Improved REEs recovery from fluorescent lamp wastes applying supported liquid membranes to the leaching solutions

S.Pavón[1], A.Fortuny[1], M.T. Coll[2], A.M. Sastre[3]

[1]Chemical Engineering Department, EPSEVG, Universitat Politècnica de Catalunya, Vilanova i la Geltrú, Víctor Balaguer 1, 08800, Spain
[2]Agri-Food Engineering and Biotechnology Department, ESAB, Universitat Politècnica de Catalunya, Castelldefels, Esteve Terrades 8, 08860, Spain
[3]Chemical Engineering Department, ETSEIB, Universitat Politècnica de Catalunya, Barcelona, Diagonal 647, 08028, Spain
Presenting author email: agustin.fortuny@upc.edu

Abstract

Purpose: REEs recovery from end-of-life fluorescent lamp wastes adding a SLM step to minimize the loss of these metals in the first leaching (L1) to obtain a purified REEs reach liquor after a second stage (L2).

Methods: SEM/EDX and XPS were the used techniques to characterize the real waste. SLM using Cyanex 923 as a carrier was the chosen technique to recover the REEs from the L1 leachate because of the high affinity of this carrier for the REEs.

Results: HNO_3 or HCl 1 M are the most appropriate acid agents in the L1 stage considering the balance between the Ca impurity removal and minimizing the REEs losses. These REEs lost can be entirely recovered from L1 leachate in nitric medium using Cyanex 923 0.60 M by SLM. The optimal conditions to recover these metals from the waste are leaching with HNO_3 or HCl 2 M for 24 h in L2 stage. REEs, especially Y and Eu, have been totally recovered using a L1– SLM – L2 stages sequential process.

Conclusions: Improving the REEs recovery from fluorescent lamp wastes is possible combining the leaching process and avoiding the REEs losses in the L1 adding an SLM process using Cyanex 923 as carrier.

Keywords

Fluorescent lamp wastes; Leaching; REEs recovery; Supported liquid membranes

1. Introduction

Nowadays, the recovery and separation of rare earth metals (REEs) has become one of the main interest subjects into the scientific community due to the need of developing alternatives to relieve their increasing consumption and supply risk. Moreover, the REEs growing consumption tendency does not seem to change in the coming years because 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 [1].

In order to provide a new way to recover and recycle REEs, the use of the end-of-life products and the processing of their waste streams has turned into a promising alternative. According to the fact that the highest consumption of REEs is concentrated in fluorescent lamps [2], the use of their end-of-life products has been chosen as the subject of this research. Red phosphors $Y_2O_3:Eu^{3+}$ (YOX), blue phosphors $BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM) and green phosphors $LaPO_4:Ce^{3+},Tb^{3+}$ (LAP), $(Gd,Mg)B_5O_{12}:Ce^{3+},Tb^{3+}$ (CBT), $(Ce,Tb)MgAl_{11}O_{19}$ (CAT) are the three main different phosphors of the fluorescent lamps [3]. Our investigation is focused on the halophosphate phosphors rich on YOX phosphors because they contain a high REEs content, specially yttrium and europium.

The characterization and leaching of a fluorescent lamp waste for the REEs recovery have been carried out in the current study. The fact that a real waste has been used, force us to propose, step by step, all the processes required to achieve a complete REEs recovery, starting from a sample containing different impurities. However, the disadvantage of working with a real waste is how to remove these impurities. In this sense, it is necessary to carry out a preliminary leaching (soft leaching) to separate most of the base metals, but in this stage some REEs are also lost. The added value provided by this investigation is the use of supported liquid membranes (SLM) to recover the REEs from the liquor obtained after this first leaching (L1) which contains REEs at low concentrations.

Mechanical separation is the easy way to remove components such a plastics, glass and aluminum end caps. Then, acid leaching is the most common method in the metal recovering from an end-of-life product real scratch resulting from the fluorescent lamps [4,5], although it is still in an incipient stage in industrial-scale applications yet. Due to the REEs interest and the deficit between consumption and exploitation, take 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 scare. A review regarding the yttrium recovery by leaching and SX from spent fluorescent lamps was recently published [6]. This review suggests a hydrometallurgical process to separate yttrium and calcium from acid leach liquor (leaching conditions 2 M of sulfuric acid, 70ºC, 15% w/v pulp density and 2 h of reaction) 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 was 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 4 M showed better efficiency for mercury [7]. Apart from the leaching study, another important point is the extractant choice, since it must be selective to achieve the complete REEs separation. In this sense, literature studies depict a wide range of different extractants that can be used to separate the rare earth selectively by the SX technique. Adding TBP into the binary mixture of Cyanex 272 and Alamine 336 a better Nd/Pr separation factor was obtained [8]. The separation factors between Ce(IV), Y(III) and Yb(III) from aqueous nitrate solution are in the order: Cyanex 923/kerosene < TBP/kerosene < HQ+Cyanex 302/heptane [9]. Besides the commercial extractants, the ionic liquids can be 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 at the same working time. 99% of Dy(III) and Nd(III) extraction in nitric acid medium using [C_8mim][Tf_2N] containing N,N-dioctyldiglycolamic acid (DODGAA) was obtained by SLM [12].

In order to evaluate the leaching efficiency for the REEs recovery from the fluorescent lamp waste, 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 complete recuperation. Several studies suggest an only 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 [13], the calcium become an insurmountable problem. As a consequence, as is 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 purpose, SLM was chosen to minimize the REEs losses, because this technique is economically viable to separate the metals presents at low concentrations, as has been demonstrated by the vast literature in the field of the REEs recovery [11,14]. The solid obtained in the L1 stage will be undergone to a second leaching (L2) using high acid concentration to obtain a liquor reach in REEs which will be mixed with the permeate fraction coming from the SLM experiment.

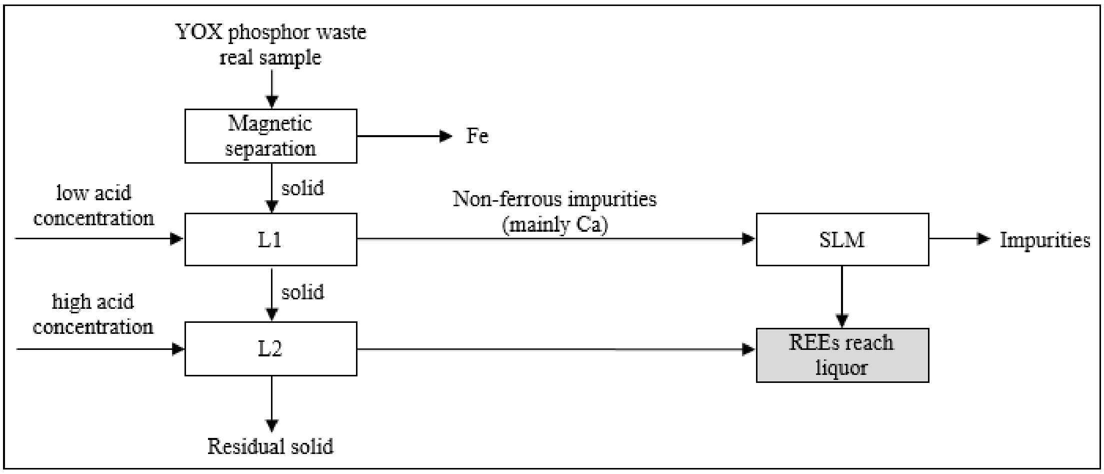


Figure 1. *Flow-sheet of the process to recover REEs from YOX fluorescent lamps wastes.*

2. Material and methods

2.1. Reagents

The end-of-life fluorescent lamps sample was obtained from Recyberica Ambiental. The acids used as leaching solutions, 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) were prepared using pure water as a diluent.

Cyanex 572 (Cy572), D2EHPA and Cyanex 923 (Cy923) were tried as carriers in the SLM experiments since the acidic and neutral carriers are the most used in the rare earths field. Both Cyanex carriers were kindly supplied by Cytec Canada Industries, D2EHPA was provided for Sigma-Aldrich (Ref. 237825) and they were used as received. Detailed specifications of these carriers are summarized in Table 1. Kerosene from Sigma-Aldrich as a diluent (Ref. 607010) and hydrochloric acid as stripping agent were used.

Table 1. Physical properties of Cy572, D2EHPA and Cy923.

Commercial name	Content %	Density $kg \cdot m^{-3}$	Viscosity (25ºC) mPa·s	Av. Mol. Weight $g \cdot mol^{-1}$
Cy572 [15]	100	933	<50	310 [a,b]
D2EHPA [16]	97			322
Cy923 [17]	93	880	40	348

[a] As a monomer.

[b] Experimental data by potentiometric titration in water/ethanol

2.2. Characterization of the waste

The end-of-life fluorescent lamps waste supplied by Recyberica Ambiental 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) (SPECS, XR-50 Dual anode source, non-monochromated (Al k-alpha, Mg k-alpha)) were the chosen techniques to know the sample composition.

Aqua regia was used to estimate the maximum leachable metals amount in 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 dm^3 of aqua regia at 90 ± 2ºC for 2h. When the solution was cold, it was filtered (Filter Paper 1001 070, Whatman International Ltd) and the volume was adjusted to 0.1 dm^3 with pure water (MilliQ, Millipore, > 18 MΩ/cm). The concentration of the metals was determined by atomic emission spectrometry using a 4100 MP AES System (Agilent Technologies) with an analytical error less than 5%.

2.3. Screening of leaching agents

Pure water, gluconic acid 1 M, acetic acid 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 dm^3 of leaching solutions (S:L ratio of 10% w/v), using magnetic stirring (200±50 rpm) at different contact times and room temperature (20±2 ºC). The non-dissolved solids were dried overnight at 100 ºC in an oven (Selecta, Conterm Ref. 2000209). In most of the cases, a second leaching (L2) was done using the dry non-dissolved solids from L1 with a higher acid concentration and the same S:L ratio.

2.4. Supported liquid membrane procedure

Due to the higher affinity of the carrier for a chemical species at low concentration, SLM is the most appropriate technique to recover the REEs from the L1 leachates. Transport experiments were carried out using the same experimental set up depicted by Pavon et al. in a previous study [11].

The organic phase was prepared dissolving Cy572, D2EHPA or Cy923 in kerosene. The neutral species are only formed when nitric acid medium is used. In contrast, using hydrochloric acid only cationic species are formed. That is why the L1 was carried out in nitric medium when Cy923 was used and Cy572 or D2EHPA were the chosen carriers in the SLM experiments in HCl media. A microporous polytetrafluoroethylene film (Fluoropore™ FHLP04700, Merck Millipore), 0.45 µm pore size, porosity of 80%, thickness 150 µm, 4.7 cm diameter and effective membrane area of 11.4 cm^2 was used as a support.

The feed and strip solutions were magnetically stirred at 1000 rpm at room temperature (20 ± 2ºC). Samples from both solutions were taken every hour up to 8 h. The metal concentrations were quantified by atomic emission spectrometry.

The permeability of each metal was obtained from the Eq. (1), derived from the feed cell metal mass balance and the Fick's law.

$$ln\frac{[Me]}{[Me]_0} = -P \cdot \frac{A}{V} \cdot t \qquad (1)$$

Where $[Me]$ and $[Me]_0$ are the metal concentration (g·dm^{-3}) in the feed cell at time (t) and initial time (t_o), respectively; P is the permeability coefficient (m·h^{-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 (h).

3. Results and discussion

3.1. Waste characterization

Firstly, the waste was dried at 60 ± 1 ºC for 24 h, and after this period, a 0.3% weight loss was observed. The sample complexity, consequence of the particle size and the wide range of elements present in it, force us to use different analytical techniques to take advantage of the information given from every one of them.

In this sense, SEM/EDX technique was the technique chosen to have an idea of how heterogeneous the sample is. For this purpose, a first screening was carried out. As can be seen in Fig. 2, the sample is very heterogeneous and the size of the particles is quite different. That is why exhaustive spectra taking into account the possible differences between the small and large particles were done. Moreover, as is shown in the Fig. 2.b a contrast was applied to the same region shown in the Fig. 2.a and the results confirm that the bigger particles correspond to elements which are in glass such as Al-Si and the smaller and more luminous ones are the REEs such a Y, Eu, La and Gd as can be seen in the spectra depicted in Fig 2.c and Fig 2.d.

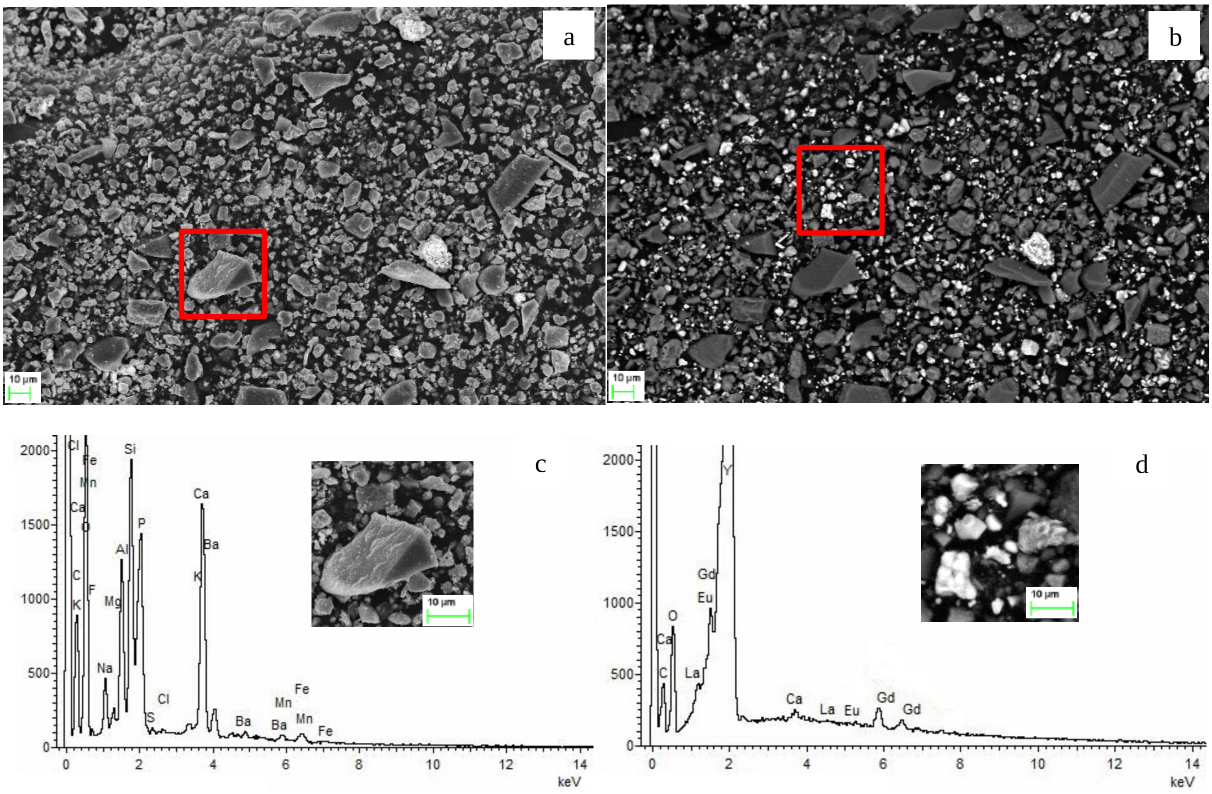


Figure 2. *SEM images of the fluorescent lamp wastes. a) 1.00 kx magnification (Signal InLens). b) 1.00 kx magnification using light contrast applied (Signal QBSD). c) Magnification (2.00 kx) of the largest particles in the red-framed area shown in a). d) Magnification (2.00 kx) of the smallest particles in the red-framed area shown in b).*

The utilization of the XPS technique as a screening of the metals present in the sample seemed a good option but the relative composition of the detected metals showed a high dispersion in function of the analyzed sample point. In this case, the results only has been used as a reference of the metals presents in the waste. XPS analysis revealed the existence of yttrium and europium as the REEs with high content in the waste. Moreover, the total REEs relative percentage in the end-of-life fluorescent lamps is 6.3 ± 0.04%.

Element	% Concentration
Al	12.3 ± 0.9
C	20.0 ± 2.1
Ca	5.8 ± 0.1
Ce	0.003 ± 0.001
Co	0.5 ± 0.1
Dy	0.01 ± 0.03
Gd	0.1 ± 0.01
Eu	0.5 ± 0.1
F	2.6 ± 0.4
Fe	0.3 ± 0.2
La	0.2 ± 0.1
Na	5.5 ± 0.1
O	43.1 ± 1.0
P	3.7 ± 0.2
Y	5.4 ± 0.1
Total REE	6.3 ± 0.04

Table 1. *Analyzed elements and their content in the waste before any treatment. The error represents the standard deviation of triplicate measurements.*

The chemical treatment with aqua regia has been applied to determine the elements that can be leached from the real sample. After this leaching, the concentration of 26 metals in the waste before the partial separation of large impurities such as glass and plastic was analyzed by atomic emission spectrometry (Table 2).

Metal	Average metal content in the waste (g metal·kg^{-1} waste)
Al	11.0 ± 0.1
B	0.7 ± 0.1
Ba	4.0 ± 0.2
Ca	79.0 ± 3
Ce	0.1 ± 0.1
Co	Not detected
Cu	0.1 ± 0.1
Dy	0.1 ± 0.01
Eu	6.0 ± 0.1
Er	Not detected
Fe	5.0 ± 0.01
Gd	1.1 ± 0.8
Hg	Not detected
K	0.9 ± 0.1
La	1.6 ± 0.3
Mg	1.5 ± 0.01
Mn	2.0 ± 0.1
Na	1.7 ± 0.1
Ni	0.1 ± 0.1
Nd	0.1 ± 0.01

Sb	0.4 ± 0.1
Si	0.1 ± 0.01
Sr	4.0 ± 0.1
Tb	0.2 ± 0.1
Y	84.0 ± 8
Yb	Not detected

***Table 2**. Content of metals in the waste. The results are obtained after aqua regia leaching (90 ± 2ºC, 2h), S:L ratio of 10% w/v. The error represents the standard deviation of triplicate tests.*

The average REEs content was 93.2 ± 1.2 $g \cdot kg^{-1}$. Calcium and Yttrium are the metals in the largest amounts with an average of 79.0 ± 3 and 84.0 ± 8 g $metal \cdot kg^{-1}$ waste, respectively. Moreover, as was expected, Y(III) and Eu(III) were the most REEs presents in this waste because they are the relevant REEs in the red phosphors ($Y_2O_3:Eu^{3+}$) [7].

Because of the similar amount of Ca and Y and taking into account the REE recovery and separation aim, a selective leaching process which allows firstly removing the Ca is essential. For this reason, a screening of different leaching agents has been carried out.

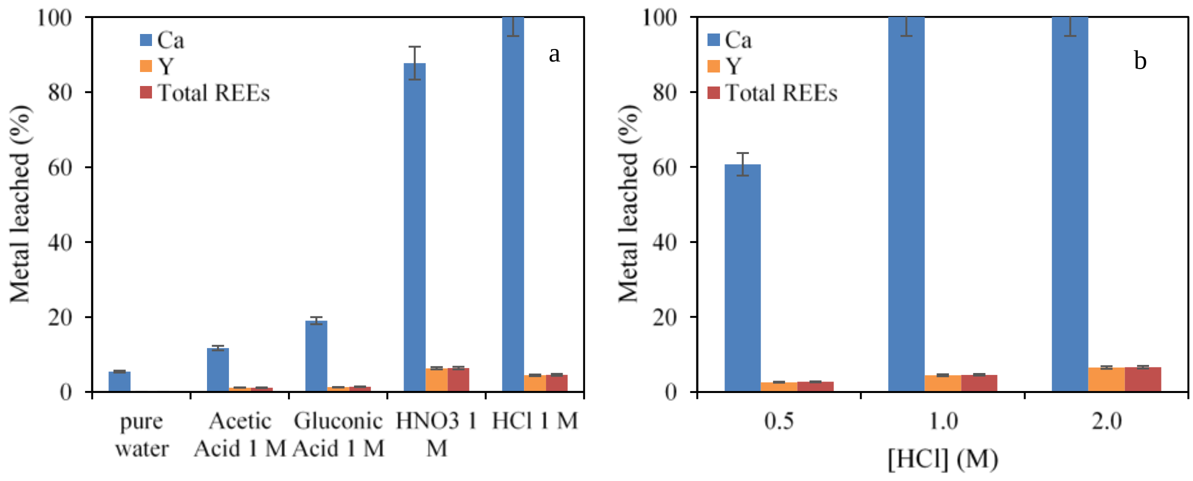
3.2. Screening of leaching agents

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

3.2.1. Leaching 1 (L1)

The L1 leaching was carried out keeping in mind the aim of maximizing the Ca elimination and losing the minimum of REEs. Pure water, acetic acid 1 M, gluconic acid 1 M, hydrochloric and nitric acid 1 M was the five leaching agents investigated using a contact time of 10 min. As is shown in Fig. 3.a, the efficacy in removing Ca was: pure water < acetic acid < gluconic acid < nitric acid < hydrochloric acid. Taking into account that the aqua regia leaching had 7.9 g $Ca \cdot dm^{-3}$, the nitric and the hydrochloric acid were the optimal leaching agents because the leached Ca was higher than 87%. However, in order to minimize the REEs losses in this leaching step, HCl 1 M seems to be the best choice.

The HCl and HNO_3 concentration and contact time for both leaching agents were parameters studied. As can be seen in Fig. 3.b and Fig. 3.c, the difference of Ca recovered when 1 M or 2 M of HCl and HNO_3 were used, was unimportant because using 1 M of both leaching agents, the Ca recovery was higher than 88%. However, when 0.5 M was used, the Ca recovered was significantly less than when 1 M or 2 M were utilized. Moreover, using 2 M of HCl or HNO_3, the REEs recovery was higher than when 1 M of these leaching agents were used. For these reasons, the best concentration of HCl or HNO_3 is 1 M. The contact time experiments show that 10 min is enough to maximize the Ca elimination maintaining at the minimum the losses of REEs (Fig. 3.d and Fig. 3.e).



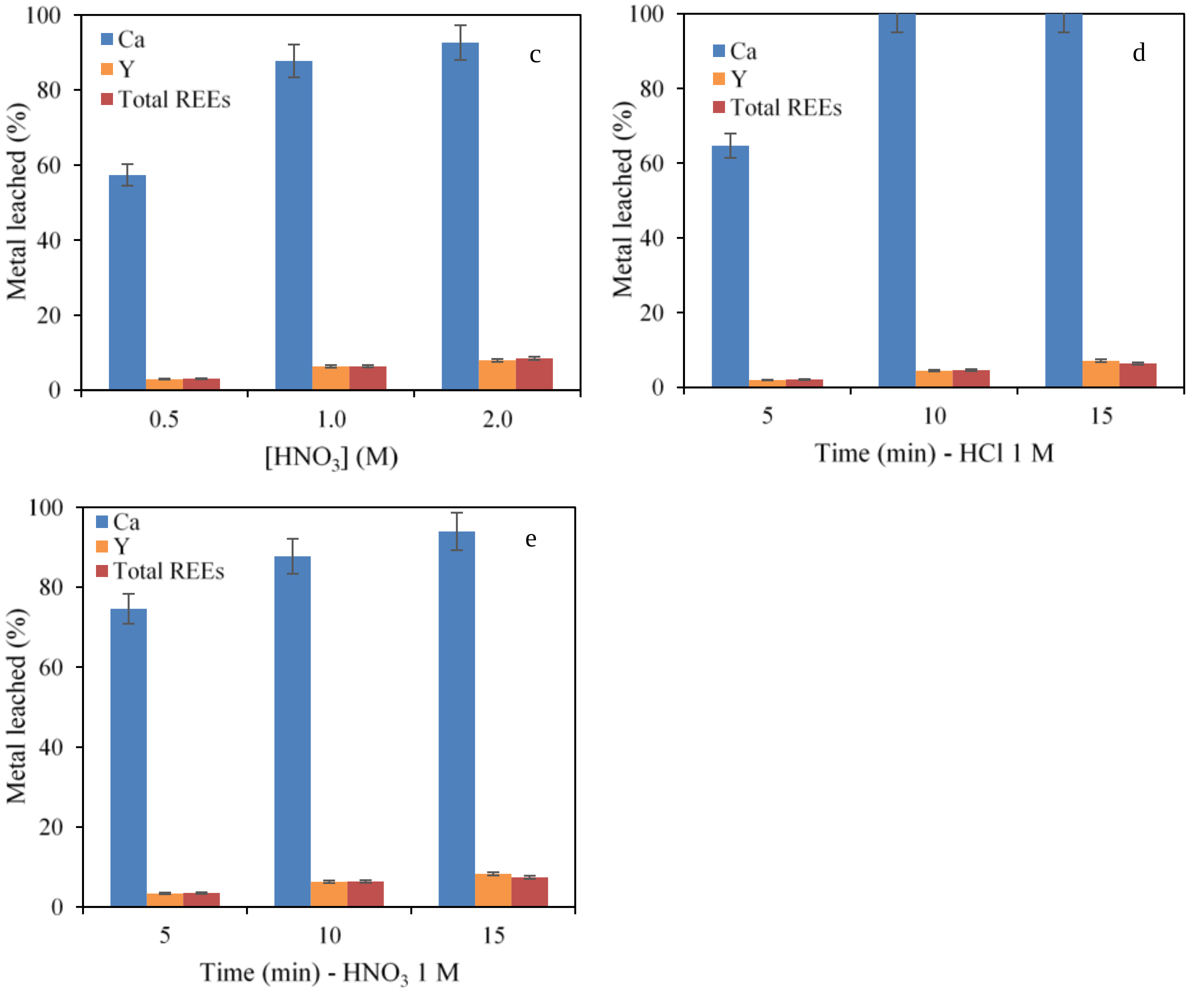


Figure 3. *Leaching 1 behaviour of Ca, Y and total REEs. S:L ratio of 10% w/v, magnetic stirring – 100 rpm. a) Leaching agents: pure water, acetic acid 1 M, gluconic acid 1 M, hydrochloric acid 1 M and nitric acid 1 M. Time contact: 10 min. b) Leaching agent: hydrochloric acid 0.5, 1.0 and 2.0 M. Time contact: 10 min. c) Leaching agent: nitric acid 0.5, 1.0 and 2.0 M. Time contact: 10 min. d) Leaching agent: hydrochloric acid 1 M. Time contact: 5, 10 and 15 min. e) Leaching agent: nitric acid 1 M. Time contact: 5, 10 and 15 min. The error represents the standard deviation of triplicate tests.*

3.2.2. Leaching 2 (L2)

The second leaching has as the purpose the REEs recovery. To achieve it, HCl and HNO$_3$ were the chosen leaching agents to investigate. The studied parameter was the contact time, maintaining the hydrochloric and nitric acids concentration at 2 M. The leaching behaviours are presented in Fig 4. For the Eu and Y, the equilibrium was achieved after 48 h. However, the Gd and La leachings were slower and the equilibrium was not reached in the investigated time (168 h). Moreover, the metal leached was higher than 80% for Eu and Y but the La leached, using HCl or HNO$_3$ was less than 13%. These results are similar to the Tunsu et al. investigation because the Eu and Y leached is higher than 90% after 168h using both acids while the percentage of the metal leached for La is around 10% [7]. However, the results presented in the Tunsu et al. study were a little different related to the Gd behaviour. Although the Gd behaviour was similar when nitric and hydrochloric acid were used, the percentage of metal leached are around 70 and 85%, respectively while in this investigation the Gd leached not exceeded the 50%.

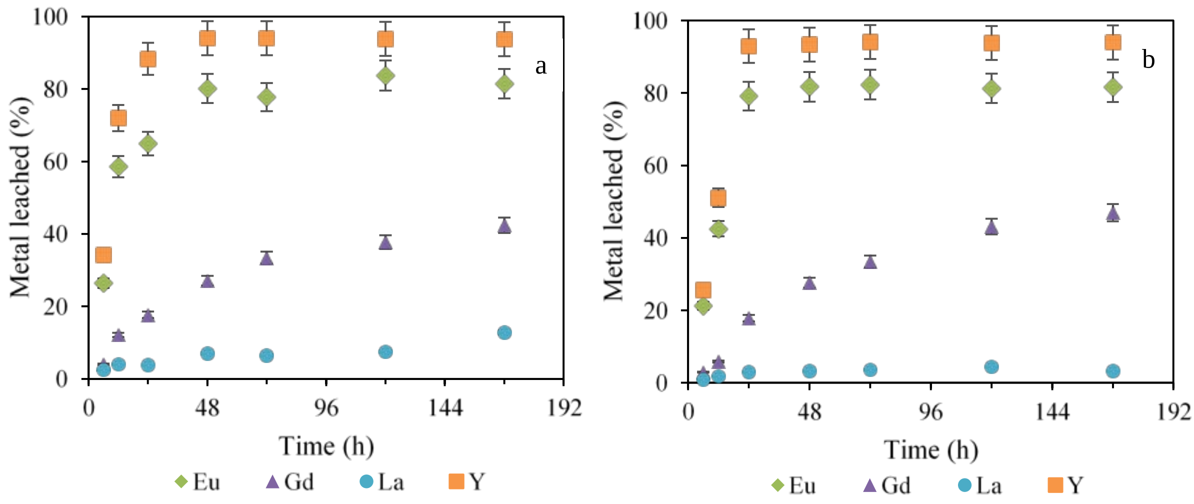


Figure 4. *Leaching 2 behaviour of Eu, Gd, La and Y over 168 h, S:L ratio of 10% w/v, magnetic stirring – 100 rpm. a) Leaching agent: hydrochloric acid 2 M. b) Leaching agent: nitric acid 2.0 M. The error represents the standard deviation of triplicate tests.*

In order to recover Y and Eu from L1 solid waste, HCl and HNO_3 2 M could be used for 48 h. If it was interesting, the Ga and La could be recovered at higher extension using more drastic conditions in a 3rd leaching (L3).

3.3. Supported liquid membrane

Cyanex 572, D2EHPA and Cyanex 923 have been chosen to recover by SLM the REEs present in the L1 leachate. 10 min of contact with 1 M of hydrochloric or nitric acid showed the better results taking into account a balance between impurities elimination and REEs losses. Cyanex 572 and D2EHPA were used to recover REEs from hydrochloric media, whereas Cyanex 923 was used from nitric acid as previous studies recommend [18].

A recent publication reports that D2EHPA and Cyanex 272 are able to separate Y/Ca mixture. This fact is possible when the pH less than 2.5 [6]. Taking into account that the pKa of the Cy572 is between the pKa of the D2EHPA and the Cyanex 272, the pH L1 leachate was set to 1.0. However, at this pH there was no metal transport using neither cationic carriers, Cy572 or D2EHPA 0.30 M. To achieve the REEs recovery, the initial pH was increased, but unfortunately, a precipitate appeared when the pH value was 1.50. This fact can be explained using the MEDUSA software because $REEPO_4(s)$ ($YPO_4(s)$ or $EuPO_4(s)$) is obtained when the initial pH is higher than 1 (Fig. 5). For this reason, nitric acid as leaching agent and Cy923 as a carrier were chosen since in this case, any pH conditioning is required to extract the REEs.

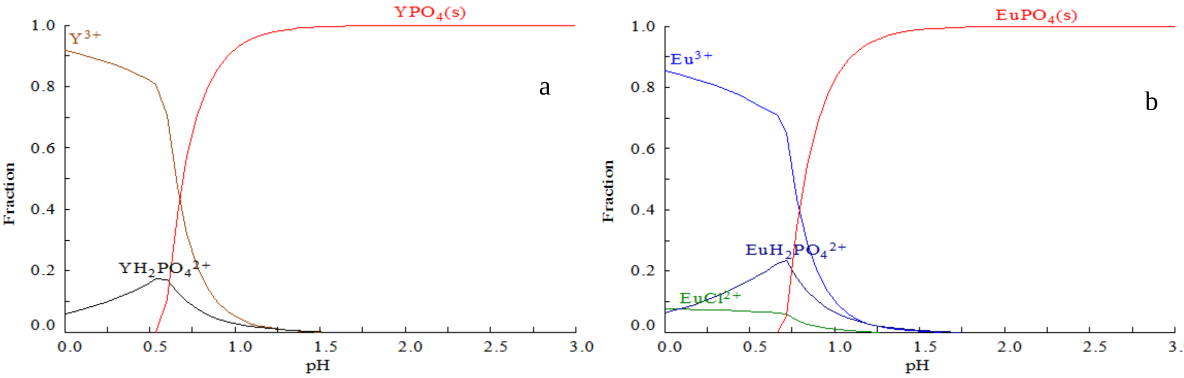


Figure 5. *Speciation diagram using MEDUSA software* [19]. *$[PO_4{}^{3-}]$=0.2 M, $[Ca^{2+}]$ = 0.2 M, $[Cl^-]$ = 1 M, Ionic Force: 1 M. a) Y $6{\cdot}10^{-3}$ M b) Eu $3.3{\cdot}10^{-4}$ M*

The SLM experiments using Cy923 were carried out using the leachate obtained from the L1 using 1 M of HNO_3 during 10 min. The pH of the feed solution was adjusted to 0.97 and four different concentrations of Cy923, 0.30, 0.60, 0.90 and 1.20 M, were investigated. The stripping phase was HCl 0.1 M.

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 for any of the Cy923 concentration used. After 8 hours, the percentage of Y was 27%, using the highest Cy923 concentration. The Eu behavior followed the same tendency that Y. This means that REEs could be separate from the L1 liquor using 0.30, 0.60, 0.90 and 1.20 M of Cy923. However, using 1.20 M of Cy923, the selectively for the same working time is higher. Comparing the metal appeared in the stripping phase with the metals disappeared from the feed phase we can affirm that the metals loaded were wholly stripped in both experiments using HCl 0.1 M.

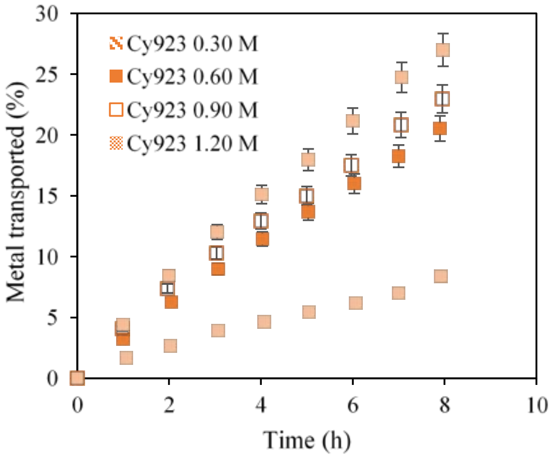


Figure 6. *Effect of Cy923 concentration on the transport of Y. Feed pH = 0.97. Receiving solution: 0.1 M HCl. The error represents the standard deviation of duplicate experiments.*

As a conclusion, to avoid the REEs losses after the first leaching process, where the higher impurity in Ca form is removed, Cy923 is the optimum carrier instead of Cy572 or D2EHPA. Because of the Cy923 choice, the leaching agent to achieve the REEs separation must be nitric acid 1 M.

Considering that Yttrium and Europium are the most representative REEs of the real sample, their permeability coefficients were determined using Eq. (1) considering P as the slope of the lineal function of $(-V/A)\cdot ln([Me]/[Me_0])$ vs t for the different Cy923 concentration experiments.

As shown in Fig. 7, the permeability increases when the carrier concentration also increases. 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, from 0.60 M of Cy923, the viscosity increases, reducing the apparent permeability. Although this fact appears for both REEs, the viscosity effects are less pronounced for the Eu. The permeation coefficients values are similar to those obtained for Cd(II) transport through hollow fiber supported strip dispersion (HFSD) by N.S. Rathore et al. using Cyanex 923 [20] and for different metals and extractants in the E. Bringas et al. review [21].

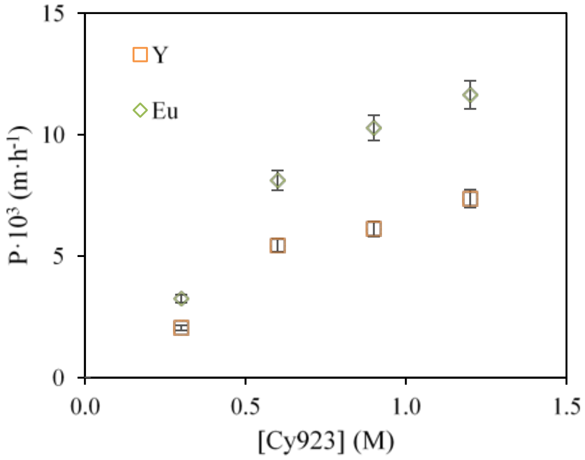


Figure 7. *Effect of the Cy923 concentration on the permeability of Y and Eu. The error represents the standard deviation of duplicate experiments.*

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.

HNO_3 is the most appropriate leaching agent and Cy923 as a carrier in the SLM to recover the REEs because of the $REEPO_4$ precipitation avoidance prior to the SLM experiments. The REEs losses in the L1 stage have been minimized adding an SLM stage. The Cy923 concentrations investigated are able to recover REEs from the L1 leachate. 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, adding the REEs recuperated from the L1 to the L2 stage, the REEs recovery can be achieved.

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

Acknowledgments

This research was supported by the MINECO with its [grant number CTM2017-83581-R]. We express our gratitude to Recyberica Ambiental and Cytec Industries Inc. for providing free samples of the fluorescent lamp wastes, Cyanex 572 and Cyanex 923, respectively. The authors would like to thank M. Dominguez and T. Trifonov (from Universitat Politecnica de Catalunya) for their technical assistance in this work.

References

[1] U.S. Department of Energy, “U.S. Department of Energy: Critical materials strategy,” 2012.

[2] N. M. Ippolito, V. Innocenzi, I. De Michelis, F. Medici, and F. Vegliò, “Rare earth elements recovery from fluorescent lamps: A new thermal pretreatment to improve the efficiency of the hydrometallurgical process,” *J. Clean. Prod.*, vol. 153, pp. 287–298, 2017.

[3] X. Song, M.-H. Chang, and M. Pecht, “Rare-Earth Elements in Lighting and Optical Applications and Their Recycling,” *JOM*, vol. 65, no. 10, pp. 1276–1282, Oct. 2013.

[4] F. Yang, F. Kubota, Y. Baba, N. Kamiya, and M. Goto, “Selective extraction and recovery of rare earth metals from phosphor powders in waste fluorescent lamps using an ionic liquid system,” *J. Hazard. Mater.*, vol. 254–255, pp. 79–88, Jun. 2013.

[5] H. Liu, S. Zhang, D. Pan, J. Tian, M. Yang, M. Wu, and A. A. Volinsky, “Rare earth elements recycling from waste phosphor by dual hydrochloric acid dissolution,” *J. Hazard. Mater.*, vol. 272, pp. 96–101, May 2014.

[6] V. Innocenzi, I. De Michelis, F. Ferella, and F. Vegliò, “Secondary yttrium from spent fluorescent lamps: Recovery by leaching and solvent extraction,” *Int. J. Miner. Process.*, vol. 168, pp. 87–94, 2017.

[7] C. Tunsu, C. Ekberg, and T. Retegan, “Characterization and leaching of real fluorescent lamp waste for the recovery of rare earth metals and mercury,” *Hydrometallurgy*, vol. 144–145, pp. 91–98, Apr. 2014.

[8] Y. Liu, H. S. Jeon, and M. S. Lee, “Solvent extraction of Pr and Nd from chloride solutions using ternary extractant system of Cyanex 272, Alamine 336 and TBP,” *J. Ind. Eng. Chem.*, vol. 31, pp. 74–79, 2015.

[9] M. I. Aly, B. A. Masry, M. S. Gasser, N. A. Khalifa, and J. A. Daoud, “Extraction of Ce (IV), Yb (III) and Y(III) and recovery of some rare earth elements from Egyptian monazite using CYANEX 923 in kerosene,” *Int. J. Miner. Process.*, vol. 153, pp. 71–79, 2016.

[10] E. Padhan and K. Sarangi, “Recovery of Nd and Pr from NdFeB magnet leachates with bi-functional ionic liquids based on Aliquat 336 and Cyanex 272,” *Hydrometallurgy*, vol. 167, pp. 134–140, 2017.

[11] S. Pavon, M. Kutucu, M. T. Coll, A. Fortuny, and A. M. Sastre, “Comparison of Cyanex 272 and Cyanex 572 on the separation of Neodymium from a Nd/Tb/Dy mixture by pertraction,” *J. Chem. Technol. Biotechnol.*, Sep. 2017.

[12] Y. Baba, F. Kubota, N. Kamiya, and M. Goto, “Selective Recovery of Dysprosium and Neodymium Ions by a Supported Liquid Membrane Based on Ionic Liquids,” *Solvent Extr. Res. Dev. Japan*, vol. 18, pp. 193–198, 2011.

[13] I. De Michelis, F. Ferella, E. F. Varelli, and F. Vegliò, “Treatment of exhaust fluorescent lamps to recover yttrium: Experimental and process analyses,” *Waste Manag.*, vol. 31, no. 12, pp. 2559–2568, Dec. 2011.

[14] P. Ramakul, T. Supajaroon, T. Prapasawat, U. Pancharoen, and A. W. Lothongkum, “Synergistic separation of yttrium ions in lanthanide series from rare earths mixture via hollow fiber supported liquid membrane,” *J. Ind. Eng. Chem.*, vol. 15, no. 2, pp. 224–228, 2009.

[15] CYTEC Industries Inc., “CYANEX 572 Extractant. Technical Brochure,” Canada, 2013.

[16] Sigma-Aldrich, “D2EHPA Extractant. Technical Brochure,” 2002.

[17] CYTEC Industries Inc., “CYANEX 923 Extractant. Technical Brochure.”

[18] C. Tunsu, M. Petranikova, M. Gergorić, C. Ekberg, and T. Retegan, “Reclaiming rare earth elements from end-of-life products: A review of the perspectives for urban mining using hydrometallurgical unit operations,” *Hydrometallurgy*, vol. 156, pp. 239–258, Jul. 2015.

[19] I. Puigdomenech, “MEDUSA software.” KHT Royal Institute of Technology, 2013.

[20] N. S. Rathore, A. Leopold, A. K. Pabby, A. Fortuny, M. T. Coll, and A. M. Sastre, “Extraction and permeation studies of Cd(II) in acidic and neutral chloride media using Cyanex 923 on supported liquid membrane,” *Hydrometallurgy*, vol. 96, no. 1–2, pp. 81–87, 2009.

[21] E. Bringas, M. F. San Román, J. A. Irabien, and I. Ortiz, “An overview of the mathematical modelling of liquid membrane separation processes in hollow fibre contactors,” *J. Chem. Technol. Biotechnol.*, vol. 84, no. 11, pp. 1583–1614, 2009.