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Separation of neodymium and dysprosium from nitrate solutions by solvent extraction with Cyanex272

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ABSTRACT

The separation of Nd and Dy from nitrate solutions using bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272) was investigated. Selective extraction of Dy(III) over Nd(III) was achieved with Cyanex272 when the HNO_3 concentration was 0.001 mol/L. Small amounts of co-loaded Nd(III) were removed by scrubbing with 0.05 mol/L dysprosium nitrate solution. Subsequently, stripping of Dy(III) from loaded Cyanex272 was accomplished using 0.3 mol/L HNO_3. The McCabe-Thiele diagrams were constructed for both extraction of Dy(III) with Cyanex272 and stripping with HNO_3. Finally, a process to separate Nd and Dy was proposed.

1. Introduction

Neodymium(Nd) is the raw material for high-strength permanent magnets (Nd–Fe–B), which are widely used in voice coil motors, power hybrid vehicles, electric motors, wind turbines, spindles for computer hard drives, etc. (Zepf, 2013). There is great demand for the Nd(III) used in Nd–Fe–B magnets because of its excellent magnetic properties and functions, compact shapes, and light weight; however, the abundance of neodymium in natural ores is limited (Padhan and Sarangi, 2017; Binnemans, 2014). During the production of the Nd–Fe–B magnets, one-fourth of the alloy materials are left over as scraps (Yoon, et al., 2016). Both scraps and end-life Nd–Fe–B magnets are important secondary sources of Nd(III). Dysprosium (Dy) is used as an additive in the Nd–Fe–B magnets to improve their high-temperature performance and increase their intrinsic coercivity, which is an important parameter for many industrial applications such as motors and generators (Seo and Morimoto, 2014). Furthermore, Dy(III) is ∼5–6 times more expensive than Nd(III), which makes it one of the important cost actors for the Nd-Fe-B magnets. Therefore, recovery of Nd(III) and Dy(III) from end-life Nd–Fe–B magnets is important from both economic and environmental perspectives.

Hydrometallurgical methods have been widely employed for recycling Nd(III) and Dy(III) from various secondary resources, such as scraps and alloys (Yoon et al., 2016; Binnemans et al., 2013). Recovery of Nd(III) from permanent magnets by leaching and solvent extraction processes has been studied. (Lee et al., 2013; Yoon et al., 2014, 2015a, 2015b; Kikuchi et al., 2014) Some researches on the extraction of Nd and Dy from various aqueous solutions were summarized in Table 1. The solvent extraction process offers significant advantages as a potential technique for recovering metal ions from solutions (Laki et al., 2016). In particular, when the concentration of the metal ion to be separated is higher than 1 g/L, solvent extraction is considered better than the ion exchange process in terms of process efficiency (Zeng and Cheng, 2009).

Bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272) is totally miscible with common aromatic and aliphatic diluents, and is extremely stable to both heat and hydrolysis. Furthermore, it is considered as a non-toxic material. In the other hand, its active component is a phosphinic acid, a variety of cations can be extracted depending upon the solution pH.

In the present investigation, Cyanex272 was used to separate Nd(III) and Dy(III) from nitrate solutions. The effect of HNO_3 and extractant concentrations on the extraction efficiency of Cyanex272 was examined. Scrubbing of Nd(III) from co-loaded Cyanex272 was carried out using HNO_3 and dysprosium nitrate solutions. McCabe-Thiele diagrams were constructed for both extraction and stripping of Dy(III). Simulated counter-current extraction and stripping experiments were also performed to validate the results.

2. Experimental

2.1. Materials

In our previous study, the Nd–Fe–B permanent magnet was leached from a camera module using 1 mol/L of HNO_3 at 80 °C. The pulp density used for leaching was 50 g/L. The composition of the leach solution was 0.07 mol/L Nd, 0.005 mol/L Dy, 0.57 mol/L Fe, and 0.046 mol/L B. Iron can be removed from the solution by a precipitation method using

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Table 1
Some of the reported studies on the extraction of Nd and Dy from various aqueous solutions.

Extractant	Aqueous solution	Diluent	Note	Reference
1-Phenyl-3-methyl-4-benzoyl-pyrazolone-5 (HPMBP)	pH ~ 2.5–6.5	Carbon tetrachloride	Dy extraction behavior was reported	Czakis-Sulikowska et al. (1991)
Di-(2-ethyl-hexyl)phosphoric acid	HCl media	Benzene	TOPO and TBP were used as synergist; TOPO-slight positive synergism; TBP-no synergistic effect	El-Kot (1993)
2-Ethyl-hexyl phosphonic mono-2-ethyl-hexylester	HCl media	Kerosene	Saponified PC 88A gave a good increment of distribution ratio of Nd; The 40% saponified PC88A was optimized	Lee et al. (2005)
2-Ethyl-hexyl phosphonic acid, mono-2-ethyl-hexyl ester (EHEHPA)	HCl media	Kerosene	Nuclear grade Dy_2O_3 has been produced with > 98% purity	Singh et al. (2008)
PC 88A (2-ethyl-hexyl phosphonic acid mono-2-ethyl-hexyl ester)	Nitrate media	Shellsol D70	Extraction mechanism was investigated	Ying and Mikiya (2010)
Cyanex 921 (tri-n-octyl-phosphine oxide)	Nitrate media	Kerosene	Extraction mechanism was investigated	Panda et al. (2012)
Tri-octyl-phosphine oxide (TOPO) + Tri-alkyl-phosphine oxide (TRPO)	Nitrate media	Kerosene	The extracted species of Nd,Nd $(NO_3)_3$(TOPO)(TRPO) was discussed	El-Nadi (2012)
Tri-octyl-methyl-ammonium di-octyl-di-glycolamate [A336][DGA]	Nitrate media	Tri-octyl-methyl-ammonium Nitrate [A336][NO_3]	Test and proved that, nitrate media was better than chloride media for Nd(III) extraction up to ~100%	Rout and Binnemans (2014)
Tri-iso-octyl-amine (Alamine 308, R_3N) Bis(2,4,4-Tri-methyl-pentyl) mono-thio-phosphinic acid (Cyanex 302, $(HX)_2$)	Chloride media	Kerosene	The synergistic enhancement coefficient was reported as 44.1 and the extraction equilibrium species at organic phase was reported as $NdClX_2 \cdot 2R_3N$	Kumar et al. (2014)
Trihexyl(tetradecyl) phosphonium nitrate	Nitrate media pH 0.25–6	–	Dy and Nd was co-loaded and separated by scrubbing of Dy with 0.03 mol/L Na_2EDTA and precipitation stripping of Nd with 76 g/L oxalic acid	Riaño and Binnemans (2015)
D2EHPA(Di-2-rthylhexyl phosphoric acid)	Chloride media pH1.91–5.87	Kerosene	Extraction mechanism and effect parameters were investigated. Dy and Nd was co-loaded and separated by scrubbing of Nd with 0.1 mol/L HCl and stripping of Dy with 2 mol/L HCl	Yoon et al. (2015a)
D2EHPA (Di-2-rthylhexyl phosphoric acid) + Cyanex272 (bis(2,4,4-tri-methyl-pentyl) phosphinic cid)	pH = 4.0	Kerosene	Extraction mechanism and effect parameters were investigated. D2EHPA: cyanex272 (more ratio) = 3:2 gave the highest synergistic enhancement factor R = 2.97	Zaheri et al. (2015)