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Solvent extraction of Pr and Nd from chloride solutions using ternary extractant system of Cyanex 272, Alamine 336 and TBP

Yang Liu [a], Ho Seok Jeon [b], Man Seung Lee [a,*]

[a] Department of Advanced Material Science & Engineering, Institute of Rare Metal, Mokpo National University, Chonnam 534-729, Republic of Korea
[b] Division of Minerals Utilization and Materials, Korea Institute of Geoscience and Mineral Resources (KIGAM), Daejon 305-350, Republic of Korea

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ABSTRACT

Synergistic extraction and separation of Pr and Nd in chloride medium using a ternary mixture containing Cyanex 272, Alamine 336 and TBP has been investigated. Compared to the binary mixture (Cyanex 272 + Alamine 336), the ternary mixture showed a remarkable synergism on metals and increased the separation factor. The highest synergistic enhancement factors were obtained for Pr (17.0) and Nd (14.6). The mechanism of the synergistic extraction reaction and the role of Alamine 336 and TBP in reaction were proposed. Furthermore, metals in the ternary mixture were easily stripped by using HCl or H_2SO_4 solution with lower acidity.

Introduction

Recently the demand for rare earth metals rises sharply because they provide the advanced materials with peculiar physical properties [1,2]. Solvent extraction is now a commonly used technique in industrial processes for the separation and purification of rare earth elements (REEs) due to its high selectivity and significant capital and operation cost savings [3–8]. Among the commercial acidic organophosphorus extractants used in the extraction of metals, such as Cyanex 272 (bis(2,4,4-trimethylpentyl) phosphinic acid), EHEHPA (2-ethylhexyl 2-ethylhexylphosphonate) and D2EHPA (di-(2-ethylhexyl) phosphoric acid), Cyanex 272 shows the best separation efficiency between adjacent REEs [9]. However, the extractability of Cyanex 272 for REEs is low because of its high pK_a value [10–12]. One method to overcome the low extractability of Cyanex 272 is to add an extractant which can form adduct with the extracted species during extraction [13].

The extraction of metals by mixtures of two extractants has attracted much interest owing to the possibility to enhance extraction efficiency and to improve the separation degree. Different kinds of extraction systems, such as mixtures of acidic extractants [14–17], mixtures of neutral extractants [18] and combination of acidic and neutral extractants [19–22], have been applied to the extraction of REEs. According to the synergistic extraction of Nd from nitrate medium using Cyanex 272 and Cyanex 921 (trioctylphosphine oxide)/Cyanex 923 (trialkylphosphine oxide) was studied [23], the addition of neutral extractants exhibits significant synergism on the extraction of Nd. However, the addition of neutral extractants to acidic extractant might cause an antagonistic effect. In the extraction of Y from chloride solutions with the mixture of EHEHPA and Cyanex 921, the addition of Cyanex 921 suppressed the extraction of Y and this might be attributed to the interaction between EHEHPA and Cyanex 921 which hinders the extraction [24].

As mentioned above, the extractants used in synergistic systems are usually composed of a mixture of acidic extractant with a neutral or another acidic one. In applying these extractant mixtures, the hydrogen ion liberated during the extraction of metals with acidic extractants adversely affects the metal extraction. During the recovery of REEs from the leach liquor of monazite sand at Korea, the chloride solution containing Pr-1.17 g/L (0.008 M) and Nd-3.28 g/L (0.023 M) was obtained after recovery of Ce and La by precipitation and solvent extraction, respectively [25]. In our previous work on the extraction and separation of Pr and Nd from this chloride solution [26], we have reported that the mixture of Cyanex 272 and Alamine 336 (tri-octyl/decylamine) or TOA (trioctylamine) showed a synergistic effect on the extraction of Pr and Nd. The synergistic extraction was ascribed to the

* Corresponding author. Tel.: +82 61 450 2492; fax: +82 61 450 2498.
E-mail address: mslee@mokpo.ac.kr (M.S. Lee).

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extraction of hydrogen ions by amines during the reaction and thus to promote the extraction of Pr and Nd by Cyanex 272. However, the separation factor between Nd and Pr by the mixture of Cyanex 272 and Alamine 336 was less than that by single Cyanex 272. Although the synergistic extraction of REEs by the binary mixtures of acidic extractants and tertiary amines have been reported, such as the extraction of REEs by the mixtures of bis(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302) and tri-isooctylamine (Alamine 308) [27], thenoyltrifluoroacetone (HTTA) and TOA [28], and 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one (HPMBP) and TOA [29], the effect of amines was explained as an adduct which increased the hydrophobic character of the extracted metal complexes.

Much attention has been paid on the development of synergistic extraction of REEs by binary mixtures. However, to the best of our knowledge, few works have been reported on the ternary system for the synergistic extraction of REEs. Although some papers have been reported on the ternary systems for the extraction of metals, in most cases, neutral extractant in these ternary systems plays a role as a modifier only [11,30]. According to literatures, the addition of neutral extractants to acidic extractants can lead to synergism or antagonism and the effect depends on the extraction system. This prompted us to investigate a ternary synergistic extraction system involving TBP (tributylphosphate) as a synergist in the extraction of REEs with the mixture of Cyanex 272 and Alamine 336. Hence, in the present work, the effect of adding TBP to the mixture of Cyanex 272 and Alamine 336 on the extraction of Pr and Nd from chloride solutions was examined in an effort to investigate synergistic effect and to obtain improved metal separation compared to those obtained by the binary mixture of Cyanex 272 and Alamine 336. Apart from the synergistic effect caused by Alamine 336 in the binary mixtures, the effect of TBP was different, which increased the hydrophobic character of the extracted metal complexes.

Experimental

Reagents and chemicals

Cyanex 272 (Cytec Inc., 85%), Alamine 336 (BASF Co., 95%) and TBP (Yakuri Pure Chemical Co., Ltd., 99%) were used without purification. The chemical structures of the extractants used in the present work and some important properties of them are listed in Table 1. Kerosene obtained from Daejung Chemicals, Korea was employed as diluent. The synthetic solution containing Pr (0.008 M) and Nd (0.023 M) was prepared by dissolving the corresponding chloride salts (Alfa Aesar, A Johnson Mattery Company, 99.9%) in deionized water. The initial pH of the aqueous solutions was adjusted using concentrated HCl and NaOH solutions. All other reagents used were of analytical grade.

Solvent extraction procedure

Extraction experiments were performed at room temperature by mixing equal volume (20 ml) of organic and aqueous phase in a screwed cap bottle and the mixtures were shaken for 30 min (previous experiments showed 10 min was sufficient to attain the equilibrium) with a Burrell wrist action shaker (model 75, USA). Solution pH values were measured with a pH meter (Orion Star A221 model). Metal concentration in the aqueous phase before and after extraction was determined by ICP-AES (OPTIMA 8300, Perkin Elemer) [31]. Metal concentration in the organic phase was obtained by mass balance. These concentrations thus obtained were used to calculate the distribution ratio (D) (the ratio of the concentration of metal present in the organic phase to that in the aqueous phase at equilibrium), which states the distribution condition of metals between two different phases [32]. The distribution ratio is related to the percent extraction (%E), which was calculated from the D values by using $\%E = D \times 100/[D + (V_{aq}/V_{org})]$, where V_{aq} and V_{org} are the volumes of aqueous and organic phases, respectively [33]. The separation factor (SF) refers to the possibility of separation of two metals from each other, which was calculated from the D values ($SF = D_{Nd}/D_{Pr}$). Two replicate experiments were carried out for each condition and the errors associated with the extraction and stripping percentage varied more or less $\pm$5%.

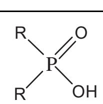
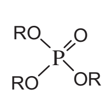
In subsequent sections, the term “binary” represents the mixture of Cyanex 272 and Alamine 336, while the term “ternary” represents the mixture of Cyanex 272, Alamine 336 and TBP.

Results and discussion

Extraction of Pr and Nd by single extractants and mixtures of two extractants

Cyanex 272, Alamine 336 and TBP alone and mixtures containing two of them were tested for the solvent extraction of Pr (0.008 M) and Nd (0.023 M) from chloride solution (pH = 5.02). For this purpose, the concentration of each extractant was varied from 0.1 to 1 M in experiments with single extractants. In our experimental ranges, the percent extraction of Pr and Nd was varied from 2 to 15 and 4 to 22 with single Cyanex 272, respectively, while the extraction of these two metals by single Alamine 336 or TBP was negligible (Fig. 1). Furthermore, studies have been carried out on the extraction of REEs using the mixtures of Cyanex 272 + TBP and Alamine 336 + TBP. The experimental data showed that the extraction of Pr and Nd by Alamine 336 + TBP was also negligible (Fig. 1). In extraction with the mixture of Cyanex 272 and TBP, the percent extraction of REEs decreased with increasing TBP concentration when the concentration of Cyanex 272 was kept at 0.7 M (see Fig. 2). This might be due to the interaction between Cyanex 272 and TBP, which decreases the effective concentration of Cyanex 272 [24,34,35]. It can be said that

Table 1
Chemical structures and properties of extractants.

Extractant	Structure	*R*	Molar mass ($g\,mol^{-1}$)	Density ($g\,cm^{-3}$)	Viscosity (25 °C) (mPa s)	Solubility in water ($g\,m^{-3}$)	Flash point (°C)
Cyanex 272		$CH_2CH(CH_3)CH_2C(CH_3)_3$	290	0.92	14.2	38	108
TBP		$CH_3CH_2CH_2CH_2$	266	0.97	3.7	5.8	146
Alamine 336	R_3N	Tri-octyl/dodecyl	136–144	0.81	10.4	5	97