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Study of the Separation of Samarium and Europium Through Solvent Extraction

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Abstract: The growing importance of rare earth elements (REEs) in recent decades is due to the large number of high technology applications. Currently, the separation of the REEs in industry is carried out mainly by solvent extraction (SX), and among the most common types of extractant are organophosphorus acids. The separation of adjacent rare earth elements is a major challenge due to the similarity in their chemical behavior, resulting in low selectivity of the extraction process. The addition of lactic acid in the extraction system can improve the extraction and selectivity of separating the elements europium (Eu) and samarium (Sm). The objective of this work was to compare the continuous solvent extraction of Sm and Eu with or without lactic acid in the extraction system. Continuous solvent extraction experiments showed that the addition of lactic acid favored extraction and selectivity of Sm/Eu separation. The best performance was achieved with a mixture of P507 (8%), D2EHPA (2%) and 0.3 mol L^{-1} of lactic acid, at pH 3.0, resulting in 96.5% recovery of europium in the organic phase. Future experiments will focus on the scrubbing of the loaded organic phase produced in the extraction stage.

Key words: samarium, europium, solvent extraction, rare earth elements

1. Introduction

Rare earth elements (REEs) are essential to high-technology industries. Among their most important applications are the manufacture of catalysts of chemical reactions such as crude oil cracking, lasers, special metal alloys, and magnets to generate high-intensity magnetic fields (used in mobile devices), hard drives for computers, aerogenerators and electric motors. These applications are expected to expand dramatically with the progressive shift from reliance on fossil fuels to greater use of renewable energy sources, such as wind and solar power, including the growing use of electric and hybrid vehicles [1].

Solvent extraction is the most widely employed technique to separate REEs, and organophosphorus acids are the most common extractants used industrially [2]. The separation of REEs by solvent extraction has been studied in recent years at the Center for Mineral Technology (CETEM) from Brazil. CETEM is a Research Center under the Ministry of Science, Technology, Innovation and Communication. These studies have focused on, among other topics, the separation of light and heavy REEs [3] and the separation of light REEs employing organophosphorus acid extractants [4, 5].

A research project was recently started at the CETEM involving the separation of medium and heavy REEs from a chloride liquor of these elements. In a previous study, batch solvent extraction tests were performed to define the best conditions for separation of samarium and europium (pH of the feed solution; concentration, saponification degree and pH of the extractant; and concentration of lactic acid in the aqueous feed solution) [6, 7]. This work is a continuation of that study for Eu/Sm separation, now starting a new step, analysis of the separation in continuous solvent extraction.

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The rare earth element samarium is mainly used to make permanent magnets of Sm_2Co_{17}, and although samarium magnets are being replaced by less expensive neodymium alloy magnets, they are still valuable due to their superior performance at high temperatures. In turn, europium is employed to make various red phosphors for color monitors and display panels and fluorescent lamps. Its luminescence is also valuable in medical, surgical and biochemical applications [1].

The objectives of this study were to investigate the continuous separation of the REEs europium and samarium using organophosphorus acids. In particular, we determined the number of stages and the A/O ratio for continuous solvent extraction of Eu/Sm based on extraction isotherms and application of the McCabe-Thiele method. The continuous solvent extraction of Sm/Eu was carried out in semi-pilot scale with and without the addition of lactic acid in the extraction medium.

2. Material and Methods

2.1 Chemical Reagents

The REE feed solution was prepared from digestion with concentrated HCl PA (12 mol L^{-1}) of the oxides of the respective elements. The concentrations of the REEs in the feed liquor, expressed as oxide, were 15.34 g L^{-1} of Sm_2O_3 and 11.32 g L^{-1} of Eu_2O_3. The elements Sm and Eu present in the chloride medium mainly consisted of free ions (M^{3+}) and chloride complexes, with a smaller quantity of 1 or 2 chlorine atoms (MCl^{-2}, MCl^{2-}). The REE oxides were acquired from Pacific Industrial Development Corporation. The pH of the feed solution was adjusted with solid NaOH PA. The reagents (concentrated HCl, solid NaOH, and lactic acid) were purchased from Vetec Química/Sigma-Aldrich.

The extractants used were P507 (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) and D2EHPA (di-(2-ethylhexyl) phosphoric acid), supplied by Aodachem (China). Commercial kerosene, supplied by Ypiranga (Brazil), was used as diluent.

2.2 Batch and Bench-Scale Solvent Extraction Tests to Obtain the Extraction Isotherm

Batch and bench-scale extraction experiments were carried out to construct the extraction isotherm by varying the volumetric ratio between the aqueous and organic phases (A/O) between 0.125 and 10. The REE and extractant feed solutions were stirred for 30 minutes at 250 rpm in separation funnels. The phase disaggregation time was 30 minutes and the tests were performed at room temperature. The P507 concentration was 0.3 mol L^{-1} (10% v/v), and when using the mixture of P507 and D2EHPA, the respective concentrations were 0.24 mol L^{-1} (8% v/v) and 0.06 mol L^{-1} (2% v/v).

2.3 Continuous Solvent Extraction Tests

The continuous solvent extraction experiments were carried out with countercurrent using mixer settlers arranged in series (mixer volume of 240 mL and decanter volume of 370 mL).

The continuous solvent extraction tests of Sm and Eu were performed under the following conditions:

1) Extractant P507 10% (v/v) and Sm/Eu liquor without lactic acid at pH 2.0.
2) Extractant P507 10% (v/v) and Sm/Eu liquor containing 0.3 mol L^{-1} of lactic acid at pH 3.0.
3) Extractants P507 8% (v/v) and D2EHPA 2% (v/v) and Sm/Eu liquor containing 0.3 mol L^{-1} of lactic acid at pH 3.0.

2.4 Chemical Analyses and Calculation of Parameters

The concentrations of samarium and europium in aqueous solution were determined by UV-Vis spectrophotometry. The absorbance was read at wavelengths of 401 nm and 394 nm for Sm and Eu, respectively.

The concentrations of Sm and Eu in the aqueous phase in each extraction cell were used to determine the

concentration of the organic phase in each cell (Eq. (1)) and the quantity extracted of each element in each cell (Eq. (2)). Besides this, three other parameters were calculated: separation factor (βEu/Sm) and recovery percentages of Sm and Eu in the organic and refined extract (%REC) (Eqs. (3)-(6)).

$$[M]_{N\,(org)} = {}^{A}/_{O}\,x\,\left([M]_{N+1\,(aq)} - [M]_{N\,(aq)}\right) + [M]_{N-1\,(org)} \quad (1)$$

$$\%E = \frac{[M]_{feed} - [M]_{N\,(aq)}}{[M]_{feed}} \quad (2)$$

$$D = \frac{[M]_{extract}}{[M]_{raffinate}} \quad (3)$$

$$\beta_{M1/M2} = \frac{D_1}{D_2} \quad (4)$$

$$\%\ REC = \frac{[Q_m]_{extract}}{[Q_m]_{feed}} \times 100 \quad (5)$$

$$\%\ REC = \frac{[Q_m]_{raffinate}}{[Q_m]_{feed}} \times 100 \quad (6)$$

In those equations, $[M]_{N(org)}$ (g L^{-1}) and $[M]_{N\,(aq)}$ (g L^{-1}) denote the concentrations of each REE at the outlet of cell N in the organic and aqueous phases, respectively; and $[Qm]_{extract}$ (mg min^{-1}) and $[Qm]_{raffinate}$ (mg min^{-1}) represent the mass flows of each element at the outlet of the extraction circuit in the organic and aqueous phases, respectively.

3. Results and Discussion

3.1 Extraction Isotherms

The McCabe-Thiele diagrams of the extraction of Sm and Eu from an aqueous solution of Sm/Eu at pH 2.0 without adding lactic acid are shown in Fig. 1. According to the McCabe-Thiele method, after 7 counter current stages using an A/O ratio of 1/10, the corresponding extraction percentages of Sm and Eu were 66% and 84%.

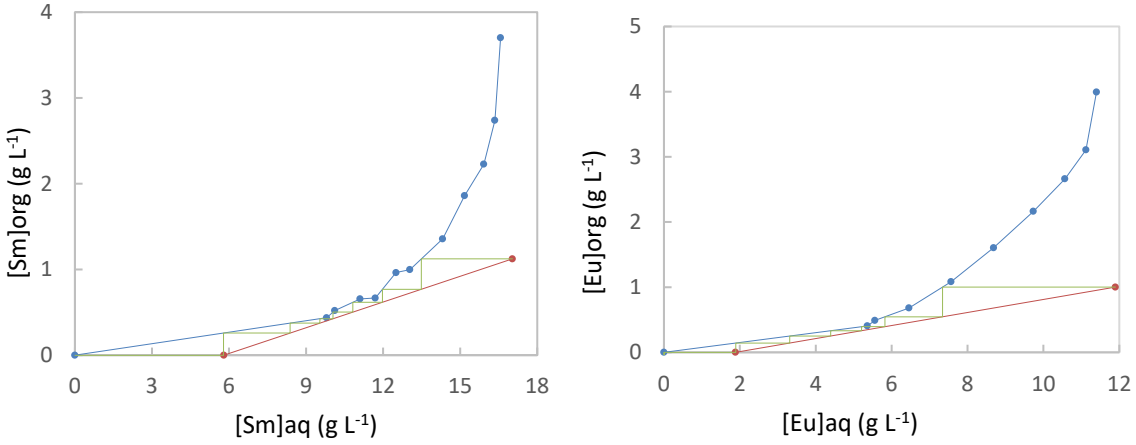

Fig. 1 Extraction isotherms of Sm and Eu obtained in batch solvent extraction tests: Extractant P507 10% (v/v); feed Sm_2O_3 15.34 g L^{-1} and Eu_2O_3 11.32 g L^{-1}; pH 2.0; HLac 0.0 mol L^{-1}.

The McCabe-Thiele diagrams of the extraction of Sm and Eu from the aqueous solution of Sm/Eu containing 0.3 mol L^{-1} of lactic acid at pH 3.0 show that 11 stages were necessary with an A/O ratio of 3/10 to extract 90% and 99% of Sm and Eu, respectively (Fig. 2). The extraction of the REEs increased in the presence of lactic acid. Although the number of stages increased from 7 (without lactic acid) to 11 (with lactic acid), there was an increase in the A/O ratio from 0.1 to 0.3. This three-fold increase means lower extractant cost.

Lactic acid (HLac) is a weak acid that partially ionizes in water, and its pKa is 3.86. At the pH value of the feed solution (pH 3.0), lactic acid is 13.6% ionized in the form of lactate ions (Lac^-) (Eq. (7)). The organophosphorus acids (H_2A_2) hydrogen ions with the ions of the REEs present in the aqueous phase (Eq. (8)). In aqueous solution, the lactate ions combine with the hydrogen ions released by the organic extractant (Eq.

(9)). Thus, the lactate ions neutralize part of the H+ ions and prevent a drastic increase in the acidity of the aqueous solution, enhancing the separation of the REEs.

$$HLac_{(a)} = Lac^{-}_{(a)} + H^{+}_{(a)} \quad (7)$$

$$REE^{3+}_{(a)} + 3\,H_2A_{2\,(o)} = REE(HA_2)_{3\,(o)} + 3\,H^{+}_{(a)} \quad (8)$$

$$H^{+}_{(a)} + Lac^{-}_{(a)} = HLac_{(a)} \quad (9)$$

3.2 Continuous Solvent Extraction

Continuous Sm/Eu extraction was carried out in the absence and presence of lactic acid (Figs. 3 and 4). The number of stages and A/O ratio were determined previously based on the McCabe-Thiele diagrams (Figs. 1 and 2).

The continuous solvent extraction test conditions and the results are presented in Tables 1 and 2.

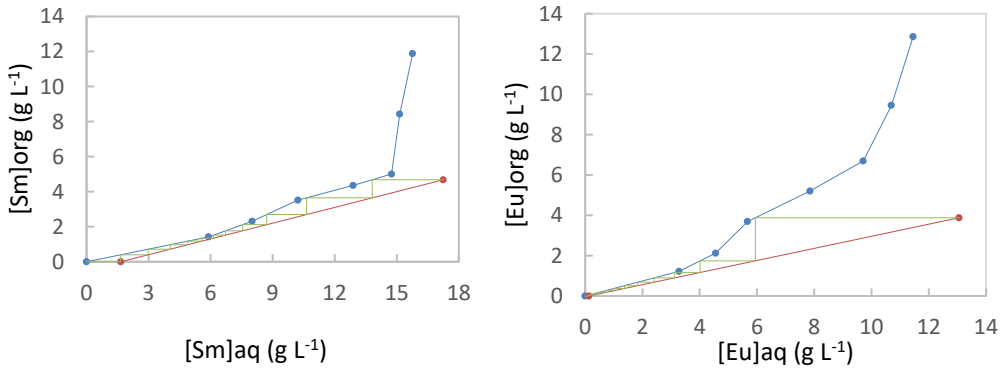

Fig. 2 Extraction isotherms of Sm and Eu obtained in batch solvent extraction tests: Extractant P507 10% (v/v); feed Sm_2O_3 15.34 g L^{-1} and Eu_2O_3 11.32 g L^{-1}; pH 3.0; HLac 0.3 mol L^{-1}.

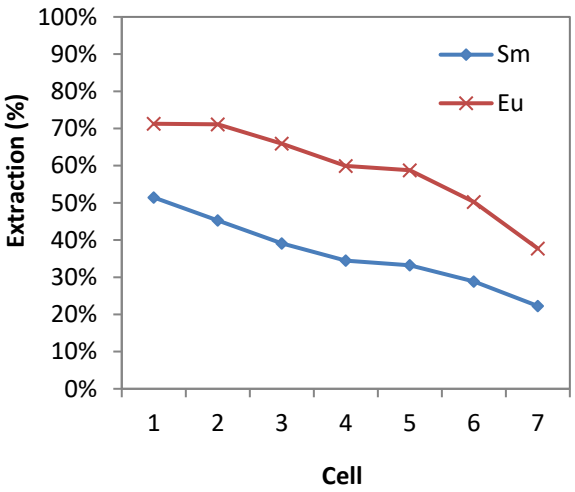

Fig. 3 Cumulative extraction of Sm and Eu obtained in the countercurrent solvent extraction circuit: Extractant P507 10% (v/v); feed Sm_2O_3 15.34 g L^{-1} and Eu_2O_3 11.32 g L^{-1}; pH 2.0; [HLac] 0.0 mol L^{-1}; A/O ratio 1:10.

Despite the higher extraction of Eu with addition of lactic acid (0.3 mol L^{-1}), the element was not completely extracted. Since the objective was to extract 100% of the Eu, a new continuous solvent extraction test was conducted using a mixture of P507 and D2EHPA as extractant. D2EHPA has greater affinity for the REEs than does P507, which increases their extraction. The number of stages, A/O ratio, concentration of HLac, and pH of the feed solution were the same as in the test with P507 at 10% (v/v) in the presence of lactic acid (Fig. 5).

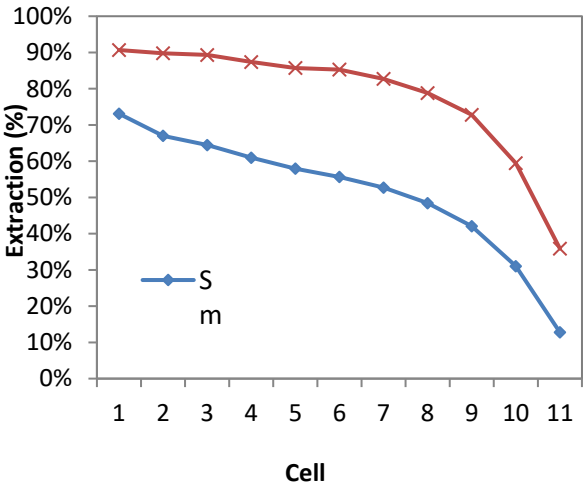

Fig. 4 Cumulative extraction of Sm and Eu obtained in the countercurrent solvent extraction circuit: Extractant P507 10% (v/v); feed Sm_2O_3 15.34 g L^{-1} and Eu_2O_3 11.32 g L^{-1}; pH 3.0, [HLac] 0.3 mol L^{-1}; A/O ratio 3:10.

Table 1 Conditions and results of the continuous solvent extraction tests of Sm and Eu.

Conditions						Results			
Test	Extractant (%)	pH	Number of Stages	A/O	[HLac] (mol L^{-1})	Extraction (%)	Eu/Sm	Extract Composition (g L^{-1})	Extract Purity (%)
1	P507 10%	2.0	7	0.13	0.0	Sm: 51.5 Eu: 71.3	2.48	Sm: 1.16 Eu: 1.14 Total: 2.3	Sm: 50.4 Eu: 49.6
2	P507 10%	3.0	11	0.31	0.3	Sm: 73.1 Eu: 90.7	3.58	Sm: 4.13 Eu: 3.89 Total: 8.01	Sm: 51.5 Eu: 48.5
3	P507 8% + D2EHPA 2%	3.0	11	0.29	0.3	Sm: 94.4 Eu: 95.8	1.36	Sm: 4.90 Eu: 3.65 Total: 8.54	Sm: 57.3 Eu: 42.7

Table 2 Results of the continuous solvent extraction tests of Sm and Eu.

	Results					
Test	Mass Flow of Extract (mg min^{-1})	Recovery in Extract (%)	Composition of Raffinate (g L^{-1})	Purity in Raffinate (%)	Mass Flow of Raffinate (mg min^{-1})	Recovery in Raffinate (%)
1	Sm: 115.8 Eu: 113.9 Total: 229.7	Sm: 57.6 Eu: 76.1	Sm: 8.52 Eu: 3.58 Total: 12.1	Sm: 70.4 Eu: 29.6	Sm: 85.2 Eu: 35.8 Total: 121.0	Sm: 42.4 Eu: 23.9
2	Sm: 165.1 Eu: 155.5 Total: 320.6	Sm: 73.7 Eu: 90.9	Sm: 4.90 Eu: 1.29 Total: 6.19	Sm: 79.2 Eu: 20.8	Sm: 58.8 Eu: 15.5 Total: 74.3	Sm: 26.3 Eu: 9.1
3	Sm: 195.9 Eu: 145.8 Total: 341.7	Sm: 95.3 Eu: 96.5	Sm: 0.55 Eu: 1.00 Total: 1.55	Sm: 64.4 Eu: 35.6	Sm: 9.7 Eu: 5.3 Total: 14.9	Sm: 4.7 Eu: 3.5

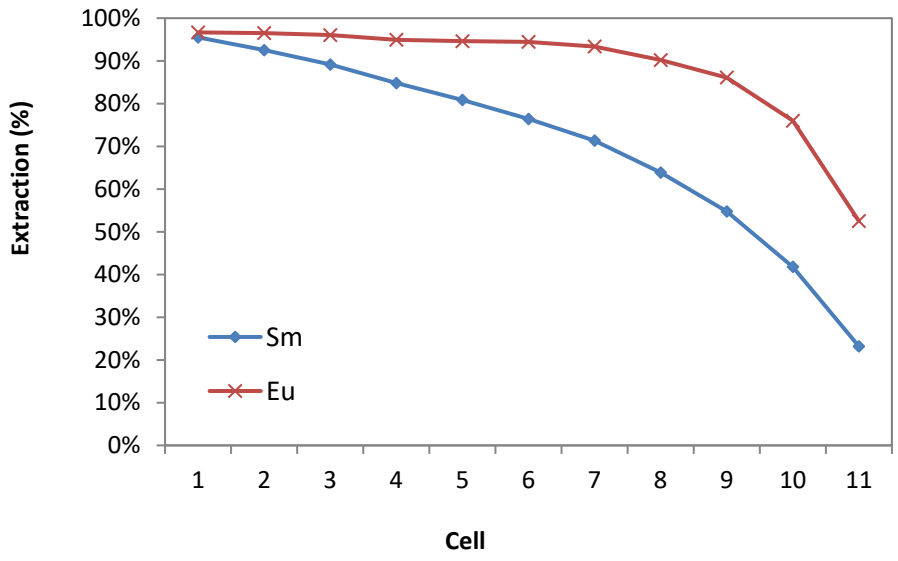

Fig. 5 Cumulative extraction of Sm and obtained in the counter current solvent extraction circuit: Extractant P507 8% (v/v) + D2EHPA 2% (v/v); feed Sm_2O_3 15.34 g L^{-1} and Eu_2O_3 11.32 g L^{-1}; pH 3.0; [HLac] 0.3 mol L^{-1}; A/O ratio 3:10.

The extraction preference of the REEs in this case was Eu > Sm. The cumulative extraction of the lanthanides increased with the addition of lactic acid to the feed solution. The cumulative extraction of Eu increased from 71.0% to 90.7% and that of Sm rose from 51.0% to 73.1% when the lactic acid concentration increased from 0 to 0.3 mol L^{-1}. The Eu/Sm separation factor increased from 2.48 to 3.58

when adding lactic acid to the extractant system. The use of the mixture of extractants D2EHPA (2%) and P507 (8%) increased the extraction rates of Sm and Eu to 94.4% and 95.8%, respectively, but considerably reduced the extraction selectivity by diminishing the Eu/Sm separation factor to 1.36.

The aqueous feed solution used in the SX tests was composed of 57.5% Sm_2O_3 and 42.5% Eu_2O_3. The objective of these tests was to separate the elements Sm and Eu so as to concentrate the Eu as much as possible in the aqueous phase.

Of the three tests conducted, that using P507 10% and HLac 0.3 mol L^{-1} (Test 2, Tables 1 and 2) produced the organic extract with highest concentration of Eu (3.89 g L^{-1}) and obtained the highest mass flow of Eu in the organic extract (155.5 mg min^{-1}). The organic extract with the greatest purity of Eu was obtained in the test without addition of HLac (Test 1), but the concentration of Eu obtained in this test was approximately 3 times lower than that obtained in Test 2. The greatest recovery of Eu in the organic extract was obtained in Test 3 (96.5%).

The SX test using P507 (10%) without adding lactic acid (Test 1, Tab. 1 and 2) produced raffinate with the highest concentration of Sm (8.52 g L^{-1}), greatest mass flow of Sm in the raffinate (85.2 mg min^{-1}) and highest recovery of Sm in the raffinate (42.4%). The greatest purity of Sm in the raffinate was obtained in Test 2 (79.2%) (Tables 1 and 2).

Since in any test conducted it will be necessary to wash the organic phase after the extraction step to remove the Sm present in the extract, the objective should be to remove as much of the Eu as possible from the feed solution so that it is not lost in the raffinate. Therefore, we believe that Test 3 is more suitable to achieve the objectives of separating Eu and Sm, despite its lower selectivity.

4. Conclusion

This study investigated the continuous solvent extraction of the REEs europium and samarium using organophosphorus extractants. The number of stages and A/O ratio of the continuous solvent extraction of Eu and Sm were determined based on extraction isotherms and application of the McCabe-Thiele method. The maximum extraction levels of Eu and Sm were 66% and 84%, respectively, when using 7 extraction stages and an A/O ratio of 0.1. When adding lactic acid, the maximum extraction levels of Sm and Eu were 90% and 99%, respectively, when using 11 stages and an A/O ratio of 0.3. Continuous solvent extraction of Sm/Eu was carried out in a semi-pilot scale with and without the addition of lactic acid in the extraction medium. Under the conditions studied, the best results were obtained using a mixture of P507 (8%) and D2EHPA (2%) with addition of lactic acid in the extractant system. Under these conditions, 96.5% of the europium in the organic phase was recovered. In future experiments we will analyze the washing of the loaded organic extract produced in the extraction step.

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