Solvent Extraction of Pr and Nd from Chloride Solution by Mixtures of Acidic Extractants and LIX 63

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Abstract: Mixtures of acidic extractants and LIX 63 were employed to improve the extraction efficiency of Pr and Nd from chloride solutions. The effect of the composition of the extractant mixtures has been studied. The order of metal extraction by single acidic extractant was D2EHPA > PC88A > Cyanex 272 > Cyanex 301. The addition of LIX 63 to the acidic extractants resulted in a synergistic effect, and the strength of the effect was the reverse order of that found for extraction by single extractants. Moreover, mixing of saponified Cyanex 272 and LIX 63 enhanced the extraction, while the addition of Alamine 336 to the mixtures of Cyanex 272 and LIX 63 depressed the extraction.

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1. INTRODUCTION

In recent years, there has been a sharp increase in demand for rare earth elements (REEs), owing to their high consumption in applications in many advanced industries [1, 2]. Due to their importance, it is highly desirable to develop effective methods to recover REEs. Solvent extraction is one of the most efficient methods used in the recovery of REEs, and has been widely studied using various kinds of extractants [3-8].

In the last decades, synergistic solvent extraction systems have drawn considerable attention in efforts to improve the efficiency of REEs extraction [9-16]. Jia et al. [17] reported the synergistic extraction of REEs from chloride solutions by mixtures of bis (2,4,4- trimethylpentyl) dithiophosphinic acid (Cyanex 301) and sec-octylphenoxy acetic acid. The mixtures show significant synergism during the extraction of REEs. The synergistic solvent extraction of REEs using a mixture of sec-octylphenoxy acetic acid and 8-hydroxyquinoline was investigated [18]. Panda et al. [19] studied the solvent extraction of Nd from a nitric acid medium using mixtures of bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) and

trioctylphosphine oxide, TOPO (Cyanex 921) or a mixture of four trialkylphosphine oxides (Cyanex 923) and the synergism reaction were determined by slope analysis. Kumar et al. [20] observed synergism for the extraction of Nd with a mixture of bis(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302) and triisooctylamine (Alamine 308) from chloride solutions, and the synergistic enhancement factor was calculated to be 44.1.

Furthermore, it was found that the addition of 5,8-diethyl-7-hydroxydodecan-6-one oxime (LIX 63) to acidic extractants would result in synergism during the extraction of metals. This phenomenon was first reported in the solvent extraction of Co and Ni by a mixture of di-2-ethyihexyl phosphoric acid (D2EHPA) and LIX 63 [21]. After that finding, the synergistic extraction of Co, Ni and other metals with mixtures of several carboxylic/ organophosphorus acids and LIX 63 was widely studied [22]. In those works, one reagent in the mixture might act as an extractant for some metals, while acting as an adduct for other metals to increase the hydrophobicity of the extracted species [23-25]. For example, LIX 63 acts as an extractant for Cu and Ni and as an adduct for other metals like Co, Zn and Mn [26,27], while the acidic extractants act as an extractant for the latter metals and an adduct for the former metals [23, 28].

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Fig. 1. Extraction of Pr and Nd using single extractants, Cyanex 272, PC 88A, D2EHPA, and Cyanex 301. Concentration of extractants was varied from 0.1 to 0.9 M. [Pr] = 1.17 g/L, [Nd] = 3.28 g/L, and pH = 5.0.

Synergistic extraction systems depend on the nature of the metal ions and the medium. Although many papers have been reported on the extraction of REEs with acidic extractants, such as D2EHPA, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC88A), Cyanex 272, and Cyanex 301, few works have been reported using a mixture of these extractants with LIX 63. In order to increase the extraction percentage of Nd and Pr, mixtures of LIX 63 and acidic extractants (D2EHPA, PC88A, Cyanex 272, and Cyanex 301) were investigated as a function of the composition of the mixture and saponification degree.

2. EXPERIMENTAL PROCEDURES

2.1. Reagents and chemicals

Cyanex 272 and Cyanex 301 were purchased from Cytec Industries, Canada. D2EHPA and PC88A were obtained from Daihachi Chem. Industries, Japan. LIX 63 and Alamine 336 were received from BASF Co, USA. Kerosene (Daejung Co., Korea) was employed as a diluent for the present work. All reagents were used as received without any further purification.

Praseodymium and neodymium chlorides (99.9%) were purchased from Alfa Aesar (A Johnson Matthey Company). The synthetic solutions were prepared by dissolving the

corresponding chloride salts. Concentrated HCl and NaOH solutions were used to adjust the initial pH of the aqueous solutions to 5.0. All other reagents used were of analytical grade.

2.2. Hydrometallurgical treatment of monazite sand

In our previous studies on the recovery of REEs from monazite sand, the sand was digested with NaOH solution followed by leaching with dilute HCl solution in order to dissolve the REEs. The thorium (Th) and other impurities (Fe and Al) in the leach solution were separated from the light REEs by adjusting solution pH. After that, a solution containing Pr-1.17 g/L and Nd-3.28 g/L was obtained after recovery of Ce and La by oxidation precipitation and solvent extraction, respectively [29].

2.3. Solvent extraction procedure

The extraction was carried out by shaking equal volumes of aqueous and organic phases in a screwed cap bottle for 20 minutes with a wrist action shaker (Burrell, USA). The concentration of metal ions in the aqueous phase was determined using ICP-AES (OPTIMA 8300, Perkin Elmer). The concentration of metal ions in the organic phase was calculated by mass balance. These concentrations were used to calculate the distribution ratio (D) (the ratio of the concentration of metal present in the organic phase to that part in the aqueous phase at equilibrium). The extraction percentage ($E\%$) was calculated from the D values by $E\% = D \times 100/[D+1]$.

3. RESULTS AND DISCUSSION

3.1. Extraction of metals by single extractants

In the solvent extraction of metals by mixtures of extractants, the synergistic enhancement factor (R) is defined as $R = D_{\text{mix}}/(D_A + D_B)$, where D_A and D_B are the distribution ratios when a metal ion is extracted by the single extractants A and B, while D_{mix} represents the distribution ratio obtained by the mixture of A and B [30]. $R > 1$ indicates the occurrence of synergism, while $R < 1$ indicates antagonism. In order to calculate the synergistic enhancement factor for the mixtures of extractants employed in

Table 1. Synergistic enhancement factors (R) of Pr and Nd using mixture of acidic extractants (D2EHPA, PC88A, Cyanex 272, and Cyanex 301) and LIX 63. Total concentration of extractants was 1.0 M. $[Pr] = 1.17$ g/L, $[Nd] = 3.28$ g/L, and pH = 5.0.

Mole fraction of Acidic extractant	D2EHPA + LIX 63		PC88A + LIX 63		Cyanex 272 + LIX 63		Cyanex 301 + LIX 63	
	R_{Pr}	R_{Nd}	R_{Pr}	R_{Nd}	R_{Pr}	R_{Nd}	R_{Pr}	R_{Nd}
0.1	1.16	0.93	1.41	1.10	2.27	1.11	0.82	1.15
0.3	1.09	0.99	1.67	1.46	1.13	1.38	1.62	1.62
0.5	1.28	1.28	1.83	1.77	2.33	2.10	6.48	5.23
0.7	1.32	1.30	2.00	2.09	1.30	1.30	1.91	2.12
0.9	0.94	0.94	1.48	1.67	1.28	1.40	1.26	1.58

Fig. 2. Extraction of Pr and Nd by the mixture of D2EHPA and LIX 63. Total concentration of extractants was 1.0 M. $[Pr] = 1.17$ g/L, $[Nd] = 3.28$ g/L, and pH = 5.0.

this study, data on the extraction of Nd and Pr by single extractant is necessary. For this purpose, the extraction of Nd and Pr by single Cyanex 272, PC88A, D2EHPA, Cyanex 272, Cyanex 301 and LIX 63 was investigated.

The composition of that aqueous solution was Pr 1.17 g/L Pr and 3.28 g/L Nd and the initial pH was fixed at pH 5.0. As shown in Fig. 1, the extraction percentage of Pr and Nd increased gradually with the increase in extractant concentration, in the following order: D2EHPA > PC88A > Cyanex 272 > Cyanex 301. The extraction order of the metals in the three organophosphorus extractants is related to the acidity of the extractant. In general, a stronger acid can extract more metals at a given pH. The acidity of the three organophosphorus extractants was in the following order: D2EHPA ($pK_a = 3.24$) > PC88A ($pK_a = 4.51$) > Cyanex 272 ($pK_a = 6.37$) [31]. Although the acidity of Cyanex 301 ($pK_a = 2.61$) was stronger than the three organophosphorus

extractants [32], the extraction percentage of metals with Cyanex 301 was the lowest.

According to HSAB theory (hard and soft acids and bases) [33], REEs are hard acids, while above mentioned extractants are hard bases except for Cyanex 301. Therefore, hard bases (D2EHPA, Cyanex 272, and PC88A) would lead to a higher extraction of hard acids (REEs) compared to a soft base (Cyanex 301). On the other hand, the extraction percentage of metals was zero with LIX 63. Further investigations using mixtures of D2EHPA, PC88A, Cyanex 272, and Cyanex 301 with LIX 63 were explored to examine the possibility of enhancement of the extraction of Pr and Nd.

3.2. Extraction of Pr and Nd with mixtures of acidic extractants and LIX 63

In the current study, extractant mixtures such as D2EHPA + LIX 63, PC88A + LIX 63, Cyanex 272 + LIX 63, and Cyanex 301 + LIX 63 were investigated by varying the concentration of each extractant from 0.1 to 0.9 M, while keeping the total concentration of the mixtures to 1.0 M. The achieved results for these mixtures are depicted in Figs. 2 – 5. Figure 2 presents the extraction of Pr and Nd by the mixture of D2EHPA and LIX 63. The addition of LIX 63 did not enhance the extraction percentage of Pr and Nd compared to single D2EHPA (Table 1). The extraction of Pr and Nd using a mixture of PC88A and LIX 63 was studied and is presented in Fig. 3. As shown in Fig. 3, the extraction percentage of Pr and Nd was greater than that of metals by individual extractants. This means that the addition of LIX 63 to PC88A caused synergism during the extraction of Pr and Nd.

The highest synergistic enhancement factors (2.0 for Pr and 2.1 for Nd) were obtained with mixtures of PC88A and LIX

Fig. 3. Extraction of Pr and Nd by the mixture of PC88A and LIX 63. Total concentration of extractants was 1.0 M. [Pr] = 1.17 g/L, [Nd] = 3.28 g/L, and pH = 5.0.

Fig. 4. Extraction of Pr and Nd by the mixture of Cyanex 272 and LIX 63. Total concentration of extractants was 1.0 M. [Pr] = 1.17 g/L, [Nd] = 3.28 g/L, and pH = 5.0.

63 when the mole fraction of PC88A was 0.7 (Table 1). Figure 4 depicts the solvent extraction of Pr and Nd using the mixture of Cyanex 272 and LIX 63. Although the extraction percentage of metals was low, these mixtures showed synergism. When the concentration ratio of Cyanex 272 to LIX 63 was unity, the highest synergistic enhancement factor was 2.33 for Pr and 2.10 for Nd, respectively (Table 1).

Mixtures of Cyanex 301 and LIX 63 also led to significant synergism during the extraction of Pr and Nd (Fig. 5). The

Fig. 5. Extraction of Pr and Nd by the mixture of Cyanex 301 and LIX 63. Total concentration of extractants was 1.0 M. [Pr] = 1.17 g/L, [Nd] = 3.28 g/L, and pH = 5.0.

highest values of synergistic enhancement factor were 6.48 for Pr and 5.23 for Nd at a Cyanex 301 mole fraction of 0.5 (Table 1). From the above investigations it was found that the addition of LIX 63 to the studied acidic extractants would produce synergism during the extraction of Pr and Nd. In summary, the maximum synergistic enhancement factors were in the following order : Cyanex 301 + LIX 63 (6.48 for Pr, 5.23 for Nd) > Cyanex 272 + LIX 63 (2.33 for Pr, 2.10 for Nd) > PC88A + LIX 63 (2.00 for Pr, 2.09 for Nd) > D2EHPA + LIX 63 (1.32 for Pr, 1.30 for Nd), which is the reverse of the order for extraction by single extractants.

The synergism in extraction may be attributed to the increase in the hydrophobicity of the extracted species due to the replacement of the coordinated water molecules when LIX 63 was added [34]. The synergistic solvent extraction of Pr and Nd using mixtures of acidic extractants ((HA)₂) and LIX63 (HB) can be represented as in [34]:

In our previous work, the addition of Alamine 336 (R₃N) to Cyanex 272 (H₂A₂) enhanced the extraction of rare earth elements [35]. In that work, the maximum synergistic enhancement factors were 14.2 for Pr and 12.2 for Nd at the

Table 2 Effect of the ternary mixtures of Cyanex 272, LIX 63 and Alamine 336 on the extraction of Pr and Nd. Concentration of Cyanex 272 and Alamine 336 was 0.3 M. [Pr] = 1.17 g/L, [Nd] = 3.28 g/L, and pH = 5.0.

Concentration of LIX 63, M	Extraction percentage, %	
	Pr	Nd
0.2	8.1	12.5
0.3	7.5	11.6
0.5	3.8	6.2
0.7	2.9	4.0

Cyanex 272 mole fraction of 0.5. The synergistic effect was caused by the extraction of hydrogen ions released from Cyanex 272 during the extraction of metals. The solvent extraction reaction of Pr and Nd by Cyanex 272 from chloride solution could be represented as [35,36]:

The released hydrogen ions could then be extracted by amine extractants:

In order to increase the extraction of Nd and Pr using the mixture of Cyanex 272 and LIX 63, Alamine 336 was added to this mixture and solvent extraction experiments were done with this ternary extraction system. In those experiments, the concentration of LIX 63 in the mixture was varied, while keeping the concentration of Cyanex 272 and Alamine 336 at 0.3 M. The results are presented in Table 2. The addition of LIX 63 to the mixture of Cyanex 272 and Alamine 336 caused a decrease in the extraction of metals. This might be due to the interaction between LIX 63 and Alamine 336 in the organic phase. The addition of Alamine 336 to the mixture of Cyanex 272 and LIX 63 had a negative effect on the extraction of Pr and Nd.

Another method to increase the extraction of metals is to saponify the acidic extractants. Therefore, a mixture of saponified Cyanex 272 and LIX 63 was tested on the extraction of Pr and Nd. For comparison, single saponified Cyanex 272 was also tested. The concentration of Cyanex 272 was varied from 0.1 to 0.9 M and the degree of saponification

Fig. 6. Extraction of Pr and Nd by the mixture of saponified Cyanex 272 and LIX 63. Total concentration of extractants was 1.0 M and saponification degree of Cyanex 272 was 20%. [Pr] = 1.17 g/L, [Nd] = 3.28 g/L, and pH = 5.0.

of Cyanex 272 was kept at 20%. In the experimental range, when the concentration of Cyanex 272 was higher than 0.5 M, clear phase separation was not observed. The extraction percentage of Pr and Nd with saponified Cyanex 272 increased sharply compared to that with unsaponified Cyanex 272. The extraction percentage of Pr and Nd increased from 20% to 99.2% and 26.8% to 99.4%, respectively (Fig. 6). After mixing with LIX 63, the extraction percentage of Pr and Nd increased from 40.9% to 64.4%, and from 50.8% to 67.0%, respectively, when the mole fraction of saponified Cyanex 272 was 0.3. The highest synergistic enhancement factors were 2.30 for Nd, and 1.96 for LIX 63. The enhancement of the extraction of metals by saponified extractant after adding LIX 63 indicated that LIX 63 acts as an adduct to increase the hydrophobicity of the extracted species.

It is important to point out that the synergism and antagonism caused by the mixtures studied in the present work provide valuable information for understanding the effects of various mixtures. It would be interesting to investigate the interaction between components in the mixtures and the nature of the extracted species by spectroscopic and other advanced methods.

4. CONCLUSIONS

In the present work, Pr and Nd were extracted from chloride solutions using acidic extractants and LIX 63, and the effect of their mixtures was reported. The mixtures of acidic extractants with LIX 63 enhanced the extraction of metals to different extents, and followed the order: D2EHPA + LIX 63 (1.32 for Pr, 1.30 for Nd) < PC88A + LIX 63 (2.00 for Pr, 2.09 for Nd) < Cyanex 272 + LIX 63 (2.33 for Pr, 2.10 for Nd) < Cyanex 301 + LIX 63 (6.48 for Pr, 5.23 for Nd), respectively. This sequence was the reverse of the order of extraction obtained by a single acidic extractant. The addition of Alamine 336 to the mixtures of Cyanex 272 and LIX 63 had a negative effect on the extraction of metals. Mixtures of saponified Cyanex 272 and LIX 63 enhanced the extraction of metals.

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