Research article

Neodymium recovery from NdFeB magnet wastes using Primene 81R·Cyanex 572 IL by solvent extraction

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ABSTRACT

The necessity of Rare Earth Elements (REEs) recycling is crucial to minimizing their supply risk and provide an alternative to greener technologies. Hence, the REEs recovery from NdFeB magnet wastes using cationic extractants by solvent extraction technique has been investigated in this research. Due to the difficulty in maintaining the aqueous pH in the industrial counter-current devices when extractants like Cyanex 272 or Cyanex 572 are used, the Primene 81R·Cyanex 572 ionic liquid has been synthesised to overcome this. 99.99% Nd(III) recovery with a purity of 99.7% from an aqueous mixture of Nd/Tb/Dy in chloride medium, the three representative REEs present in the NdFeB magnets wastes, has been achieved after two stages counter-current extraction process using 0.30 M of Primene 81R·Cyanex 572 ionic liquid (1:4 A:O ratio) diluted in Solvesso 100, without any aqueous pH conditioning.

1. Introduction

Rare earth permanent magnets are increasingly playing a relevant role in clean energy applications.

In fact, this sector holds first place in the priority of recycling taking into account the difficulty in finding substitutes, the critical use of REEs in magnets which are neodymium, praseodymium, dysprosium, terbium and samarium and the potential value of the waste stream (European Commission, 2014; U.S. Department of Energy, 2012). Therefore, the magnets growing tendency does not seem to be changing in the near future, because nowadays, there is a high dependence on the REEs from different sectors and applications, like the motor industry, automation, technology devices, e-mobility, renewable energies and wind power. Although prices and demand are high, only a small fraction of REEs are being recycled. In 2011, just 1% was recycled (Tsamis and Coyne, 2015). Nevertheless, recycling and recovering these metals from urban mines is economically and environmentally beneficial because these wastes are reduced and it brings some independence from REEs producing countries.

Permanent magnets are divided into four categories: (1) Neodymium-Iron-Boron (NdFeB), (2) Samarium-Cobalt (SmCo), (3) Ferrite and (4) Aluminium-Nickel-Cobalt (AlNiCo). The formers are stronger than the other ones and their sizes are not restricted due to brittleness problems. Thus they are more appropriate for large

applications (Smith Stegen, 2015). Therefore, the NdFeB magnets are used more than the SmCo ones, and approximately 26,000 tons per year of REEs are used in the manufacture of NdFeB permanent magnets (Rare et al., 2015). Although NdFeB magnets are more expensive than ferrite and AlNiCo magnets, which are commonly used in wind turbine generators (WTGs), they can produce a higher magneto-motive force in smaller magnet sizes (Rao et al., 2017). Due to the advantages of permanent magnet generators (PMG) based on the REEs use, the average annual demand growth rate forecast for NdFeB in WTGs will increase by 10% in the 2020–2030 period (Schulze and Buchert, 2016). For this reason, it is necessary to study these magnets and find efficient separation and recovery processes.

Up to now, there are many separation and recovery processes for REEs. Among them, the solvent extraction is the most common technique using a wide range of extractants. Cyanex 272 (bis(2,4,4-trimethylpentyl)phosphinic acid, Cy272) (Liu et al., 2014), DEHPA (di-(2-ethylhexyl)phosphoric acid) and EHEHPA (2-ethylhexylphosponic acid mono-2-ethylhexyl ester, PC88A, P507) (Mohammadi et al., 2015), Cyanex 923 (mixture of trialkylphosphine oxides) (Batchu et al., 2017), TBP (tributyl phosphate) (Chen et al., 2016) and the ionic liquids (Larsson and Binnemans, 2015; Chen et al., 2017) are but a few examples. Liu et al. suggest that by adding TBP into the binary mixture of Cyanex 272 and Alamine 336 a better Nd/Pr separation factor is obtained (Liu et al., 2015). The extraction of neodymium and

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Table 1
Physical properties of Cy272, Cy572 and P81R.

| Commercial name	Content %	Density kg·m^{-3}	Viscosity (25 °C) mPa·s	Av. Mol. Weight g·mol^{-1}
Cyanex 272 (CYTEC Industries Inc, 2008)	85	920	14.2	290[a]
Cyanex 572 (CYTEC Industries Inc, 2013)	100	933	< 50	310[a,b]
Primene 81R	100	860	2.58[c]	191[b]

[a] As a monomer.
[b] Experimental data by potentiometric titration in water/ethanol.
[c] Viscosity data by Rohm HA&AS (ROHM HA&AS, 1961).

praseodymium abilities in using different ionic liquid were investigated by Padhan and Sarangi and they proposed the Cyanex 272·Alamine 336 IL > DEHPA·Alamine 336 IL > Cyanex 272 > DEHPA > Aliquat 336 extraction order (Padhan and Sarangi, 2017). Cyanex 572 (Cy572) is a commercial extractant that has been specially developed for the extraction and purification of REEs (CYTEC Industries Inc, 2013). It is a mixture of Cy272 and PC88A and it allows the stripping of REE using lower acid concentrations rather than using phosphonic acids due to the complex strength formed by the REEs (CYTEC Industries Inc, 2013; Quinn et al., 2015; Wang et al., 2015). Tunsu et al. reported that the separation of Yttrium and Europium from solutions of fluorescent lamp waste was successfully achieved using Cy572 (Tunsu et al., 2016). Th was recovered using Cy572 with two different processes depending on its concentration. 95% and 99.9% purity of Th were respectively obtained by Wang et al. recovering from low and high Th concentrations using different extraction, scrubbing and stripping stages (Wang et al., 2017). The extraction and separation of Heavy Rare Earth Elements (HREEs) from ion-adsorbed deposits using Cy572 was more effective than using P507; considering the stripping efficiency, the lower acid requirements and also from an environmental point of view (Wang et al., 2015).

Taking into account that 30% of the NdFeB magnets are REEs (Tunsu et al., 2015; Binnemans et al., 2013) and Nd, Dy and Tb, are critical REEs according to their supply risk and importance in clean energy markets (Tunsu et al., 2015), the current research has been focused on how to recover and separate these REEs from magnet wastes.

In order to evaluate the selectivity to separate the REEs from a mixture containing neodymium, terbium and dysprosium in chloride media, extractants such as Cyanex 272 and Cyanex 572 have been studied using the solvent extraction technique. However, extrapolating the results obtained in this study to set up an industrial separation process, it appears the difficulty in maintaining the pH in a counter-current process using cationic extractants, as can be seen in Eq. (1) where a possible extraction mechanism considering the dimeric form of the extractant involved in the extraction process is shown (Tunsu et al., 2016). Although there are many industrial processes, where the pH is controlled when cation extractants are used, this research suggests an alternative to avoid the necessity of the inter-step pH control using an ionic liquid as an extractant.

$$Me^{3+} + 3\,\overline{(HA)_2} \overset{K_1}{\longleftrightarrow} \overline{Me(HA_2)_3} + 3\,H^+ \qquad (1)$$
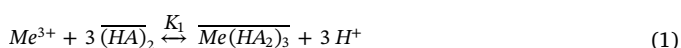
For this reason, the investigation of Primene 81R·Cyanex IL behaviour as the extractant to selectively recover REEs from magnet wastes is promising. As shown in Eq. (2), there is no proton exchange to the aqueous phase when rare earths are extracted with this IL, and consequently, the aqueous phase pH is not modified after extraction.

$$3\,\overline{RNH_3^+A^-} + Me^{3+} + 3\,Cl^- \overset{K_2}{\longleftrightarrow} \overline{MeA_3 \cdot 3\,RNH_3^+Cl^-} \qquad (2)$$
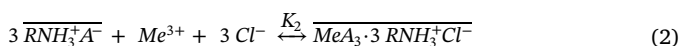
According to this, the first part of the study was focused on the Cyanex choice (C272 or C572) to form the ionic liquid taking into account its selectivity HREEs/neodymium and its behaviour on the neodymium separation. When the Primene 81R·Cyanex IL was synthesized, different parameters were studied, such as contact time, pH, ratio of IL, IL concentration and diluent used, to achieve the Nd(III) separation

from a mixture of Nd/Tb/Dy using an aqueous phase concentration coincident with the real concentration of these REEs in the magnet wastes by a counter-current extraction process.

2. Experimental

2.1. Reagents

The aqueous phase solutions were prepared by dissolving Nd$_2$O$_3$ (Sigma Aldrich Ref. 228656, 99.9%), Tb$_2$O$_3$ (Sigma Aldrich Ref. 590509, 99.99%) and Dy$_2$O$_3$ (Sigma Aldrich Ref. 289264, 99.9%) in hydrochloric acid. NaCl, NaOH or HCl were added to adjust the pH and the chloride concentration. Citric acid (Sigma Aldrich Ref. 251275, 99.5%) and hydrochloric acid were used as stripping agents. Cy272, Cy572 and Primene 81R·Cyanex 572 IL (P81R·Cy572 IL) were used as extractants. Both Cyanex extractants and P81R were kindly supplied by Cytec Canada Industries and Dow Chemical, respectively, and they were used as received. Detailed specifications of these extractants are summarized in Table 1. Kerosene, from Sigma-Aldrich, was used mainly in the majority of the experiments as a diluent. Toluene (methylbenzene), Cumene (isopropylbenzene), Solvesso 100 (a mixture of alkyl (C$_3$)-benzenes) and Solvesso 200 (a mixture of alkyl(C$_4$-C$_7$)-benzenes) were also used to investigate the effects of the diluent on the extraction. ExxonMobil supplied both Solvesso diluents and they were used as received.

2.2. Primene 81R·Cyanex 572 IL preparation

P81R·Cy572 IL is a home-made ionic liquid that was produced by mixing these two commercial extractants, Primene 81R (primary t-alkyl amine, P81R) and Cy572. In order to prepare the P81R·Cy572 IL, stoichiometric quantities of P81R and Cy572 were mixed in kerosene as can be seen in Eq. (3) below.

$$2\,\overline{RNH_2} + \overline{(HA)_2} \leftrightarrow 2\,\overline{RNH_3^+A^-} \qquad (3)$$

2.3. Solvent extraction procedure

For the extraction experiments, the concentration of Nd(III), Tb(III) and Dy(III) in the aqueous phase was 1 g dm^{-3} of each metal (or specified concentration) in 4 M Cl$^-$. 10 cm^3 of this aqueous phase were equilibrated at room temperature (20 ± 2 °C) with an equal volume of organic phase in a separatory funnel using a horizontal mechanical shaker (SBS Mechanical Shaker) at 140 rpm for 10 min, until the equilibrium was achieved. In order to evaluate the effect of the citric acid and HCl as stripping agents, 5 cm^3 aliquots of the organic phase were placed in two new separatory funnels to make the stripping process using citric acid 1 M and HCl 1.2 M. After the separation phases, the concentration of the REEs in the aqueous phase was determined by atomic emission spectrometry using a 4100 MP AES System (Agilent Technologies) with an analytical error ≤ 5%. A triplicate test was made.

Extraction efficiency (%E), stripping efficiency (%S), distribution ratio (D) and separation factor (β) are defined in Eqs. (4)–(7) to