Separation and Purification Technology 194 (2018) 265–271

Contents lists available at ScienceDirect

Separation and Purification Technology

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

# NdFeB magnet recycling: Dysprosium recovery by non-dispersive solvent extraction employing hollow fibre membrane contactor

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## ARTICLE INFO

*Keywords:*
Recycling
NdFeB magnets
Hollow fibre membrane
Dysprosium

## ABSTRACT

Hollow Fibre Membrane (HFM) operation in non-dispersive solvent extraction (NDSX) mode has been successfully employed for the separation of dysprosium from NdFeB magnetic scrap material using EHEHPA as an extractant. Effect of various hydrodynamic parameters including aqueous phase acidity, extractant concentration, Dy concentration in feed, phase ratio and flow rate were investigated to optimize the condition for quantitative recovery of dysprosium from the leach liquor obtained by the dissolution of hard disk drive (HDD) in nitric acid media. 0.5 M EHEHPA, 0.3 M $HNO_3$ as aqueous feed phase, 100 ml/min flow rate and phase ratio of 1:1 were found to be optimum for both the cycle test runs. Taking the advantage of fast extraction kinetics of dysprosium, two cycle HFM-NDSX approach was adopted to concentrate Dy from 20 to 83% in first cycle while raising its purity > 97% in the second cycle. The overall process also yielded neodymium rich by-product for its further purification.

## 1. Introduction

Rare earth elements are critical raw material for wide range of modern age products ranging from catalysts, phosphors, magnet, lasers, fibre optics and several more [1]. There is a great research interest growing in rare-earth (RE) recycling due to increase in demand for REs and associated complexity of REs separation from primary ores [2]. Neodymium Iron Boron magnet (NdFeB) is one of the major consumer for rare earth elements which include Nd, Dy and Pr. NdFeB magnets are best available magnets due to their superior energy product (with a theoretical maximum of 512 kJ/$m^3$) and fulfil almost 70% of permanent magnetic material demand worldwide. NdFeB permanent magnet contains about ~32 wt% REEs (mainly 21–31 wt% (Nd/Pr), 0–10 wt% Dy and small amounts of Gd and Tb) [3]. Dysprosium added to NdFeB magnets plays a crucial role in preserving the performance of the magnet at elevated temperature which is essential for high-temperature applications [4]. Apart from NdFeB magnets, dysprosium also finds an important place in the manufacturing of laser materials, nuclear reactors, hybrid cars and colour television tubes [5].

Du and Graedel [6] have recently published very interesting fact about the global stock in use for four REs in NdFeB permanent magnets, i.e., neodymium (Nd), praseodymium (Pr), terbium (Tb), and dysprosium (Dy), which amount to a total of 97.0 kilotons (kt): 62.6 kt Nd, 15.7 kt Pr, 15.7 kt Dy, and 3.1 kt Tb. This vast resource of RE elements could augment the existing supply as they are quantitatively almost four times the 2007 annual production of the individual elements, if recycled efficiently. RE recycling not only supplements existing demand but can also reduce the geopolitical impact on economic aspects due to supply risk. Less than 1% of the REEs were recycled by 2011, and developmental researches for new large-scale processes are scanty [7]. The scarcity of data on the current quantity of REE materials from magnets in the waste streams and the fate of the magnets after shredding has hampered the possible development of REE recycling processes [8]. There are various metallurgical processes practised to separate and recover the REEs in the NdFeB magnet scrap such as liquid metal extraction [9], hydrometallurgical processing [10,11], and pyrometallurgical slag extraction [4,12]. Hydrometallurgical, an important route, involves leaching of magnetic scraps with acids at room temperature, leading to dissolution of all the components in NdFeB magnets. Subsequently rare earth can be precipitated as double sulphate salt which could be easily converted to corresponding fluoride or oxide [13]. The resultant oxide consists majority of rare earth elements mostly Nd, Pr and Dy present in magnetic scrap. However subsequent purification of dysprosium can enhance the value as well as importance of the recycling process due to its invariably high cost and demand. There are various conventional methods available for purification of individual rare earth elements such as solvent extraction, ion exchange and fractional precipitation [14]. Solvent extraction is the industrially accepted method for purification of rare earth elements. In solvent extraction process, organophosphorous acids based organic extractants

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https://doi.org/10.1016/j.seppur.2017.11.025
Received 1 September 2017; Received in revised form 23 October 2017; Accepted 10 November 2017

are employed for separating REE, due to their solvation properties as well as their chemical stability and low aqueous solubilities [15]. Acidic organophosphorous extractants, such as 2-ethylhexyl 2-ethyhexylphosphonic acid (EHEHPA also known as PC88A), di-2-ethyl hexyl phosphoric acid (D2EHPA) are widely used for the extraction and separation of individual rare earths including dysprosium [16]. However, Dy recovery from NdFeB magnet scrap is difficult with solvent extraction process owing to requirement of multiple stages and low Dy content in feed source [17]. The present scenario consisting shortfall in supply of critical rare earths elements has attracted a lot of research interest in the field of rare earth separation by alternative methods i.e. membrane based separation, solvent impregnated resins and ionic liquids from waste and secondary sources [18–21].

Membrane assisted solvent extraction employing hollow fibre membrane modules can provide suitable alternative to recover and purify dysprosium from mixed rare earths feed [22]. Membrane based techniques eliminates the disadvantages of conventional solvent extraction process such as lean source, environmental hazard associated with loss of organic extractant, loss of diluents in aqueous streams and third phase formation [23]. In the case of hollow fibre membrane operation mode, individual separation of rare earth elements is enhanced in non-equilibrium conditions due to the continuous high driving forces over extended periods of time compared to equilibrium limited conventional solvent extraction [24]. Hollow fibre membrane modules provide high surface area contact per unit volume resulting in high RE extraction rate and can be employed in two modes namely supported liquid membrane and non-dispersive solvent extraction (NDSX) mode. In NDSX mode an organic extractant phase passing through one side of the membrane wets the microporous hydrophobic membrane. A non-wetting aqueous phase is passed through other side of the membrane at a pressure higher than that of the organic phase, but lower than that needed for the aqueous phase to displace the organic phase in the pores of the membrane. The aqueous–organic (aqueous–membrane) interface is essentially immobilized at the pore mouth of the hydrophobic membrane support through which the solute mass transfer takes place. Here, the membrane support does not function as a size selective sieve, but it merely prevents the dispersion of one phase into the other. Among them only few have explored hollow fibre membrane module for rare earth separation [25]. However non dispersive solvent extraction mode which has promising potential for scale up among membrane based separation methods has not yet been explored extensively. Therefore it is desirable to develop an efficient separation method to process the leach solution obtained from NdFeB magnet scrap material to get high purity rare earth oxides.

Accordingly the objective of the present study is to explore the HFM-NDSX under wide range of experimental variables to address the complexity involved in Dy separation from NdFeB magnet scrap by solvent extraction process by employing hollow fibre membrane module in non dispersive mode to recover the same.

## 2. Experimental

### 2.1. Materials

2-Ethylhexyl 2-ethylhexyphosphonic acid (EHEHPA) shown in Fig. 1 also known as EHEHPA having molecular weight of 306.4 and purity of 95% has been received from Heavy Water Board and used as it is. Experiments performed during the recovery of rare earth by employing hollow fibre membrane required organic extractant to be used as carrier phase. The extractants were diluted to optimize hydrodynamic conditions of the process. Petroffin (heavy normal paraffin) having specification shown in Table 1 has been used as diluent. Rare earth (such as Dy (III), Nd(III), Pr(III) etc.) solutions were prepared by dissolving their oxides (> 99% purity, received from Indian Rare Earth Limited, India) in concentrated nitric acid and individual working solution were prepared by the appropriate dilution of the stock solutions. NdFeB magnetic scraps shown in Fig. 2 were recovered from end of life Hard Disk Drive obtained from Computer Division, Bhabha Atomic Research Centre, Mumbai. The magnets were first demagnetized by heating well above the Curie temperature (30 min at 350 °C) and then fed into a jaw crusher resulting in magnetically-neutral particles ready for chemical processing. Subsequently the same was crushed in mortar and pestle to powder form for efficient leaching of metal into corresponding acids.

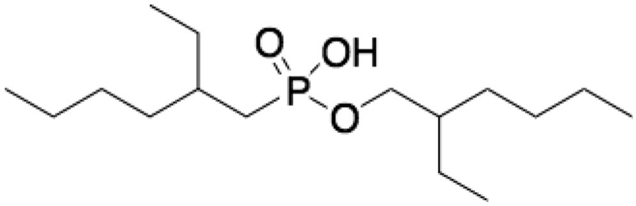

**Fig. 1.** Structure of 2-Ethylhexyl 2-ethylhexyphosphonic acid.

**Table 1**
Characteristic properties of petrofin.

| Characteristics | Specifications |
|---|---|
| Density (at 15 °C) | 0.75 ± 0.01 |
| Purity | 99% |
| *Carbon distribution* | |
| C11 | 20–30% |
| C12 | 25–35% |
| C13 | 20–30% |
| C14 | 20–25% |
| Flash point | 70 °C |

### 2.2. Non-dispersive solvent extraction studies

HFM contactor (Liqui Cell 2.5 × 8) used in the present work was procured from Polypore, USA and it consists of hydrophobic microporous polypropylene hollow fibres enclosed in a polypropylene shell of 2.5″ × 8″ dimension as shown in Fig. 3. The module contained about 10,000 fibres of 40% porosity and had an effective surface area of 1.4 $m^2$ with other specifications, listed in Table 2. The aqueous and organic phases (agitated continuously in the reservoir for uniform concentration) were contacted in counter-current mode in the hollow fibre module pores. The flow rates of aqueous and organic phases were kept at 100 ml/min with the help of gear pumps (cole-palmer) through the lumen side and shell side of the HFM module, respectively. The polypropylene membrane is hydrophobic in nature so the organic phase wets and even passes through the membrane fibres. To prevent the dispersion of the organic phase into the aqueous feed phase a small trans-membrane pressure in the lumen side is applied.

### 2.3. Sample analysis

The evaluation of rare earth elements extraction/stripping was studied by monitoring its concentration in aqueous phase by using Inductively Coupled Plasma-Atomic Emission Spectrophotometer, ICP-AES (JY-Ultima 2). The experiments were performed thrice and the mean values are reported. The errors in non dispersive solvent extraction experiments and metal ion concentration analysis were less than 4%.

## 3. Results and discussion

### 3.1. Batch extraction of Dy by EHEHPA

Separation of heavy rare earth (Dy) by Hollow fibre membrane