Metallurgy and materials
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Separation of rare earths by solvent extraction using DEHPA

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Abstract

This paper presents results or the analysis of process variables for separating light REE and heavy REE, in chloride media, by solvent extraction. DEHPA-Isoparaffin was used as the extraction system and the liquor was produced in the laboratory by dissolving REE oxides in HCl to simulate leaching liquor originating from monazitic ores after cerium removal. The following parameters were determined: pH of work, extractant concentration, reaction time, and number of extraction stages. A continuous extraction circuit was operated and its behavior was similar to that shown by batch extraction tests.

Keywords: solvent extraction, rare earths, DEHPA.

1. Introduction

The rare earths (REE) are a group of 17 elements of atomic numbers 57 to 71, scandium and ytrium. Relatively abundant in nature, they have similar chemical properties and are used in many high tech industries (Long *at al*. 2010).

The availability and price of these elements in the market are oscillating due to the location of their reserves, vulnerability to supply disruptions and lack of suitable substitute materials.

The United Nations Program for the Environment has already reported about the vulnerability of the green economy to shortages of rare earth minerals because many so-called clean energy technologies, such as wind turbines and components of electric vehicles, depend on the unique properties of these materials (US Department of Energy Critical Materials Strategy, 2010). At the beginning of the 20th century, Brazil became the world's main producer, exploring monazitic sands, which are rich in rare earths, particularly cerium and lanthanum that occur from the coast of the state of Rio de Janeiro to the south of the state of Bahia. Loureiro (1994) reported that, in 1960, the United States became the world's largest producer, but was over taken by Australia the following decade. In the 80s, China became the market leader with massive investments in the sector, and production in Bayan Obo, Mongolia. During the 90s,

Brazil totally ceased its production of rare earths due to the low prices of the Chinese product (Buys, 2012). China is currently responsible for the majority of world production of elements like lanthanum, cerium and neodymium, a market worth about 15 billion dollars a year (Tse, 2011).

Currently, Brazil does not produce any rare earth compound, being completely dependent on imports. The production of rare earth concentrates in Brazil had a prominent position in the 40's, but today the production is practically nil. (Andrade, 2012). However, the country has a variety of deposits and technological capability, and as such, presents good potential for processing rare earth from mainly the

polymetallic minerals.

Currently, according to official government information, Brazil has around 164 requests filed for research about rare earth deposits (Andrade, 2012).

A current technological problem in the research for processing rare earth minerals is the separation of the mineral containing rare earth from the remaining minerals. For some mineral sources, these strategic elements can appear in very small particles, which creates a problem for the process of beneficiation. In the following steps of the process, the market value of these elements depends on their effective separation and purity. To ensure these characteristics of purity in the final products, the application of the technique of solvent extraction (SX) is the traditional technique for the fractionation of rare earth elements.

The solvent extraction of the trivalent lanthanides by reagents of different types has been extensively studied since the 1940s, and this technique is widely accepted in the commercial processing of rare earth compounds (Preston and du Preez, 1990).

The separation of the natural REE mixtures into individual elements is very difficult to achieve, due to the very low separation factors involving the adjacent REE, and because the chemical properties of the individual elements are very similar.

The use of organophosphorous extractants (Thakur, 2000) and phosphine oxide (Shaibu et al., 2006) has been the most common approach. DEHPA, PC 88A (Gupta and Krishnamurthy, 2004), Cyanex 272 (Komatsu and Freiser, 1989; Li and Freiser, 1986; Banda *et al.*, 2012a, 2012b), Cyanex 302 (Wu et al. 2004) and synergistic mixtures (Reddy *at al.*, 1999; El-Nadi 2012; Wu *et al.*, 2007) efficiently extract rare earths from different aqueous medium solutions.

Recent research on rare earth solvent extraction has been done in Brazil. Morais and Ciminelli (2004)report a process to obtain a high-grade La_2O_3 with a yield of 99.9% using continuous experiments at 8 stages for extraction, scrubbing and 6 stages for stripping with the 2-ethyl hexyl phosphonic acid mono-2-ehylhexylester (PC 88A) as an extractant.

In the year 2000, a hydrometallurgical demonstration of a leaching and solvent extraction plant unit, which produced rare earth compounds, was operated by the Nuclear Industries of Brazil – INB in Minas Gerais state (MG) and was closed after a period of experimental operation (Rosental, 2005).

The Centre for Mineral Technology - CETEM, in Rio de Janeiro (RJ), worked in the 80s in the design and implementation of a pilot plant for solvent extraction to separate the rare earths, yielding high purity oxides of samarium, neodymium and gadolinium from leach liquors originating from monazite ore (Barbosa, 2008). In Brazil, the processing of rare earths, and the production of compounds, metals or alloys partially developed in the past, needs to be renewed, updated and expanded to include new sources and new technologies minerals.

As a target of the Brazilian government, the Ministry of Science, Technology and Innovation - MCTI is currently promoting initiatives for the resumption of research on rare earths in Brazil. Thus, the present study shows results of research conducted by the Centre for Mineral Technology - CETEM aiming at contributing to the structuring and development of a rare earth supply chain, considered as promising and strategic for Brazil. A synthetic liquor of rare earths was produced with a rare earth composition similar to an actual liquor corresponding to the leaching stage of a Brazilian monazite. The liquor was treated by solvent extraction for separation of the light fraction of rare earth elements(La-Nd) or LREE, from medium and heavy fractions (Sm-Lu) or HREE. Beyond batch laboratory tests for investigation of process variables, a micro continuous pilot plant was operated for monitoring of performance at each stage of extraction.

2. Material and Methods

2.1 Reagents and solutions

The tests had as their main objective to verify the best conditions for the separation of LREE from other rare earth elements in a synthetic liquor. The quantitative analysis was performed for the elements La, Pr, Nd and Sm. Sm was used as a reference for the separation between light and heavy elements. In the case of the pilot plant, Gd was also analyzed. It was considered that the elements of atomic number higher than Gd were 100% removed.

The synthetic liquor of rare earth chlorides was prepared from their oxides with added in stoichiometric excess HCl and heated. Before the addition of HCl, a paste was made with the mixture of oxides and distilled water in a beaker to facilitate the solubility of the same. After the preparation of this paste, the beaker was heated on a hot plate and HCl was added slowly. The rare earth elements are completely solubilized when the solution becomes clear. Af-

ter this process, the beaker should be heated to reduce the initial volume and form a wet and compact paste. The final mixture should then be transferred to a flask and the final volume completed with distilled water.

Table 1 shows the quantities of each rare earths and yttrium oxides used for the preparation of a synthetic solution based on leach liquors from a Brazilian monazite (Awwal & Filgueiras, 1988).

Table 1
Composition of species present in the sample used in the tests.

Rare earth oxide	La_2O_3	Pr_6O_{11}	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3	Tb_4O_7	Dy_2O_3	HO_2O_3	Er_2O_3	Y_2O_3
%	42.04	9.74	34.94	4.84	0.64	3.04	0.74	0.94	0.44	0.44	2.24

All the rare earth compounds were supplied by Nuclear Industries of Brazil S.A. – INB/Caldas plant in the state of Minas Gerais. The absence of cerium in the synthetic liquor was designed to simulate a liquor from which cerium had been previously removed by precipitation.

The extraction system was com- posed of organic solutions of DEHPA (Di-(2-ethylhexyl)phosphoric acid), in different concentrations. The dilution was realized in isoparaffin17/21. Isoparaffin

17/21 is a commercial type of kerosene and it was used without any previous treatment.

Concentrations of rare earth in the aqueous phases were determined by optical emission spectrometry with inductively coupled plasma – ICP-OES (Agilent), and the concentrations of the organic phase were determined by mass balance. The pH was measured by a pHmeter DIGIMED.

Replicate experiments were carried out for each condition.

2.2. Experimental procedure
2.2.1 pH on extraction

The tests were performed varying the initial pH of the liquor to investigate the influence in the percentages of extraction and separation factor. The pH of the liquor was initially set to a value determined in each test with addition of HCl 6.0 mol/L.

The experiments were conducted using 50 mL of aqueous and organic solutions (phase relationship 1/1). The concentration of organic phase was 20% v/v (0.6 mol/L). The extraction tests were performed in Erlenmeyer flasks under agitation of 250 rpm in a reciprocal shaker (IKA), 15 minutes and at room temperature. After this time the solution was put at rest for 40 minutes in a separation funnel for the separation phase.

2.2.3 Extractant concentration

These tests were performed to investigate the influence of the concentration of extractant in the organic phase (5 - 25% v/v or 1.5 – 0.75 mol/L) on the percentage of extraction and separation factors. The tests followed the same methodology described in section 2.2.1, using 50mL of aqueous and organic solutions and the initial pH of the aqueous solution was adjusted to 1.0.

2.2.4 Reaction time

The time influence (between 15 and 240 seconds) on the percentage of extraction was studied. In all tests, the pH was maintained at 1.0 in aqueous solution (50 g/L RE total). A volume of 50mL of aqueous and organic solutions wasused. The tests were also conducted in a beaker with magnetic stirring.

2.4 Extraction isotherm

These tests were performed to construct the McCabe-Thiele diagram for determining the number of stages required in a circuit of extraction for the separation of heavy rare earths from other lighter elements. Seven tests were performed at three different pH values (0.5, 1.0 and 1.5) varying the ratio O/A from 1/3 to 1/5. The tests were conducted following the same methodology of the other previous tests.

2.5 Continuous experiments

The continuous counter-current experiments were carried out in a sequence of mixer-settler stages, with mixers of 180 mL and settlers of 380 mL. Six stages for extraction were used as shown in Figure 1. The experiment was conducted under the following conditions: O/A ratio 2/1; Initial pH of the liquor 1.0; Initial concentration of liquor 50 g/L for total rare earth and extractant concentration 20% v/v.
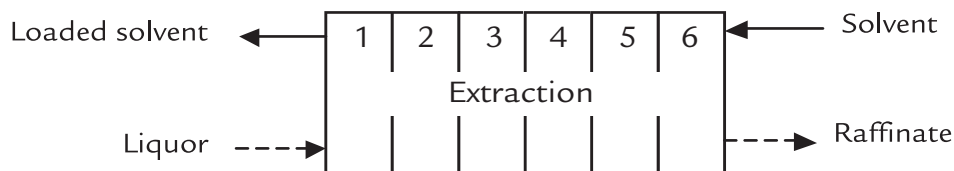

Figure 1
Proposed flow diagram illustrating the successive extraction.

3. Results

3.1 pH extraction

The DEHPA (Di-(2-ethylhexyl) phosphoric acid) is a kind of typical organic phosphoric acid extractant, widely used for rare earth separation because of its higher extraction efficiency. This reagent is a liquid cationic extractant and the metal is exchanged by the hydrogen ion of its hydroxyl group. In general, on industrial solvent extraction application concentrations, the DEHPA form dimmers in kerosene solutions (Hirashima, *et al.* 1982;Lundqvist *et al.* 1983).

Figure 2 shows the performance of extraction of light elements and samarium by DEHPA as a function of initial aqueous phase pH. The extraction efficiency at an equal volume of organic and aqueous phases is commonly defined by:

(1)

$$\text{Extraction (\%)} = 100 \times [M]_{org}/[M]_0$$

where $[M]_{org}$ is the concentration of metal in organic phase and $[M]_0$ is the concentration of metal in initial aqueous phase. As expected, the extraction increases with increasing aqueous pH.

It was observed that at pH 1.0, considerable separation between the light elements and Sm was obtained. This reveals the much stronger affinity of Sm to that of LREE. The preference for the DEHPA extraction of rare earth elements increases with increasing atomic number.

The distribution ratio (D) was calculated as the ratio of the concentration of metal present in the organic phase

$([M]_{org})$ to that in the aqueous phase $([M]_{aq})$ at equilibrium:

$$D = [M]_{org}/[M]_{aq} \tag{2}$$

From the D value, theseparation fac- tor (F) between two metals (1 and 2) can be calculated by:

$$F_{1-2} = D_1/D_2 \tag{3}$$

It is of considerable interest to quantitatively compare the separation ability. The values of the separation factors for the pair of elements Sm-Nd are represented in Figure 3. We can observe that an increase in pH tends to increase the separation factor for the pairs tested with the exception of pair Pr/Nd that remains unchanged. There was a slight decline in the separation factor for the pair Nd/La in the final values of pH tested. The separation factor values calculated confirm the optimum pH value to be between 0.8 and 1.0, where allocated was the highest distribution coefficient of the pair Sm/Nd, indicating a better separation of LREE from the other elements. The small values for the separation factor obtained for the other two pairs analyzed (Pr/La and Nd/Pr) indicates the difficulty in separating these elements, in particular for Nd/Pr.
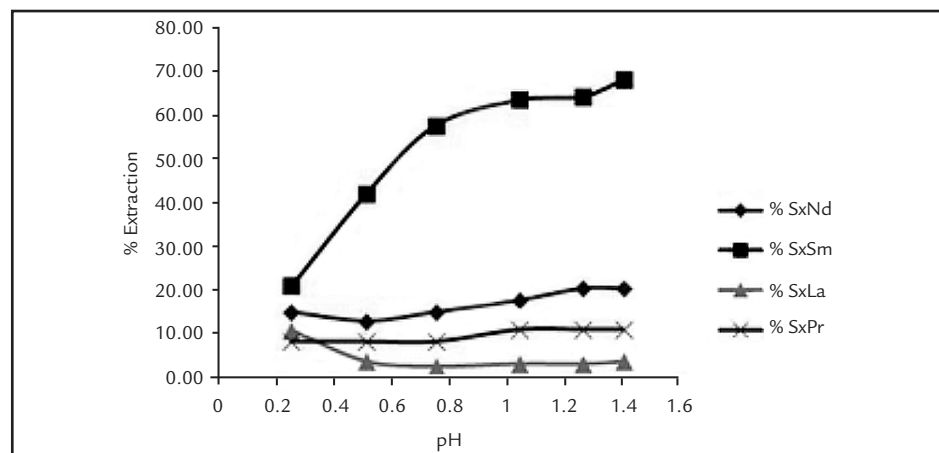

Figure 2
Extraction efficiencies of La(III), Pr(III), Nd(III) and Sm(III) from system DEHPA-Isoparaffin 17/21 at different initials pH.
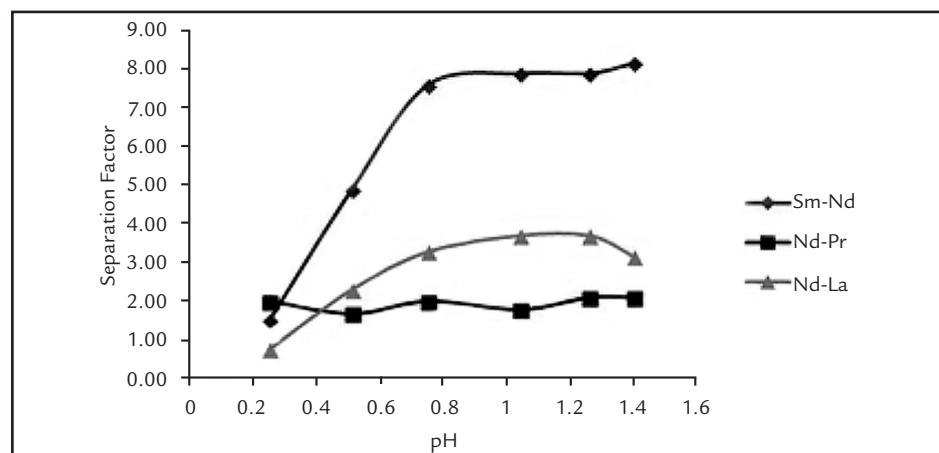

Figure 3
Influence of pH in the separation factor.

3.2 Extractant concentration

This step aims to verify the effect of working extractant concentration - DEHPA - in percentage of extraction of REE and Sm. From the extraction data, it was possible to observe the separation factors for the pair Sm/Nd, and they are represented graphically in Figure 4. From a concentration of 15% of DEHPA, no increase in the separation factor was ob-served. It is believed that the observed fact relates to the formation of complex species extracted. It is known that acid extractants of a chelating nature or monobasic such as DEHPA release a hydrogen from each molecule that combines with the metal extracted. The number of molecules of extractant involved in the formation species extracted depends, among other things, onthe oxidation state or the co-ordination number of the metal ion in solution. Thus the volume occupied by these species in the organic phase can be a limiter to promote extraction.

The best separation factors were obtained in the concentrations between 15 and 20% (0.45-0.60 mol/L).

3.3 Reaction time

The different times of extraction evaluated in this test, and the percentage of extraction are shown in Figure 5. The chemical equilibrium of extraction is reached very quickly with no significant difference in the percentage of extraction after 30 seconds. In subsequent experiments, a contact time of 15 minutes is adopted to ensure complete equilibration.

3.4 Extraction isotherm

The isotherms were plotted in the three pH values, 0.5, 1.0 and 1.5, with reference to the element Sm, and the curves can be observed in Figure 6. However, only the McCabe-Thiele isotherm at 1.0 pH will be discussed in detail to determine the number of theoretical stages required for the pilot plant. In Figure 7, notice that the isotherm at pH 1.0 already has some operating lines. For example, with feed liquor at around 1.6 E-2 mol/L Sm (corresponding to a liquor 50 g/L total TR) and a line operation of O/A equal at 1/2, two stages of extraction can be determined.

The first point of the curve, in reality is not an experimental point but rather a continuation of the trend line in order to mark the beginning of the operating line.

It should also be noted that the curve is shifted to the right, meaning that case one still likely have residue of Sm in the raffinate.

Figure 4
Effect DEHPA concentration on Separation factor between LREE in Isoparaffin 17/21 diluent. Experimental conditions: aqueous phase concentration in Table 1 and A/O ratio = 1.
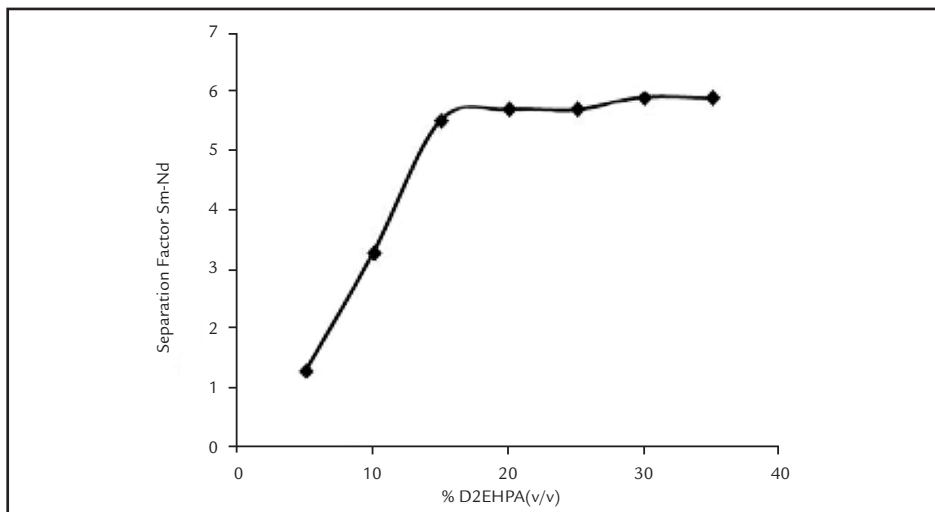

Figure 5
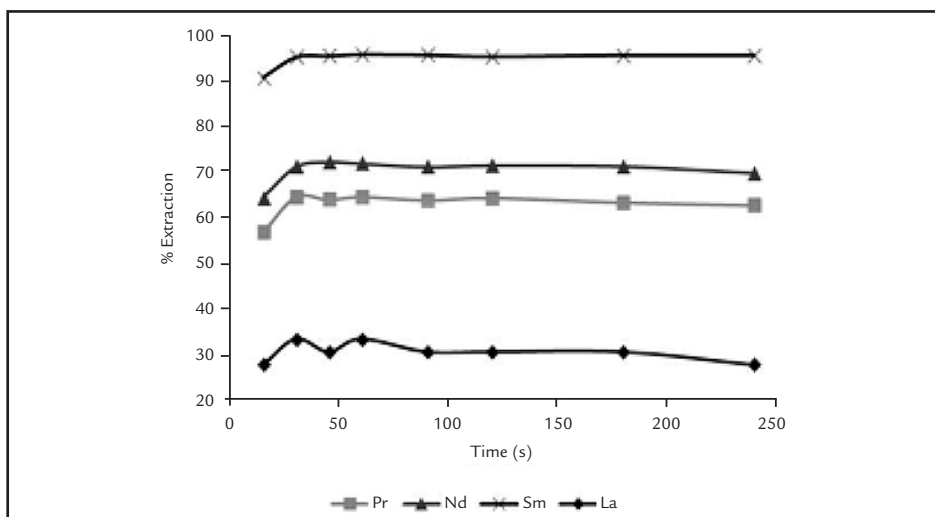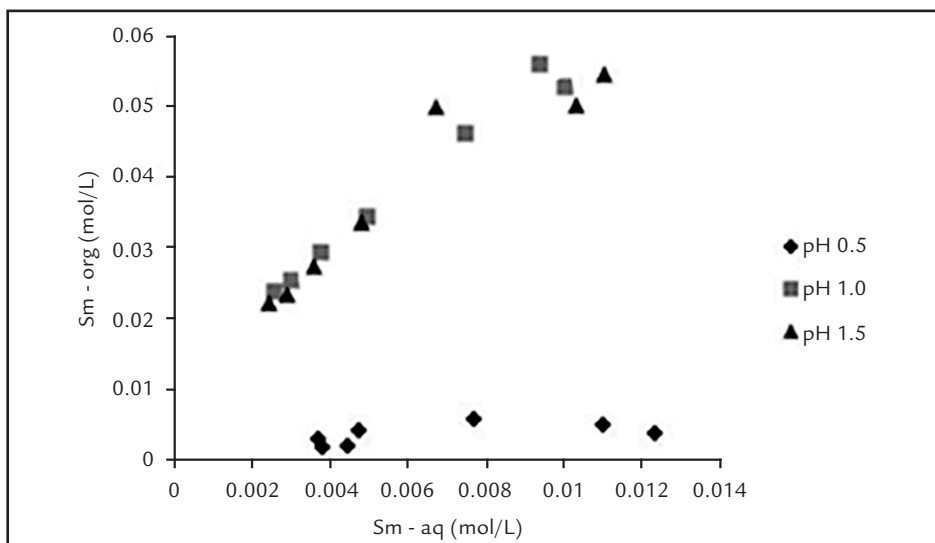Reaction kinetics of extraction of some LREE and Sm.

Figure 6
Isotherm for Sm.
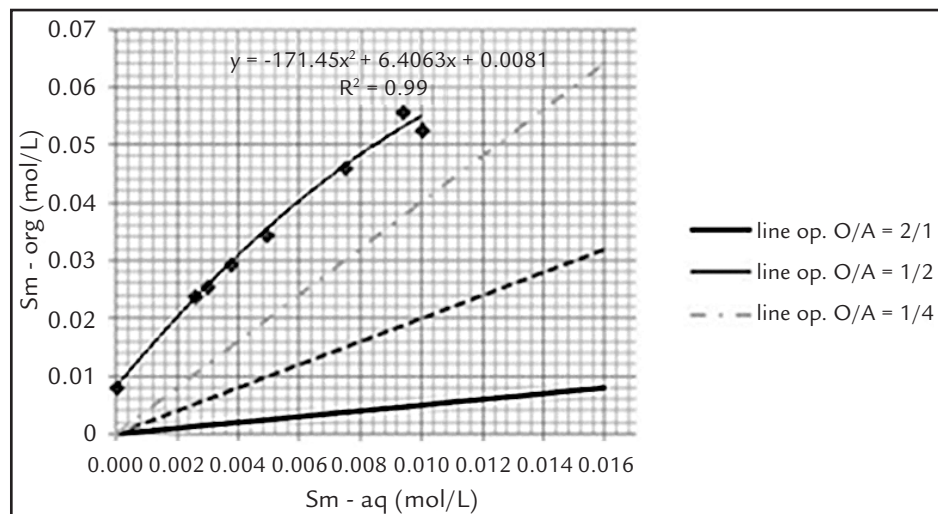
$$y = -171.45x^2 + 6.4063x + 0.0081$$
$$R^2 = 0.99$$

Figure 7
Determination of the
number of extraction stages.

3.5 Continuous experiments

Figure 8 shows the results of average extraction by stage, for the elements La, Pr, Nd, Sm and Gd for two days of operation. We highlight the good extractions Sm and Gd in the first stage, while the other metals, the light ones, feature extraction increased over the subsequent stages. With these observations, we note that the separation factor between the medium and light REE will decrease along the circuit.
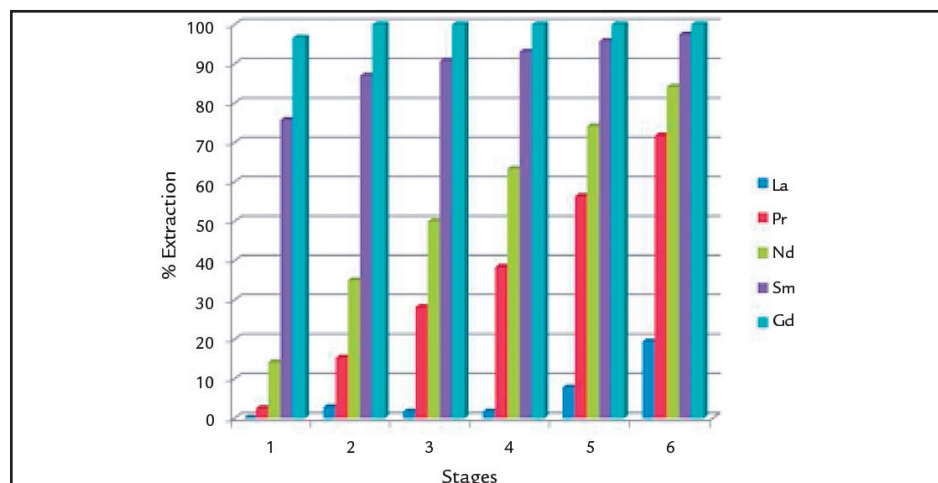

Figure 8
Analytical results
of the pilot plant, by stage.

4. Conclusions

This paper presents results for the analysis of technical indexes for separating light REE from the medium and heavy REE, in hydrochloric media, by solvent extraction. The system DEHPA-Isoparaffin was used as extractant and the spent liquor was produced in the laboratory by dissolving oxides REE in HCl in order to simulate a liquor originating from monazitic ores, free of Ce. The following parameters were determined at pH of work extractant concentration (20%), reaction time, loading of the organic and number of extraction stages.

The extraction increases with increasing aqueous pH, particularly for Sm. It was observed that at pH 1.0, considerable separation between the light elements and Sm was obtained. The separation factor calculated confirm the optimum pH value between 0.8 and 1.0, where the highest allocated distribution coefficient was the pair Sm/Nd, indicating a better separation of LREE for the other elements. From a concentration of 15% v/v of DEHPA, no increase in separation factor was observed. The best separation factors were obtained in the concentrations between 15 and 20% v/v.

The chemical equilibrium of extraction is reached very quickly with no significant difference in the percentage of extraction after 30 seconds.

McCabe Thiele diagram for the separation of LREE of the HREE was plotted and the number of theoretical stages can be drawn from the different operating line. The result of the continuous circuit presents similarities with the information showing the possibility of separation for these elements.

5. Acknowledgements

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