the insignificant effects were removed, the ANOVA results were modified (Table 10.13) decreasing the $R^2$ by 58%. Hence, considering only one significant effect for Y yield optimization, a mathematical model equation was determined as a function of the temperature (Eq. (10.18)) achieving the 70% Y as the maximum under the following reaction conditions: $300^\circ C$, 90 min, $2 \text{ g}_{\text{NH}_4\text{Cl}}/\text{g}_{\text{solid}}L$.

**Table 10.13.** ANOVA results from the $3^3$ Box-Behnken design with three central point removing the insignificant effects.

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>DF*</th>
<th>Mean square</th>
<th>F-value</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Temperature</td>
<td>7815.63</td>
<td>1</td>
<td>7815.63</td>
<td>18.00</td>
<td>0.0010</td>
</tr>
<tr>
<td>Total error</td>
<td>5644.05</td>
<td>13</td>
<td>434.158</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total (corr.)</td>
<td>13459.7</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.5807</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R^2$ adjusted for DF</td>
<td>0.5484</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


\[
Y \text{ yield} = -305.17 + 1.25025 \cdot A
\]  

(10.18)

where:

\[
A: \text{ Temperature in } ^\circ C.
\]

Since considering a single effect as a determinant does not generate a good optimization model, the results are presented in Fig. 10.24 in order to examine how factors and factor levels could be modified to obtain a better model. The growing trends obtained in Figs. 10.24. a and b are expected to be seen, since kinetics of chemical reactions depend on temperature and time cause of the Arrhenius equation and reaction rates, respectively. However, at lowest temperature, $250^\circ C$, the Y yields are close to zero. These results in a loss of information.
reducing the extent in which each effect can influence Y yield. Consequently, effects might have been determined insignificant, because of the fact that temperature range was set too low.

Fig. 10.24. All four pair of experiments differing only in one of the chosen factors. a) Temperature. b) Residence time. c) g\(_{NH_4Cl}/g_{solid,L1}\).

Regarding the influence of the g\(_{NH_4Cl}/g_{solid,L1}\) ratio, three different trends can be seen in Fig. 10.24. c. At 250 °C, Y yields are almost zero disguising the influence the ratio may have on Y yield. Therefore, the temperature range requires adjustment. Furthermore, Y yields also show a decreasing trend when more NH\(_4\)Cl\(_{(s)}\) is introduced in the reactor. These results are consistent to Lorenz and Bertau who obtained the same trend in their investigation [19]. Considering the composition of the fluorescent lamps wastes, the influence of the g\(_{NH_4Cl}/g_{solid,L1}\) ratio on the Y yield in a negative way could be explained by the precipitation of the YPO\(_4\). Since the Ca\(^{2+}\) is one of the most representative element, due to the halophosphate as main source
of this element, and the solubility of YPO_4 is much lower than for Ca_3(PO_4)_2 [19]. the precipitation of the Y^{3+} could be increased with rising amounts of Ca^{2+} entering the solution. However, evidence cannot be gathered using the organic leaching solution, as the formed CaCl_2 remains undisolved in the residue. Thus, different solid-state chlorination experiments should be carried out using water as leaching solution to confirm that while the most g_{NH_4Cl}/g_{solidL1} ratio is used, the more Ca yield is obtained, the Y yield is increased reaching to a maximum and then, it decreases due to the precipitation.

To sum up, a new 3³ Box-Behnken design has to be carried out with adjusted factor levels. In this regard, the lowest temperature limit must be higher than 250ºC allowing effects influencing Y yield significantly. The g_{NH_4Cl}/g_{solidL1} ratio has to be adjusted too in order to take the possible YPO_4(s) precipitation into account. Despite the necessity of adjusting the optimization to the new findings, it has been demonstrated that the L2 stage in Fig. 10.17 can be improved via SSC process with regard to chemical consumption and acidity of wastewater. Additionally, REE recovery becomes selective when a mixture of 10% of 2,4 pentanedione diluted in ethanol is utilized for leaching.

10.4. Conclusions

REEs recovery and separation process from fluorescent lamp wastes can be improved by using solid-state chlorination to reduce the chemical consumption and the acidity of the leachate. It also means cost savings since (1) NH_4Cl(s) costs 23% less than HCl(aq) and (2) the SSC reduces the cost of using waste water with low acidity by around a third.

Moreover, 2,4 pentanedione diluted in ethanol as the leaching solution has been proven as an effective alternative to aqueous nitric/hydrochloric acids to REEs recovery from end-of-life products such as fluorescent lamps. In addition, using this organic mixture, the REEs can be recovered selectively avoiding a further stage to separate the REEs from other metals which are also recovered by using aqueous leaching solutions.

However, the 3³ Box-Behnken design has to be adjusted by shifting the lowest temperature level to a temperature above 250ºC and by focusing on lower g_{NH_4Cl}/g_{solidL1} ratios. Eventually, these changes will allow for developing a final model describing how Y yield depends on temperature, residence time and g_{NH_4Cl}/g_{solidL1} ratio. Based on his model, maximum Y yield can be estimated. This work will be conducted in a future scientific research for which the present work has developed the fundamental principles.
Acknowledgment

This research was supported by the MINECO with its [grant number CTM2017-83581-R]. We express our gratitude to Recyberica Ambiental S.L. for providing free samples of the fluorescent lamp wastes. Further thanks are owed to Andrea Schneider and Dipl. Chem. Sebastian Hippmann, Institute of Chemical Technology for conducting ICP-OES and TGA/DTA analyses.
References


10. RECOVERY OF RARE EARTH ELEMENTS FROM FLUORESCENT LAMP WASTES BY USING SOLID-STATE CHLORINATION


11. RESULTS
11. RESULTS
11. Results

11.1. NdFeB magnets

Since the raw material for this REEs application was synthetic, the purpose was to separate the neodymium from a Nd/Tb/Dy mixture, because it is the main REEs compound found in NdFeB magnets. Significant outcomes of the Nd separation are set out below depending on the applied separation technique.

Key findings in liquid membranes

FSSLM is a suitable membrane process to separate Nd from a Nd/Tb/Dy mixture using molecular cationic extractants such as Cyanex 272 and Cyanex 572 in chloride media. By means of this membrane technique, the Nd separation was possible depending on the carrier concentration, the feed pH and the agent used in the receiving solution and its concentration.

Although both extractants were able to completely separate the Nd from a mixture of Nd/Tb/Dy containing 0.1 g/L of each REE in 0.4 M of Cl\(^-\), the metals transport was higher with the same working time when Cyanex 572 was used. For this reason, it was especially designed for the HREEs extraction. Hence, it had a more acidic character and it was required a less stripping agent concentration. Despite the fact that Cyanex 572 seemed to be more appropriate for the REEs separation, if the membrane area or the working time were increased using Cyanex 272 as carrier in the membrane experiments, similar results should be obtained.

As the cation exchanger mechanisms are strongly pH dependent, this parameter was key to obtain the Nd selective separation. The optimal feed pH conditions when the carrier concentration was fixed to 0.30 M were 1.5 and 2.0 using Cyanex 572 and Cyanex 272, respectively. Setting these pH values, the Nd separation was achieved using a range of Cyanex 272 concentration from 0.14 to 0.68 M. However, a higher transport of these LREE using Cyanex 572 concentrations ≥ 0.45 M, a selective separation was gained using carrier concentrations less or equal than this value.

Citric acid 1 M or HCl 1.2 M were suitable to recover the Me-loaded in the receiving solution due to mainly the complexing and acidic effect, respectively. Furthermore, although the HCl concentration had influence on the metals transport, 1.2 M was chosen to be used in the receiving solution. 0.5 and 2.0 M of HCl were discarded due to low metal transport and to avoid working with severe conditions, respectively.

The permeability coefficients of Nd, Tb and Dy were determined to predict the transport of these REEs as a function of the carrier concentration and the required area. Since the viscosity
of both carriers was not a parameter that restricted the metal transport in the working range concentration studied; the dependence on the Cyanex concentration and permeability was linear. Thus, the diffusion process controlled the metal transport through the membrane. This transport was 35% faster using Cyanex 572 than using Cyanex 272.

To sum up, the Nd separation from a Nd/Tb/Dy mixture containing in the aqueous solution 0.1 g/L of each metal in 0.4 M of Cl⁻ was achieved after 8 h by a flat sheet liquid membrane Fluoropore™ FHLP04700 using (1) 0.14-0.68 M of Cyanex 272, feed pH=2, HCl 1.2 M as receiving solution or (2) 0.15-0.45 M of Cyanex 572, feed pH=1.5, HCl 0.5 M as receiving solution. Considering the scale-up industrial process using hollow fibre membrane modules, 7 h would have required to recover the 95% of REEs from 1 m³ of the NdFeB magnet waste using 11 and 15 m² membrane area when Cyanex 572 and Cyanex 272 were used, respectively, if the permeability coefficients had been 1.3 times less than those obtained by FSSLM according to the relationship of both membranes in fluorescent lamps experiments.

Key findings in solvent extraction process

To avoid the inter-step pH control, an alternative was developed using ionic liquid as an extractant since there was no proton exchange to the aqueous phase when REEs were extracted, and consequently, the aqueous phase pH was not modified after extraction. Thus, an industrial counter-current process was developed to recover neodymium from synthetic magnet waste leachings using Primene 81R·Cyanex 572 IL as extractant.

In order to find the optimal working conditions to achieve the selective REEs separation, the effect of the Primene 81R/Cyanex 572 ratio, IL concentration, the aqueous pH and the diluent were investigated. As a result, neodymium was selectively separated from the Nd/Tb/Dy mixture containing 1 g/L of each REE in 4 M of Cl⁻ using 0.3 M of the IL (1:1 molar ratio), initial pH=0.10 and kerosene as diluent. The REE-loaded in the organic phase were completely stripped using HCl 4 M. However, to set up an industrial separation process, the metal concentrations in the feed solution were modified to the representative REE concentrations on magnet wastes: 9.00, 0.50 and 2.55 g/L of Nd, Tb and Dy, respectively. Furthermore, a diluent’s change was required to avoid the third phase formation in the organic phase in the counter-current process.

The counter-current process results showed that at least two stages were required (A:O ratio of 1:4) to separate Nd from the Nd/Tb/Dy mixture using 0.3 M of Primene 81R·Cyanex 572 IL and Solvesso 100 as the organic phase because it allowed the elimination of 99.99% and 99% of the initial Tb and Dy, respectively, without any aqueous pH conditioning, since it was remained constant around 1.20 for the extraction.
11.2. Fluorescent lamps

An available hydrometallurgical process to recover and separate REEs from end-of-life fluorescent lamps was designed testing a lab-scale taking halophosphor rich in YOX as the raw material in powder form. The flow-sheet of the process separation is shown in Fig. 11.26.

![Flow-sheet of the separation process of REEs from fluorescent lamp wastes.](image)

The fluorescent lamp powders had a REEs content of 93.2 g\text{metal}/kg\text{waste}. Due to the high amount of Y and Eu in the waste, the fluorescent lamps seemed to come from red phosphors (Y₂O₃:Eu³⁺). However, 79 gCa/kg\text{waste} meant that the waste was a mixture of different phosphors with the red ones as predominant. The powders were treated with a magnetic separation to remove the Fe ions. Then, the solid was undergone to acidic leaching processes. Two leaching stages were required; firstly, the calcium had to be removed in the Y/Eu rich liquor to avoid the CaSO₄(s) in the oxalate precipitation step. For this purpose, 86% of calcium metal ion was
11. RESULTS

recovered using 1 M of HNO₃, 10 min of contact time and 10% w/v of S:L ratio in the L1 leaching stage. Unfortunately, 6% of the REEs content was washed-up in the liquid fraction too. In order to recover this amount, a membrane step was used because of the economic viability to separate the metals at low concentrations.

Then, the membrane experiments were carried out with a flat sheet supported liquid membranes to be assured the success and to find the optimal conditions to the REEs recovery spending the least amount of reagents. The feed solution, which contained 548 mg/L of REEs, was the leachate from L1 and Cyanex 923 diluted in kerosene was the organic solution. The results disclosed that the metal transport was only controlled by the diffusion through the membrane at low Cyanex 923 concentrations. However, at higher carrier concentrations, the effect of the shear stress became predominant reducing the apparent permeability. Since adding a modifier like 2,6-Dimethyl-4-heptanone, the organic solution viscosity decreased obtaining higher REEs permeability coefficients and the study of the diffusivity on the dynamic viscosity showed decreasing lines with slopes closed to (-2/3). For these reasons, it can be affirmed that the reduction of the permeability at high carrier concentrations was due to the viscosity.

Furthermore, a transport model for yttrium and europium was developed using the permeability coefficient as the characteristic parameter considering three more parameters: Cyanex 923 concentration, 2,6-Dimethyl-4-heptanone percentage (v/v) and viscosity of each mixture. As it was expected, the metal transport was meaningful favoured using 40 % (v/v) of the modifier reaching the maximum value of the permeability (only 2,6-Dimethyl-4-heptanone as solvent) due to the notably viscosity decrease at high concentrations of Cyanex 923 when the modifier concentrations increased. The optimal permeability coefficient values when 1.19 and 1.18 M of Cyanex 923 adding 40% of modifier were 4.38∙10⁻⁶ and 7.00∙10⁻⁶ m/s for Y and Eu, respectively.

Once the improvement of the REEs recovery from the fluorescent lamp wastes was demonstrated adding a FSSLM step, then this membrane step was optimized so the whole recovery and separation process could be industrially implemented. So, a hollow fibre module was used. To guarantee the membrane stability, it was working in renewal configuration, but, the experiments could not be carried out at the found optimal conditions owing to the chemical incompatibility of the 2,6-Dimethyl-4-heptanone with the membrane PP material fibres and avoiding sampling time errors due to fast REEs transport.
As it was expected, the dependence on the permeability from the Cyanex 923 concentration is linear because the diffusion controls the transport process instead of the viscosity when Cyanex concentration range was 0.1-0.3 M. To minimize the efforts on the optimization membrane process since determining experimentally the optimal conditions was labourious and time-consuming, so, the proposed model for the FSSLM was modified. It has been considered that the permeability differences when both membranes were used can be justified in terms of tortuosity, thickness and porosity differences. Finally, considering the transport modelling, the highest permeability values of Y, 2.80⋅10^{-6} m/s, and Eu, 4.10⋅10^{-6} m/s could be achieved using 1.18 M of Cyanex 923. As a conclusion, the REEs amount washed-up in the L1 leachate can be completely recovered using hollow fibre membranes. The REEs-EDTA complex had to be treated with HNO_3 concentrated to get the EDTA precipitation to use it in successive membrane stage.

The solid obtained from the L1 stage was tested with a second leaching (L2) using 2 M of HNO_3 up to 48 h of contact time and 10% w/v of S:L ratio obtaining a liquor rich in REEs, mainly Y/Eu, which were mixed with the permeate fraction coming from the membrane stage. Although the experiments showed that HCl and HNO_3 were available to recover more than 94 and 82% of Y and Eu, respectively, the HNO_3 was chosen to the industrial process since the liquor coming from the membrane step was in nitrate media. Unfortunately, using these conditions, Gd and La were not completely recovered (47 and 5%, respectively) because these REEs need more drastic conditions in the leaching process.

A mathematical modelling of the Y/Eu/Ce extraction was developed to predict the extraction behaviour of these metals. The proposed models took into consideration the proton, the chloride and the extractant concentrations. They were derived from the mass balance and equilibria equations involved in the extraction processes considering the most suitable ones for the REEs when a cationic extractant was used. The extraction of yttrium, europium and cerium in chloride media using D2EHPA diluted in kerosene were firstly individually simulated following twelve different models whose parameters were estimated by minimizing the deviations between the experimental data and the proposed model using the Matlab R2017b software. Three proposed models obtained a standard deviation < 5:

\[
Me^{3+} + 3 \cdot HA \overset{K_{a1}}{\leftrightarrow} MeA_3 + 3 H^+ \quad (R.a_1)
\]

\[
Me^{3+} + 3 \cdot (HA)_2 \overset{K_{b1}}{\leftrightarrow} Me(HA_2)_3 + 3 H^+ \quad (R.b_1)
\]

\[
Me^{3+} + 3 \cdot (HA)_2 \overset{K_{c1}}{\leftrightarrow} MeA_3(HA)_3 + 3 H^+ \quad (R.c_1)
\]
These three models were tested for a mixture of Y/Eu/Ce to determine if they were useful to reproduce their competitive extraction. Obtaining a standard deviation of 5.8 and 6.7 for $a_1$ and $b_1-c_1$, respectively, it can be affirmed that the model accuracies are similar in the whole range of the three studied parameters (pH, chloride and D2EHPA concentrations). According to the most frequently used coordination numbers for REEs and the dimeric consideration of cationic extractants like D2EHPA, the selected extraction mechanism was the corresponding to R.c1. The stepwise stability formation constants for the Ce-Cl, Eu-Cl and Y-Cl species formed in the aqueous phase in equilibrium and the metal extraction equilibrium constants values were obtained. Furthermore, the results disclosed that the Y could be selectively separated from the Y/Eu/Ce mixture using D2EHPA as extractant when the chloride concentration in the aqueous phase was higher than 4 M maintaining the proton concentration above 3 M.

Once the REEs behaviour was studied in the extraction modelling, the recovery and separation of the REEs were achieved experimentally. Both Y/Eu rich liquors can be mixed to obtain the REEs oxalate precipitation by adding oxalic acid. The metals in oxide form can be obtained after the REEs oxalate calcination at 600°C for 1 h. Then a synthetized Y/Eu/Ce mixture was dissolved with HCl 2 M and NaCl 2 M and was used as feed solution. Eventually, the Y/Eu/Ce separation with purity ≥ 99.9% was achieved combining the use of two ILs as extractants, such as Primene 81R-D2EHPA and Primene 81R-Cyanex 572, by using a four-stages cross-flow solvent extraction process. The first three stages were necessary to obtain 98% of Y in the organic phase using Primene 81R-D2EHPA IL and Primene 81R-Cyanex 572 to selectively separate Eu/Ce. Since Y is HREE, the IL composed by D2EHPA was more suitable for its separation from the REEs mixture. This IL was used at 0.30 M in the two first stages instead of the third one (0.15 M) to avoid the Eu/Ce extraction. Cerium and europium were separated using 0.30 M of Primene 81R-Cyanex 572 in the last stage, obtaining 99.99% of Eu in the organic phase. 4 M of HCl was enough to recover the Eu and the Y from the organic phases and 99.99% of Ce was recovered in the raffinate flow.

Although the properly REE yield optimization could not be achieved by using solid-state chlorination process due to the selection of the levels of temperature and $g_{NH_4Cl}/g_{waste}$ ratio on the $3^3$ Box-Behnken design, it has been demonstrated that the REEs recovery and separation process from fluorescent lamp wastes (Fig. 11.27) can be improved.
Bearing in mind that using SSC instead of L2 acid leaching stage, the chemical consumption and the acidity of the leachate are reduced, this unconventional process seems to be promising in the REEs recovery field. As can be seen in Fig. 11.27, using the 2,4 pentanedione diluted in ethanol as the leaching solution, the REEs can be selectively recovered avoiding further stages (precipitation using oxalic acid, calcination and redissolution) to separate the REEs from other metals which can be also recovered by using other aqueous leaching solutions. Finally, once the Y/Eu liquor in nitrate medium is obtained, the selective separation should be studied.
12. CONCLUSIONS
12. Conclusions

Different techniques have been studied to recover and separate REEs from end-of-life products to provide more industrial sustainable processes and potential management solutions. For this purpose, solvent extraction and liquid membrane processes have been developed to obtain these key metals with high purity to close a circular economy loop reusing end-of-life fluorescent lamps and NdFeB magnets. Then, it has proved that:

**NdFeB magnets**

- It was possible to separate Nd from Nd/Tb/Dy synthetic mixture at 4 M of Cl⁻ using Cyanex 272 or Cyanex 572 diluted in kerosene by using FSSLM. The feed solution should be at 1.5 pH value when Cyanex 572 is used, instead of 2.0 for Cyanex 272 due to the higher acidic character of the former. The transport through the liquid membrane using Cyanex 572 is about 35% faster than using Cyanex 272. Thus, to achieve similar results to those obtained with Cyanex 572, the membrane area or the working time should be increased for Cyanex 272.

- 99.99% of Nd recovery with a purity of 99.7% from an aqueous Nd/Tb/Dy mixture, containing the REEs concentrations on magnet wastes, in chloride medium was achieved after two stages counter-current extraction process using 0.30 M of Primene 81R·Cyanex 572 IL (1:4, A:O ratio) diluted in Solvesso 100 without any aqueous pH conditioning since the pH remained constant around 1.2.

To sum up, it can be affirmed that these experiments disclosed two different processes to separate the most common REEs present in the end-of-life NdFeB magnets and the results obtained allowed consideration of (1) applying both proposed techniques using real NdFeB magnet wastes and (2) a scale-up industrial process using hollow fibres module with 11 or 15 m³ when Cyanex 572 or Cyanex 272 are used, respectively.

**Fluorescent lamps**

- REEs can be recovered from their leachates optimizing the leaching process adding a membrane step. For this reason, the main impurities content was removed using magnetic separation and an acidic leaching stage for iron and calcium, respectively. 86% of Ca was removed using 1 M of HNO₃ or HCl for 10 min and S:L ratio of 10% too. The solid obtained from the L1 stage was undergone to a second leaching using high acid concentration (2 M) to recover completely the REEs, especially Y and Eu. HNO₃ could recover as well as HCl for 48 h the 100 and 86% of Y and Eu, respectively. For
the recovery of Gd and La could be acquired at higher extensions using more drastic conditions in a 3rd leaching (L3).

- The REEs losses in nitrate media from the L1 leachate were recovered by liquid membranes (FSSLM and HFRLM). Using FSSLM, the highest available carrier concentration to recover these REEs losses was 0.90 M since at higher Cyanex 923 concentrations, the viscosity was the parameter which controlled the transport process instead of the diffusion. Thus, the permeability coefficients remained constant. To avoid it, it was demonstrated that adding 2,6-Dimethyl-4-heptanone as modifier, the organic solution viscosity decreased favouring the metal transport. Moreover, a transport modelling was developed taking as characteristic parameter the permeability reaching $4.38 \times 10^{-6}$ and $7.00 \times 10^{-6}$ m/s for Y and Eu, respectively, using 40% of modifier and 1.19 M of Cyanex 923. However, since the FSSLM were not suitable to an industrial scale-up, the membrane experiments were also carried out using hollow fibre module working in renewal configuration. Since the REEs permeability differences using FSSLM or HFRLM can be justified by the tortuosity, thickness and porosity differences, the modelling was modified considering the membrane characteristics. The highest permeability coefficient values ($2.80 \times 10^{-6}$ m/s for Y and $4.10 \times 10^{-6}$ m/s for Eu) were achieved using 1.18 M of Cyanex 923, without modifier due to its incompatibility with the PP material of the membrane fibres.

- A solvent extraction modelling for Y/Eu/Ce was developed to predict the behavior of these metal ions in a mixture and to study the feasibility of using a molecular extractant like D2EHPA instead of Primene 81R-D2EHPA IL in the cross-flow solvent extraction process minimizing from the first three stages to one. The results disclosed that Y could be separated from the mixture using 0.10 M D2EHPA, acidity above of 3 M of protons and chloride concentration higher than 4 M.

- REEs were selectively separated from the rich liquor which came from L2 and HFRLM stages. A feed solution containing a mixture of Y/Eu/Ce in chloride medium was synthetized and used to achieve the individual metals with purities ≥ 99.9% combining the use of Primene 81R-D2EHPA and Primene 81R-Cyanex 572 as extractants in a four-stages cross-flow solvent extraction process. The first three stages were required to recover 98% of Y in the organic phase using Primene 81R-D2EHPA IL. 99.99% of Eu in the organic phase was obtained in the last step using Primene 81R-Cyanex 572 IL. Both REEs were recovered from the organic phase using 4 M of HCl and 99.99% of Ce was obtained in the raffinate flow.
Solid-state chlorination process is a promising alternative instead of acid leaching on the REEs recovery since reduction of chemical consumption and the acidity of the leachate and avoidance of stages to separate REEs from other metals present in the fluorescent lamps are achieved.

As a final conclusion, this research has demonstrated different ways to provide REEs from urban mining by integration of solvent extraction and membrane process. So, recycling REEs from secondary resources encourage the green technologies development, the supply stability and a circular economy. Furthermore, although there are some hydrometallurgical processes for recovery and separation of REEs in the literature, this thesis proposes a process combining two different separation techniques such as solvent extraction and membrane processes to optimize the REEs recovery and separation process from fluorescent lamp wastes.
13. FUTURE RESEARCH
13. Future research

Although finding substitute materials for the REEs may help to mitigate supply pressures, it does not offer any solution because, as mentioned above, there are many REEs applications without alternative. In this sense, to design new REEs recovery processes from the end-of-life products is indispensable to guarantee their supply and their use in the high-tech applications development.

Considering the results obtained and the processes designed to recover and separate the REEs, some recommendations for future research to answer some arising questions are listed below bearing in mind both end-of-life products studied in this PhD thesis.

NdFeB magnets

- To test different extractants to separate Tb/Dy by solvent extraction processes.
- To study the feasibility of the Nd/Tb/Dy transport using Cyanex 572 by HFRLM, instead of FSSLM, adding a pH conditioning in the experimental set-up.
- To develop a mathematical model to describe Nd/Tb/Dy transport when the hollow fibre module is in renewal configuration.
- To design a whole hydrometallurgical process to recover and separate the REEs present in NdFeB permanent magnets.

Fluorescent lamp wastes

- To investigate the influence of temperature, time and acid concentration on the Gd and La leached to try to recover completely these REEs in the L2 stage.
- To test different complexing agents such as lactic acid to avoid the REEs precipitation at pH=1-1.5 from L1 leachate using HCl as leaching agent.
- To re-design the $3^3$ Box-Behnken for the REE yield optimization via solid-state chlorination process using 2,4 pentanedione diluted in ethanol as organic leaching solution.
- To verify the REEs separation designed process using real samples in whole the process.