Diluents Role in Extraction and Possible Separation of Light Rare Earth Elements from Chloride Solutions by using Cyanex[®] 272 used as an Extractant

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Abstract: The present paper deals with liquid-liquid extraction studies and the possible separation of light rare earths (LREs) from chloride solutions. Aromatic diluents such as benzene, toluene and xylene were tested for LREs extraction and possible separation from chloride solutions. Bis(2,4,4-triethylpentyl)phosphinic acid (trade name Cyanex[®] 272) was used as an extractant and dissolved in the diluents. Various experimental parameters such as time effect, influence of pH, extractant concentration variation and maximum loading capacity of the target LREs to Cyanex[®] 272 were examined. Finally, the separation potential of each of the other LREs was calculated, and a suitable diluent system was proposed. The highest separation factors were found using the present systems.

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Keywords: light rare earth elements, chloride solutions, extraction, separation, Cyanex[®] 272

1. INTRODUCTION

Rare earth (RE) elements have similar chemical properties, making them difficult to separate from each other. REs are utilized in clean energy, advanced electronics [1,2] and environmental technology applications [3]. REs such as dysprosium, neodymium, terbium and yttrium are the most important elements for clean energy technologies (including wind turbines, electric vehicles, fluorescent lighting, and photovoltaic cells). The global reserves of REs are in China (38%, 36 Mt), the Former Soviet Union (19%, 19 Mt), the USA (22%, 22 Mt), Australia (5%, 5.4 Mt), India (3%, 3 Mt), and other countries worldwide (22%, 22 Mt). China produced 97% of the world's rare earth oxides (REOs) in 2009, followed by India (2.1%), Brazil (0.5%), and Malaysia (0.3%) [4].

The literature reports that few attempts have been made to develop light rare earth (LRE) processing and separation. Mainly phosphorus-based extractants, 2-ethylhexyl phosphonic acid mono-2-ethyl hexyl ester (HEHEHP, Daihachi Chem-

ical), di-2-ethylhexyl phosphoric acid (D2EHPA) and bis(2,4,4-trimethylpentyl)phosphinic acid Cyanex[®] 272 (from Solvay) have been utilized for LRE processing. Recently studies have been reported of LRE separation using continuous liquid-liquid extraction (CLLE) with HEHEHP extractants, and lactic acid added to the feed aqueous. Adding lactic acid increased Pr and Nd extraction efficiencies from 22% to 92% and 30% to 96% respectively [5]. Another study determined the separation possibilities of heavy metals and LRE's from phosphoric acid solutions using an acidic organophosphorus reagent, Talcher organo phosphorus solvent (TOPS 99) which is more effective at low acidities [6].

A work has been done on saponification of Cyanex[®] 272 to minimize lanthanum co-extraction and it was found that 50% saponification (replacing the H⁺ on the organic with Na⁺) could suppress La extraction. A McCabe-Thiele diagram was generated with 2 mol/L Cyanex[®] 272 in Escald[®] 110 (Exxon) diluent. It predicted that at an A/O ratio of 2, three extraction stages are required for the maximum Pr and Nd extraction. A counter-current extraction (CCE) study using 2 mol/L Cyanex[®] 272 (50% saponified) gave results of 77 mg/L La, 230 mg/L Pr and 657 mg/L Nd in the loaded organic. The co-extracted lanthanum was scrubbed off the

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loaded organic using a Nd solution (780 mg/L Nd, pH 0.5). The scrubbed organic, now holding only Pr and Nd, was stripped with 1 mol/L HCl [8].

In another study, a 10% saponified Cyanex[®] 272 (1 mol/L) in Escald[®] 110 single system as well as a mixed system, were tested with the addition of either Versatic-10 or tri-n-butyl phosphate (TBP). Best results were obtained using 1 mol/L Cyanex[®] 272 (10% saponified) mixed with 0.5 mol/L TBP. With this mixture, the produced loaded organic contained 300.5 mg/L Nd, 95.3 mg/L Pr but only 16.2 mg/L La. The organic was well stripped by 1 mol/L HCl [9].

The diluent effect on rare earths extraction was studied a long time ago (1976), using methyl-n-diheptyl amine dissolved in various diluents such as mesitylene, p-xylene, toluene, benzene and nitro-benzene [10]. The highest separation coefficient 84 calculated in benzene diluent in between cerium and lutetium; whereas, cerium between praseodymium, separation coefficient was 2.3 and cerium and neodymium, separation coefficient was 4.6 reported in benzene diluent. This old report disclosed that solvation energy plays a key role in rare earths extraction and separation [10]. Another more recent attempt (2012) of rare earths extraction, from the behavior of chloride solutions in various diluents, was reported using N,N,N',N'-tetrabutyl-3-oxy-glutaramide (TBDGA) as an extractant system [11]. The extraction efficiency of rare earths followed the order: toluene < n-octane < CCl₄ < CHCl₃. All the extraction reactions were exothermic by nature. Solvent extraction of RARE EARTHS (Pr & Na) from chloride solutions was developed by L1 × 63 of an extractant system [12].

The literature survey led to the further investigation of a viable extractant system for LRE processing. The present study focuses on the effect of the nature of the diluent on extraction, as well as on the separation of lanthanum, cerium, praseodymium and neodymium from each other.

2. EXPERIMENTAL

2.1 Apparatus and reagents

A master synthetic leach liquor was used here, prepared by dissolving LRE oxides in hydrochloric acid solutions. In

every experiment, after pH adjustment with NaOH solution, the adjusted feed solution was separately analyzed. The LRE concentrations on the loaded organic were calculated by mass balance using feed and raffinate assays. The average of all the feed assays was: La-125 ± 5; Ce-21 ± 2; Pr-27 ± 2, and Nd-72 ± 2 mg/L.

For the LRE analysis, an inductively coupled plasma optimal emission spectrometer (ICP-OES, Thermo Scientific, USA, model iCAP 6000 Series) was used. An Orion Star A215 pH/conductivity meter was used for the pH measurements. A shaking incubator (model: SI-300/300R/600/600R) was used for the liquid-liquid extractions. The commercial-grade Cyanex[®] 272 was supplied by Cytec, Canada and used as received. It was diluted to the desired concentration in the three aromatic diluents (GR Grade), benzene, toluene and xylene that were investigated. The diluents were obtained from Aldrich Chemicals. All other reagents used were of analytical reagent grade.

2.2 Liquid-Liquid-Extraction procedure

Equal volumes of the organic mixture being tested and a chloride aqueous phase containing four LRE's (La, Ce, Pr, and Nd) were shaken in a separatory funnel mounted in a shaking incubator. The set-point temperature was 25 ± 1 °C and the shaking speed was 250 rpm. Except for the extraction kinetics experiment, the extraction time was set to 10 min. Separation time after shaking was 30 sec. The feed and raffinate solutions were analysed for LRE content by ICP-OES. The loaded organic LRE concentration was calculated by mass balance.

2.3 Formulas

$$Metal_{organic} = Metal_{feed} - Metal_{raffinate} \quad (1)$$

$$\text{Distribution ratio, } D = Metal_{organic} / Metal_{aq} \quad (2)$$

$$\text{Extraction, \%} = 100 \times D / (D + A/O \text{ ratio}) \quad (3)$$

where D = Distribution ratio (concentration of the metal in organic phase / concentration in aqueous phase)

$$\text{Separation factor, } \beta = D_{M1} / D_{M2} \quad (4)$$

where, DM1 = Distribution ratio of metal 1 and DM2 = Distribution ratio of metal 2

3. RESULTS AND DISCUSSION

3.1 Kinetic studies

Kinetic studies are needed to determine the test conditions for equilibrium studies. Metal extraction processes are governed by the mass transfer and diffusion rates. The very fast kinetics of extraction allows the use of contactors which have retention times on the order of seconds. A series of kinetics tests were conducted under standard conditions ($A/O = 1$, 25°C) and the initial pH condition of the aqueous feed solutions, 5.6 ± 0.1 . Samples were taken at different contact times. The obtained experimental data are presented in Figure 1. From the figure, it is clear that the extraction of all four LRE's reached equilibrium quickly in all three diluent systems. Therefore, in all of the subsequent experiments, extraction time was set to 10 min.

3.2 The Influence of pH

The effect of pH in the range from 1 to 5.6 ± 0.1 was studied in tests using 0.7 mol/L Cyanex[®] 272 dissolved in the three diluents, benzene, toluene or xylene. All contacts were at a phase ratio (O/A) of 1 at 25°C . The LRE synthetic solution feed analysis was (in mg/L): Ce = 26, La = 126, Pr = 27, and Nd = 66.

The obtained results are presented in Figure 2. The four LRE's are adjacent in the lanthanide series in terms of atomic numbers from 57 for La to 58 for Ce, 59 for Pr and 60 for Nd. The extraction efficiency of the four LRE's followed the order from heaviest (Nd) to lightest (La). Extraction was unsatisfactory at pH's below 2.0 and it was concluded that mid-range pH values from 3 to 5.6 (equilibrium pH 2.6 ± 0.2) gave the best extractions of the LRE's in all three diluent systems.

3.3 Effect of the extractant concentration

The extractant concentration was varied in the range between 0.01 and 1.0 mol/L (Cyanex[®] 272) while other parameters were kept the same, as in the work at 0.7 mol/L extractant. The feed pH range studied was 3 to 5.6. The percent extracted increased with increasing extractant concentration. In the case of lanthanum, even 1.0 mol/L of the extractant was not able to extract more than 30% (Figure 2 to 4).

Fig. 1. Kinetics of LRE extraction using 1 mol/L Cyanex[®] 272 in the three diluents tested

Fig. 2. Influence of the pH on the extraction and possible separation of LRE's using Cyanex[®] 272 as an extractant diluted in benzene.

Fig. 3. Influence of the pH on the extraction and possible separation of LRE's using Cyanex[®] 272 as an extractant diluted in toluene.

Fig. 4. Influence of the pH on the extraction and possible separation of LRE's using Cyanex[®] 272 as an extractant diluted in xylene.

3.4 Studies of separation factors (SFs)

The potential for separation of the LRE's is presented in Tables 1 to 3. As noted, extraction of LRE's was generally poor below pH 2. Table 1 presents the benzene diluent system. Separation of Nd from La showed the highest calculated SF of 65.7 at an initial pH of 4 (Eq. pH 2.5) with 1.0 mol/L Cyanex[®] 272. This is expected because Nd is the most strongly extracted and La is the most weakly extracted. Separation factors for Nd/Pr and Nd/Ce were around 2.6-2.8 and 1.3-1.4 respectively, again following the order of elements preferred by the extractant.

In the toluene system, the separation factors were about the same as in the benzene system. The xylene system produced the highest Nd/La separations, but in a pH range where overall extraction was not as good. It was also found that the highest SFs were those of the xylene system (up to SF with a D_{Nd} / D_{La} ratio of 192 at lower pH conditions (not shown here)), followed by benzene (SF with a D_{Nd} / D_{La} ratio of 65.6) and toluene (SF with a D_{Nd} / D_{La} ratio of 30.3). The SF data indicate that the studied benzene and xylene systems are feasible in the pH range of 3 to 5.6; whereas the toluene system at pH 2 is feasible, but under this condition the extraction efficiencies were very low.

3.5 Possible extraction mechanism

Based on the influence of pH and extractant concentration on LRE extraction the processing mechanism can be predicted. The reported literature indicates that the ion-exchange mechanism was observed in many cases [13,14]. Similar extraction behavior was observed in the present study and the following extraction reaction is proposed:

Here, LRE = Light rare earths such as Lanthanum, Cerium, Praseodymium and Neodymium, H_2A_2 = Cyanex 272, n (or) m = Numerical numbers such as 1, 2, 3....

3.6 Loading capacity of the extractant (Cyanex[®] 272)

The loading capacity of the extractant is significant from industrial and commercial standpoints. In the present study, 0.7 mol/L of Cyanex[®] 272 was dissolved in different diluents, in this case benzene, toluene and xylene. They were tested to

Table 1. Separation factor data for Cyanex® 272-benzene system.

Separation of Nd from La, $\beta_{Nd/La} = D_{Nd} / D_{La}$			Separation of Nd from Ce, $\beta_{Nd/Ce} = D_{Nd} / D_{Ce}$			Separation of Nd from Pr, $\beta_{Nd/Pr} = D_{Nd} / D_{Pr}$		
0.5 mol/L Ex	0.7 mol/L Ex	1.0 mol/L Ex	0.5 mol/L Ex	0.7 mol/L Ex	1.0 mol/L Ex	0.5 mol/L Ex	0.7 mol/L Ex	1.0 mol/L Ex
30.8	29.7	36.0	2.6	2.6	2.7	1.2	1.3	1.3
20.7	28.3	65.7	2.6	2.6	2.7	1.2	1.4	1.3
28.9	28.7	34.2	2.4	2.4	2.6	1.2	1.3	1.3

Ex = Cyanex® 272

Table 2. Separation factor data for Cyanex® 272-toluene system.

Separation of Nd from La, $\beta_{Nd/La} = D_{Nd} / D_{La}$			Separation of Nd from Ce, $\beta_{Nd/Ce} = D_{Nd} / D_{Ce}$			Separation of Nd from Pr, $\beta_{Nd/Pr} = D_{Nd} / D_{Pr}$		
0.5 mol/L Ex	0.7 mol/L Ex	1.0 mol/L Ex	0.5 mol/L Ex	0.7 mol/L Ex	1.0 mol/L Ex	0.5 mol/L Ex	0.7 mol/L Ex	1.0 mol/L Ex
19.4	22.8	27.6	2.0	2.1	2.3	1.1	1.1	1.2
17.1	23.5	28.5	2.0	2.3	2.4	1.1	1.2	1.3
28.1	29.7	30.2	2.0	2.2	2.5	1.2	1.2	1.3

Ex = Cyanex® 272

Table 3. Separation factor data for Cyanex® 272-xylene system.

Separation of Nd from La, $\beta_{Nd/La} = D_{Nd} / D_{La}$			Separation of Nd from Ce, $\beta_{Nd/Ce} = D_{Nd} / D_{Ce}$			Separation of Nd from Pr, $\beta_{Nd/Pr} = D_{Nd} / D_{Pr}$		
0.5 mol/L Ex	0.7 mol/L Ex	1.0 mol/L Ex	0.5 mol/L Ex	0.7 mol/L Ex	1.0 mol/L Ex	0.5 mol/L Ex	0.7 mol/L Ex	1.0 mol/L Ex
37.6	37.8	39.0	3.1	3.2	3.2	1.5	1.5	1.5
45.5	40.3	37.1	3.0	3.1	3.0	1.3	1.3	1.3
16.2	22.5	30.6	2.0	2.2	2.6	1.2	1.3	1.4

Ex = Cyanex® 272

Fig. 5. Loading capacity of extractant (Cyanex® 272) of light rare earth elements extraction from chloride solutions.

Fig. 6. Effect of the phase ratio (aqueous / organic) on light rare earth extraction rate from chloride solutions using Cyanex[®] 272 as an extractant system with the diluents of benzene, toluene, and xylene.

assess the maximum loading capacity by adding them simultaneously in an aqueous feed to an identical organic phase, up to the metal saturation point. All three systems, up to fifteen extraction stages (one-by-one), were not saturated by the maximum loading of the LRE's. The total extraction stages tested individually for up to seventeen stages (Fig. 5). Overall, the order of loading capacity extraction efficiency was as follows: toluene > xylene > benzene.

3.7 Effect of the phase ratio on the extraction process for light rare earth elements

Various phase ratios were changed and tested to assess the LRE extraction and potential for separation using Cyanex[®]

272 as an extractant system, and the three different diluents of benzene, toluene and xylene were utilized to determine the best organic phase media. The aqueous versus organic phases were varied from 0.2 to 5.0 at a temperature of 25 °C, and the initial pH condition was 5.6 ± 0.1 (the equilibrium pH was 2.5 ± 0.1), with 0.7 mol/L of Cyanex[®] 272 dissolved individually in the three different diluents of benzene, toluene and xylene to determine the phase ratio effect. For all three diluents, the percentage of extraction of the LRE's increased with an increase in the phase ratio (Figure 6). Except for lanthanum, the remaining three LRE's reached 97%, whereas for lanthanum the highest extraction observed was between 78% and 83%. It started to saturate at the maximum loading of the

Fig. 7. Extraction isotherm for LRE's using Cyanex® 272 as an extractant system with diluents of benzene, toluene, and xylene.

metal from a phase ratio of A/O 3 onwards. Even for metals such as Pr and Nd, A/O 2 is enough of a load to reach the maximum capability of the metal.

3.8 Extraction isotherms for LRE's using Cyanex® 272 as an extractant

The extraction isotherm will give information about the required phase ratio and the number of extraction stages to reach the maximum metal extraction rate from an aqueous to an organic phase. In the present study, the A/O was varied from 1 to 10. The obtained data are presented in Fig. 7. The data indicate that lanthanum was extracted at a negligible rate (and sometimes nil); the present experiment determined the number of extraction stages for Nd, Pr, and Ce. With the Cyanex® 272-benzene system, two extraction stages are required for Nd and Pr when the A/O ratio is 2 for Nd and 2.9 for Pr, whereas the toluene system requires four extraction stages for Nd, three for Pr and two for Ce with corresponding phase ratios of 2, 1.8, and 1. The other system, xylene, requires three extraction stages for Nd with a phase ratio of three and two for Pr or Ce with a phase ratio of 2 (Fig. 7).

4. CONCLUSIONS

Three different types of aromatic diluents were tested in the present study. These were benzene, toluene and xylene, and the difference between each diluent was the addition of one methyl group. A kinetic study concluded that the three diluents could rapidly reach equilibrium within one minute. The influence of the initial pH study concluded that 3 to 5.64 is the better range when compared to a lower range (1 to 2). The extractant concentration was varied from 0.1 to 1.0 mol/L of Cyanex® 272, and the percentage of extraction increased with an increase in the extractant concentration. The maximum loading capacity test found the following order of preference (Nd loading): toluene > xylene > benzene. Overall separation factors were calculated, finding a diluent order as follows: xylene > benzene > toluene. Extraction isotherm studies concluded that two extraction stages with A/O equal to 2 are required in the Cyanex® 272-benzene system for Nd, whereas a phase ratio of 2.9 for Pr was observed in the same system. In the toluene system, four extraction stages are

required for Nd with an A/O ratio of 2 and three stages are required for Pr with, an A/O ratio of 1.8. For the Cyanex[®] 272-xylene system, three extraction stages for an A/O ratio of 3 for Nd and two stages for an A/O ratio of 2 for Pr or Ce are needed. This study indicates that the benzene system is more suitable for good extraction and possible separation. Future studies will concentrate on the development of counter-current and stripping processes. Future studies will also focus on metal extraction enrichment and possible separation of adjacent rare earths.

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