



Regeneration of a binary mixture of Cyanex 272 and Alamine 336 for the solvent extraction of rare earths elements by treatment with sodium hydroxide solution

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ARTICLE INFO

Article history:

Received 14 October 2015
Received in revised form 3 December 2015
Accepted 19 March 2016
Available online xxxx

Keywords:

Binary mixture
Cyanex 272
Alamine 336
Regeneration
Sodium hydroxide

ABSTRACT

A binary mixture of Cyanex 272 and Alamine 336 has synergism on the solvent extraction of La, Pr and Nd from chloride solution. The binary mixture not only enhanced the extraction percentage of these metal ions but also improved the separation factors between Pr and Nd over La compared to Cyanex 272 alone. However, the stripped binary mixture could not extract the metals owing to the extraction of HCl by Alamine 336 during stripping as well as the interaction between Cyanex 272 and protonated Alamine 336. Although adding TBP to the binary mixture enhanced the stripping of metals from loaded organic, it hardly improved the regeneration of the binary mixture. The treatment of the stripped binary mixture with NaOH solution resulted in the regeneration of the mixture, which was verified by 6 cycles of extraction-stripping-regeneration. The interaction between the constituents in the binary mixture after extraction, stripping and regeneration was analyzed by employing the FT-IR spectra of the mixture.

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1. Introduction

Solvent extraction processes generally consist of extraction, scrubbing, and stripping step. In some cases, degradation of extractants occurs due to oxidation, hydrolysis or other chemical reactions during the solvent extraction process [1]. In order to restore the extraction power of the degraded extractants, regeneration step of the stripped extractants is necessary [2,3]. In the Queensland process for the separation of cobalt and nickel, nickel is selectively extracted from cobalt (III) by hydroxyoxime LIX 84I (2-hydroxy-5-nonylacetophenone oxime) after the oxidation of cobalt (II) to cobalt (III) [2]. Cobalt (III) caused oxidative degradation of the extractant. An additional regeneration step for re-oximation was carried out to maintain the extractant capacity [4,5]. In the recovery of neptunium, uranium and plutonium from nitrate solutions by TBP ((RO)₃PO) in PUREX process, the extractant was degraded by hydrolysis and radiolysis, resulting in the formation of dibutylphosphoric acid ((RO)₂PO(OH)), monobutylphosphoric acid ((RO)PO(OH)₂), and phosphoric acid (PO(OH)₃) in the organic phase [6,7]. Since degraded extractants affect the extraction of metals, degraded TBP was treated by either sodium carbonate or sodium hydroxide in order to convert acidic phosphate species to their sodium salt form and remove them from degraded extractants [8]. Although part

of degraded products could be removed by alkali washing, other degradation products could be accumulated to reduce the extractant performance and then fresh extractants had to be employed to replace the old [9]. Furthermore, in the extraction of metals by saponified extractants, stripping with strong acid may convert the saponified extractant into its acid form, which will decrease the extraction of metals. Therefore, a regeneration step should be employed to convert the acid form of the extractant to the saponified form [10,11].

Recently, synergistic solvent extraction has drawn much attention in the separation of rare earths elements (REEs) because it enhances the extraction percentage and sometimes improves the separation selectivity [12–14]. In order for synergistic solvent extraction systems to be commercially applied, the organic constituents should be chemically stable and reused under expected operating conditions [15]. It has been reported that the addition of acidic extractant to LIX 63 would cause the degradation of LIX 63, and increase in extractant acidity augments the degradation of LIX 63 [16,17]. Binary mixtures of Cyanex 272 and Alamine 336 has shown significant synergistic effect on the extraction of rare earth elements from chloride solution (La (7.56 g/L), Pr (1.17 g/L), Nd (3.28 g/L)) [18]. The synergistic enhancement factors (R) were 8.0 for La, 24.0 for Pr and 22.1 for Nd by using this mixture compared to single Cyanex 272 (the extraction percentage of these three metals by Alamine 336 alone was zero). The separation factors (SF) increased from 6.9 for SF_{Pr/La} and 10.0 for SF_{Nd/La} by single Cyanex 272 to 37.3 for SF_{Pr/La} and 43.4 for SF_{Nd/La} by binary mixture of 0.5 M

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Cyanex 272 and 0.5 M Alamine 336 [18]. This synergism was caused by the extraction of hydrogen ions released from Cyanex 272 during extraction of metals. The extraction reaction can be represented as



where subscript org represents the organic phase. Extracted metals could be stripped from loaded organic by 0.7 M HCl solution. Further work showed that the addition of TBP into the binary mixture of Cyanex 272 and Alamine 336 not only enhanced the extraction of Pr and Nd, but also improved the stripping of them with lower concentration of acid [19].

In our work on the reusability of these binary mixtures on the extraction of REEs, it was found that the extraction percentage of REEs by the stripped mixtures was nearly zero. This problem might be ascribed to the extraction of HCl during stripping. Therefore it is necessary to reduce the amount of the extracted HCl in the stripped mixture after stripping. Normally, a water treatment method might be a good option for the stripping of acid from the amine extractants [20]. However, the extracted acid could not be stripped from Alamine 336 by water [21]. Literature survey shows that stripping of HCl from Alamine 336 could be achieved by sodium hydroxide solution [21]. This might be employed to remove HCl from the stripped binary mixtures in the present work.

In order to investigate the reactions occurring in the mixture, the FT-IR spectra of the mixture together with the variation in the pH of the aqueous solution after stripping and successive extraction was analyzed. From the FT-IR spectra, the interaction between components in the binary mixtures was proposed. The effect of adding TBP to the binary mixture on the stripping and regeneration of the mixtures was also investigated. In the treatment of the stripped binary mixture by NaOH solution, the effect of NaOH concentration on the regeneration of the mixture was investigated. After obtaining an optimum condition for the regeneration of the stripped mixture, cyclic tests on the performance and stability of the regenerated binary mixture were performed on the extraction of REEs from chloride solutions.

2. Experimental

2.1. Reagents and chemicals

Cyanex 272 (85%), Alamine (95%) and TBP (99%) were purchased from Cytec Inc., BASF Co., and Yakuri Pure Chemical Co., Ltd, respectively. Kerosene (Daejung Co., Korea) was employed as a diluent. The chemical structures of these three extractants are presented in Table 1. Stock solutions containing La (7.56 g/L), Pr (1.17 g/L) and Nd (3.28 g/L) were prepared by dissolving their chloride salts (Alfa Aesar, A Johnson Matthey Company, 99.9%) in deionized water. Reagent grade NaOH was purchased from Duksan Pure Chemicals Co. The binary mixtures were prepared by mixing Cyanex 272 and Alamine 336.

Table 1
Chemical structures of extractants used in the present work.

Extractant	Structure	R
Cyanex 272		$\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\text{CH}-\text{CH}_2-$
Alamine 336		$\text{C}_8\text{H}_{21} \text{ } \overline{\text{A}}_{10}\text{H}_{27}$
TBP		$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$

Table 2

Determination of the loading capacity of the binary mixture of 0.5 M Cyanex 272 and 0.5 M Alamine 336 for La, Pr and Nd from chloride solution.

A/O	Metal concentration in loaded organic (g/L)			
	La	Pr	Nd	Total
0.5	0.65	0.56	1.58	1.94
1	0.93	0.98	2.81	4.72
2	1.53	1.37	4.29	7.19
3	1.66	1.55	5.02	8.23
5	1.68	1.57	5.08	8.33

2.2. Solvent extraction procedure

Extraction and stripping 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 that 10 min was sufficient to attain the equilibrium) with a Burrell wrist action shaker (model 75, USA). The stripped extractants were treated at an equal volume (20 mL) ratio of stripped organic solutions and sodium hydroxide solution with different concentrations. The pH of the aqueous phase was measured with a pH meter (Orion Star A221 model, USA). The concentration of metal ions in the aqueous phase was determined using an OPTIMA 8300 (Perkin Elmer, USA) inductively coupled plasma-optical emission spectrometer (ICP-OES). The wavelengths used for analyzing La, Pr, and Nd by using ICP-OES were 408.672 nm, 390.844 nm, and 406.109 nm, respectively. FT-IR measurement of organic phases was performed with a Microscopic FT-IR/Raman Spectrometer (Vertex 80V, Bruker, Germany) in a KBr demountable cell.

The concentration of metal ions extracted into the organic phase was obtained by mass balance. The extraction percentage was calculated by using $\text{EX}\% = [(C_{\text{ini}} - C_{\text{Raf}}) / C_{\text{ini}}] \times (V_{\text{Org}} / V_{\text{Aq}}) \times 100$, where C_{ini} and C_{Raf} are the concentrations in the initial and raffinate aqueous solutions, respectively. V_{Aq} and V_{Org} are the volumes of the aqueous and organic phase, respectively. Stripping percentage (Strip%) was calculated according to $\text{Strip}\% = (C_{\text{Strip}} / C_{\text{L.O.}}) \times (V_{\text{Aq}} / V_{\text{Org}}) \times 100$, where C_{Strip} is the equilibrium concentration of metal in the stripping solution and $C_{\text{L.O.}}$ is the concentration of metals loaded in the organic phase.

2.3. Reusability evaluation of extractant mixtures

The reusability of the extractant mixtures was evaluated by carrying out the successive extraction and stripping experiments of REEs. The aqueous solution containing La (7.56 g/L), Pr (1.17 g/L), and Nd (3.28 g/L) with pH 5 was contacted with the extractant mixtures at a 1:1 phase ratio. After the separation of two phases, the loaded organic phase was stripped with HCl solution at a 1:1 phase ratio. Then the extractant mixtures were employed for further cycles of extraction and stripping tests.

Table 3

Equilibrium pH in each process in different cycles in the extraction and stripping of metals by mixtures of 0.5 M Cyanex 272 and 0.5 M Alamine 336.

Cycle number	Equilibrium pH	
	Extraction	Strip
1	3.38	1.38
2	1.28	1.13
3	1.28	1.13
4	1.28	1.13
5	1.28	1.13

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