



HAL
open science

Selective recovery of rare earth elements from acetic leachate of NdFeB magnet by solvent extraction

Sahar Belfqueh, Simon Chapron, Fabrice Giusti, S Pellet-Rostaing, Alain Seron, Nourredine Menad, Guilhem Arrachart

► To cite this version:

Sahar Belfqueh, Simon Chapron, Fabrice Giusti, S Pellet-Rostaing, Alain Seron, et al.. Selective recovery of rare earth elements from acetic leachate of NdFeB magnet by solvent extraction. Separation and Purification Technology, 2024, 339, pp.126701. 10.1016/j.seppur.2024.126701 . hal-04610359

HAL Id: hal-04610359

<https://hal.umontpellier.fr/hal-04610359v1>

Submitted on 13 Jun 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License



Selective recovery of rare earth elements from acetic leachate of NdFeB magnet by solvent extraction

Sahar Belfqueh^{a,b}, Simon Chapron^b, Fabrice Giusti^a, Stéphane Pellet-Rostaing^a, Alain Seron^b, Nouredine Menad^b, Guilhem Arrachart^{a,*}

^a ICSM, Univ Montpellier, CEA, CNRS, ENSCM, Marcoule, France

^b BRGM, Direction de l'Eau, de l'Environnement, des Procédés et Analyses, Orléans, France

ARTICLE INFO

Editor: Luo Guangsheng

Keywords:

Acetic acid
NdFeB magnets
Recycling
Solvent extraction
TODGA

ABSTRACT

Due to their indispensable role in a wide range of advanced technologies, rare earth elements (REEs) are becoming increasingly essential. As a result, there is a growing need to develop optimised processes for the recovery of these elements, whether from primary or secondary sources. This need extends to the recovery of REEs from a variety of sources, including mine tailings, the recycling of end-of-life products and the management of urban and industrial waste. The recovery of REEs from NdFeB permanent magnets from end-of-life computers hard disk drives (HDDs) is a great opportunity if separation from iron is effective. For this purpose *N,N,N',N'*-tetraoctyldiglycolamide (TODGA) has been used for the selective extraction of REEs from a real leachate, obtained by NdFeB magnet powder dissolution in acetic acid. Process parameters such as TODGA concentration, ionic strength, time, and temperature have been investigated highlighting the complete selective recovery of REEs from the acetic acid leachate. The results show that TODGA at a concentration of 0.25 mol/L in aliphatic diluents allows the selective extraction of rare earths from an acetic acid feed solution at 1.6 mol/L, when NaNO₃ is added, with high separation coefficients for REEs in regards to iron, boron and nickel respectively. After a stripping step, the recyclability of the extractant phase was also demonstrated for at least 9 cycles. The complete process allows the recovery of the REEs from the NdFeB leachate with efficiencies of approximately 92 %, 88 % and 99 % for Nd, Pr and Dy respectively.

1. Introduction

Rare earths (REEs) are a group of metals with similar properties, namely scandium (Sc), yttrium (Y) and all the lanthanides, the latter corresponding to the 15 chemical elements listed in the periodic table of elements from atomic number 57 for lanthanum (La) to atomic number 71 for lutetium (Lu) [1]. The special electronic configuration of REEs, in particular their unsaturated 4f electron sublayer, gives them unique chemical, structural and physical properties. These properties have been exploited in many sophisticated industrial applications: glass and ceramics, polishing, catalysis, production of high-tech alloys, permanent magnets, optical equipment, luminescent materials, rechargeable batteries for electric or hybrid vehicles, generators for wind turbines, etc. [2]. REEs are therefore among the “technology metals” whose supply is strategically important. However, as only a few countries produce rare earths from mines (China alone currently accounts for almost 60 % of the world’s annual production of REEs), there is a significant risk of

supply disruptions in the long term, so we need to optimise all production routes [3,4].

At the same time, growing environmental awareness is prompting a constant search for alternatives to mining, such as substitution of the chemical elements used, reduction of demand or recycling of used products or production waste [5]. Recycling is one of the pillars of the circular economy, which consists of optimising the value generated by resources, thus reducing the need for primary resources and avoiding the landfilling of end-of-life products.

One of the leading REEs recycling markets in terms of volume and potential market value is for NdFeB permanent magnets, which are used in a variety of high-tech products such as electric and hybrid vehicles, wind turbines, hard drives and induction motors [6,7]. This resource for REEs recycling is particularly interesting because these magnets contain a large amount of light REE (about 30 % by mass of a neodymium/praseodymium mixture) and a smaller amount of heavy REE with high economic value, including dysprosium. In addition to containing large

* Corresponding author.

E-mail address: guilhem.arrachart@umontpellier.fr (G. Arrachart).

<https://doi.org/10.1016/j.seppur.2024.126701>

Received 18 December 2023; Received in revised form 29 January 2024; Accepted 5 February 2024

Available online 8 February 2024

1383-5866/© 2024 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

amounts of iron and smaller amounts of boron, NdFeB permanent magnets are usually coated with a protective anti-corrosion coating based on nickel and other transition metals such as cobalt. The challenge is to separate the rare earths from the other metals, in particular iron, as efficiently as possible.

Most of the work aiming at recovering REEs from natural or urban ores by liquid–liquid extraction has been carried out on aqueous solutions obtained by treating these ores with inorganic acids such as nitric acid, hydrochloric acid, sulphuric acid or phosphoric acid followed by a liquid–liquid extraction with specific extractant such as these based on phosphorus ((tri-*n*-butyl phosphate (TBP), (2-ethylhexyl)phosphoric acid (D2EHPA), 2-ethyl-hexyl phosphonic acid mono-2-ethyl-hexyl ester (PC 88A), Cyanex phosphate extractants) [8,9].

The use of lipophilic diglycolamides such as *N,N'*-dimethyl-*N,N'*-di-*n*-octyldiglycolamide (MODGA) [10], *N,N,N,N'*-tetraoctyl-3-oxapentanediamide (TODGA) [11] and *N,N,N,N'*-tetradodecyl-3-oxapentanediamide (TdddGA) [12] as extractants, has been proposed for the selective recovery of REEs from aqueous solutions simulating or resulting from the leaching of used or scrap NdFeB permanent magnet powder by an inorganic acid, which is preferably nitric acid but can also be sulphuric acid, hydrochloric acid or phosphoric acid.

Studies have demonstrated the possibility of the effective leaching of NdFeB permanent magnet powders with organic acids. The advantages of using organic acids over inorganic acids such as nitric, hydrochloric or sulphuric acids are numerous, namely that organic acids, which are generally derived from biological sources, are less corrosive or non-corrosive, produce fewer toxic gases than inorganic acids and are mostly biodegradable, which significantly reduces the environmental impact of leaching.

Gergoric *et al.* used glycolic acid, maleic acid and ascorbic acid as organic acids lixivants, followed by a liquid–liquid extraction step in order to recover the REEs from neodymium magnet powder [13]. After further investigating the possibility of extracting REEs from glycolic and maleic acid leachates and testing several types of extractants (TBP, D2EHPA, TODGA, Cyanex™ 272 and Cyanex™ 923) was demonstrated. They also showed that TODGA at a concentration of 1 mol/L in organic solution selectively extracts neodymium, dysprosium and praseodymium from iron, cobalt and boron, but only from maleic acid leachate [13].

More recently, acetic acid, formic acid, citric acid and tartaric acid have been investigated as alternative leaching reagents for rare earth elements recovery from NdFeB magnets [14].

It was highlighted that acetic acid shows the highest leaching performance of the REEs, with leaching yields of over 90 % of Nd, Dy and Pr in the acid concentration range of 1.6–10 mol/L and the solid/liquid ratio range of 0.5 %–5 % at a temperature of 60 °C. In this context, the present study considers the possibility of using TODGA as an extractant for the recovery of REEs from such acetic acid aqueous solutions resulting from the processing of NdFeB permanent magnets from end-of-life computers hard disk drives (HDDs). Process parameters such as TODGA concentration, ionic strength, time, and temperature alongside various diluents have been investigated with the aim of evaluating the performance in terms of selective extraction of REEs from the acetic acid leachate.

2. Experimental part

2.1. Materials and methods

Chemicals and Reagents: *N,N,N,N'*-tetraoctyl-3-oxapentanediamide (TODGA) and *N,N,N,N'*-tetraethyl-3-oxapentanediamide (TEDGA) were synthesised based on a procedure adapted from the literature [15,16], with ¹H and ¹³C NMR characterisations in agreement with those referenced in the literature. All other chemicals were purchased from Sigma-Aldrich and used without any further purification.

Instrumentation and Analysis: Metal concentrations in the aqueous

phase were measured by inductively coupled plasma/atomic emission spectroscopy (ICP/OES Thermo Scientific iCAP) or mass spectroscopy (ICP/MS Thermo Scientific iCAP RQ). ICP calibration samples were prepared from 1000 ± 4 mg/L iron, neodymium, praseodymium, dysprosium, cobalt, boron and nickel standard solutions (SCP Science PlasmaCal). Uncertainties in metal concentration were determined by repeated measurements of different samples of the same concentration. These uncertainties were estimated to be in the order of ±5 %. The typical limits of quantification obtained for the analyses are as follows for ICP-OES: B (5.1 µg/L at 249.773 nm); Fe (6.4 µg/L at 240.488 nm); Co (1.7 µg/L at 228.616 nm); Ni (2.6 µg/L at 221.647 nm); Pr (17.9 µg/L at 390.844 nm); Nd (6.8 µg/L at 406.109 nm); Dy (4.4 µg/L at 353.170 nm); and for ICP-MS: ¹¹B STD (43 ng/L); ⁵⁶Fe KED (586 ng/L); ⁵⁹Co KED (5.1 ng/L); ⁶²Ni KED (15.4 ng/L); ¹⁴¹Pr STD (4.3 ng/L); ¹⁴⁴Nd STD (4.1 ng/L); ¹⁶²Dy STD (2.5 ng/L).

2.2. Extraction experiments

The aqueous feed solutions were prepared after the leaching of NdFeB powder. The leachate of the NdFeB powder obtained from end-of-life computers hard disk drives (HDDs) was prepared according to the procedure described in the literature [14], typically a 0.5 % solid/liquid ratio was used with acetic acid concentration of 1.6 mol/L at 60 °C for 24 h. With this condition, more than 90 % of all the REEs (Nd, Pr and Dy) initially present in the NdFeB powder can be leached with a co-leaching of Fe, Co, B and Ni. The composition of the acetic acid feed solution was determined by ICP-OES and ICP-MS, the results are provided in the Table 1.

The organic phases were prepared by dissolving the TODGA extractant in aliphatic diluents (dodecane, isooctane, hydrogenated tetrapropylene) at the desired concentration.

Each extraction was carried out by contacting an aqueous phase with an organic phase in a 5 mL flask stirred at 400 rpm in a thermostatically controlled cell (Infor-ht® ecotron at 20 °C–60 °C). Unless otherwise indicated, the volume ratio of aqueous phase to organic phase (A/O) was 1 and the contact time was 60 min. At the end of the stirring period, the mixture was centrifuged (10,000 rpm–5 min) and the aqueous and organic phases were separated from each other. The aqueous phases obtained from the extractions were diluted in 1 % nitric acid and analysed by ICP-OES, while the organic phases were mineralised by microwave (Milestone ETHOS) in a mixture of 69 % nitric acid and 35 % hydrogen peroxide (HNO₃/H₂O₂ = 9/1, v/v), then diluted in 1 % nitric acid and analysed by ICP-MS. The yielded compositions of the different phases were compared to check the mass balance. All extraction experiments were carried out in triplicate.

Based on the results of these analyses, the distribution coefficients were determined according to the conventions of liquid–liquid extractions and the distribution law, derived by W. Nernst in 1898. In the context of liquid–liquid extraction, the distribution coefficient (D_M) for an element M is commonly defined as the ratio of its concentrations in the organic phase to this in aqueous phase at equilibrium. The concentration of the metal in the organic phase, denoted as $[M]_{org}$, is

Table 1

Composition of the acetic acid feed solution after the leaching of the NdFeB powder.

Elements	Concentration	
	mg/L	mmol/L
Fe	3258	58.3
Nd	1307	9.1
Pr	167	1.2
Co	80	2.9
Dy	62	0.4
B	55	5.1
Ni	25	0.4

determined after mineralisation of the organic phase or by the variance between the initial concentration in the aqueous phase ($[M]_{aq,ini}$) and the equilibrium concentration ($[M]_{aq,eq}$). This relationship is expressed as follows for an aqueous / organic volume ratio (A/O) of 1:

$$D_M = \frac{[M]_{org,eq}}{[M]_{aq,eq}} = \frac{[M]_{aq,ini} - [M]_{aq,eq}}{[M]_{aq,eq}}$$

Furthermore, the separation factor for a specific metal concerning another metal is defined by the ratio of their respective distribution coefficients:

$$SF_{M1/M2} = \frac{D_{M1}}{D_{M2}}$$

Each back-extraction was carried out by contacting an aqueous stripping phase with the organic loaded phase in a 5 mL flask stirred at 400 rpm in a thermostatically controlled cell (Infor-ht® ecotron at 20 °C–60 °C). At the end of the shaking period, the mixture was centrifuged (10,000 rpm–5 min) and the aqueous and organic phases were separated from each other. The conditions under which the aqueous and organic phases obtained after the back-extractions were analysed were identical to those mentioned above for the extractions. The back-extraction yields were also determined in accordance with the conventions in the field of liquid–liquid extractions, namely that the back-extraction yield of a metallic element M , denoted BE and expressed in %, from an organic loaded phase is equal to:

$$\%BE = \frac{[M]_{aq,st}}{[M]_{org,load}} \times \frac{V_{aq,st}}{V_{org,load}} \times 100$$

where $[M]_{aq,st}$ and $[M]_{org,load}$ are the concentrations of the metal ions in the stripping aqueous phase after stripping and in the loaded organic phase before stripping, respectively.

The recyclability of the organic phase was evaluated through a cycle consisting of the following four stages:

- 1) Liquid-liquid extraction: The organic phase consisting of 0.25 mol/L TODGA, 5 % v/v octanol dissolved in dodecane was brought into contact with a leachate of NdFeB magnet powder in acetic acid containing 0.6 mol/L NaNO_3 . Contact was made at 20 °C for 5 min using an O/A ratio equal to 1.
- 2) Back-extraction: The REEs-loaded organic phase was brought into contact with a 0.01 mol/L EDTA solution. Contact is made at 20 °C for 5 min using an O/A ratio equal to 1.
- 3) Acid wash: The organic phase was brought into contact with a 4 mol/L H_2SO_4 solution at 40 °C using an O/A ratio equal to 1 for a period of 30 min in order to extract the trace elements (Fe, Ni, Co and B) remaining in the organic phase.
- 4) Water wash: The organic phase was brought into contact with deionised water at 40 °C for 30 min to re-equilibrate it.

After stripping, the REEs were precipitated by adding oxalic acid to the aqueous phase, aiming for an oxalic acid/REE molar ratio of around 2. The solutions were stirred at 30 °C for 2 h. The resulting precipitate was filtered. The supernatant was analysed by ICP-OES to perform a mass balance and to evaluate the efficiency of the precipitation step. The precipitate was then heat treated in air at a heating rate of 5 °C/min from 25 to 1000 °C. The powder composition was determined by ICP-OES analysis after mineralisation in aqua regia.

3. Results and discussion

3.1. Extraction process

3.1.1. Effect of TODGA concentration

The effect of TODGA concentration on the extraction performance of the elements was evaluated by varying it in dodecane at concentrations between 0.05 mol/L and 1 mol/L. Octanol (5 % v/v) was added to the

system to prevent the formation of the third phase. The distribution coefficients of the extracted elements are shown in Fig. 1. Fe and the other elements (Co, B and Ni) were not extracted ($D_M < 1 \cdot 10^{-3}$) regardless of the concentration of TODGA used in the system. The efficiency of REEs extraction was found to be closely related to the strong oxygen donor atoms present in the TODGA molecule [17,18]. The strong affinity of TODGA's oxygen donor atoms for REEs contributes significantly to the efficiency of complex formation, thereby enhancing the distribution coefficient observed in comparison to the other elements. The importance of the ionic radius as a key determinant influencing the efficiency and selectivity of TODGA in the extraction of REEs, has been highlighted by Zhu *et al.* [19]. Indeed, they show that divalent ions characterised by ionic radii less than 80 pm and trivalent ions with ionic radii less than 70 pm exhibit significantly weak extraction when subjected to TODGA in dodecane. These low-extracted metals include Fe, Al, Ni, Co, Cu and Zn, which are also elements often present in leachates from NdFeB magnets. In addition, REEs with larger ionic radii are preferentially treated in the extraction process. Thus, in line with what is reported in the scientific literature, extraction increases by increasing the atomic number or decreasing the ionic radius of rare earths [8].

TODGA also shows a preference for the extraction of heavy rare earths (Dy) over light rare earths (Nd and Pr). This phenomenon can be attributed to the increased charge density associated with the heavy rare earth elements due to their smaller ionic radii, which facilitates their complexation [20]. This characteristic facilitates the formation of complexes, thereby influencing the observed distribution coefficient. At TODGA concentrations lower than or equal to 0.1 mol/L, only Dy is extracted, but with a low D of less than 1. The evolution of the Dy/Nd and Dy/Pr selectivity factors is shown in Fig. S1. This selectivity is optimal at a concentration of about 0.2 mol/L TODGA, where the distribution coefficient $D_{Dy} > 1$, $SF_{Dy/Nd} > 70$ and $SF_{Dy/Pr} > 60$. In comparison, the extraction of Nd and Dy with a Dy/Nd selectivity factor of about 20 was achieved by liquid–liquid extraction and separation of Nd and Dy in 0.3 mol/L nitric acid solution using 0.1 mol/L TODGA diluted in dodecane [21]. Therefore, using the TODGA extraction phase, it seems possible to separate REEs from other elements and from each other from an acetic acid feed solution. Despite these advantages, the distribution coefficients of REEs obtained during extraction are relatively low, and therefore an improvement in extraction efficiency is required.

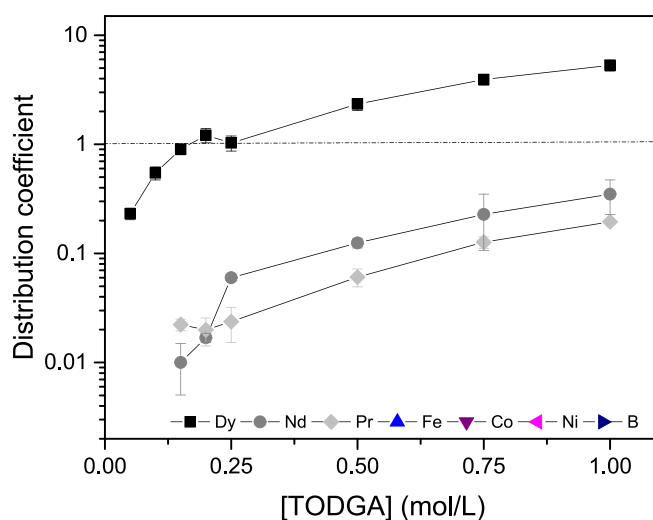


Fig. 1. Distribution coefficient of metals as a function of TODGA concentration (NdFeB powder leachate [CH_3COOH] = 1.6 mol/L; [TODGA] = 0.05–1 mol/L (dodecane + 5 % v/v *n*-octanol); O/A = 1; $T = 20$ °C. Extraction time: 60 min.

3.1.2. Effect of aqueous medium

In general, the distribution coefficient for a neutral complex would increase with increasing the ionic strength, this salting-out effect is frequently attributed to a reduction in the amount of free water molecules in the system leading to an increase in the activity of the extracted species [22]. Also the salting-out agent can reduce the dielectric constant of the aqueous phase, which leads to a reduction in the polymerisation of metal ions.

Therefore, to investigate the influence of adding a salting-out agent to the system, sodium nitrate (NaNO_3) was added to the leachate. This choice was made because numerous studies have shown that TODGA performs well in extracting REEs from nitrate-containing media [19,23]. NaNO_3 was dissolved in the aqueous phase, after the leaching with acetic acid, at various concentrations ranging from 0.25 to 1 mol/L. These aqueous phases were contacted for 1 h at 20 °C with three organic phases corresponding to three concentrations of TODGA (0.05, 0.1 and 0.25 mol/L) dissolved in dodecane containing 5 % v/v octanol. The distribution coefficients obtained from these tests are shown in Fig. 2. The results show that the addition of NaNO_3 to the system results in a significant increase in the distribution coefficients of the REEs. This increase is maximal for the 0.25 mol/L TODGA system where the addition of 0.25 mol/L NaNO_3 multiplies the distribution coefficients of

Dy, Nd and Pr by factors of 80, 116 and 200 respectively.

In addition, increasing the concentration of NaNO_3 in the aqueous phase further increases the REEs distribution coefficients. Thus, at 1 mol/L NaNO_3 , a single extraction step allows the quantitative extraction of all rare earths (Nd, Pr and Dy). On the other hand, in other experiments, sodium acetate (CH_3COONa) was added to the leachate, in which case the extraction of Nd and Pr was only slightly improved and the distribution coefficients remained below 1 even when 1 mol/L sodium acetate was added to the leachate. These results suggest that nitrates are extracted in the organic phase and are present in the metal complexes [24]. The addition of NaNO_3 to the system also results in the extraction of other metals (Fe, B, Co and Ni). However, the distribution coefficients of these metals remain very low ($D < 0.1$) whatever the concentration of TODGA or NaNO_3 used. Thus, the addition of a salting-out agent such as NaNO_3 to the system does not change the selectivity towards Fe, Co, Ni and B. The selectivity REEs/other metals and REEs between them therefore tends to increase with increasing concentrations of NaNO_3 in the system (Fig. S2).

Extraction efficiency depends on a number of factors, including the nature and concentration of the acidic leachate, the concentration of the extractant, the nature of the diluent and the experimental parameters involved in the extraction experiment, such as metal ion concentration,

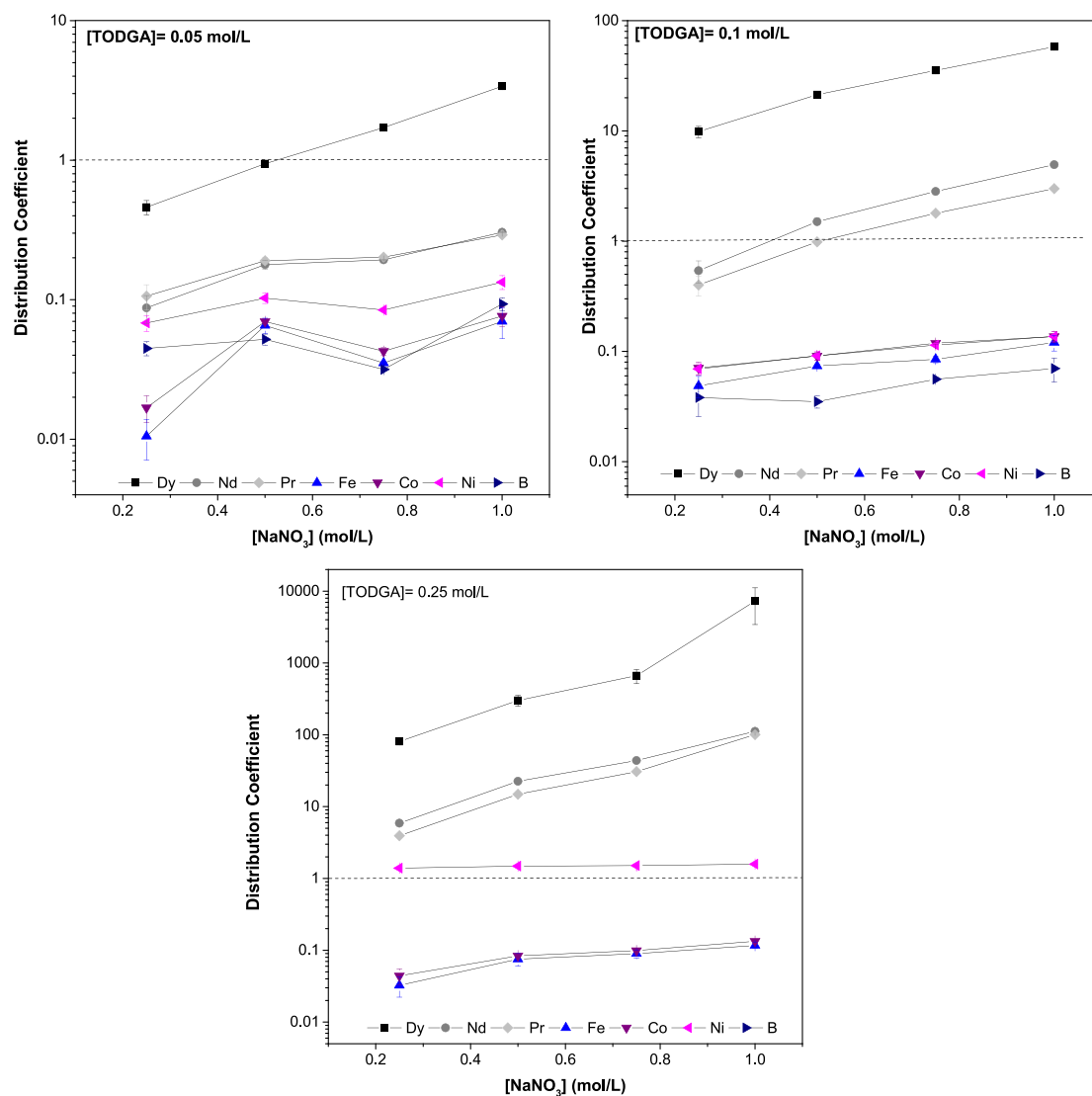


Fig. 2. Distribution coefficient of metals as a function of NaNO_3 concentration for various TODGA concentrations. NdFeB powder leachate $[\text{CH}_3\text{COOH}] = 1.6$ mol/L + $[\text{NaNO}_3] = 0.25$ –1 mol/L; $[\text{TODGA}] = 0.05$ –0.25 mol/L (dodecane + 5 % v/v *n*-octanol); O/A = 1; $T = 20$ °C. Extraction time: 60 min.

A/O ratio, pH, ionic strength and temperature. It is therefore difficult to evaluate different extraction systems in a relevant way. As an indication, it has been shown that from leachates of permanent magnet powder obtained with organic acid (maleic or glycolic acid) at 1 mol/L with a TODGA phase at 1 mol/L in Solvent 70, distribution coefficients of the order of $D_{Nd} \approx 140$, $D_{Pr} \approx 82$; $D_{Dy} \approx 162$, $D_{Fe} \approx 0.18$, $D_{Co} \approx 0.22$, $D_B \approx 0.22$ and $D_{Nd} \approx 0.6$, $D_{Pr} \approx 0.3$; $D_{Dy} \approx 4.4$, $D_{Fe} \approx 0.13$, $D_{Co} \approx 0.12$, $D_B \approx 2.5$ can be obtained respectively from maleic or glycolic leachate [13]. In this study, similar trends to those observed for maleic acid were observed for acetic acid leachate with $NaNO_3$, but with a much higher affinity for Dy than for the other REEs with lower TODGA concentration in the extracting phase. It is difficult to draw tendencies from the nature of the acid, whether mono- or dicarboxylic, or from their pKa.

The essential role of ionic strength in the TODGA-mediated solvent extraction process is highlighted from the collective results of the present study. This point out the importance of the addition of $NaNO_3$ in the acetic acid leachate as a key determinant influencing the efficiency and selectivity of TODGA in the extraction of REEs.

3.1.3. Effects of time and temperature

In order to study the kinetics of the REEs extraction, an organic solution containing 0.25 mol/L TODGA and 5 % v/v octanol dissolved in dodecane was brought into contact with the leachate of NdFeB magnet powder containing 0.6 mol/L $NaNO_3$ at 20 °C with an O/A ratio equal to 1 for different times ranging from 1 min to 60 min. It can be seen from Fig. S3 that thermodynamic equilibrium is reached in less than 5 min for the rare earths and the other metals, with the exception of Ni, for which equilibrium is reached after 10 min of contact. Thus, under these conditions, in less than 5 min, approximately 99 % of Dy, 96 % of Nd and 94 % of Pr are extracted in the organic phase, while more than 99 % of the other metals remain in the aqueous phase. The temperature applied during the extraction process can have a significant effect on the overall extraction process. It is therefore important to determine the thermodynamic parameters for the extraction system and whether the free energy of partition between the organic and aqueous phases is dominated by an enthalpy (solvation process) or an entropy term (solvent orientation and restructuring) providing information about hydration and solvation. In order to investigate the effect of temperature on rare earth extraction, extractions were carried out by varying the temperature between 10 and 60 °C while maintaining an O/A ratio of 1. For each temperature value, contact was maintained for three different contact times, namely 5 min, 30 min and 60 min, using an organic phase containing 0.25 mol/L TODGA and 5 % v/v *n*-octanol dissolved in dodecane and a leachate of NdFeB magnets in 1.6 mol/L acetic acid containing 0.6 mol/L $NaNO_3$. Fig. 3 shows the metal partition coefficients as a function of temperature for a contact time of 60 min. The results show that the REE distribution coefficients tend to decrease with increasing temperature, indicating an exothermic nature of the extraction process. On the other hand, temperature had very low influence on the extraction of the other metals Fe, Co and Ni.

It should be noted that for all REEs the distribution coefficients tend to decrease with time for temperatures above 20 °C.

Furthermore, the extraction results obtained at different temperatures were used to calculate the thermodynamic extraction parameters ΔH and ΔS using the Van't Hoff equation (Eq. (1)) and taking into account the direct proportionality between the distribution coefficient D and the equilibrium constant K . Thus, the enthalpy ΔH could be calculated from the slope of the $\ln(D_M)$ curve as a function of the reciprocal of the temperature, and the entropy of ΔS was calculated from the y-intercept obtained from the data in Fig. 3. These data were then used to estimate ΔG using the Gibbs-Helmholtz equation (Eq. (2)).

$$\ln(K) = \frac{\Delta H^0}{R} \times \frac{1}{T} + \frac{\Delta S^0}{R} \quad (1)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = -RT\ln(K) \quad (2)$$

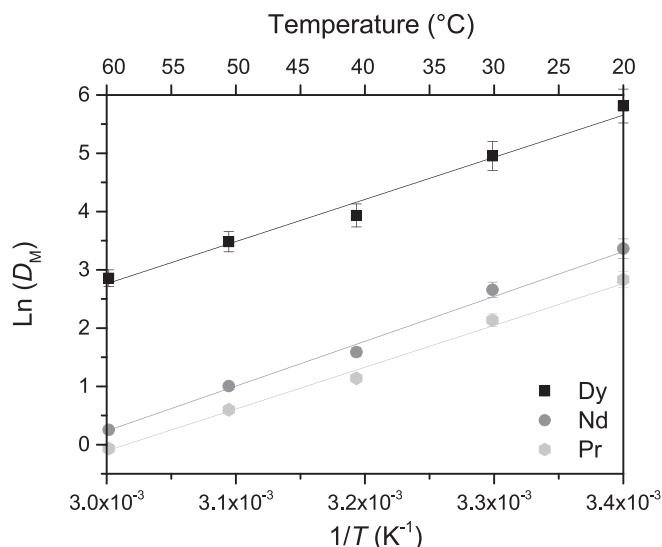


Fig. 3. Logarithm of the distribution coefficient D_M as a function of the reverse of the temperature T . NdFeB powder leachate $[CH_3COOH] = 1.6$ mol/L + $[NaNO_3] = 0.6$ mol/L; $[TODGA] = 0.25$ mol/L (dodecane + 5 % v/v *n*-octanol); O/A = 1; $T = 20$ °C–60 °C. Extraction time: 60 min. $\ln(D_M) = f(1/T)$: Dy ($y = -18.943(\pm 1.466)x + 7234.7(\pm 457.7)$; $R^2 = 0.988$); Nd ($y = -22.851(\pm 1.092)x + 7695(\pm 341)$; $R^2 = 0.994$); Pr ($y = -21.639(\pm 1.019)x + 7177.5(\pm 318.1)$; $R^2 = 0.994$).

The thermodynamic parameters ΔH and ΔS and the values of ΔG as a function of temperature are presented in Table 2.

The results show that the extraction of the Nd, Pr and Dy is controlled by the enthalpy ΔH . The value of ΔH is negative for all REEs, indicating exothermic extraction. Based on the ΔH values, the REEs are classified as follows Nd > Dy > Pr. The enthalpy changes depend on several contributing factors, including dehydration of metal ions, formation of neutral extracted species and dissolution of metal complexes in the organic phase. On the other hand, the entropy ΔS has an unfavourable effect on the extraction, as it is negative in the case of the three rare earths. This can be explained by a loss of translational and rotational entropy of TODGA during complexation in a medium containing bulky extracted species. Negative entropy values may also indicate the presence of water molecules in the formed metal complexes [25,26]. On the other hand, between 10 °C and 60 °C, ΔG values are generally negative, indicating that REEs extraction reactions are spontaneous. However, the ΔG increases considerably as the temperature rises, becoming positive for Pr at 60 °C. In all cases, based on the ΔG values, the rare earths are classified as follows: Dy > Nd > Pr. Although Nd has a higher ΔH than Dy, its extraction is less favoured due to the greater negative contribution of ΔS . Thus, even though extraction is governed by exothermic enthalpy, the order of rare earth extraction is partly governed by entropy. To illustrate this, Fig. S4 shows the evolution of ΔH , $-T\Delta S$ and ΔG as a function of REEs. As already mentioned, the results show that the extraction of rare earths decreases with increasing temperature, while the following order of extraction preference is maintained Dy > Nd > Pr. Therefore, a series of extraction tests were carried out at 60 °C using low concentrations of $NaNO_3$ in the leachate in order to increase the extraction selectivity of Dy over light rare earths. Fig. S5 shows the evolution of the selectivity factors of Dy with respect to Nd and Pr at 20 °C and 60 °C as a function of the concentration of $NaNO_3$ present in the leachate of the NdFeB magnetic powder. The results show that the selectivity factors $SF_{(Dy/Nd)}$ and $SF_{(Dy/Pr)}$ tend to increase significantly at high temperatures and with the use of low concentrations of $NaNO_3$, allowing maximum separations characterised by a $SF_{(Dy/Pr)} = 44.5$ with 0.01 mol/L $NaNO_3$ at 60 °C and a $SF_{(Dy/Nd)} = 17.5$ with 0.05 mol/L $NaNO_3$ at 60 °C.

Table 2
Thermodynamic parameters (ΔH , ΔS , and ΔG) for the extraction of REEs.

REEs	ΔS (J/mol)	ΔH (KJ/mol)	ΔG (KJ/mol)					
			10 °C	20 °C	30 °C	40 °C	50 °C	60 °C
Nd	-190.0	-64.0	-10.2	-8.3	-6.4	-4.5	-2.6	-0.7
Pr	-179.9	-59.7	-8.7	-6.9	-5.1	-3.3	-1.5	0.3
Dy	-157.5	-60.2	-15.6	-14.0	-12.4	-10.8	-9.3	-7.7

NdFeB powder leachate [CH_3COOH] = 1.6 mol/L + [NaNO_3] = 0.6 mol/L; [TODGA] = 0.25 mol/L (dodecane + 5 % v/v *n*-octanol); O/A = 1; $T = 20\text{ }^\circ\text{C} - 60\text{ }^\circ\text{C}$. Extraction time: 60 min.

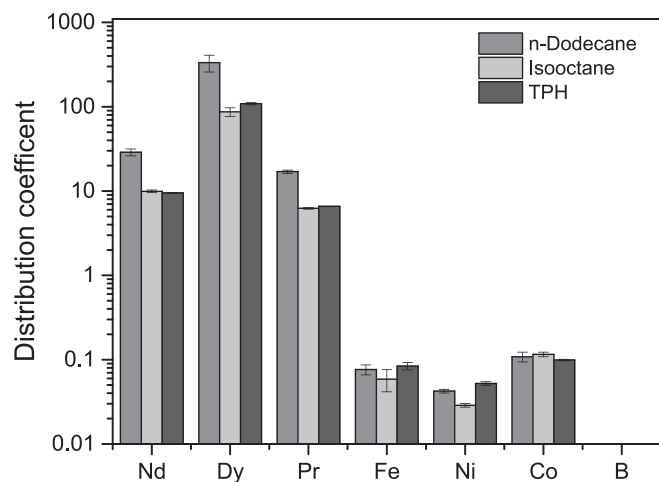


Fig. 4. Distribution coefficient of metals as a function of the diluent. NdFeB powder leachate [CH_3COOH] = 1.6 mol/L + [NaNO_3] = 0.6 mol/L; [TODGA] = 0.25 mol/L (dodecane + 5 % v/v *n*-octanol; isooctane or TPH); O/A = 1; $T = 20\text{ }^\circ\text{C}$. Extraction time: 5 min.

3.1.4. Effect of diluent

The nature of the diluent can influence the extracting phase through different interactions such as van der Waals, dipole–dipole, pi electron and hydrogen bonding. The liquid–liquid extraction of REEs using TODGA was investigated using various aliphatic diluents: dodecane, isooctane, and hydrogenated tetrapropylene (TPH). For these experiments, the NdFeB magnet powder leachate containing approximately 0.6 mol/L NaNO_3 was brought into contact with the organic phase containing 0.25 mol/L TODGA dissolved in the chosen diluent. The O/A ratio was set at 1 and the two phases were stirred at $20\text{ }^\circ\text{C}$ for 5 min according to the result of the kinetic study. Fig. 4 shows the distribution coefficients for REEs and other metals as a function of the diluent used. It should be noted that octanol (5 % v/v) was added when using dodecane in order to avoid the appearance of the third phase. In the case of the other diluents, the addition of the phase modifier was not necessary, as the third phase was not observed.

Although different from one diluent to another, the extraction of rare earths is efficient, enabling distribution coefficients close to or greater than 10 for Nd, 6 for Pr and 100 for Dy to be achieved. The distribution coefficients for the REEs slightly decrease in the following order:

Table 3
Loading capacity of REEs as a function of the diluent.

Diluent	Loading capacity					
	Dy		Nd		Pr	
	mmol/L	g/L	mmol/L	g/L	mmol/L	g/L
Dodecane (+5 % v/v <i>n</i> -octanol)	61	9.9	50	7.2	40	5.6
Isooctane	39	6.3	30	4.3	28	3.9
TPH	48	7.8	31	4.5	26	3.7

NdFeB powder leachate [CH_3COOH] = 1.6 mol/L + [NaNO_3] = 0.6 mol/L; [TODGA] = 0.25 mol/L (dodecane + 5 % v/v *n*-octanol); Isooctane or TPH; $T = 20\text{ }^\circ\text{C}$. Extraction time: 5 min.

dodecane (+5 % octanol v/v) > Isooctane \approx TPH. The purpose of the addition of octanol is to prevent the formation of a third phase, but it also increases the polarity of the diluent. Thus, the distribution coefficients tend to decrease when the polarity of the diluent is lower which suggests that it would have a role to play in the extraction mechanism. It is important to note that the use of a branched diluent has the advantage of avoiding the need for a phase modifier while maintaining good extraction properties for TODGA.

The REEs loading capacity of 0.25 mol/L TODGA in dodecane, isooctane and TPH, was investigated by contacting these organic solutions with NdFeB magnet powder leachate containing 0.6 mol/L NaNO_3 at different A/O ratios varying between 1 and 30. All contacts were made at $20\text{ }^\circ\text{C}$ for 5 min. As in previous studies, 5 % v/v octanol was added to the dodecane-containing system to avoid the appearance of the third phase. Fig. S6 shows the concentrations of REEs in the organic phase after the extraction step as a function of A/O ratio and diluent. For all the diluents investigated, the loading capacity of the REEs tended to increase with atomic number, in direct proportion to the extraction performance observed for heavy REEs compared to light REEs. For Nd and Pr, the loading capacity tends to increase with the polarity of the diluent, in the same way as the extraction efficiency. Furthermore, in the case of Dy, the loading capacity increases in the following order: dodecane > TPH > isooctane, as observed for the partition coefficients. Maximum loading capacities are obtained using dodecane with values of about 60 mmol/L (10 g/L) for Dy, 50 mmol/L (7 g/L) for Nd and 40 mmol/L (6 g/L) for Pr (Table 3).

3.2. Back-extraction (Stripping)

The use of TODGA has shown great potential for the extraction of Nd, Pr and Dy contained in the leachate of NdFeB magnet powder in acetic acid. In order to recover these elements and ensure that the extractant phase could be recycled, a study was carried out to determine the optimum performance and conditions for stripping. Water-soluble complexing agents with a high affinity for rare earths must be considered for effective stripping. The main complexing agents used are polyamino acids such as ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA) and *N*-hydroxyethylenediaminetriacetic acid (HEDTA) [27,28]. In addition, given the high potential of diglycolamides (DGA) for REE extraction, it would be interesting to investigate water-soluble DGAs such as *N,N,N,N*-tetraethyldiglycolamide (TEDGA) as complexing agents in the aqueous phase to implement the back-extraction step [29–32]. Table S1 shows the concentrations of

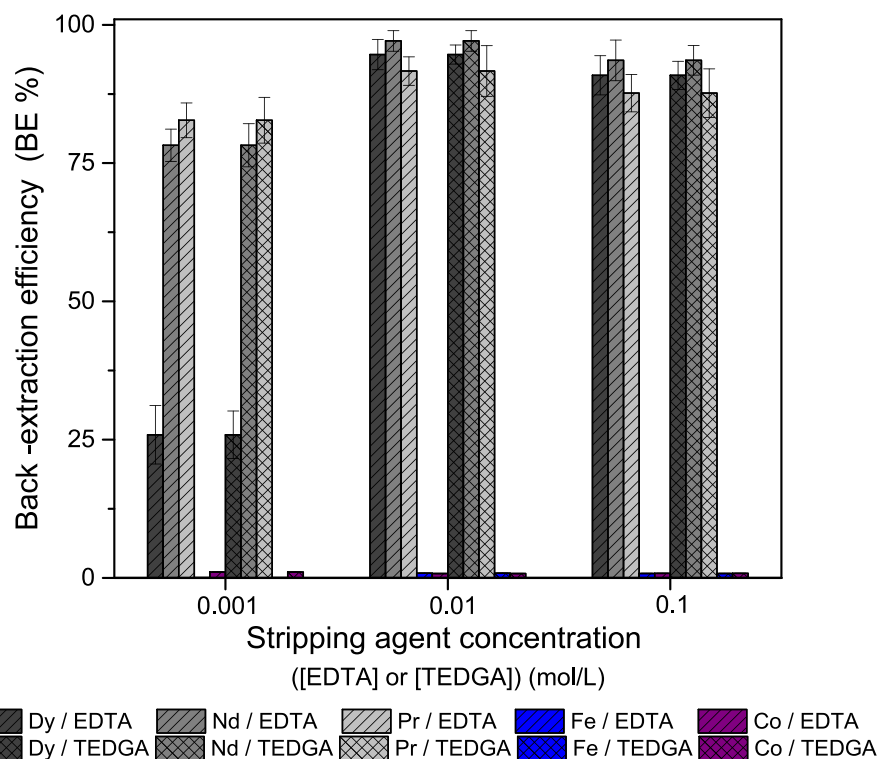


Fig. 5. Recovery of metals from an organic TODGA phase by various aqueous stripping solution. Extraction condition: NdFeB powder leachate $[\text{CH}_3\text{COOH}] = 1.6$ mol/L + $[\text{NaNO}_3] = 0.6$ mol/L; $[\text{TODGA}] = 0.25$ mol/L (dodecane (+5 % v/v *n*-octanol)); O/A = 1; $T = 20$ °C. Extraction time: 60 min. Back-extraction condition: Organic phase: $[\text{TODGA}] = 0.25$ mol/L (dodecane (+5 % v/v *n*-octanol)) loaded with metals (see Table S1 for composition); Stripping phase: $[\text{EDTA}]$ or $[\text{TEDGA}] = 0.001$ – 0.1 mol/L; A/O = 1; $T = 20$ °C. Stripping time: 60 min.

REEs and other metals present in the organic loaded phase after the extraction stage.

3.2.1. Total stripping of REEs

The REEs contained in the organic phase were first stripped by contacting this phase with aqueous solutions containing EDTA and TEDGA at the following concentrations 0.1 mol/L, 0.01 mol/L and 0.001 mol/L. In all these experiments, the A/O was fixed at 1 and the contacts were made at 20 °C for a period of 60 min. Fig. 5 shows the back-extraction yields, which indicate that both EDTA at 0.01 mol/L and TEDGA at 0.1 mol/L allowed almost all (>95 %) of the REEs to be extracted in one step and selectively compared to the other metals present in the organic phase.

Also, the kinetic study of REEs stripping using EDTA at 0.01 mol/L demonstrated that this step reaches equilibrium in less than 5 min for all the metals. Thus, in less than 5 min, more than 95 % of the Nd, Pr and Dy were back-extracted from the organic phase into the aqueous phase; while more than 99 % of the other metals (Fe, Ni, B and Co) remained in the organic phase.

3.2.2. Selective stripping between REEs

Back-extraction of the REEs contained in the organic phase was achieved by contacting this phase with deionised water using A/O ratios between 0.3 and 10 (at a fixed temperature of 20 °C), and using temperatures between 20 °C and 60 °C (at a fixed A/O ratio of 0.5). Preliminary tests have shown that back-extraction equilibrium with water is achieved in 5 min. Fig. 6 shows the evolution of the back-extraction yields of the metals contained in the organic phase as a function of the A/O ratio and temperature. The results show that under these conditions, the back-extraction of light rare earths (Nd and Pr: didymium) is favoured over that of Dy. This can be explained by the more pronounced affinity of the TODGA extractant phase for heavy rare earths, which makes it more difficult to extract them.

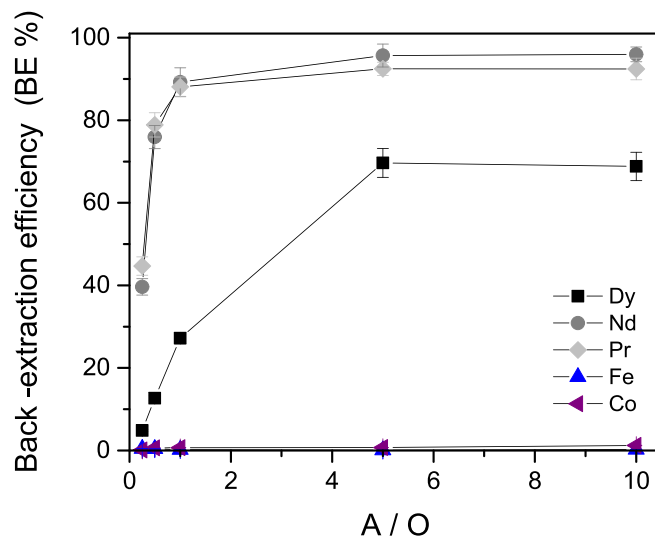


Fig. 6. Recovery of metals from an organic TODGA phase using water as stripping solution. Extraction condition: NdFeB powder leachate $[\text{CH}_3\text{COOH}] = 1.6$ mol/L + $[\text{NaNO}_3] = 0.6$ mol/L; $[\text{TODGA}] = 0.25$ mol/L (dodecane (+5 % v/v *n*-octanol)); O/A = 1; $T = 20$ °C. Extraction time: 60 min. Back-extraction condition: Organic phase: $[\text{TODGA}] = 0.25$ mol/L (dodecane (+5 % v/v *n*-octanol)) loaded with metals (composition in Table S1); Stripping phase: Water; A/O = 0.25–10; $T = 20$ °C. Stripping time: 60 min.

Using deionised water, a maximum back-extraction selectivity can be achieved using an A/O ratio of around 0.5. Furthermore, as mentioned previously, the TODGA used in the liquid–liquid extraction step is exothermic, so increasing the temperature favours the back-extraction of all the REEs and hinders the selective back-extraction of didymium

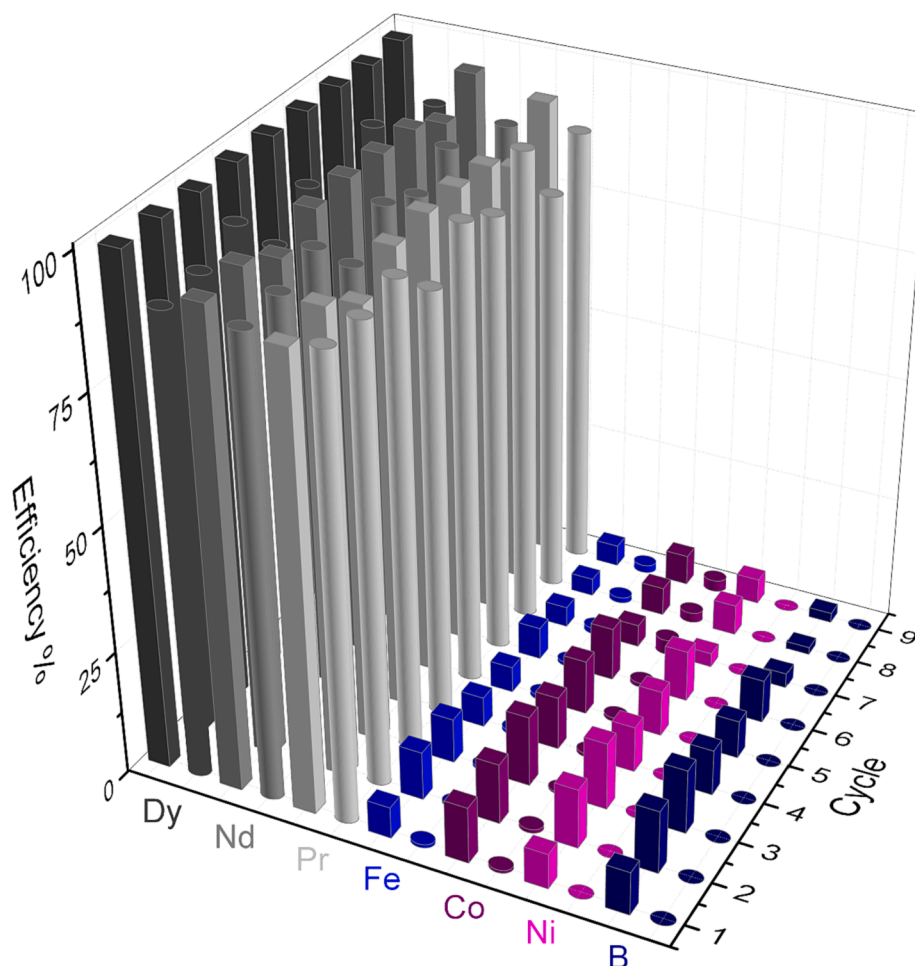


Fig. 7. Extraction (bars) and stripping (cylinders) percentages obtained for different numbers of extraction–stripping cycles. Extraction condition: NdFeB powder leachate $[\text{CH}_3\text{COOH}] = 1.6 \text{ mol/L} + [\text{NaNO}_3] = 0.6 \text{ mol/L}$; $[\text{TODGA}] = 0.25 \text{ mol/L}$ (dodecane + 5 % v/v *n*-octanol); O/A = 1; $T = 20 \text{ }^\circ\text{C}$. Extraction time: 60 min. Back-extraction condition: Organic phase: $[\text{TODGA}] = 0.25 \text{ mol/L}$ (dodecane + 5 % v/v *n*-octanol) loaded with metals (composition in Table S1); Stripping phase: $[\text{EDTA}] = 0.01 \text{ mol/L}$; A/O = 1; $T = 20 \text{ }^\circ\text{C}$. Stripping time: 60 min.

and Dy (Fig. S7). It should also be noted that back-extraction with deionised water maintains excellent selectivity for the other metals (Fe, Co, Ni and B), the majority of which (>99 %) remain in the organic phase.

3.3. Recyclability of the organic phase

In order to study the recyclability of the organic phase, the cycle consisting of four stages (see experimental part) was repeated nine times on the same organic phase. The Fig. 7 summarises the extraction efficiencies of stage I (bars) and the back-extraction yields of stage II (cylinders) for the metals obtained for each cycle. The results show that the efficiencies of the REEs remain high and in the same order of magnitude for all the cycles, while maintaining selectivity with respect to the other metals. In addition, for all the cycles, the back-extraction with EDTA made it possible to recover about 90 % of the REEs extracted in the organic phase, while maintaining the selectivity with respect to the extracted trace elements. This means that the organic phase can be perfectly reused at least 9 times. This excellent recyclability could be partly due to the limited transfer of material between the two phases during the extraction stage. [supporting information](#)

3.4. Recovery of REEs

In order to recover the REEs contained in the aqueous phase after the stripping step, in the form of oxides, a first step consists of precipitating them in the form of oxalate salts. Table S2 shows the concentrations of REEs and trace elements in the aqueous solutions after the stripping. Oxalic acid was added to the aqueous phase to give a molar ratio of oxalic acid to rare earths of around 2. The solutions were then stirred at $30 \text{ }^\circ\text{C}$ for 2 h. These conditions enabled all the REEs to be precipitated, as ICP-OES analysis of the filtrates did not show the presence of REEs in solution. The oxalates thus obtained were then subjected to heat treatment in air up to $1000 \text{ }^\circ\text{C}$ in order to form the corresponding oxides. The powder was totally dissolved in an aqua regia solution in order to evaluate its composition by ICP-OES, which shows that it contains mainly REEs (82.3 %). In addition to REEs, the analysis revealed the presence of trace elements Fe (0.03 %) and Co (0.01 %) while B and Ni, were not detected in the powder.

Based on the various results obtained during the different stages a flowsheet was proposed with an overall recovery yield of REEs, from NdFeB permanent magnet powder from HDD, of about 92 %, 88 % and 99 % for Nd, Pr and Dy respectively (Fig. 8).

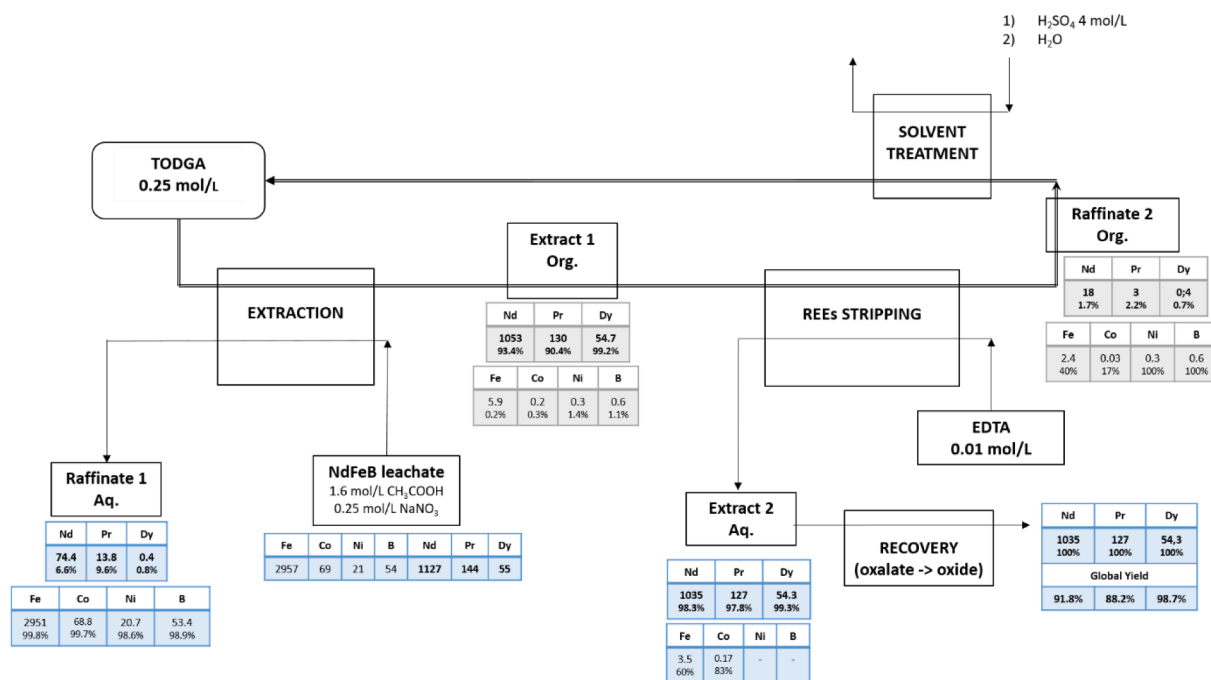


Fig. 8. Flowsheet illustration for the recovery of REEs from NdFeB permanent magnet powder. Compositions in tables are expressed in mg/L, % correspond to the yields of each step. Extraction condition: NdFeB powder leachate [CH₃COOH] = 1.6 mol/L + [NaNO₃] = 0.6 mol/L; [TODGA] = 0.25 mol/L (Dodecane (+5 % v/v octanol)); T = 20 °C. Extraction time: 60 min. Back-extraction condition: Organic phase: [TODGA] = 0.25 mol/L (dodecane +5 % v/v n-octanol) loaded with metals; Stripping phase: [EDTA] = 0.01 mol/L; A/O = 1; T = 20 °C. Stripping time: 60 min.

4. Conclusion

The possibility of using an extractant phase with TODGA for the selective recovery of REEs from an acetic acid leachate of NdFeB permanent magnet powder from HDDs was demonstrated in this study. The distribution coefficients, extraction yields and extraction kinetics obtained during TODGA extractions of REEs from an aqueous solution resulting from the leaching of NdFeB permanent magnet powder with an organic acid, such as acetic acid, are significantly improved when a salting-out agent (NaNO₃) is added to this aqueous solution. This does not affect the extraction selectivity towards other metal elements (iron, cobalt, boron, etc.) and the TODGA preference for heavy REEs remains unaffected. Indeed, in addition to its selectivity for iron, cobalt, nickel and boron, TODGA has a greater affinity for heavy REEs such as dysprosium than for light REEs such as neodymium and praseodymium, which is interesting from the point of view of selective recovery of these REEs. Based on these experimental results, a flow sheet has been proposed that allows the recovery of REEs from NdFeB permanent magnet powder from HDDs, achieving approximately 92 %, 88 % and 99 % recovery rates for Nd, Pr and Dy, respectively.

CRedit authorship contribution statement

Sahar Belfqueh: Writing – original draft, Investigation, Formal analysis, Data curation, Conceptualization. **Simon Chapron:** Validation, Supervision, Project administration, Methodology, Funding acquisition. **Fabrice Giusti:** Methodology. **Stéphane Pellet-Rostaing:** Validation, Methodology. **Alain Seron:** Supervision, Methodology. **Nourredine Menad:** Validation, Supervision, Project administration, Funding acquisition. **Guilhem Arrachart:** Writing – review & editing, Writing – original draft, Validation, Supervision, Project administration, Methodology, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

The authors are grateful to the Occitanie Region (RETREAT project ALDOCT 000443) and the French Geological Survey (BRGM) for the PhD scholarship and financial support. The authors acknowledge Béatrice Baus-Lagarde, for her help regarding the ICP-OES and ICP-MS experiments.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2024.126701>.

References

- [1] N.G. Connelly, T. Damhus, R.M. Hartshorn, A.T. Hutton, Nomenclature of inorganic chemistry – IUPAC recommendations 2005, R. Soc. Chem. 27 (2005) 25–26, <https://doi.org/10.1515/ci.2005.27.6.25>.
- [2] V. Balaram, Rare earth elements: a review of applications, occurrence, exploration, analysis, recycling, and environmental impact, Geosci. Front. 10 (2019) 1285–1303, <https://doi.org/10.1016/j.gsf.2018.12.005>.
- [3] K. Binnemans, P.T. Jones, T. Müller, L. Yurramendi, Rare earths and the balance problem: how to deal with changing markets? J. Sustain. Metall. 4 (2018) 126–146, <https://doi.org/10.1007/s40831-018-0162-8>.
- [4] K. Binnemans, P.T. Jones, Rare earths and the balance problem, J. Sustain. Metall. 1 (2015) 29–38, <https://doi.org/10.1007/s40831-014-0005-1>.

- [5] K. Binnemans, P.T. Jones, B. Blanpain, T. Van Gerven, Y. Yang, A. Walton, M. Buchert, Recycling of rare earths: a critical review, *J. Clean. Prod.* 51 (2013) 1–22.
- [6] Y.X. Yang, A. Walton, R. Sheridan, K. Guth, R. Gauss, O. Gutfleisich, M. Buchert, B. M. Steenari, T. Van Gerven, P.T. Jones, K. Binnemans, REE recovery from end-of-life NdFeB permanent magnet scrap: a critical review, *J. Sustain. Metall.* 3 (2017) 122–149, <https://doi.org/10.1007/s40831-016-0090-4>.
- [7] C. Tunsu, 8 - Hydrometallurgy in the recycling of spent NdFeB permanent magnets, in: F. Vegliò, I. Birloaga (Eds.), *Waste Electrical and Electronic Equipment Recycling*, Woodhead Publishing, 2018, pp. 175–211, <https://doi.org/10.1016/B978-0-08-102057-9.00008-1>.
- [8] F. Xie, T.A. Zhang, D. Dreisinger, F. Doyle, A critical review on solvent extraction of rare earths from aqueous solutions, *Miner. Eng.* 56 (2014) 10–28, <https://doi.org/10.1016/j.mineng.2013.10.021>.
- [9] H.-S. Yoon, C.-J. Kim, K.-W. Chung, S.-D. Kim, J.-Y. Lee, J.R. Kumar, Solvent extraction, separation and recovery of dysprosium (Dy) and neodymium (Nd) from aqueous solutions: waste recycling strategies for permanent magnet processing, *Hydrometall.* 165 (2016) 27–43, <https://doi.org/10.1016/j.hydromet.2016.01.028>.
- [10] H. Narita, M. Tanaka, Separation of rare earth elements from base metals in concentrated HNO₃, H₂SO₄ and HCl solutions with diglycolamide, *Solvent Extr. Res. Dev., Jpn.* 20 (2013) 115–121, <https://doi.org/10.15261/serdj.20.115>.
- [11] M. Gergoric, C. Ekberg, M.R.S.J. Foreman, B.-M. Steenari, T. Retegan, Characterization and leaching of neodymium magnet waste and solvent extraction of the rare-earth elements using TODGA, *J. Sustain. Metall.* 3 (2017) 638–645, <https://doi.org/10.1007/s40831-017-0122-8>.
- [12] M. Miguiditchian, V. Haquin, V. Pacary, R. Laucournet, M. Montuir, Processes for selective recovery of rare earth metals present in acidic aqueous phases resulting from the treatment of spent or scrapped permanent magnets, WO/2016/046179, 2016.
- [13] M. Gergoric, A. Barrier, T. Retegan, Recovery of rare-earth elements from neodymium magnet waste using glycolic, maleic, and ascorbic acids followed by solvent extraction, *J. Sustain. Metall.* 5 (2019) 85–96, <https://doi.org/10.1007/s40831-018-0200-6>.
- [14] S. Belfqueh, A. Seron, S. Chapron, G. Arrachart, N. Menad, Evaluating organic acids as alternative leaching reagents for rare earth elements recovery from NdFeB magnets, *J. Rare Earths* 41 (2023) 621–631, <https://doi.org/10.1016/j.jre.2022.04.027>.
- [15] E.A. Mowafy, H.F. Aly, Synthesis of some N, N, N', N'-tetraalkyl-3-oxa-pentane-1,5-diamide and their applications in solvent extraction, *Solvent Extr. Ion Exch.* 25 (2007) 205–224, <https://doi.org/10.1080/07366290601169352>.
- [16] D.D. Dicholkar, P. Kumar, P.K. Heer, V.G. Gaikar, S. Kumar, R. Natarajan, Synthesis of N, N, N', N'-tetraoctyl-3-oxapentane-1,5-diamide (TODGA) and its steam thermolysis-nitrolysis as a nuclear waste solvent minimization method, *Ind. Eng. Chem. Res.* 52 (2013) 2457–2469, <https://doi.org/10.1021/ie302603q>.
- [17] Y. Sasaki, Y. Sugo, S. Suzuki, S. Tachimori, The novel extractants, diglycolamides, for the extraction of lanthanides and actinides in HNO₃-n-dodecane system, *Solvent Extr. Ion Exch.* 19 (2001) 91–103, <https://doi.org/10.1081/SEI-100001376>.
- [18] S. Tachimori, Y. Sasaki, S. Suzuki, Modification of TODGA- n -dodecane solvent with a monoamide for high loading of lanthanides(III) and actinides(III), *Solvent Extr. Ion Exch.* 20 (2002) 687–699, <https://doi.org/10.1081/SEI-120016073>.
- [19] Z.-X. Zhu, Y. Sasaki, H. Suzuki, S. Suzuki, T. Kimura, Cumulative study on solvent extraction of elements by N, N, N', N'-tetraoctyl-3-oxapentanediamide (TODGA) from nitric acid into n-dodecane, *Anal. Chim. Acta* 527 (2004) 163–168, <https://doi.org/10.1016/j.aca.2004.09.023>.
- [20] M. Mohammadi, K. Forsberg, L. Kloof, J. Martinez De La Cruz, Å. Rasmuson, Separation of ND(III), DY(III) and Y(III) by solvent extraction using D2EHPA and EHEHPA, *Hydrometall.* 156 (2015) 215–224, <https://doi.org/10.1016/j.hydromet.2015.05.004>.
- [21] Y. Sasaki, M. Matsumiya, Y. Tsuchida, Basic research on batchwise multi-stage extractions using TODGA for Dy/Nd separation, *Anal. Sci.* 36 (2020) 1303–1309, <https://doi.org/10.2116/analsci.20P129>.
- [22] A.M. Hyde, S.L. Zultanski, J.H. Waldman, Y.-L. Zhong, M. Shevlin, F. Peng, General principles and strategies for salting-out informed by the hofmeister series, *Org. Process Res. Dev.* 21 (2017) 1355–1370, <https://doi.org/10.1021/acs.oprd.7b00197>.
- [23] Y. Sasaki, Y. Tsubata, Y. Kitatsuji, Y. Sugo, N. Shirasu, Y. Morita, T. Kimura, Extraction behavior of metal ions by TODGA, DOODA, MIDOA, and NTAamide extractants from HNO₃ to n-dodecane, *Solvent Extr. Ion Exch.* 31 (2013) 401–415, <https://doi.org/10.1080/07366299.2013.800431>.
- [24] Q. Tian, M.A. Hughes, The mechanism of extraction of HNO₃ and neodymium with diamides, *Hydrometall.* 36 (1994) 315–330, [https://doi.org/10.1016/0304-386X\(94\)90029-9](https://doi.org/10.1016/0304-386X(94)90029-9).
- [25] G.R. Choppin, Solution chemistry of the actinides, *Radiochim. Acta* 32 (1–3) (1983) 43–54, <https://doi.org/10.1524/ract.1983.32.13.43>.
- [26] G.R. Choppin, A. Morgenstern, Thermodynamics of solvent extraction, *Solvent Extr. Ion Exch.* 18 (2000) 1029–1049, <https://doi.org/10.1080/07366290008934721>.
- [27] J. Mackey, *A Study of the Rare-Earth Chelate Stability Constants of Some Aminopolyacetic Acids*, Iowa State University, 1960.
- [28] D.L.G. Rowlands, Observations on the separation factors of the rare earths with various ligands, *J. Inorg. Nucl. Chem.* 29 (1967) 809–814, [https://doi.org/10.1016/0022-1902\(67\)80338-5](https://doi.org/10.1016/0022-1902(67)80338-5).
- [29] Y. Sasaki, H. Suzuki, Y. Sugo, T. Kimura, G.R. Choppin, New water-soluble organic ligands for actinide cations complexation, *Chem. Lett.* 35 (2006) 256–257, <https://doi.org/10.1246/cl.2006.256>.
- [30] Y. Sasaki, Y. Sugo, Y. Kitatsuji, A. Kirishima, T. Kimura, G.R. Choppin, Complexation and back extraction of various metals by water-soluble diglycolamide, *Anal. Sci.* 23 (2007) 727–731, <https://doi.org/10.2116/analsci.23.727>.
- [31] M.-C. Charbonnel, C. Berthon, L. Berthon, N. Boubals, F. Burdet, M.-T. Duchesne, P. Guilbaud, N. Mabile, S. Petit, N. Zorz, Complexation of Ln(III) and Am(III) with the hydrosoluble TEDGA: speciation and thermodynamics studies, *Proc. Chem.* 7 (2012) 20–26, <https://doi.org/10.1016/j.proche.2012.10.005>.
- [32] S. Chapron, C. Marie, G. Arrachart, M. Miguiditchian, S. Pellet-Rostaing, New insight into the americium/curium separation by solvent extraction using diglycolamides, *Solvent Extr. Ion Exch.* 33 (2015) 236–248, <https://doi.org/10.1080/07366299.2014.1000792>.