Hydrometallurgy 150 (2014) 61–67

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

Solvent extraction of Pr and Nd from chloride solution by the mixtures of Cyanex 272 and amine extractants

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ARTICLE INFO

Article history:
Received 20 May 2014
Received in revised form 29 August 2014
Accepted 19 September 2014
Available online 5 October 2014

Keywords:
Pr
Nd
Synergistic extraction
Cyanex 272
Alamine 336

ABSTRACT

In the separation of rare earth elements by solvent extraction with organophosphorus extractants, bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) leads to lower extraction percentage but higher separation factor. In order to increase the extraction of Pr and Nd by Cyanex 272, its mixtures with amine extractants, such as tri-octyl/decyl amine (Alamine 336), trioctylamine (TOA) and tri-2-ethylhexyl amine (TEHA) have been employed from chloride solution. Among the studied extractant mixtures, the combination of Cyanex 272 and Alamine 336 showed that the best extraction ability and the maximum synergistic enhancement factors were 14.2 for Pr and 12.2 for Nd at Cyanex 272 mole fraction of 0.5. The role of Alamine 336 in this mixture was to extract hydrogen ions released from Cyanex 272. The overall solvent extraction reaction was identified by applying a slope analysis method to the experimental data. Moreover, it was found that the concentration ratio of Alamine 336 to chloride ion affected the enhancement in the extraction of the two metals. The quantitative stripping of both Pr and Nd was possible from the loaded mixture by using HCl or H_2SO_4 solution.

1. Introduction

Rare earths are extensively used in various important fields, such as metallurgical industry, ceramic technology, electronics and catalysts (Humphries, 2013; Sabot et al., 1996). In recent years, the extraction and separation of rare earth elements (REEs) have gained considerable attention due to the increasing demand for REEs with higher purity. Owing to the similar chemical properties among REEs, separation of individual REEs from each other is very difficult. Among the REEs, the separation of praseodymium (III) and neodymium (III) is the most difficult due to similar ionic radii ($r^{3+}_{\mathrm{Pr}} = 101.3$ pm, $r^{3+}_{\mathrm{Nd}} = 99.5$ pm) (Dean, 1991).

Among several separation techniques for REEs, solvent extraction is considered to be competitive (Bhattacharyya and Ganguly, 1993; Gupta and Krishnamurthy, 2005; Thakur et al., 1993; Lee et al., 2005; Xie et al., 2014). Recently synergistic extraction has drawn more attention in the separation of REEs because of its enhancement in extraction efficiency together with improvement in separation selectivity. Many types of synergistic systems have been reported for the extraction and separation of REEs, such as mixtures of acidic extractants, mixtures of neutral extractants and combinations of acidic and neutral extractants (Li and Wang, 1998; Santhi et al., 1991; Tian et al., 2012, 2013; Tong et al., 2013; Wang et al., 2006). Torkaman et al. (2013) reported that the addition of di-2-ethylhexyl phosphoric acid (D2EHPA) to bis-2,4,4 trimethylpentyl dithiophosphinic acid (Cyanex 301) leads to an increase in extraction efficiency and to better stripping performance of Sm. El-Nadi (2012) studied the synergistic extraction of Ln and Nd from nitric acid solutions using a mixture of two neutral extractants, namely trioctylphosphine oxide (TOPO, Cyanex 921) and trialkylphosphine oxide(TRPO, Cyanex 923). The extracted species for both Ln and Nd has been identified as $RE(NO_3)_3(TOPO)(TRPO)$. Reddy et al. (1999) reported the synergistic extraction of REEs from nitrate solutions, and the results showed that La and Nd are extracted by the mixture of Cyanex 301 (HA) and Cyanex 923 (L) as $REA_2 \cdot NO_3 \cdot L$, while Eu, Y and heavier rare earths are extracted as $REA_3 \cdot HA_2 \cdot L$.

Sun et al. (2006) investigated the effect of Cyanex 272 and Sec-nonylphenoxy acetic acid (CA 100) on the extraction of REEs (Sc, Y, La, Gd, Yb) from hydrochloric acid medium. This mixture exhibited significant synergism on the extraction of REEs, and the extracted species of Y is found to be $YH_5A_4L_4$. Higher extraction efficiency and larger separation factor are obtained by using a mixture of Cyanex 272 and sec-octylphenoxy acetic acid (CA 12) during the extraction of Y from chloride medium of heavy REEs (Sun et al., 2005). The synergistic extraction of Nd from nitric acid medium using the mixture of Cyanex 272 and Cyanex 921/Cyanex 923 (B) has been studied by Panda et al. (2013). The composition of extracted species in the organic phase is proposed to be $Nd(NO_3)A{\cdot}3HA{\cdot}B$ with the binary mixtures.

Although various extractant mixtures have been employed in the separation of REEs, only few papers have been reported on the

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http://dx.doi.org/10.1016/j.hydromet.2014.09.015
0304-386X/

synergistic extraction of REEs by the mixture of acidic extractants and tertiary amines (Kim et al., 2012; Kumar et al., 2014). Kumar et al. (2014) investigated the synergistic solvent extraction of Nd with the mixture of bis(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302) and triisooctylamine (Alamine 308) from chloride solutions. An overall reaction for the solvent extraction of Nd by this mixture is proposed by applying a slope analysis method to the experimental data but the exact mechanism has not been given.

In our study on the recovery of rare earths from monazite sand, a chloride leach solution with pH 5 was obtained by digestion of monazite sand with NaOH followed by leaching with HCl. The chemical composition of the leach solution was La–7.8 g/L, Ce–12.4 g/L, Pr–1.17 g/L and Nd–3.28 g/L. The recovery of Ce and La from this solution was achieved by oxidation precipitation and solvent extraction, respectively (Banda et al., 2014). The solution after the removal of La and Ce contained Pr–1.17 g/L (0.008 mol L^{-1}) and Nd–3.28 g/L (0.023 mol L^{-1}).

It has been reported that the extraction capability for REEs by the organophosphorus extractants follows D2EHPA > PC88A > Cyanex 272. However, the separation factor between adjacent REEs follows Cyanex 272 > PC88A > D2EHPA (Banda et al., 2012). Although the separation factor between Pr and Nd by Cyanex 272 is the highest among the above-mentioned three extractants, the problem lies in the fact that the extraction percentage of REEs by Cyanex 272 is low. Therefore, in order to obtain high separation factor together with high extraction efficiency, solvent extraction experiments have been performed from chloride solution containing Nd and Pr by using mixtures of Cyanex 272 and tertiary amines. For this purpose, effects of various parameters, such as composition of the extractant mixtures, aqueous phase acidity, chloride concentration, and diluents on the extraction have been investigated. From the preliminary solvent extraction experiments with the mixture of Cyanex 272 and some tertiary amines, a synergistic system for Nd and Pr was selected and the extraction reaction of both metals by this mixture was identified. The extraction and separation efficiency of Nd and Pr by the mixture of Cyanex 272 and amine extractant have been compared.

2. Experimental

2.1. Reagents

Bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) was purchased from Cytec Industries, Canada. Tri-octyl/decyl amine (Alamine 336) and tri-2-ethylhexyl amine (TEHA) was received from BASF Co., and trioctylamine (TOA) was purchased from Samchun Pure Chem Co., Ltd., respectively. All the extractants were used as received without any further purification. Kerosene (Daejung Co.) was employed as a diluent for the present work except for the study on the effect of diluents.

Praseodymium and neodymium chlorides (99.9%) were purchased from Alfa Aesar (A Johnson Mattery Company). The synthetic solution containing Pr and Nd was prepared by dissolving the corresponding chloride salts in deionized water. Concentrated HCl and NaOH solutions were used to adjust the initial pH of the aqueous solutions. All other reagents used were of analytical grade. In this work, the chemical composition of Pr and Nd was fixed at 0.008 mol L^{-1} and 0.023 mol L^{-1}, respectively.

2.2. Apparatus

A thermo scientific pH meter (Orion Star A221 model) was used for the measurement of pH values. An inductive coupled plasma optical emission spectroscopy (ICP-OES, Spectro arcos model) was used for the determination of metal ions concentration in the aqueous phase.

2.3. Procedures

The extraction experiments were carried out by mixing equal volumes (20 mL) of organic and aqueous phase in a screwed cap bottle and shaken for 30 min (previous experiments showed 10 min was sufficient to attain the equilibrium) with a Burrell wrist action shaker (model 75 USA). The metal concentration in the aqueous phase before and after extraction was determined by ICP-OES and metal contents in the organic phases were obtained 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 was calculated from the D values by $E\% = D \times 100/[D + (V_{aq}/V_{org})]$ where V_{aq} and V_{org} are the volumes of aqueous and organic phases, respectively. The separation factor (SF) was calculated from the D values ($SF = D_{Nd}/D_{Pr}$).

3. Results and discussion

3.1. Extraction of Pr and Nd by either single Cyanex 272 or amine extractants

In preliminary experiments by single Cyanex 272, there was little difference in the extraction percentage of Pr and Nd when the initial pH of the solution was controlled from 4 to 6. Therefore, extraction of Pr and Nd from chloride solutions was studied by using Cyanex 272 and tertiary amines alone at the initial pH of 5.02. The variation in the extraction percentage of the two metals with the concentration of Cyanex 272 is shown in Table 1. The extraction percentage of Pr and Nd increased constantly with increasing Cyanex 272 concentration up to 1 mol L^{-1}, where the highest extraction of Pr and Nd was 15.2% and 21.5%, respectively. Nd was extracted better than Pr due to the difference in the acidity of the metal ions in aqueous chloride solutions (Gschneidner, 1979; Sundaram, 1987).

The variation in separation factor between Pr and Nd with Cyanex 272 concentration is also presented in Table 1. Although the extraction percentage was low, the highest separation factor of 1.86 was obtained at 0.1 mol L^{-1} Cyanex 272 and afterwards it decreased to a constant value of about 1.56.

The extraction of Pr and Nd by amine extractants (Alamie336, TOA and TEHA) alone was investigated under similar experimental conditions to those with Cyanex 272. The experimental data showed that the extraction of Pr and Nd by amine extractant alone was negligible. In our experimental conditions, no anionic species of REEs is present and thus the extraction of Nd and Pr by single tertiary amine is negligible.

3.2. Synergistic solvent extraction of Pr and Nd with mixtures of Cyanex 272 and amine extractants

The extraction of Pr and Nd with the mixtures of Cyanex 272 and TEHA, TOA and Alamine 336 was investigated from chloride solutions with initial pH 5.02 and their extraction percentage vs. mole fraction of Cyanex 272 ($X_{Cyanex\ 272}$) is represented in Figs. 1–3, respectively. In each experiment, the total concentration of the mixtures was fixed at 1.0 mol L^{-1}. Although the extraction percentage of Pr and Nd with

Table 1
Effect of Cyanex 272 concentration on extraction and separation of Pr and Nd at initial pH 5.02.

Cyanex 272, mol L^{-1}	$E\%$, Pr	$E\%$, Nd	$SF_{Nd/Pr}$
0.1	2.2	4.1	1.86
0.3	5.7	8.5	1.55
0.5	6.5	9.6	1.51
0.7	11.6	17.0	1.56
0.9	12.3	18.3	1.57
1.0	15.2	21.5	1.53