Research Article

Received: 14 July 2017 Revised: 18 September 2017 Accepted article published: 29 September 2017 Published online in Wiley Online Library: 15 November 2017

(wileyonlinelibrary.com) DOI 10.1002/jctb.5458

# Comparison of Cyanex 272 and Cyanex 572 for the separation of Neodymium from a Nd/Tb/Dy mixture by pertraction

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## 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.**


*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

## INTRODUCTION

Society moving towards an ultra-connected world has changed the intercommunication paradigms that have been established for centuries. The amount of technology used by the mainstream consumer has increased significantly over the last few years due to exponential advances in IT; the need for communication by globalization; the cheapness of raw materials and the easy access to information. Many of these new devices are possible because of the use of new materials that were not commonly used a couple of decades ago.[1] Rare earth elements (REEs) are one of these materials and there are currently different applications for these materials in fields such as electronic devices, electric and hybrid-electric vehicles, permanent magnet generators for wind turbines and medical imaging devices.[2] Specifically, REEs are present in magnets, battery alloys, phosphors, auto catalysts, polishing powders and glass additives.[3] The first three applications represent about 35% of the consumption of REEs: magnets 20%, batteries 8% and phosphors 7%. However, magnets are the most important application generating 37% of the total value of the REEs market.[4] The magnets market is dominated by neodymium-iron-boron (NdFeB)[4] with 25–30% neodymium, 3–4% dysprosium, 60–70% iron, 1% boron and 1–4% of other REEs.[5]

The importance of these elements has skyrocketed due to high demand, uncertain supply and no alternatives. The stable supply of such metals is becoming a concern because almost all of the rare earth element resources are found in a few specific areas on Earth.[3] In 2015, five REEs, dysprosium, terbium, europium, neodymium and yttrium, were found to be critical in the short term based on two vectors: importance of clean energy and supply risk.[5–7] For this reason, it is important to find effective mechanisms and techniques that separate the REEs from urban mines.

The REEs can be recovered and separated by different techniques. In metallurgy there are several methods of recovery and separation of REEs from the solid phase. Each REE is obtained, dissolved, concentrated, separated and returned to a solid phase. Gravity and magnetic separation are the two most important techniques for concentrating REE minerals.[8] To increase the concentration of each REE we can use wet high-intensity magnetic separation (WHIMS) in combination with gravity pre-concentration steps.[8] Leaching is a process used to extract metals from a solid by dissolution in a liquid[9,10] and has been used to recover REEs from fluorescent lamp wastes.[11,12] Liquid–liquid

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extraction is a conventionally employed technique for the separation of REEs.[13–16]

Literature studies show that different extractants can be used to separate REEs by extraction. Thus Dy(III) can be separated in nitrate media using 2-ethylhexylphosponic acid mono-2-ethylhexyl ester (PC88A) as an extractant and Shellsol D70 as a diluent.[16] Yoon *et al.* obtained separation factors ($D_{Dy}/D_{Nd}$) of 247.2 and 125.37 using 0.1 mol $L^{-1}$ di-(2-ethylhexyl)phosphoric acid (D2EHPA) or PC88A, respectively, as extractants.[17] Using PC88A 87.5% of Nd(III) was recovered from a mixture of La, Ce, Pr, Nd and Sm from nitric acid medium.[17] Cyanex 572 plays an important role in industrial applications of heavy rare earth element (HREEs) enrichments from ion-adsorbed deposits because of its lower acid requirements and higher stripping efficiency compared to P507 (PC88A).[18] However, Quinn *et al.* suggested less acid consumption in the plant stripping section using Cyanex 572, but an increase in the size of the process equipment is required.[19] Kolar *et al.* proposed the use of Cyanex 572 to achieve selective extraction of HREEs from light rare earth elements (LREEs) with an aqueous feed of pH = 0.7 by microfluidic solvent extraction.[20] Solvent extraction of neodymium was studied by Yazaki *et al.* in a continuous stirred vessel using PC88A as an extractant and kerosene as a diluent and the results confirmed that the distribution ratio of Nd(III) increased as pH increased and the fractional yield of the metal ion increased as the flow rate and pH in the feed phase decreased.[21] Swain and Otu reported that lanthanide elements could be extracted in the following order: La < Ce < Pr < Nd < Sm < Eu < Gd < Tb < Dy < Ho < Er < Tm < Yb < Lu using bis (2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272, C272) as a ligand starting at high acidity and progressively increasing the pH in the perchloric acid media.[22]

Supported liquid membranes (SLM) are an effective separation technique which can achieve high affinity of the liquid membrane for a particular chemical species.[23,24] Also, SLM have many advantages as a separation technique compared to liquid–liquid extraction as extraction and stripping are carried out simultaneously, the organic phase volume is reduced, and it is economically viable to separate metals or molecules present in a mixture at low concentrations.[24–26] Flat sheet supported liquid membrane (FSSLM) is the chosen technique used in this study to compare metal transport with both extractants. The operating principle is to contact the two liquid phases separated by an immiscible liquid membrane. The transported species come from the feed phase through the membrane to reach the receiving phase.[27–29]

Selective recovery of dysprosium and neodymium in the presence of ferric ions by SLM was studied by Baba *et al.* in nitric acid medium using [$C_8$mim][$Tf_2$N] containing N,N-dioctyldiglycolamic acid (DODGAA) and 99% extraction of Dy(III) and Nd(III) was obtained in the receiving phase.[30] Zaheri *et al.* found that separation of Dy(III) and Eu (III) in nitrate medium was highly dependent on the pH of the feed solution when using a mixture of D2EHPA and C272 as extractant and kerosene as diluent. The membrane was stable for six operation cycles.[31] The highest permeability coefficient value for europium by SLM using 0.60 mol $L^{-1}$ D2EHPA + Cyanex 272 at a 1:1 mole fraction ratio was $3.48\times10^{-5}$ m $s^{-1}$ at feed pH 4, stripping phase 2 mol $L^{-1}$ $HNO_3$ and a stirring rate of 500 rpm.[32] Hollow fiber supported liquid membrane (HFSLM) extraction allows the selective extraction of praseodymium from a feed solution at pH 5.5. After 6 cycles of 300 min the results gave extraction 91.7% and stripping 78% using as extractant Cyanex 272 10% (v/v), strip solution HCl 0.60 mol $L^{-1}$ and flow rates of feed and stripping solutions 100 mL $min^{-1}$.[33]

The synthetic solution used in the current investigation simulates the result of leaching waste magnets containing Nd, Tb and Dy. Cyanex 272 and Cyanex 572 (C572) were used as the carriers to separate neodymium, terbium and dysprosium in chloride media as C272 is a common extractant to separate REEs[22,34] and C572 is a newly created extractant to improve extraction performance compared to traditional phosphonic acid extractants. It has been specially formulated for the extraction and purification of REEs.[35]

## EXPERIMENTAL

### Reagents

Neodymium, terbium and dysprosium solutions were prepared by dissolving $Nd_2O_3$ (Sigma Aldrich Ref. 228656), $Tb_2O_3$ (Sigma Aldrich Ref. 590509), $Dy_2O_3$ (Sigma Aldrich Ref. 289264) using hydrochloric acid. The chloride concentration in the aqueous phase and pH in the medium were adjusted adding NaCl, NaOH, HCl or a combination of any two. The organic compounds used as carriers were C272 and C572. Both were kindly supplied by CYTEC Canada Industries. Detailed specifications of these extractants are summarized in Table 1. The diluent was kerosene (Sigma-Aldrich). Citric acid (Sigma Aldrich Ref. 251275) and EDTA disodium salt (Panreac AppliChem Ref. 131669) have been used to study the effect of different stripping agents.

### Liquid–liquid extraction

The critical parameter to separate REEs using cationic extractants is the pH. In order to choose the pH range to successfully separate Nd(III) from the mixture, the extraction/pH curves were determined for both carriers; the optimum range being where there is a greater difference between the extraction of neodymium and the other two REEs.

For these experiments, the aqueous phase was a mixture of 1 g $L^{-1}$ of each metal in 4 mol $L^{-1}$ $Cl^-$ and it was equilibrated with the same volume of organic phase in a separatory funnel using a horizontal mechanical shaker (SBS Mechanical Shaker). The phases were shaken at 140 rpm for 20 min at room temperature (20 ± 2 °C) until equilibrium was achieved. After phase separation, the aqueous phase concentrations of Nd(III), Tb(III) and Dy(III) were determined by atomic emission spectrometry using a 4100 MP AES System (Agilent Technologies) with an analytical error < 5%.

### Flat sheet supported liquid membrane

Transport experiments were carried out in an experimental set-up which has two cylindrical compartments (one for feed solution and the other for the receiving solution) connected by a lateral window where the FSSLM was placed (Fig. 1). Each compartment contained 220 mL of the respective solutions and has an independent stirrer.

A microporous polytetrafluoroethylene film (Fluoropore™ FHLP04700, Merck Millipore), 4.7 cm diameter, thickness 150 $\mu$m, 85% porosity, 0.45 $\mu$m pore size and effective membrane area of 11.4 $cm^2$ was used as a support.

The feed was a mixture of Nd(III), Tb(III) and Dy(III) with 0.1 g $L^{-1}$ of each metal in 0.4 mol $L^{-1}$ $Cl^-$ and the receiving phase was HCl 1.2 mol $L^{-1}$ for C272 and HCl 0.5 mol $L^{-1}$ for C572.

The solutions were stirred at 1000 rpm for 24 h at room temperature (20 ± 2 °C). Samples were taken every half hour up to 4 h, then sampling every hour up to 8 h; a final sample was taken after 24 h to determine membrane stability. Nd(III), Tb(III) and Dy(III) concentration in the feed and receiving cells were determined using the same procedure described earlier.



  

**Table 1.** Physical properties of C272 and C572

| Commercial name | Content % | Density kg m$^{-3}$ | Viscosity mPa s | Av. Mol. Weight g mol$^{-1}$ |
|---|---|---|---|---|
| C272[37] | 85 | 920 | 14.2[a] | 290 |
| C572[35] | 100 | 933 | <50[a] | 310[b] |

[a] At 25 °C.
[b] Experimental data by potentiometric titration in water/ethanol.

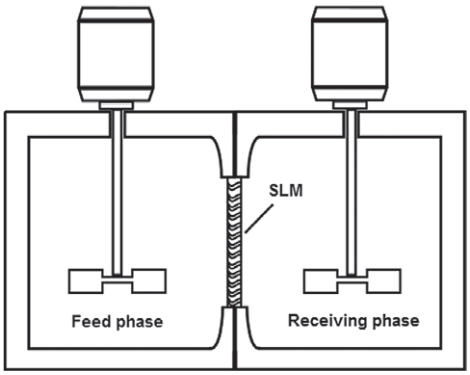


**Figure 1.** Scheme of FSSLM experimental set-up.[38]

Even though 24 h is not sufficient to determine the long-time membrane stability, it does give a good indicator. FSSLM mainly suffer from problems of stability and limited lifetime due to leaching of the carrier. In order to overcome these problems, the strip dispersion renewal membrane technique can be used in an industrial process scale up.[36]

Equation (1) derived from the metal mass balance in the feed cell and Fick's law, was used to calculate the permeability of each metal:

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

where *[Me]* and $[Me]_0$ are the metal concentration (g L$^{-1}$) in the feed cell at time ($t$) and initial time ($t_o$), respectively; $A$ is the membrane area (m$^2$); $V$ is the volume of the feed solution in the cell (m$^3$); $P$ is the permeability coefficient (m h$^{-1}$); and $t$ is the time (h).

## RESULTS AND DISCUSSION

### Solvent extraction

Prior to FSSLM experiments, the appropriate pH for Nd(III) separation was determined following the solvent extraction procedure described previously. Figure 2 shows the extraction percentage vs equilibrium pH curves obtained using C272 and C572 at a concentration of 10% (v/v) and an aqueous phase containing 1 g L$^{-1}$ of each metal in 4 mol L$^{-1}$ Cl$^-$ medium. The results using C272 showed the same percentage extraction for all REEs up to pH 1.0. Increasing pH above this value, the extraction of Nd(III) is lower than Tb(III) and Dy(III) and the extraction of Tb(III) and Dy(III) increases quickly with pH, achieving 100% at pH 2.0. As can be seen in Fig. 2(a) the optimum pH range is between 1.4 and 1.8 for C272 because this range shows greater difference between the extraction of Nd(III) and the other two REEs.

On the other hand, Fig. 2(b) shows that using C572 the extraction of Tb(III) and Dy(III) increases faster compared to C272, and achieved close to 100% at pH 1.0. Nd(III) shows similar behaviour for both extractants up to this pH, but after this value the extraction suddenly increases despite the fact that for all pH values studied it is below the Tb(III) and Dy(III) yields. These results are consistent with those reported by CYTEC Canada Industries,[35] although these liquid–liquid extractions were carried out under different conditions. Evaluating the results, the optimum pH range to separate Nd(III) from the mixture using C572 appears to be between 0.4 and 1.3.

### Flat sheet supported liquid membrane

To evaluate the feasibility of separating Nd/Tb/Dy using C272 or C572 in supported liquid membranes, the effect of parameters pH, carrier concentration, stripping agents and receiving phase HCl concentration have been studied. Also, the permeability was determined by Equation (1) and can be used to predict the REEs transported by both extractants at any carrier concentration.

#### *Effect of pH*

As stated in above, pH is a crucial parameter to separate Nd(III) from the mixture using this kind of extractant. The results obtained by solvent extraction show the behaviour for each carrier and it allows the working conditions of this parameter to be used in FSSLM to be established.

Thus feed solutions containing 0.1 g L$^{-1}$ of each metal at different pHs were prepared in 0.4 mol L$^{-1}$ Cl$^-$. The effect of feed pH on metal transport through the membrane was studied using 10% (v/v) of C272, at initial feed pH values of 1.5, 2.0 and 2.5 with HCl 1.2 mol L$^{-1}$ used as the receiving solution. In the case of C572, the initial pH values chosen were 1.5 and 3.5 and the receiving solution was HCl 0.5 mol L$^{-1}$.

When the feed phase is pH = 1.5, using C272 as carrier, transport of the three REEs is less than 15% with after 8 hours (Fig. 3). However, this percentage increases to 43% for Tb(III) and 55% for Dy(III) when C572 is used.

Using C272, Tb(III) and Dy(III) were transported at pH values of 2.0 and 2.5, but in these pH conditions, Nd(III) transport was less than 9%, which makes it possible to separate these metals. On the other hand, in Fig. 3(a), the difference in Tb(III) and Dy(III) transport is more significant at pH values above 1.5. Terbium transport increases from 47% to 53% while the transport of Dy(III) increases from 48% to 66% at pH 2.0 and 2.5, respectively.

As noted previously, it is possible to separate Nd(III) from the mixture at pH 2.0 and 2.5 and taking into account the results shown in Fig. 2(a), the optimum pH is 2.0 because the transport of Nd(III) in these conditions was around 50% of that obtained at pH 2.5.

Working with C572 and pH 3.5, it is possible to transfer 12%, 65% and 75% of Nd(III), Tb(III) and Dy(III) from the feed to the receiving cell, but to separate Nd(III) from the mixture, pH 1.5 has been chosen because the transport of Nd(III) was less than at pH 3.5. (Fig. 3(b)).

The stability of the membrane was demonstrated with the results obtained at 24 h and compiled in Table 2. The percentages of extraction of the three metals increased when both the pH and the working time were increased. However, in order to separate Nd(III) from the mixture, the optimum conditions must be chosen according to a balance between REEs transport and selectivity.

The pH influence on metal transport can be explained by the type of extractant used. C272 and C572 are acid extractants and the reaction with REEs is:

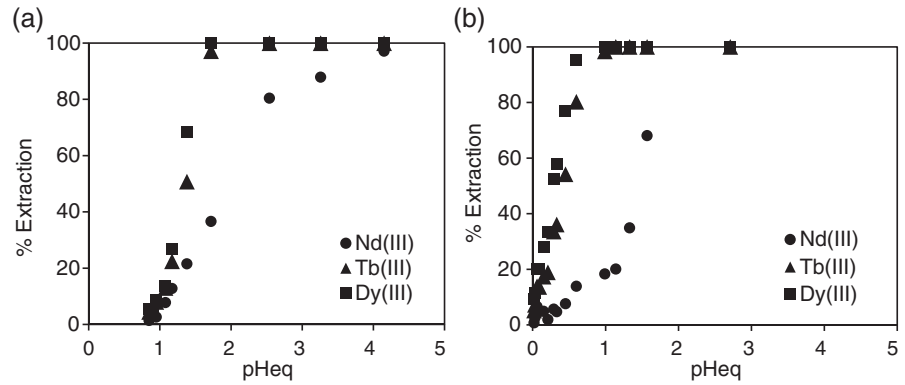


**Figure 2.** Effect of equilibrium pH on the extraction. Aqueous phase: 1 g $L^{-1}$ of each REE in 4 mol $L^{-1}$ $Cl^-$. (a) C272 10% (v/v), (b) C572 10% (v/v).

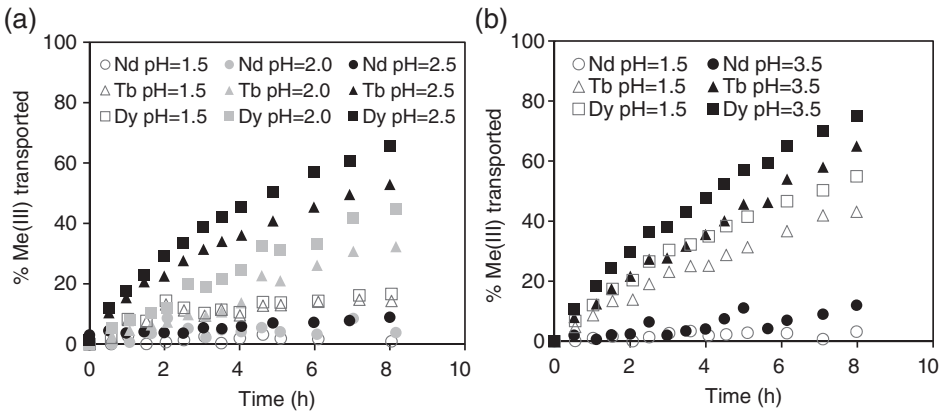


**Figure 3.** Effect of feed pH on the transport of Nd(III), Tb(III) and Dy(III). Feed phase: 0.1 g $L^{-1}$ of each metal in 0.4 mol $L^{-1}$ $Cl^-$ at different pH. **(a)** C272 10% (v/v). Receiving solution: 1.2 mol $L^{-1}$ HCl **(b)** C572 10% (v/v). Receiving solution: 0.5 mol $L^{-1}$ HCl.

**Table 2.** Percentage of metal transported after 24 h for the three REEs at different pHs using C272 or C572 10% (v/v)

| | pH | %Nd(III) | %Tb(III) | %Dy(III) |
|---|---|---|---|---|
| C272 | 1.5 | 3 | 22 | 26 |
| | 2.0 | 5 | 64 | 78 |
| | 2.5 | 12 | 78 | 92 |
| C572 | 1.5 | 6 | 74 | 85 |
| | 3.5 | 23 | 97 | 100 |

$$Me^{n+} + n\,\overline{HA} \leftrightarrow \overline{MeA_n} + n\,H^+ \quad (2)$$

When the extractant is loaded with the REEs, free protons are released to the feed phase, causing the pH to decrease. Thus this reaction will be favoured when the feed phase is less acidic and this is the reason why at high pH values, there is greater transport of the REEs. Therefore, the graphs are consistent with this explanation because it can be observed that when pH was increased the percentage of metal transported also increased.

In conclusion, pH 2.0 for C272 and pH 1.5 for C572 are the optimum conditions for the separation of Nd(III) from the mixture. Although using both carriers Nd(III) separation is possible, the percentage of Tb(III) and Dy(III) transported is 11% higher using C572 than C272 at the same time, because the former is more acidic.

*Effect of carrier concentration*

The concentration of extractant in the membrane plays a significant role in metal transport through the FSSLM. The effect of carrier concentration was investigated over the range from 5% to 25% (v/v) (0.14–0.75 mol $L^{-1}$) in kerosene. The pH of the feed solution was fixed at 2.0 for C272 and at 1.5 for C572 and the concentration of each metal in the mixture was 0.1 g $L^{-1}$ in 0.4 mol $L^{-1}$ $Cl^-$. Receiving phases were C272 1.2 mol $L^{-1}$ HCl and C572 0.5 mol $L^{-1}$ HCl. Figure 4 shows that the transported metal of REEs increased with carrier concentration.

At low extractant concentrations, <0.15 mol $L^{-1}$ (5% (v/v)), similar behaviour was observed for both extractants, but when the concentration was increased, C572 achieved higher REEs transport rates. The transport of Tb(III) and Dy(III) was more significantly influenced by the carrier concentrations using C572 than with C272.

The transport percentage of each REE using the maximum value of extractant concentrations was 10%, 60% and 68% for Nd(III), Tb(III) and Dy(III), respectively, using C272. On the other hand, the percentages using C572 were higher, reaching 17% for Nd(III), 89% for Tb(III) and 93% for Dy(III) after 8 h.

Nd(III) can be separated from the mixture over the entire range of concentration using C272. However, Nd(III) can only be separated from the mixture using C572 concentrations <0.45 mol $L^{-1}$ due to the higher transport of Nd(III) using 0.60 or 0.75 mol $L^{-1}$.

Table 3 shows the total percentages of metal transported after 24 h and membrane stability was proved because these percentages increased with the working time. Using C272, Nd(III) transport



  

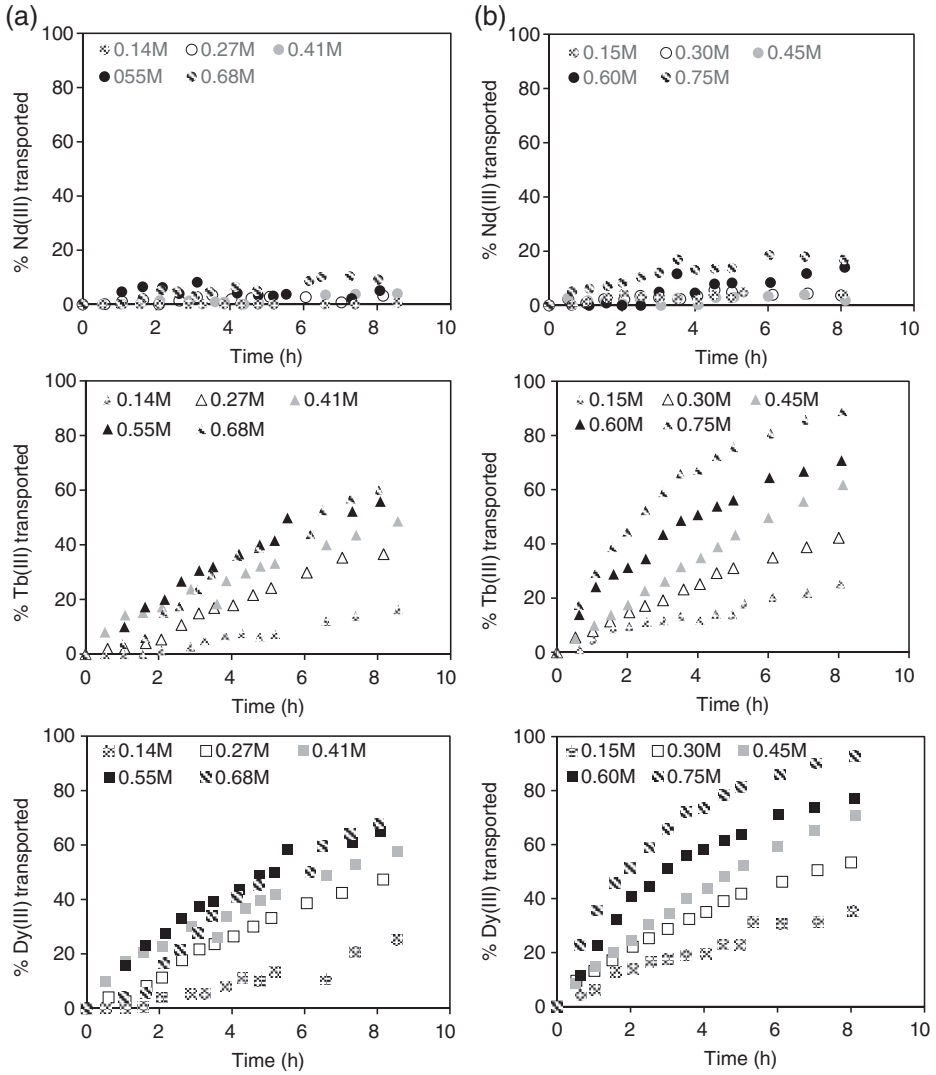


**Figure 4.** Effect of extractant concentration on the transport of Nd(III), Tb(III) and Dy(III). Feed phase: 0.1 g $L^{-1}$ of each metal in 0.4 mol $L^{-1}$ $Cl^-$. (a) C272. Feed pH = 2. Receiving solution: 1.2 mol $L^{-1}$ HCl. (b) C572. Feed pH = 1.5. Receiving solution: 0.5 mol $L^{-1}$ HCl.

was very slow with the value after 8 h very close to that after 24 h. In contrast, the transport of Tb(III) and Dy(III) using the higher concentration, increased from 60 to 93% and from 68 to 97%, respectively. In the case of C572 0.75 mol $L^{-1}$, the transport of Nd(III) was different, i.e. after 8 h 17% and after 24 h 43%, but the transport percentages of Tb(III) and Dy(III) did not change because they were already 100%.

By increasing the concentrations of C272 and C572 in the membrane, a higher amount of metal–carrier complex is formed at the feed–membrane interface and this promotes a greater flux of metal through the membrane.

*Effect of the HCl concentration in the receiving phase.*

The reaction at the interface membrane/receiving phase also has an important influence on the metal transport from the feed phase to the receiving phase. In this section, the effect of the concentration of HCl in the receiving cell over the range 0.5–2.0 mol $L^{-1}$ was studied. All the other parameters, i.e. feed pH and carrier concentration were adjusted to the optimum conditions and the concentration of metals in the feed phase were 0.1 g $L^{-1}$ in 0.4 mol $L^{-1}$ $Cl^-$. The results obtained are shown in Fig. 5.

**Table 3.** Percentage of metal transported after 24 h for the three REEs at different extractants concentrations

| | [Carrier] (mol $L^{-1}$) | %Nd(III) | %Tb(III) | %Dy(III) |
|---|---|---|---|---|
| C272 | 0.14 | 0 | 43 | 57 |
| | 0.27 | 3 | 69 | 79 |
| | 0.41 | 4 | 79 | 88 |
| | 0.55 | 6 | 88 | 94 |
| | 0.68 | 12 | 93 | 97 |
| C572 | 0.15 | 5 | 53 | 68 |
| | 0.30 | 7 | 75 | 84 |
| | 0.45 | 18 | 95 | 95 |
| | 0.60 | 28 | 97 | 98 |
| | 0.75 | 43 | 100 | 100 |

The results indicate that the transport of Nd/Tb/Dy increases as the concentration of HCl in the receiving phase increases. This has been explained previously (Equation (2)). Using both extractants the percentage of Nd(III) transported after 8 h was only 4%, while



  

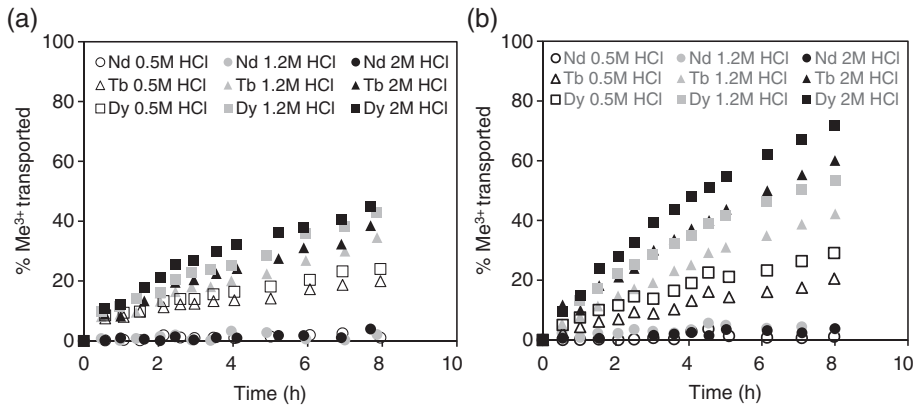


**Figure 5.** Effect of HCl concentration in the receiving phase on transport of Nd(III), Tb(III) and Dy(III). Feed phase: 0.1 g $L^{-1}$ of each metal in 0.4 mol $L^{-1}$ $Cl^-$. (a) Feed pH = 2. C272 10% (v/v). (b) Feed pH = 1.5. C572 10% (v/v).

for Tb(III) and Dy(III) there were differences between C272 and C572 because with C572 the percentage of metal transported changed significantly over the range of HCl concentration studied.

The hydrochloric acid concentration has an influence on transport but the influence on the separation efficiency is limited because the ratio between the three REEs transported in 1.2 mol $L^{-1}$ or 2.0 mol $L^{-1}$ HCl, compared to 0.5 mol $L^{-1}$, is still maintained.

The results follow the same tendency after 24 h, so the stability of the membrane is maintained. In this case, the highest percentage of Nd(III) transported using C272 was 5% but the Tb(III) and Dy(III) transport doubled using 2 mol $L^{-1}$ HCl reaching 75% and 89%, respectively. Using C572, the most Nd(III) transported was 13% and the percentage of Tb(III) and Dy(III) also doubled reaching around 100%.

In order to choose the best concentration of HCl in the receiving phase, the metal transported and selectivity have to be considered. For that reason, HCl 0.5 mol $L^{-1}$ was discarded because of low metal transport. Regarding 1.2 mol $L^{-1}$ and 2.0 mol $L^{-1}$ HCl, the former was chosen because using this concentration, it is possible to separate Nd(III) from the mixture and the operation conditions are less severe.

*Effect of different stripping agents on the transport.*

After experiments using HCl as receiving solution, other types of stripping agents were tested. Citric acid (1 mol $L^{-1}$), and $Na_2EDTA$ (0.1 mol $L^{-1}$) conditioned at pH 3.8 were chosen because of their different chemical characteristics compared to HCl. Citric acid is a weak acid but has a complexing effect, and $Na_2EDTA$ has a chelating effect.

The results in Fig. 6 show that for Nd(III) there are no significant differences in transport using these stripping agents due to the low overall transport. However, Tb(III) and Dy(III) transport is higher using 1.2 mol $L^{-1}$ HCl or 1 mol $L^{-1}$ citric acid than 0.1 mol $L^{-1}$ $Na_2EDTA$. After 8 h, transport of Tb(III) was 14%, 35% and 36% and Dy(III) transport was 19%, 48% and 49% using $Na_2EDTA$ (0.1 mol $L^{-1}$), HCl (1.2 mol $L^{-1}$) and citric acid (1 mol $L^{-1}$), respectively.

Thus $Na_2EDTA$ is not a good stripping agent because it does not possess an acidic proton to exchange with C272, an essential condition. However both HCl and citric acid showed similar receiving percentages because it is probable that the complexing effect of citric acid compensates for its lack of acidity. In order to elucidate this, a solution of HCl 0.01 mol $L^{-1}$ was prepared (pH = 2.0, the same as 1 mol $L^{-1}$ citric acid) and no stripping of any REEs was observed. Consequently, citric acid mainly strips due to the complexing effect.

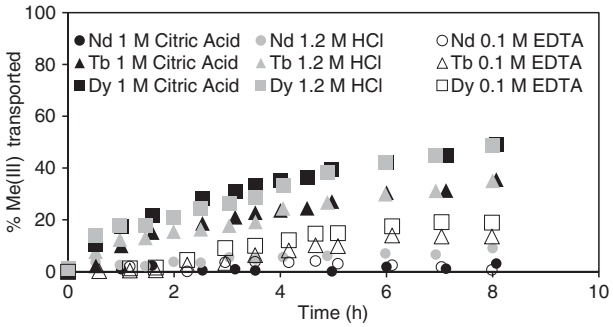


**Figure 6.** Effect of receiving solution on transport of Nd(III), Tb(III) and Dy(III). Feed phase: 0.1 g $L^{-1}$ of each metal in 0.4 mol $L^{-1}$ $Cl^-$ at pH = 2. C272 10% (v/v).

The results (Fig. 6) prove that $Na_2EDTA$ is not a good choice of stripping agent to separate Nd(III) from the mixture because the percentage transport of all the REEs is <20%. For this reason, the best decision is to use HCl (1.2 mol $L^{-1}$) or citric acid (1 mol $L^{-1}$) as stripping agents.

In these experiments, membrane stability was also demonstrated because the percentages of metals transported were the same after 24 h. The transport of Tb(III) was around 69–71% and around 76–80% for Dy(III) using HCl or citric acid while the transport of Nd(III) remained <10% using both stripping agents.

As a conclusion, the optimum stripping conditions for the separation of Nd(III) from the mixture are to use 1.2 mol $L^{-1}$ HCl or 1 mol $L^{-1}$ citric acid, but the first was chosen because it is a common stripping agent.

## Permeability determination

The permeability coefficients were determined using Equation (1), considering P as the slope of the lineal function of $\frac{-V}{A}\ln\frac{[Me]}{[Me]_0}$ vs $t$ for each experiment, the linearized graphs are included in the Supplementary content. In Fig. 7 these parameter values are shown as a function of the carrier concentration and as can be seen, permeability increases with carrier concentration. Considering that the extraction and stripping equilibrium are instantly achieved on both sides of the membrane, the metal transport is controlled by the diffusion through the membrane.



  

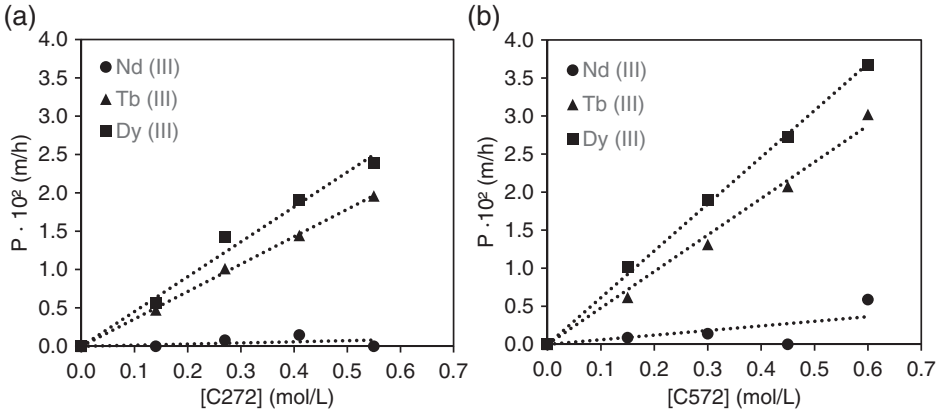


**Figure 7.** Nd(III), Tb(III) and Dy(III) permeability dependence with the extractants concentrations. Aqueous phase: 0.1 g $L^{-1}$ each metal in 0.4 mol $L^{-1}$ $Cl^-$. (a) C272. Feed pH 2.0. (b) C572. Feed pH 1.5.

The results indicate that C572–metal complex is transported more quickly than C272–metal complex. The dependence of extractant concentration and permeability is linear in this working range for both carriers (Fig. 7). This means that the viscosity of the Cyanex is not a parameter that restricts metal transport in this concentration range and it is possible to obtain an equation that relates the permeability to the carrier concentration (Equations (3)–(8)).

$$P_{Nd\,(III)} = 0.15 \times 10^{-2} \cdot [C272] \quad (3)$$

$$P_{Nd\,(III)} = 0.66 \times 10^{-2} \cdot [C572] \quad (4)$$

$$P_{Tb\,(III)} = 3.57 \times 10^{-2} \cdot [C272] \quad (5)$$

$$P_{Tb\,(III)} = 4.82 \times 10^{-2} \cdot [C572] \quad (6)$$

$$P_{Dy\,(III)} = 4.56 \times 10^{-2} \cdot [C272] \quad (7)$$

$$P_{Dy\,(III)} = 6.21 \times 10^{-2} \cdot [C572] \quad (8)$$

where $P$ is in m $h^{-1}$.

These equations allow prediction of the REEs transported as a function of the carrier concentration and the required area to make the separation. In the case of C572, as expected, the permeability is higher than when using C272. In addition, the value of permeability for Dy(III) is about 28% greater than the combined Tb(III) permeability using both carriers.

## CONCLUSIONS

Both extractants, C272 and C572, are able to separate Nd(III) from a mixture with Tb(III) and Dy(III) using FSSLM. However, using C572, more metal is transported for the same working time. If C272 were to be used to separate Nd(III) from the mixture, the membrane area or the working time should be increased to achieve similar results to those obtained with C572.

The pH dependence of metals transport was investigated using both extractants. The optimum conditions for Nd(III) separation are a feed solution with pH values of 1.5 and 2.0 using C572 and C272, respectively.

The permeability coefficients of Nd(III), Tb(III) and Dy(III) were determined for both extractants to predict the transport of these three REEs as a function of the carrier concentration and the required area. The transport through the supported liquid membrane using C572 is about 35% faster than using C272.

The order of metal transport is Dy(III) > Tb(III) > > Nd(III) in all studied conditions and the results obtained in this study suggested that to achieve Nd(III) separation from the mixture, optimizing working time and membrane area it is advisable to use C572 as the carrier.

The results obtained allowed consideration of a scaled-up industrial process using hollow fibres.

## ACKNOWLEDGEMENT

This work has been financed by the MINECO [grant number CTM20014-52770-R].

We thank Cytec Industries Inc. for providing us with free samples of Cyanex 272 and Cyanex 572.

### Supporting Information

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

## REFERENCES

1 Binnemans K, Rare earths: essential elements for the transition to a low carbon economy, in: *Proceedings of the Bauxite Residues Valorisation and Best Practices Conference 2015*, ed. by Pontikes Y. Leuven, Belgium, pp. 291–299 (2015).
2 Kumari A, Panda R, Jha MK, Lee JY, Kumar JR and Kumar V, Thermal treatment for the separation of phosphate and recovery of rare earth metals (REMs) from Korean monazite. *J Ind Eng Chem* **21**:696–703 (2015).
3 Morgan JP. *Rare Earths*. We Touch Them Everyday. [Online]. Malaysia (2010). [Available]. http://www.lynascorp.com/Shared Documents/Investors and media/Reporting Centre/Presentations/2011/Investor_Presentation_May_2011.pdf.
4 Sprecher B, Xiao Y, Walton A, Speight J, Harris R, Kleijn R *et al.*, Life cycle inventory of the production of rare earths and the subsequent production of NdFeB rare earth permanent magnets. *Environ Sci Technol* **48**:3951–3958 (2014).
5 Tunsu C, Petranikova M, Gergorić M, Ekberg C and Retegan T, Reclaiming rare earth elements from end-of-life products: a review of the perspectives for urban mining using hydrometallurgical unit operations. *Hydrometallurgy* **156**:239–258 (2015).

  

6 US Department of Energy. US Department of Energy: Critical Materials *Strategy* (2012).
7 Binnemans K, Jones PT, Blanpain B, Van Gerven T, Yang Y, Walton A *et al.,* Recycling of rare earths: a critical review. *J Clean Prod* **51**:1–22 (2013).
8 Jordens A, Sheridan RS, Rowson NA and Waters KE, Processing a rare earth mineral deposit using gravity and magnetic separation. *Miner Eng* **62**:9–18 (2014).
9 Tunsu C, Ekberg C and Retegan T., Characterization and leaching of real fluorescent lamp waste for the recovery of rare earth metals and mercury. *Hydrometallurgy* **144–145**:91–98 (2014).
10 Behera SS and Parhi PK, Leaching kinetics study of neodymium from the scrap magnet using acetic acid. *Sep Purif Technol* **160**:59–66 (2016).
11 Tan Q, Li J and Zeng X, Rare earth elements recovery from waste fluorescent lamps: a review. *Crit Rev Environ Sci Technol* **45**:749–776 (2015).
12 Tunsu C, Ekberg C, Foreman M and Retegan T, Targeting fluorescent lamp waste for the recovery of cerium, lanthanum, europium, gadolinium, terbium and yttrium. *Mineral Process Extract Metall* pp. 1–5 (2016).
13 Kubota F, Yang J and Goto M, Ionic liquid-based extraction and the application to liquid membrane separation of rare earth metals, in *Application of Ionic Liquid on Rare Earth Green Separation and Utilization*. Springer, Berlin/Heidelberg, pp. 73–83 (2016).
14 Thakur NV, Separation of rare earths by solvent extraction. *Miner Process Extr Metall Rev* **21**:277–306 (2000).
15 Radhika S, Kumar BN, Kantam ML and Reddy BR, Liquid–liquid extraction and separation possibilities of heavy and light rare-earths from phosphoric acid solutions with acidic organophosphorus reagents. *Sep Purif Technol* **75**:295–302 (2010).
16 Huang Y and Tanaka M, Solvent extraction equilibrium of dysprosium(III) from nitric acid solutions with 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester. *Trans Nonferrous Met Soc China* **20**:707–711 (2010).
17 Yoon H-S, Kim C-J, Chung K-W, Kim S-D, Lee J-Y and Kumar JR, Solvent extraction, separation and recovery of dysprosium (Dy) and neodymium (Nd) from aqueous solutions: Waste recycling strategies for permanent magnet processing. *Hydrometallurgy* **165**:27–43 (2016).
18 Wang Y, Li F, Zhao Z, Dong Y and Sun X, The novel extraction process based on CYANEX 572 for separating heavy rare earths from ion-adsorbed deposit. *Sep Purif Technol* **151**:303–308 (2015).
19 Quinn JE, Soldenhoff KH, Stevens GW and Lengkeek NA, Solvent extraction of rare earth elements using phosphonic/phosphinic acid mixtures. *Hydrometallurgy* **157**:298–305 (2015).
20 Kolar E, Catthoor RPR, Kriel FH, Sedev R, Middlemas S, Klier E *et al.,* Microfluidic solvent extraction of rare earth elements from a mixed oxide concentrate leach solution using Cyanex® 572. *Chem Eng Sci* **148**:212–218 (2016).
21 Yazaki T, Yonathan M, Habaki H and Egashira R, Solvent extraction of rare earth metal by a continuous stirred vessel. *J Eng Sci Technol* **10**:87–96 (2015).
22 Swain B and Otu EO, Competitive extraction of lanthanides by solvent extraction using Cyanex 272: analysis, classification and mechanism. *Sep Purif Technol* **83**:82–90 (2011).
23 Rathore NS, Sastre AM and Pabby AK, Membrane assisted liquid extraction of actinides and remediation of nuclear waste: a review. *J Membr Sci Res* **2**:2–13 (2016).
24 Scott K, Introduction to membrane separation, in *Handbook of Industrial Membranes*. Elsevier B.V. pp. 3–185 (1995).
25 Åke Jönsson J, Membranowa E, Środowiskowej W and Chemicznej A, Membrane extraction in environmental chemical analysis, in *Proceedings of ECOpole*. Duszniki Zdroj, Poland, pp. 37–42 (2007).
26 Gega J and Otrembska P, Separation of Ni(II) and Cd(II) ions with supporte liquid membranes (SLM) using D2EHPA as a carrier. *Sep Sci Technol* **49**:1756–60 (2014).
27 Wannachod T, Leepipatpiboon N, Pancharoen U and Phatanasri S, Mass transfer and selective separation of neodymium ions via a hollow fiber supported liquid membrane using PC88A as extractant. *J Ind Eng Chem* **21**:535–541 (2015).
28 Wannachod T, Mohdee V, Suren S, Ramakul P, Pancharoen U and Nootong K, The separation of Nd(III) from mixed rare earth via hollow fiber supported liquid membrane and mass transfer analysis. *J Ind Eng Chem* **26**:214–217 (2015).
29 Pabby AK and Sastre AM, State-of-the-art review on hollow fibre contactor technology and membrane-based extraction processes. *J Membr Sci* **430**:263–303 (2013).
30 Baba Y, Kubota F, Kamiya N and Goto M, Selective recovery of dysprosium and neodymium ions by a supported liquid membrane based on ionic liquids. *Solvent Extr Res Dev Japan* **18**:193–198 (2011).
31 Zaheri P, Abolghasemi H, Mohammadi T and Maraghe MG, Synergistic extraction and separation of dysprosium and europium by supported liquid membrane. *Korean J Chem Eng* **32**:1642–1648 (2015).
32 Zaheri P, Abolghasemi H, Ghannadi Maraghe M and Mohammadi T, Intensification of europium extraction through a supported liquid membrane using mixture of D2EHPA and Cyanex272 as carrier. *Chem Eng Process Process Intensif* **92**:18–24 (2015).
33 Wannachod P, Chaturabul S, Pancharoen U, Lothongkum AW and Patthaveekongka W, The effective recovery of praseodymium from mixed rare earths via a hollow fiber supported liquid membrane and its mass transfer related. *J Alloys Compd* **509**:354–361 (2011).
34 Reddy BR and Kumar JR, Rare earths extraction, separation, and recovery from phosphoric acid media. *Solvent Extr Ion Exch* **34**:226–240 (2016).
35 Solvent Extractant CYANEX ® 572 Solvent Extraction Reagent (2013).
36 Rathore NS, Leopold A, Pabby AK, Fortuny A, Coll MT and Sastre AM, Extraction and permeation studies of Cd(II) in acidic and neutral chloride media using Cyanex 923 on supported liquid membrane. *Hydrometallurgy* **96**:81–87. (2009).
37 CYTEC Industries Inc. CYANEX 272 Extractant. Technical Brochure (2008).
38 Castillo J, Coll MT, Fortuny A, Navarro P, Sepúlveda R and María A, Hydrometallurgy Cu (II) extraction using quaternary ammonium and quaternary phosphonium based ionic liquid. *Hydrometallurgy* **141**:89–96 (2014).




  