



Study on separation of heavy rare earth elements by solvent extraction with organophosphorus acids and amine reagents



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ABSTRACT

The present work describes a study of the separation of rare earth elements (REE) from heavy REE concentrate through solvent extraction. Seven extractants were investigated: three organophosphorus acids (DEHPA, IONQUEST[®]801 and CYANEX[®]272), a mixture of DEHPA/TOPO (neutral ester) and three amines (ALAMINE[®]336, ALIQUAT[®]336 and PRIMENE[®]JM-T). The organophosphorus extractants were investigated in hydrochloric and sulphuric media whereas the amines performance was assessed in a sulphuric medium. The variables investigated were: concentration of the extractant agent, aqueous phase acidity, aqueous/organic volumetric ratio, contact time, stripping agent concentration (hydrochloric acid solution) and the selective stripping step. In the extraction step, the best separation factors for the adjacent elements were obtained with DEHPA and IONQUEST 801. For 1.0 mol L⁻¹ DEHPA in an initial acidity of 0.3 mol L⁻¹ H⁺, the separation factor was 2.5 Tb/Dy, 2.1 Dy/Ho, 1.9 Ho/Er, 2.0 Ho/Y and 1.1 Y/Er; for 1 mol L⁻¹ IONQUEST 801 in 0.3 mol L⁻¹ of H⁺ it was 2.7 Tb/Dy, 2.4 Dy/Ho, 2.1 Ho/Er, 2.1 Ho/Y e 1.5 Y/Er. The study concluded that for the extractants investigated, IONQUEST 801 is the most indicated for the separation of heavy REE because it has lower affinity with the REE compared to the affinity of DEHPA/REE, which makes the strip of the REE from Ionquest 801 easier than from DEHPA. Moreover, the number of stages necessary for the stripping of the REE from IONQUEST 801 is much lower than that observed when DEHPA is employed.

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1. Introduction

The rare earth elements (REE) are important in many fields of advanced materials science and their application in material industries has increased significantly. As result their separation

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and purification have gained considerable importance in the last decades in order to meet demands. Studies into solvent extraction of individual REE have been extensively carried out with the use of various extractants in different media, however, only relatively few investigations are practical considering industrial application (Gupta and Krishnamurth, 2005). The researches address cationic exchanger extractants such as di-2-ethylhexyl phosphoric acid (DEHPA) and 2-ethylhexyl mono (2-ethylhexyl) ester phosphonic acid IONQUEST® 801 and carboxylic acids; neutral extractants, such as tri-n-butyl-phosphate (TBP); and anionic extractants, such as trialkyl-methyl-ammonium-chloride (ALIQAT® 336) (Gupta and Krishnamurth, 2005).

It usually takes a considerable number of separation stages in a counter-current circuit mode to produce a highly purified REE. The efficiency of the extraction of the REE by organophosphorus extractants like DEHPA and IONQUEST 801 follows the order: La < Ce < Pr < Nd < Sm < Eu < Gd < Tb < Dy < Ho < Er < Tm < Yb < Lu, i.e. it rises as the atomic number of the elements increases, whereas for anion exchange extractants such as amines like PRIMENE® JM-T an inverted order applies (Sato, 1989; Morais and Ciminelli, 2007). IONQUEST 801 was applied in order to produce a nuclear grade dysprosium oxide through a dual cycle counter-current solvent extraction in a circuit comprising 54 stages (Anitha et al., 2009). Dy and Tb were simultaneously purified from a Dy concentrate by using IONQUEST 801 as the extractant. The separation factors were determined experimentally: 14.1 Tb/Gd, 2.7 Dy/Tb, 1.8 Ho/Dy, 3.20 Y/Dy and 4.16 Er/Dy (Mishra et al., 2000). Michelsen and Smutz (1971) studied the separation of Y, Ho and Er in hydrochloric acid medium using DEHPA as extractant and an equilibrium pH of 0.1 (final acidity of 1.0 mol L⁻¹ H⁺). The separation factors obtained for Er/Y, Y/Ho and Er/Ho were 1.39, 2.02 and 2.81, respectively. Sato (1989) using the system RE³⁺ – HCl – DEHPA, obtained the following separation factors: 1.42 Tb/Dy, 1.76 Tb/Ho, 2.98 Tb/Er, 1.24 Dy/Ho, 2.10 Dy/Er and 1.70 Ho/Er. Gschneidner (1980) studied the extraction of the REE using IONQUEST 801 as extractant in hydrochloric acid medium. The separation factors obtained by Gschneidner (1980) were: 2.0 for Tb/Dy, 2.1 for Dy/Ho and 2.1 for Ho/Er. Thakur (2000) investigated the extraction of the heavy REE for both DEHPA–HCl and IONQUEST–HCl systems. For DEHPA–HCl the separation factors obtained were: 2.11 Tb/Dy, 1.94 Dy/Ho, 1.91 Y/Ho e 1.18 Er/Y and for IONQUEST–HCl were: 2.71 Tb/Dy, 1.80 Dy/Ho, 1.78 Y/Ho e 1.30 Er/Y.

In all studies cited before, the authors investigated the separation factor in the extraction step. The separation of the REE occurs in the association of the extraction and scrubbing steps. The aim of this work is to determine the best conditions to separate the heavy REE with determination of the separation factors in steps of extraction and stripping. The process variables such as feed acidity, REE concentration, phase ratio, contact time, extractant concentration and selective Tb stripping as well as the stripping conditions of the other heavy REE have been optimized in a batch scale.

2. Experimental

2.1. Materials

Commercial extractants and organic solvents were used without any further purification. The extractants DEHPA – 97 wt% (di

2-ethyl hexyl phosphoric acid) and IONQUEST® 801–96.5 wt% (2-ethyl hexyl phosphonic acid mono-2-ethyl hexyl ester) were supplied by Albright & Wilson Americas Inc. CYANEX® 272–99 wt% (Bis-2,4,4-trimethylpentyl-phosphinic acid) and TOPO (trioctyl phosphine oxide) were supplied by Cytec do Brasil Ltda. The amines (PRIMENE® JM-T – 98 wt%, ALAMINE® 336 – 98 wt% and ALIQUAT® 336 – 98 wt%) were supplied by Rohm and Haas Company. The TRIDECANOL 95 wt% used as a modifier agent for the amine extractants, were supplied by “Cognis do Brasil Ltda” and EXXSOL®-D100 (purified kerosene), used as diluent for all extractants, was supplied by Exxon Chemicals Ltda.

The sulphuric and hydrochloric acids (H₂SO₄ and HCl) used in the experiments were of analytical grade and the aqueous solutions were prepared with distilled water. Before this study, the REE liquor obtained from the monazite chemical treatment was fractioned into light, medium and heavy groups and stored in a carbonate form by the “Indústrias Nucleares do Brasil S.A.” – INB, that supplied the concentrate of the heavy RE carbonate used in this study. In order to prepare the REE liquors, the carbonate was dissolved with hydrochloric or sulphuric acid solutions. Table 1 presents the content of the REE in the carbonate and in the hydrochloric and sulphuric liquors.

2.2. Methods

The effect of seven extractant agents on the rare earth separation factor was investigated: three organophosphorus acids (DEHPA, IONQUEST® 801 and CYANEX 272), three amines (ALAMINE 336, ALIQUAT 336 and PRIMENE JM-T), and a mixture of an organophosphoric acid (DEHPA) with neutral ester (TOPO). The organophosphorus extractants were investigated in both hydrochloric and sulphuric acid media; the amines were investigated in sulphuric acid medium and, the mixture of DEHPA and TOPO in hydrochloric acid medium. The amines were investigated just in sulphuric acid medium due to the amines extract anionic and neutral species and these species are not formed in hydrochloric acid medium (Morais and Ciminelli, 2007).

Extraction, selective stripping and stripping experiments were carried out in a 150 mL beaker under mechanical agitation at room temperature (25 ± 1 °C) using equal volumes (20 mL) of aqueous and organic phases. After contact, the aqueous/organic mixture was transferred to a separation funnel and the phases were collected separately. The metal content in each phase was determined by an energy-dispersive X-ray spectrometer (KEVEX system) (Morais and Ciminelli, 2007). Replications prepared from randomly chosen experiments indicated an experimental error of around 5% at 95% of confidence level for both steps.

3. Results

3.1. Extraction

The concentration of the extractants used was 1.0 mol L⁻¹ except for the TOPO in the mixture with DEHPA, which was 0.25 mol L⁻¹. The total RE concentration in the feed was 30 g L⁻¹ and the pH was 1.0. The results of these experiments as percentage of extraction are shown in Table 2.

Table 1
REE content in carbonate, hydrochloric and sulphuric liquors.

Content	Sm	Eu	Gd	Tb	Dy	Ho	Er	Y
RE carbonate (%)	0.009	<0.003	0.043	1.96	7.59	0.92	1.61	24.4
^a RE hydrochloric liquor (g L ⁻¹)	<0.004	<0.004	0.32	4.42	16.3	1.57	3.06	55.5
RE sulphuric liquor (g L ⁻¹)	<0.004	<0.004	0.07	1.00	4.36	0.53	0.87	19.5

^a Mother solution.

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