



# Process development for the recovery of high-grade lanthanum by solvent extraction

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## Abstract

The development of a solvent extraction process for the recovery of high-grade lanthanum oxide from a light rare earth (RE) (La, Pr, Nd) chloride solution is described. In a preliminary stage, process parameters and experimental conditions were explored in bench-scale experiments. The effect of variables such as nature and concentration of the extractants (di-2-ethylhexylphosphoric acid [DEHPA] and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester [HEH(EHP)]), contact time, acidity and rare earth concentration in the extraction stage as well as the effect of the hydrochloric acid concentration in the stripping stage were investigated. The continuous counter-current experiments were carried out in a mini-battery unit of mixer-settlers. The final set-up was comprised of 22 stages: 8 for extraction, 8 for scrubbing and 6 for stripping. A high-grade oxide (>99.9% La<sub>2</sub>O<sub>3</sub>) was obtained with a yield superior to 99.9%.

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## 1. Introduction

Rare earth (RE) elements have been increasingly used in the field of chemical engineering, metallurgy, nuclear energy, optical, magnetic, luminescence and laser materials, high-temperature superconductors and secondary batteries, catalysis, red phosphors, among

others (Maestro and Huguenin, 1995; Nagaosa and Binghua, 1997; Sánchez et al., 1999). Lanthanum, one of the most abundant of the lanthanides, is an important element of mischmetal and hydrogen-absorbing alloy (Nagaosa and Binghua, 1997). The RE elements occur together in nature in some minerals like bastnaesite, monazite, xenotime and others (Gschneidner, 1980; Sundaram, 1987). The high value of these elements depends on their effective separation into high purity compounds. The separation of the natural RE mixtures into the individual elements is very difficult to achieve, due to the very low separation factors involving the adjacent RE elements. Among

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the trivalent lanthanides, Ce and Eu can be separated through changes in their oxidation state. The Ce(III) is oxidized to Ce(IV) and the Eu(III) is reduced to Eu(II) (Topp, 1965; Kedari et al., 1999; Morais and Ciminelli, 1998, 2001, 2002). The separation of the other RE elements, usually carried out by solvent extraction or ion exchange, is based on systematic differences in their basicity, which decreases from La to Lu (Gschneidner, 1980; Sundaram, 1987). Generally, a mixture of rare earths is first separated into groups of: light rare earths (La, Ce, Pr, Nd), middle rare earths (Sm, Eu, Gd) and heavy rare earths (Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, Y). This separation is favored by the relatively higher separation factor between Nd/Sm and Gd/Tb compared to the other separation factors of the adjacent elements within a lanthanides group. The separation into these three groups is usually accomplished by solvent extraction, using di-2-ethylhexylphosphoric acid (DEHPA) as the extractant (Gschneidner, 1980; Qiu et al., 1991).

The extraction behavior of rare earths has been studied since the 1950s. There are several reports on the separation of rare earth elements in different media and extractants, such as: phosphoric, phosphonic and phosphinic acids, with 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH(EHP)) also known as 2-ethylhexyl 2-ethylhexylphosphonic acid (EHEHPA) and DEHPA being the most used (Xu et al., 1992; Giles et al., 1996; Nucciarone et al., 2001); neutral phosphate, such as tri-*n*-butylphosphate (TBP) and tri-*n*-octylphosphine oxide (TOPO) (Ceconie and Freiser, 1990; Majdan, 1994; Mathur and Choppin, 1998); carboxylic acid derivative (Zheng et al., 1991; Du Preez and Preston, 1992); amines (Gorski et al., 1991; Hirai and Komasa, 1991; Preston, 1996); ketones; and others (Hirai and Komasa, 1991; Abbruzzese et al., 1992). The majority of these studies focus on the fundamentals, which include the determination of separation and extraction parameters in synthetic solutions, evaluation of kinetics and reaction mechanism, among others. There is little information in the literature regarding process development, mainly for proprietary reasons.

DEHPA is one of the first and most extensively investigated extractants in the separation of rare earth elements. In recent years, studies have also been carried out with HEH(EHP) in view of some advantages of this extractant compared to DEHPA, like

higher separation factors and easier stripping (Xu et al., 1992; Nucciarone et al., 2001). In this work, the use of DEHPA and HEH(EHP) for the separation of lanthanum from light rare earth chloride liquor was investigated. Based on the results, a process to obtain a high-grade La<sub>2</sub>O<sub>3</sub> using HEH(EHP) as extractant was developed and, for the first time, is described.

## 2. Experimental

### 2.1. Reagents and Solutions

The extractants, HEH(EHP) (96.5 wt.%), commercialized under the trade name Ionquest 801<sup>®</sup> and DEHPA (97 wt.%), were supplied by Albright and Wilson Americas. The extractants were diluted in Exxsol<sup>®</sup> (purified kerosene), supplied by “Exxon Química”. All other reagents were of analytical grade and their solutions were prepared with distilled water.

The rare earth chloride solution was supplied by “INB—Industrias Nucleares do Brasil”. Prior to the experiments, cerium was recovered through oxidation/hydrolysis with KMnO<sub>4</sub>/Na<sub>2</sub>CO<sub>3</sub> solution (Morais et al., 2003). The filtrate containing the remaining light rare earths was neutralized with Na<sub>2</sub>CO<sub>3</sub> solution in order to separate the RE from the permanganate excess and to obtain the RE carbonate. The chemical composition of the chloride liquor and the RE carbonate are shown in Table 1. The light RE solution used in the experiments was prepared by dissolving the RE carbonate in an aqueous hydrochloric acid solution (3.0 mol L<sup>-1</sup>).

### 2.2. Batch experiments

The effect of the main process parameters, such as aqueous phase acidity, RE concentration, nature and

Table 1  
Chemical composition of the light RE liquor and the RE carbonate, after cerium removal

Sample	La <sup>3+</sup>	Ce <sup>3+</sup>	Pr <sup>3+</sup>	Nd <sup>3+</sup>	Sm <sup>3+</sup>	CO <sub>3</sub> <sup>2-</sup>	Cl <sup>-</sup>	H <sub>2</sub> O
Hydrochloric liquor (g L <sup>-1</sup> )	138	17.3	29.2	110	0.42	–	550	–
RE carbonate (wt.%)	32.8	0.07	6.89	26.2	0.10	33.1	0.35	5.8

concentration of the extractant on the rare earths extraction and the effect of the hydrochloric acid concentration on the rare earths stripping from the loaded organic phase were investigated. The experiments were carried out in mechanically agitated beakers containing equal volumes (20 cm<sup>3</sup>) of the aqueous and organic phases, at (25 ± 1) °C. Following contact, the phases were separated by means of a separation funnel. All the batch experiments were carried out at a fixed contact time of 5 min, based on the results of preliminary experiments indicating that 3 min were sufficient to achieve equilibrium.

### 2.3. Continuous experiments

The continuous experiments were carried out using HEH(EHP) as the extractant, in an acrylic mini-battery unit of mixer–settlers, supplied by Sonal-Polux, with mixers of 13 cm<sup>3</sup> and settlers of 40 cm<sup>3</sup> capacities, each run lasting 30 h. The solutions were fed by peristaltic pump into six points of the circuit. These solutions were the RE and organic solutions, ammonium hydroxide solution for pH adjustment at the extraction stage, the scrubbing and the stripping solutions. The control of system stability was evaluated by lanthanides determination in the exit flows every hour. At this time, the flow rates of the feed solutions were also checked. During the process development, the lanthanide concentrations were mostly measured in the aqueous phase by using an energy-dispersive X-ray spectrometry (Kevex system). The minor constituents were determined by an atomic emission spectrometer with inductively coupled plasma (ICP/AES).

The Kevex system has a radioactive source of americium (Am<sup>241</sup>) with 100 mCi of activity for the

X-ray generation. The complete setup is built around an Si(Li) detector X-ray spectrometer, with an energy resolution of 220 eV at 5.94 keV. The peaks observed in the X-ray fluorescence spectra are fitted with a multicomponent spectrum analysis and the intensities of the characteristic X-ray lines are extracted, for calculating the elemental concentrations. Specifically for the rare earth elements, Am<sup>241</sup>, is the indicated radioisotope as source to produce the fluorescence. The X-ray spectrum formed is due to the K layer excitation, which produces simpler spectra compared to those obtained by the L layer. The detection limit of this technique depends on the atomic number of the element and the counting time. For the rare earth elements, this limit is a few micrograms per gram (Morais and Ciminelli, 2001, 2002).

### 3. Results and discussion

DEHPA and HEH(EHP) are liquid cation-exchangers, the extracted metal being exchanged by the hydrogen ion in the hydroxyl group. Fig. 1 shows the structural formulae for both reagents.

These reagents are prone to form dimers through hydrogen bonding. In dilute solutions, the dimerization increases with the decrease of solvent (diluent) polarity (Baes, 1962; Giles et al., 1996; Sánchez et al., 2001). Concentrated solutions, like those required in industrial processes, favor the formation of dimeric forms, generally represented by (HX)<sub>2</sub> or H<sub>2</sub>X<sub>2</sub>.

The mechanism involved in the extraction of rare earths by DEHPA and HEH(EHP) was first described by Peppard and collaborators (Peppard et al., 1958, 1961). The mechanism, later confirmed by others (Iglesias et al., 1999; Geist et al., 1999; Jensen and

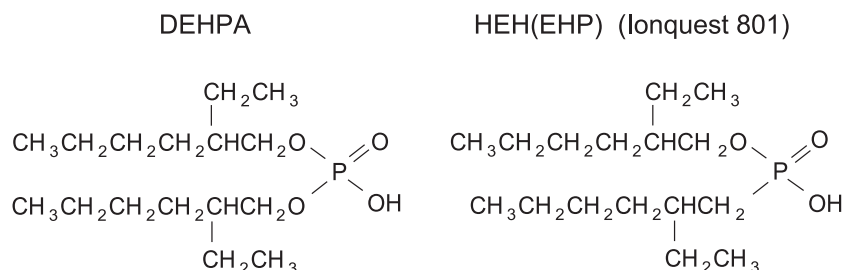


Fig. 1. Structural formulae of the extractants DEHPA and HEH(EHP).

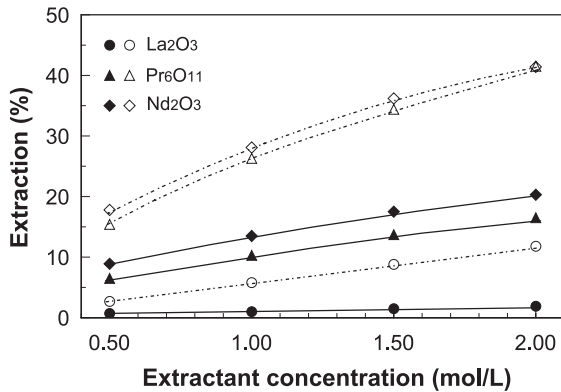
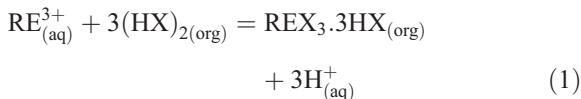


Fig. 2. Influence of DEHPA and EHE(EHP) concentration on the RE elements extraction. The dotted lines represent the experiments with DEHPA. Feed solution: 44.0 g L<sup>-1</sup> La<sub>2</sub>O<sub>3</sub>, 9.33 g L<sup>-1</sup> Pr<sub>6</sub>O<sub>11</sub>, 35.7 g L<sup>-1</sup> Nd<sub>2</sub>O<sub>3</sub>, pH 2.4.

Nash, 2001), can be represented by the following reaction:



Where HX symbolizes the extractant molecule and X its deprotonated form.

Mechanisms of rare earth extraction by DEHPA involving the formation of organic species like  $\text{REX}_3 \cdot 2\text{HX}$  and  $\text{REX}_3$  are also reported (Sato, 1989; Iglesias et al., 1999; Sánchez et al., 1999, 2001). These species are believed to occur in very dilute organic solutions, where dimerization of DEHPA is not significant and the extractant also exists as a monomer (Sánchez et al., 2001). At high organic concentrations such as those applied in this investigation, the monomer form can be neglected, with the predominance of the mechanism shown in Eq. (1).

### 3.1. Batch experiments

The batch experiments were carried out with the extractants DEHPA and HEH(EHP). The following variables were investigated: extractant concentration, acidity and concentration of rare earths in the feed solution, contact time in the metal extraction and stripping and hydrochloric acid concentration in the metal stripping. The results are presented in Figs. 2–5.

Fig. 2 shows the extraction of La, Pr and Nd as a function of extractant concentration. More concentrated feed solutions, such as those used here, required higher extractant concentration. One can observe that the extraction increases as the extractant concentration increases from 0.5 to 2 mol L<sup>-1</sup>, the increase being relatively higher in the case of DEHPA. It is also seen that for all three elements, significantly higher extraction is obtained with DEHPA. The selectivity of both extractants with respect to Pr and Nd is clearly indicated. Extractions of Pr and Nd are quite similar for both extractants. The increase in the extraction from La to Nd can be explained by the difference in the acidity of these elements, which increases from La to Lu. This difference is related to a systematic and smooth decrease in the ionic radii of the RE elements, known as the lanthanide contraction, which increases with the atomic number in the lanthanide series (Gschneidner, 1980; Sundaram, 1987). The very low extraction of La with HEH(EHP) should be emphasized as this will help separation of this rare earth from the mixture. The subsequent experiments were carried out with the extractant concentration of 1.5 mol L<sup>-1</sup>.

The pH of the aqueous phase was investigated from 0 to 2.4. As shown by (Eq. (1)), the extraction increases with the decrease of the acidity of the RE solution. With both extractants, the extraction increases up to pH 1 and then reaches a plateau (Fig. 3). For all three metals, the extraction with HEH(EHP) drops to nearly zero as pH

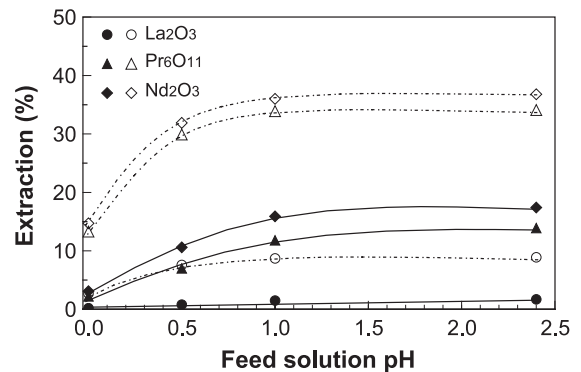


Fig. 3. Effect of the chloride solution acidity on the RE elements extraction with DEHPA and HEH(EHP). The dotted lines represent the experiments with DEHPA. Feed solution: 44.0 g L<sup>-1</sup> La<sub>2</sub>O<sub>3</sub>, 9.33 g L<sup>-1</sup> Pr<sub>6</sub>O<sub>11</sub>, 35.7 g L<sup>-1</sup> Nd<sub>2</sub>O<sub>3</sub>.

reaches values less than 0.5. This indicates that the use of this reagent would require a very effective pH control at the extraction stage.

The total rare earth concentration was investigated from 30 to 89 g L<sup>-1</sup> RE oxides. As expected, extraction increases as the total rare earth concentration decreases (Fig. 4). Among all the studied variables, this was the one that caused the most significant influence on selectivity. The effect on selectivity happens because the decrease in the RE concentration caused a relatively higher increase in lanthanum extraction as compared to the increase in the extraction of praseodymium and neodymium. Though it is not made clear from the distances between the lines shown in Fig. 4, these differences will reflect in a significant reduction in the separation factor Pr/La, as the RE concentration decreases (Table 2). The separation factor indicates the effectiveness in the separation of two elements; it is calculated by the ratio of the extraction coefficients of these elements obtained under the same experimental conditions. For the system HEH(EHP)–HCl, the separation factor Pr/La increased from 7.7 to 10.2, while for the system DEHPA–HCl, it varied from 4.6 to 5.4, as total RE concentration varied from 29.7 to 89.0 g L<sup>-1</sup>.

The separation factors Nd/Pr remained practically constant and equal to 1.3, for the system HEH(EHP)–HCl, and 1.1 for the system DEHPA–HCl. As for Pr/La, the highest separation factors were obtained with HEH(EHP)–HCl. The separation factor was not significantly affected by the other variables investigated in

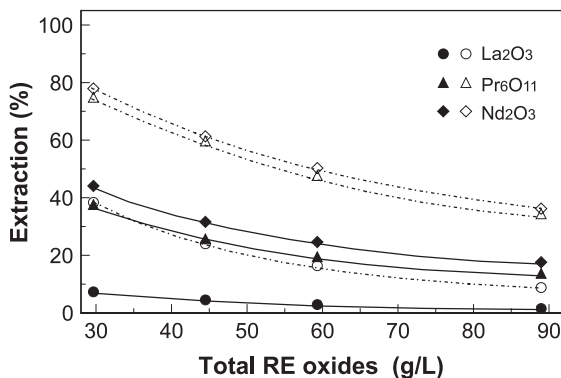


Fig. 4. Effect of the total RE concentration on the individual elements extraction with DEHPA and HEH(EHP). The dotted lines represent the experiments with DEHPA. Feed solution pH 2.4.

Table 2

Extraction coefficient of La, Pr and Nd and separation factor of Pr/La and Nd/Pr for different La, Pr and Nd concentration

Extractant	Total RE oxide (g L <sup>-1</sup> )	Extraction coefficient			Separation factor	
		LaE <sub>a</sub> <sup>o</sup>	PrE <sub>a</sub> <sup>o</sup>	NdE <sub>a</sub> <sup>o</sup>	Pr/La	Nd/Pr
HEH(EHP)	89.0	0.016	0.163	0.217	10.2	1.33
HEH(EHP)	59.3	0.026	0.242	0.324	9.31	1.34
HEH(EHP)	44.5	0.045	0.346	0.460	7.69	1.33
HEH(EHP)	29.7	0.082	0.605	0.798	7.38	1.32
DEHPA	89.0	0.096	0.520	0.570	5.42	1.10
DEHPA	59.3	0.191	0.914	1.015	4.79	1.11
DEHPA	44.5	0.316	1.484	1.622	4.70	1.09
DEHPA	29.7	0.652	2.987	3.250	4.58	1.09

Feed solution: 49.4 wt.% La<sub>2</sub>O<sub>3</sub>, 10.5 wt.% Pr<sub>6</sub>O<sub>11</sub>, 40.1 wt.% Nd<sub>2</sub>O<sub>3</sub>, pH 2.4; extractants concentration: 1.5 mol L<sup>-1</sup>.

the present study, remaining at 10.2 and 1.33 for La/Pr and Pr/Nd, respectively, with HEH(EHP) and 5.4 and 1.10 with DEHPA. The high separation factor between La and Pr is due to the absence of cerium and the higher basic character of lanthanum.

Under all conditions, the extractions obtained with DEHPA were significantly superior to those obtained with HEH(EHP). These results will be discussed on the basis of the soft and hard acid/base theory (Pearson, 1963; Huheey, 1992) and the hydrophilic character of the different extractants. DEHPA and HEH(EHP) are cation-exchange extractants, thus the analysis of their extraction behavior should take into consideration their conjugated bases. DEHPA is a stronger acid than HEH(EHP) (pK<sub>a</sub> 3.2 and 4.4 at 298 K, respectively); therefore, by the Lewis acid/base theory, it has a weaker conjugated base than HEH(EHP). For this reason, lower extractions would be expected for DEHPA, which is not the case. The pK<sub>a</sub> of the reagents was determined experimentally in the present work by titration, the pK<sub>a</sub> being the pH corresponding to half of the equivalent volume (Butler, 1964). The soft and hard acid/base theory divides acids and bases into two categories: polarizable or “soft” and nonpolarizable or “hard”. As hard acids, the lanthanide ions will prefer to bind to hard bases (Pearson, 1963). It is hypothesized here that the symmetry of the four oxygen atoms around the phosphorus atom in DEHPA would be responsible for making the conjugated base of this extractant harder than the conjugated base of HEH(EHP). In addition to this and perhaps even more relevant is the

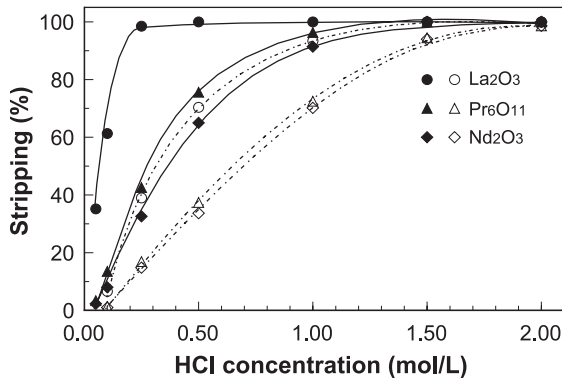


Fig. 5. Effect of the HCl concentration on the RE elements stripping from loaded DEHPA and EHE(EHP). The dotted lines represent the experiments with DEHPA. Organic phases: HEH(EHP)— $3.41 \text{ g L}^{-1} \text{ La}_2\text{O}_3$ ,  $5.64 \text{ g L}^{-1} \text{ Pr}_6\text{O}_{11}$ ,  $24.6 \text{ g L}^{-1} \text{ Nd}_2\text{O}_3$ ; DEHPA— $6.50 \text{ g L}^{-1} \text{ La}_2\text{O}_3$ ,  $4.92 \text{ g L}^{-1} \text{ Pr}_6\text{O}_{11}$ ,  $20.4 \text{ g L}^{-1} \text{ Nd}_2\text{O}_3$ .

relatively higher hydrophilic nature of the phosphate group in DEHPA as compared to the phosphonic group in HEH(EHP), thus making the former more active in the organic/aqueous interface.

As the extraction of the rare earths is higher with DEHPA compared to HEH(EHP), metal stripping, the reverse reaction, is expected to be relatively easier from the loaded HEH(EHP) as compared to DEHPA. This behavior is confirmed by the results shown in Fig. 5. Lanthanum is fully stripped from HEH(EHP) with  $0.25 \text{ mol L}^{-1}$  HCl solution while  $1.5 \text{ mol L}^{-1}$  HCl was

required for the complete stripping of lanthanum from DEHPA.

Based upon the superior separation factor Pr/La (equal to 10.2 with HEH(EHP) and 5.4 with DEHPA), the lesser extraction of the La and the easier stripping as compared to DEHPA, HEH(EHP) was selected for the experiments in a continuous mixer–settler battery.

### 3.2. Continuous experiments

The batch experiments indicated that praseodymium and neodymium are more easily extracted than lanthanum. Then, the objective of the continuous experiments was to transfer praseodymium and neodymium to the organic phase, lanthanum being kept in the raffinate.

In the continuous experiments, the variables studied were: number of stages in the extraction, scrubbing and stripping steps; organic/aqueous ratio in all steps, HCl concentration in the scrubbing and stripping;  $\text{NH}_4\text{OH}$  concentration and the extraction stage where pH was adjusted. The experimental set-up was comprised of three cycles: extraction, scrubbing and stripping (Fig. 6). The variables were progressively adjusted in consecutive runs until the desired yields and grades were achieved. Fig. 6 shows the composition and distribution of the products obtained in a continuous counter-current circuit for

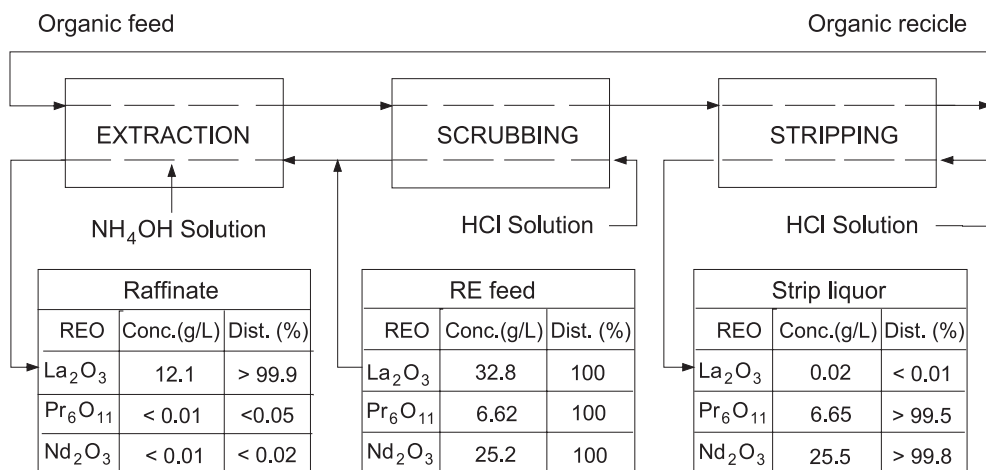


Fig. 6. Composition and distribution of the products obtained in a continuous counter-current circuit for lanthanum recovery. REO = rare earth oxide, Conc. = concentration, Dist. = distribution.

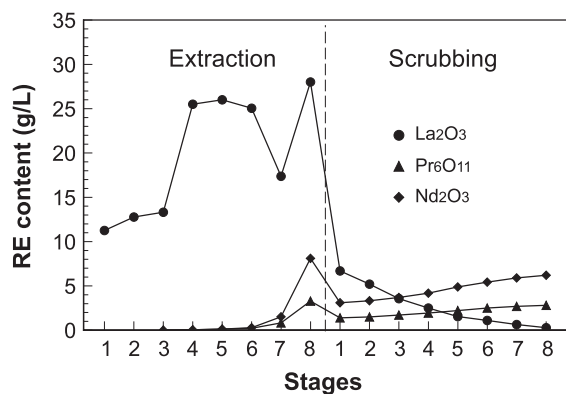


Fig. 7. Profile of the RE elements in aqueous phase of the extraction and scrubbing circuit.

lanthanum recovery of the experiment leading to the best yields.

The extraction occurred in the stages 1 to 8. The aqueous solution containing the rare earth elements was fed at the eighth stage and the organic solution was fed in the first. The scrubbing solution ( $0.25 \text{ mol L}^{-1} \text{ HCl}$ ) was added in the 16th stage in order to achieve the selective stripping of lanthanum, which was partially extracted. The pH control was made by addition of ammonium hydroxide. The ammonium hydroxide and the scrubbing solutions were combined with the RE feed solution in the raffinate, which was then removed in the first stage. The praseodymium and neodymium-loaded organic, after passing through the scrubbing stage, fed the stripping cycle, stages 17 to 22. The stripping solution ( $1.0 \text{ mol L}^{-1} \text{ HCl}$ ) was fed in the 22nd stage and the strip liquor was removed in stage 17. The organic effluent was filtered and recycled in the circuit without any additional treatment.

The high efficiency of the proposed separation process is depicted in Figs. 6 and 7. In the raffinate leaving the first stage, only lanthanum was detected, i.e.  $12.1 \text{ g L}^{-1} \text{ La}_2\text{O}_3$  and less than  $0.01 \text{ g L}^{-1} \text{ Pr}_6\text{O}_{11}$  and  $\text{Nd}_2\text{O}_3$  (Fig. 6). In the strip liquor leaving the 17th stage, basically only praseodymium and neodymium were detected:  $0.02 \text{ g L}^{-1} \text{ La}_2\text{O}_3$ ,  $6.65 \text{ g L}^{-1} \text{ Pr}_6\text{O}_{11}$  and  $25.5 \text{ g L}^{-1} \text{ Nd}_2\text{O}_3$  (Fig. 6). The profiles of lanthanum, praseodymium and neodymium concentration in the aqueous phase are shown in Fig. 7, according to the results obtained in the experiments leading to highest yields. Under those conditions, in the extraction

step, the pH varied from 1.2 in the eighth stage to 0.95 in the first stage. From the stages 3 to 8, the pH was maintained at approximately 1.2. In the scrubbing step, the pH varied from 1.0 (stage 16) to 1.25 (stage 9). In the stripping step, the pH was nearly zero. The flow rate of the RE liquor was  $0.8 \text{ mL min}^{-1}$ . The ratios of aqueous/organic phases in the extraction and stripping steps were of 0.5.

#### 4. Conclusions

The utilization of solvent extraction to obtain high-grade, high-yield lanthanum oxide from a light rare earths mixture has been demonstrated. The process consisted in extracting Pr and Nd into  $1.5 \text{ mol L}^{-1} \text{ HEH(EHP)}$  diluted in Exxsol, followed by the scrubbing of the organic phase with HCl solution and the return of the extracted La to the aqueous phase. Sixteen stages were required in this separation. Finally, Pr and Nd were stripped with another HCl solution in 6 stages, using an organic/aqueous phase ratio of two. A product assaying over 99.9%  $\text{La}_2\text{O}_3$  was obtained from a chloride liquor containing  $32.8 \text{ g L}^{-1} \text{ La}_2\text{O}_3$ ,  $6.62 \text{ g L}^{-1} \text{ Pr}_6\text{O}_{11}$  and  $25.2 \text{ g L}^{-1} \text{ Nd}_2\text{O}_3$ . The overall recovery was superior to 99.9%.

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