THESIS FOR THE DEGREE OF LICENCIATE OF ENGINEERING

The Diluent Effect on the Solvent Extraction of Rare Earth Elements from Neodymium Magnet Leachate

MARINO GERGORIĆ

Industrial Materials Recycling
Department of Chemistry and Chemical Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
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Industrial Materials Recycling
Department of Chemistry and Chemical Engineering
Chalmers University of Technology
SE-412 96 Gothenburg
Sweden
Telephone +46 (0)31-7721000

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ABSTRACT

Rare earth elements (REEs) have become vital components in a wide range of industrial applications. The demand for the REEs has grown significantly in the last few decades. This has led to increasing costs and supply chain risk. Today, despite lower prices than in 2011, they are classified as the highest supply risk elements in the EU; thus new incentives for recycling the REEs out of electronic scrap were brought forth. End-of-life neodymium magnets are a viable source for the recovery of some REEs. Although mainly iron alloys, these materials contain neodymium, dysprosium and small admixtures of praseodymium and terbium.

Leaching followed by solvent extraction of the REEs out of the leachate is an attractive and efficient way of recycling these elements out of end-of-life neodymium magnets. The issues that are encountered along this recycling path is the separation of the REEs from the other elements that are dissolved with the REEs into the leachate and achieving high separation factors between the REEs from each other. Extracting agents such as D2EHPA (di(2-ethylhexyl)phosphoric acid) and TODGA (tetraoctyl diglycolamide) have been previously used for achieving good separation of the REEs under specific extraction conditions.

This thesis has focused on the development and optimization of REE extraction from real commercial waste sources, the nitric acid and sulfuric acid media leachates of the neodymium magnet waste, using TODGA and D2EHPA as extracting agents, respectively. Selective REE extraction from the solution with minimal or no co-extraction of other elements in the leachate is hoped to provide a novel route to a commercially viable route to recyclable REE products. The composition of the organic phase was investigated in order to study the effect of the diluent on the overall extraction process, a well-known optimization parameter, however infrequently used. The effect of the diluent on the separation factors was also discussed as well as some characteristics of the aqueous phase on the overall extraction process. The named extractants were used at various concentrations in different diluents like solvent 70, hexane, octane, cyclohexanone, toluene, 1-octanol and chloroform. Both extractants demonstrated good selectivity concerning the extraction of the REEs out of the neodymium magnet waste leachates.

KEYWORDS : neodymium magnets, rare earth metals, recycling, solvent extraction, diluents, TODGA, D2EHPA

LIST OF PUBLICATIONS

The work presented in this thesis is based on the work contained in the following papers:

Paper I

Marino Gergorić, Christian Ekberg, Britt-Marie Steenari, Teodora Retegan. Separation of heavy rare-earths from light rare-earths via solvent extraction from neodymium magnet leachate – diluent effect.

Paper II

Marino Gergorić, Christian Ekberg, Mark Foreman, Britt-Marie Steenari, Teodora Retegan. Characterization and leaching of the neodymium magnet waste and solvent extraction of the rare earth elements using TODGA.

Contribution: all experimental work and data analysis

ABBREVIATIONS AND PHYSICAL QUANTITIES

$\alpha_{A/B}$	Separation factor between A and B
θ	Organic to aqueous phase ratio
Cyanex 923	Trioctylphosphine oxides; TRPO
Cyanex 925	Triisooctylphosphine oxide
D	Distribution ratio
D2EHPA	Di(2-ethylhexy)phosphoric acid
EHEHPA	2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester
EU	European Union
HDDs	Hard disk drives
HREEs	Heavy rare earth elements
ICP-OES	Inductively coupled plasma – Optical Emission Spectroscopy
LREEs	Light rare earth elements
MRI	Magnetic resonance imaging
NdFeB	Neodymium magnets
REEs	Rare earth elements
rpm	Rotations per minute
SmCo	Samarium-cobalt magnets
TALSPEAK	Trivalent Actinide/Lanthanide Separations by Phosphorus Extractants from Aqueous Komplexes
TRUEX	TRansUranium EXtraction
TBP	Tributyl phosphate
TODGA	Tetraoctyl diglycolamide
USA	United States of America
vpm	Vibrations per minute
w. %	Weight percentage

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1. INTRODUCTION

Rare earth elements (REEs) have become essential and critical materials in many modern technologies. Due to their unique magnetic, spectroscopic, electric and catalytic properties, they have played a pivotal role in the development of various products such as neodymium-iron-boron (NdFeB) permanent magnets, commonly referred to as neodymium magnets, samarium-cobalt (SmCo) permanent magnets, lamp phosphors and batteries, to name a few. During the last decades, around 95 % of the global demand for REEs was supplied by China, which has led to a significant price increase of these elements particularly since the global financial crisis in 2011. [1] With ever growing demand, fluctuating prices, and significant supply risk REEs are currently categorized as the most critical elements in the EU. [2]

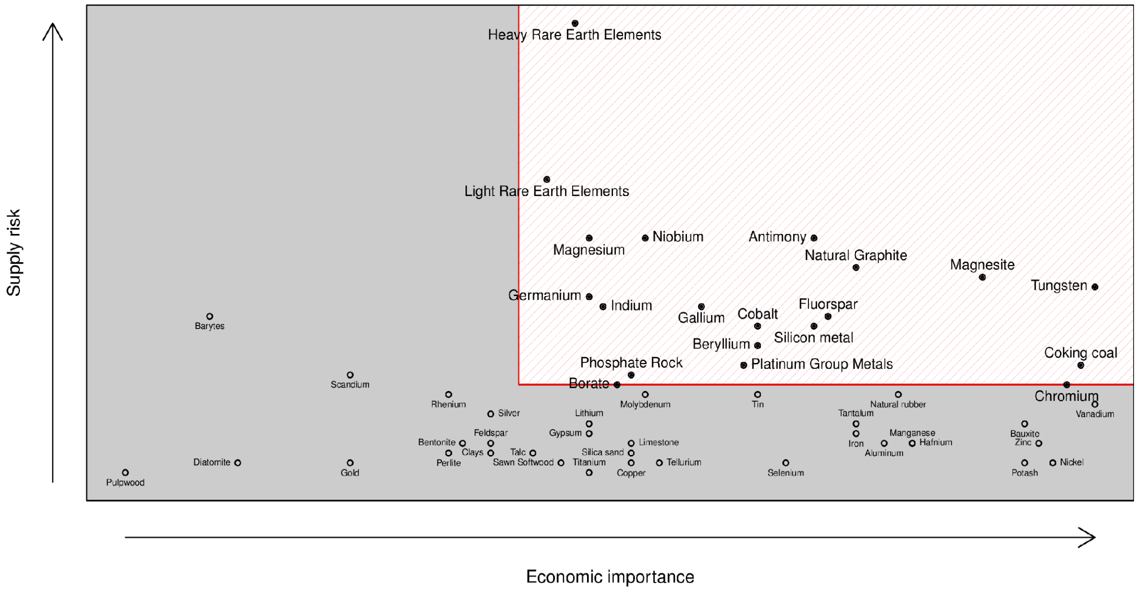


Figure 1. Critical assessment of a wide range of raw materials by the EU commission in 2013 according to economic importance and supply risk. [2]

It can be observed in Figure 1 that the REEs are considered the most critical elements with respect to supply risk in the EU, with the HREEs being at the highest risk of supply. It is thus important to assure the supply risk is eliminated, or at least minimized to the lowest possible level. Recycling of the REEs from end-of-life products could help lower the supply risk by recovering the REEs from these products.

A range of methodologies for the recovery and reuse from end-of-life products are being investigated, but industrial-scale applications are almost non-existent. [1, 3-5]. End-of-life neodymium magnets are viewed as a viable secondary source for obtaining some REEs. They are used in hard disk drives (HDDs), motors in hybrid cars, wind turbines and MRI machines, among others. [3] Since their use has increased in the last few decades and new waste is produced daily, they could be a viable stock for further reprocessing after they have been used. The recycling could, to a certain extent, help stabilize the market price. Very few large-scale recycling processes have been developed, mostly due to the lack of data about the quantities of the REEs in the waste streams and the fate of magnets after shredding. The lack of incentives for developing such a process have also been a key factor and are mostly a result of the low prices of the REEs up to 2011. [6]

The recycled and purified products of the recycling of neodymium magnets have a potential of being used as raw starting materials for the production of new neodymium magnets, other products containing REEs or can be sold as raw materials. Up to five REEs can be found in the neodymium magnets. These are neodymium, dysprosium, praseodymium, gadolinium and smaller amounts of terbium. [1] The overall goal in an industrial process is to achieve a circular system of production and eventual reuse/recycling of the neodymium magnets.

Solvent extraction or liquid-liquid extraction, a hydrometallurgical method, is a frequently used method for the recovery and removal of metal ions from aqueous solutions. [7] It is based on the phenomenon in which metal ions from the aqueous solution are distributed between organic and aqueous phase in a constant and specific ratio, dependent on the composition of the aqueous and organic phase and other external factors. Solvent extraction was used in this work as method of recovery of REEs out of aqueous solutions obtained by leaching of the neodymium magnet waste.

1.1. The scope of the thesis

The main objective of this work is to assess the feasibility of the selective extraction of the REEs from real neodymium magnet waste leachate in nitric and sulfuric media, leaving other elements in the aqueous solution. The main focus has been the effect of the solvent and the diluent making up the organic phase on the recovery of REEs out of aqueous solutions. The extractants employed were tetraoctyl-diglycolamide (TODGA) and di-(2-ethylhexyl) phosphoric acid (D2EHPA). The used diluents were Solvent 70, hexane, octane, cyclohexanone, toluene, 1-octanol and chloroform. Critical system parameters were investigated like the concentration of extractant in the organic phase, acidity of the aqueous phase, ionic strength of the aqueous phase and kinetics of extraction. Together with the investigation of bulk REEs extraction from commercial waste, studies on element specific separation of the adjacent and non-adjacent REEs were conducted. Tentative steps towards the separation of the REEs from each other were taken; whereby the extractant concentration and the diluent effect on this kind of separation were investigated.

2. BACKGROUND

2.1. RARE EARTH ELEMENTS

The REEs are a group of 17 closely related elements. These are scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium. [8] Scandium and yttrium are located in the d-block of the periodic system, while the lanthanides belong to the f-block. The REEs are separated into two groups: the so called *light rare earth elements* (LREEs), i.e. lanthanum through gadolinium, referred to as the cerium group, and the *heavy rare earth* elements (HREEs), i.e. terbium through lutetium plus yttrium, sometimes referred to as the yttrium group. LREEs are characterized by increasing number of unpaired electrons from 0 to 7, while HREEs have an increasing number of paired electrons from 8 to 14. Yttrium is added to the HREEs group due to the similarity in the ionic radius and chemical properties to the group. [9] The chemistry of the REEs in aqueous solutions is dominated by the 3 + oxidation state, with some exceptions due to the stability of the half-filled or filled f-orbitals (Ce^{4+}, Eu^{2+} and Yb^{2+}). Chemical bonding in these elements is predominantly ionic in nature, with very limited covalent character. Ln^{3+} are hard Lewis acids and exhibit fast ligand exchange in aqueous solutions. [10] Some of the characteristics of hard Lewis acids are small ionic radii, high oxidation states, low polarizability and high electronegativity. [11]

Even though they are called ʻʻrareʼʼ earths, they are comparatively abundant in the Earth's crust, but despite their abundance they are quite dispersed and the number of economically feasible exploiting sites is limited. [12] Since they are chemically similar, they occur together naturally in a wide range of ores.

REEs are found in a wide range of products, such as fluorescent lamps, magnets, superconductors, lasers, ceramics, semiconductors, catalysts, and thermal neutron absorbents. [13] The percentage of the REEs used by application is summarized in table 1.

*Table 1. Usage of REEs by application (in w. %), taking into consideration only REEs in the composition. [1]**

Application	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Other
Magnets			23.4	69.4			2	0.2	5		
Battery alloys	50	33.4	3.3	10	3.3						
Metallurgy	26	52	5.5	16.5							
Auto catalysts	5	90	2	3							
FCC	90	10									
Polishing powders	31.5	65	3.5								
Glass additives	24	66	1	3						2	4
Phosphors	8.5	11				4.9	1.8	4.6		69.2	
Ceramics	17	12	6	12						53	
Others	19	39	4	15	2		1			19	

* Average values by consumption, might vary from manufacturer to manufacturer

2.1.1. Recycling of rare earth elements

Many of the mentioned products are important for the development of environmentally friendly technologies for transport, lighting, energy storage and manufacturing of chemicals, all of which are essential to the human existence nowadays. Thus, the demand for REEs is constantly growing. Since they are mined in only a few countries and their prices have varied in the recent years, their supply is considered critical in both the EU and the USA. [1] After the sky-rocketing of the prices of REEs in 2011, it became clear to what extent the developed economies are dependent on these elements, and should do all to be less dependent on the main provider, China, which at that time and even up to this day provides over 90 % of the world's need for these elements. The fact that a very low percentage [3, 14] of the REEs are recycled to this day, mostly due to lack of incentives in the past decades, makes the recycling process investigation and development even more important and challenging.

The REEs are chemically very similar, thus they occur as mixtures in nature.[8] This means they will be hard to separate from one another from a primary source, and equally so from an end-of-life product. Since many of the applications require REEs in elemental form, the separation of the individual REEs from each other is essential for further development and production of the final products. The separation of REEs has been shown to be one of the most difficult in inorganic chemistry. On an industrial scale, this is done by solvent extraction or ion-exchange.[10, 15]

2.2. NEODYMIUM MAGNETS

One of the most important applications of the REEs are the so called neodymium magnets, sometimes referred to as the NdFeB magnets. Neodymium magnets are used in many high-tech and clean energy applications, such as HDDs, electric vehicles and electric generators in wind turbines, shown in Figure 2. [16]

Figure 2. Some of the most important applications of neodymium magnets: a) HDDs [17], b) electric vehicles [18], c) wind turbines [19]

Neodymium magnets are the strongest permanent magnets commercially available. Chemically, they are made of an alloy of neodymium, iron and boron which form a tetragonal $Nd_2Fe_{14}B$ crystalline structure. [20]

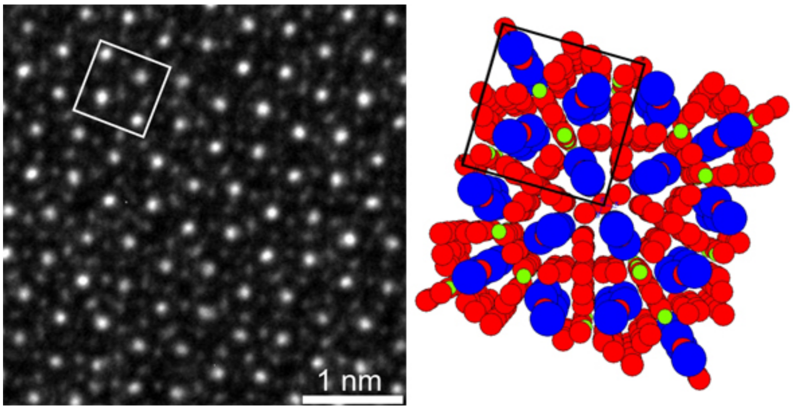


Figure 3. The $Nd_2Fe_{14}B$ crystalline structure

The $Nd_2Fe_{14}B$ matrix phase is surrounded by a neodymium rich grain boundary phase, with small admixtures of praseodymium, gadolinium, terbium and dysprosium, as well as other elements, such as aluminum, cobalt, copper, molybdenum, niobium, titanium, vanadium and zirconium [1], which are usually added to the $Nd_2Fe_{14}B$ alloy to improve certain properties of the magnet. The addition of dysprosium improves the high temperature performance of the magnet and increases their intrinsic coercitivity. Small but considerable amounts of cobalt are added to increase the Curie temperature of the magnet, the temperature at which certain materials lose their permanent magnetic properties. [21] This points out that the neodymium magnets used at higher operating temperatures will contain more cobalt and vice versa.

*Table 2. Typical composition of NdFeB magnets in w. % [3]**

Element	Elemental composition in *w.* %		
Co	4.22		
Fe	58.16	65-70	69
Nd	25.95	30	25
Pr	0.34		
Dy	4.21	3	4
B	1	1	1
Other	1		

*data obtained by total dissolution

As seen from Table 2, the neodymium magnets contain mainly iron, which makes up around two thirds of the material, and neodymium, which makes around one third of the alloy. Other elements that can be found in considerable amounts are boron, cobalt and dysprosium.

In the last two decades the neodymium magnets have largely replaced the samarium-cobalt (SmCo) permanent magnets due to better magnetic properties. Furthermore, the SmCo magnets require large amounts of cobalt, which significantly increases the cost of the material. The drawbacks of the neodymium magnets are lower operating temperature and lower corrosion resistance than that of SmCo magnets. [1] The corrosion resistance is increased by plating the surface with a protective layer, usually consisting of nickel and copper.

2.2.1 Why recycle end-of-life neodymium magnets?

Neodymium magnets are, as already stated, a good secondary source of some valuable elements. Since they make up the majority of the permanent magnets market today, more waste is expected to be produced. They are more interesting from a recycling point of view than SmCo magnets, which make up less than 2 % of the permanent magnets market. [1] The recycling process of the neodymium magnets can be further complicated by the protective coating.

The reuse of the already existing magnets is the most viable method of recycling these magnets, which is only possible with big and easily accessible magnets in electric vehicles and wind turbines, but these magnets will be in use for a long period of time and are not available in large quantities in scrap today. The main source of such end-of-life waste today are considered to be electronic goods like loudspeakers, cell phones and HDDs. [1] It is very hard to recover the neodymium magnets out of such products because of the size of the magnets in those products, they tend to stick to other ferrous components during shredding and they need to be demagnetized before reprocessing. Only a handful of industrial methods have been developed such as the the method of recycling of the neodymium magnets from HDDs and air conditioning devices via dismantling and further sorting based on magnetic properties developed by the Hitachi corporation in Japan in 2013. [22]. Some other demonstrational plants for recycling have also been developed [23], but with no successful large scale industrial applications to date. The greatest issue that is encountered, even when the method of the recycling of the REEs containing products has been developed, is the price fluctuation of the elements. [24] Since that has been the case in the last 2 years, the prices being sky-high to prices being reasonably low, a lot of up-scaling of the neodymium magnets recycling and new and old mines openings have been delayed or cancelled. As soon as the price of element of interest drops, the interest for proceeding with the project by the company seems to fade, and keeping the process alive is almost impossible, the main reason being negative profit. So the overall conclusion to this problem is, the more the price of the raw materials increases, the more profitable it will be to recycle the existing end-of-life materials at the end. Some legislations might be needed to keep the recycling business alive since the very dynamic market and the values of the individual elements can crash such ideas and dreams in a glimpse of an eye.

Recycling of REEs and other metals from magnets can be done by hydrometallurgical and pyrometallurgical methods. Pyrometallurgical methods include electroslag refining, direct melting and liquid metal extraction. [1] Hydrogen decrepitation is a method that is also being under investigation and development. [16] These methods surpass the scope of this thesis and will not be further discussed in this work.

2.2.2. Recovery of REEs out of neodymium magnets waste via hydrometallurgy

Hydrometallurgical processing neodymium magnets involves leaching of these elements with mineral acids, followed by solvent extraction, ion exchange or precipitation for isolation and separation of the desired metals. [1, 3, 7] There are many advantages of using hydrometallurgy for the recovery of REEs out of neodymium magnet waste such as the large applicability on most types of commercial magnets and the already existing knowledge since the reprocessing of the end-of-life neodymium waste is similar to the recovery of the REEs form the mining ores. The main disadvantage of the hydrometallurgical methods compared to the pyrometallurgical methods is the large volume of solvents and acids used for the recovery of the elements from the waste, however this can be mitigated by solvent recycling, e.g. organic phase, by stripping and scrubbing of the loaded phase.

During the leaching step, selectivity of the leaching agent is important since the majority of the magnet (around 72 %) consists of iron. Iron will thus make up the majority of the ions in solution, which might pose challenges in separating the REEs e.g. co-extraction by phosphine oxides during solvent extraction. Selective leaching of iron from the magnet scrap might be only a partial solution to the problem, due to the presence of other elements such as boron and the copper and nickel used in the corrosion protection layer. [3]

The idea of the selective leaching of REEs and as little as possible of other constituent materials, including iron, is of much interest. [1] Results obtained by Önal and co-workers. [25] demonstrate that powdered neodymium magnet scrap can be selectively leached, leaving iron in the solid residue. The powdered samples were transformed into a sulfate mixture by mixing the powder with sulfuric acid in alumina crucibles with the acid / magnet ratio (g/g) of 2.15 (12 M), 3.2 (13.5 M), 4.3 (14.5 M), and 8.6 (16 M). The achieved mixtures were then dried in a muffle furnace at 110 ^{o}C for 6-24 h. The dried samples were then treated at 650-800 ^{o}C for 15-120 minutes for a selective roasting process. The obtained products were later leached with demineralized water for 15 min to 24 h at 225 rpm on a shaker. This process led to 95-100 % extraction efficiencies for neodymium, praseodymium, dysprosium and gadolinium while iron remained in the residue after leaching. The whole concept was based on the different solubility product values of REEs sulfates and iron sulfate.

In 2013. Lee C. et al [26] reported on leaching neodymium magnet scrap with HCl, HNO_3, H_2SO_4 or NaOH. The process was optimized with regards to temperature, leaching time, concentration of leaching reagent and solid to liquid ratios. HCl and H_2SO_4 showed best performance. Neodymium was successfully recovered from optimized H_2SO_4 leaching solution with 75.41 % by precipitation. The optimum conditions were solid to liquid ratio (S : L) of 20 g/L, 15 minutes leaching time and 3 M hydrochloric acid or 1.5 M sulfuric acid.

In 2014. Yoon at al [27] performed a similar investigation where increasing the leaching temperature gave increased leaching effect of H_2SO_4 when leaching the neodymium magnet scrap. The optimal leaching conditions were determined to be 4 hours leaching time at 70 ^{o}C using 3 M H_2SO_4.

After the leaching step the elements from the solution are usually precipitated, extracted with an organic solvent or ionic liquid, or separated using ion exchange. The solvent extraction can be done with all the conventional extractants present on the market, like D2EHPA, TBP (tributyl phosphate), PC-88A (2-ethylexyl hydrogen 2-ethylhexyl phosphonate) and EHEHPA (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester), which have been used for REEs extraction from mineral acid media in the past. [28, 29]

The mentioned extracting agents have however shown some drawbacks concerning selectivity, stripping of the elements out of the solution and extraction kinetics. The issues in the case of conventional extractants is the co-extraction of other elements that were leached into the solution. Moreover, almost none of the today's industrially used extracting agents follow the CHON principle.[30] A promising extractant that could be employed for the extraction of the REEs out of the leachate containing all the elements leached from the neodymium magnet waste is TODGA (N,N,N',N'-tetraoctyl-diglycolamide) which showed high distribution ratios of lanthanides and actinides when extracted from highly acidic solutions.

It was also found that the loading capacity of 0.1 M TODGA-n-dodecane was 0.008 M Nd(III) with an aqueous phase of 3 M HNO3. [31] An especially interesting fact for this research is the very low distribution ratios ($< 10^{-2}$) of iron (III) and aluminum (III) that have been shown by the investigation of the extraction of with 0.1 TODGA in n-dodecane from 2.9 M HNO3. [32]

In 2015 at the Oakridge National Laboratory, Tennesee a process with the membrane solvent extraction was conducted comparing the extraction of REEs from a neodymium magnet leachate with Cyanex 923. With the TODGA, Neodymium, dysprosium and praseodymium were selectively recovered with the TODGA, resulting in no co-extraction of non-REEs such as iron and boron. [33]

2.3. SEPARATION OF REEs FROM EACHOTHER

As mentioned previously the chemistry of the REEs is very similar, making individual REEs separation from each other quite a challenging task.

There is one unique property of the lanthanide group, called the *lanthanide contraction*. The decrease in the ionic radii in the lanthanide group from lanthanum to lutetium, which is greater than expected and does not follow the same trend as in other periods in the periodic table of elements. This is the result of the poor shielding of the nuclear charge by the 4f electrons, meaning the 6s electrons are more strongly drawn to the nucleus, resulting in smaller radius.[34] This property plays an important role in the separation of the REEs, particularly in solvent extraction, since the ionic radius can lead to the formation of complexes with different stability constants and consequently their solubility in the organic phase, thus somewhat enabling their separation.

A phenomenon known as the tetrad effect is a common feature discovered in the lanthanide group of metals which is linked to the distribution of REEs in nature and in the liquid-liquid separation processes. It refers to the separation of REEs into four separate segments called tetrads (first tetrad, La-Ce-Pr-Nd; second tetrad, (Pm)-Sm-Eu-Gd; third tetrad, Gd-Tb-Dy-Ho; fourth tetrad, Er-Tm-Yb-Lu). [35]

Many attempts to separate the f-block elements have been made since the 1950s, especially in the nuclear field where it has been crucial to separate the REEs from the actinides due to the high neutron absorption cross section which lanthanides possess. That can interfere with the reuse of actinides in further nuclear operations. [29] Thus the TALSPEAK (Trivalent Actinide/Lanthanide Separations by Phosphorus Extractants from Aqueous Komplexes), a process of based on extraction of REEs with the organophosphorous extractants like D2EHPA with the aqueous phase containing diethylenetriamine N, N, N′, N′ petnaacetic acid (DTPA) as as the actinide complexating agent, and TRUEX (TRansUranium EXtraction) processes were developed.[28] But since the basic idea of f-elements separation changed through history, from the idea of creating a promising energy source to the idea of environment restoration adopted today the approach to the f-block elements separation changed as well. With the growing demands for REEs, and the requirements for their purity this separations techniques for separating the REEs from each other were further investigated.

Some attempts in separating the REES from each other are listed below.

In the separation of REEs, organophosphorous extractants are commonly used. Di(2-ethylhexyl)-phosphoric acid (D2EHPA), an acidic extractant, is commonly used on a larger industrial scale. [36] The selectivity order for extracting rare earths from 0.5 M HCl solution with 0.75 M D2EHPA in toluene was found by Peppard and coworkers to be Lu > Yb > Tm > Tb> Eu >Pm> Pr> Ce> La with the log of the distribution coefficient increasing linearly with the atomic number of the rare earth. [37]

D2EHPA has also been used to separate samarium, europium, and gadolinium from the other REEs in a mixed nitrate-chloride leachate from monazite. [38] Furthermore, in many studies [28] it was shown that a typical separation factor between adjacent REEs using the D2EHPA extractant is in the region of 2.5.

Many studies have been conducted on the separation of REEs with D2EHPA and other related extractants in various mineral acid media like nitric, sulfuric and nitric. [39] They have shown the best mutual separation properties in lanthanide separation so far.

Cyanex 925 in n-heptane was used for the extraction of REEs out of nitric acid media. The separation between the LREEs and HREEs was possible, in a few stages. The REEs were stripped back using nitric acid. [40]

It is known that by changing the diluent in the organic phase, the properties of the extraction change as well. It is thus important to investigate the effect of the diluent on the separation of the REEs from each other.

In a study from Oakridge National Laboratory (1961) the separation of Am and Eu with TIOA (triisooctylamine) in various diluents. It was shown that the separation factors do indeed change with the diluents composition change.

In a study by Dukov et. al. [41] an investigation of the separation of La, Nd, Eu, Ho and Lu using HTTA (thenoyltrifluoroacetone) and the quaternary ammonium salt Aliquat 336 in chloride or perchlorate form was studied. Chloroform, benzene, tetrachloromethane and cyclohexane were used as diluents. The study did not show a direct connection about the diluent effect of the separation factors, but the separation factors between lanthanum and neodymium increased when chloroform was changed with benzene, cyclohexanone and tetrachlorometane.

TODGA has been tested for extraction in various diluents and it has been shown that the stoichiometric factors vary by changing the diluent (toluene, 1-octanol, chloroform and others), which could have effects on the separation factors and should be further investigated. [29]

3. THEORY

3.1. SOLVENT EXTRACTION

The term solvent extraction or liquid-liquid extraction refers to the distribution of a solute between two immiscible or partially miscible liquid phases, usually one organic and one aqueous phase. [11]

In solvent extraction, the solvent, or organic phase, is made up of an extractant dissolved in a diluent. In some cases, pure extractant is used, but it is more common to use a diluent since many extractants are viscous materials in their undiluted form. A third component, a modifier, may be added to the organic phase to prevent third phase formation. The solute is usually a metal ion that is extracted into the organic phase.

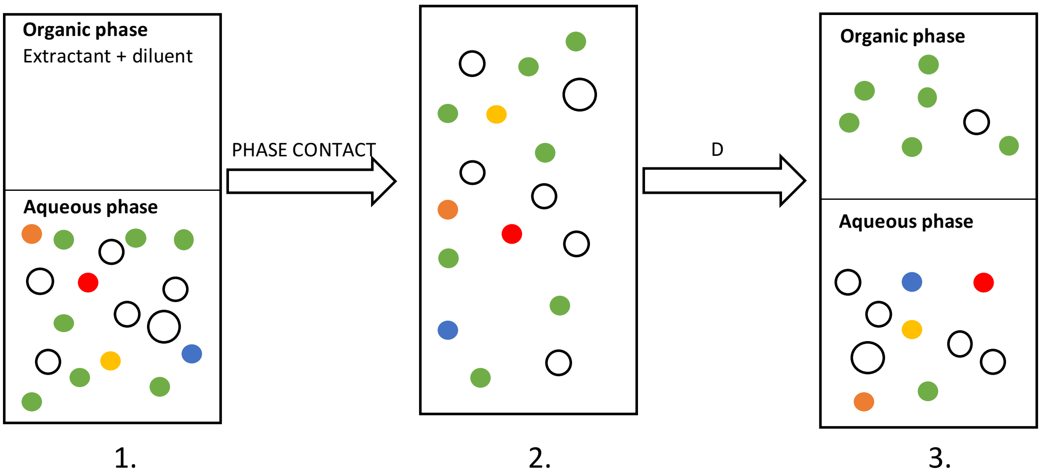


Figure 4. Schematic display of a solvent extraction process. (1) Two immiscible phases (aqueous and organic), the aqueous phase containing the metals of interest. (2) The two phases are put in contact by vigorous shaking or stirring. (3) The two phases are disengaged and the metals of interest are transferred into the organic phase.

The parameter representing the distribution of the metal of interest between the two immiscible phases is called distribution ratio (*D*). It is defined as the ratio of the total concentration of the metal A in the organic phases and the total concentration of the metal A in the aqueous phase.

$$D_A = \frac{[A]_{org}}{[A]_{aq}} \tag{1}$$

The parameter showing the degree of separation between the two solutes in the same extraction system is called the separation factor (α). It can be calculated from equation (2).

$$\alpha_{\mathrm{A/B}} = \frac{D_A}{D_B} \tag{2}$$

In order for the metal to be extracted into the organic phase, the aqueous metal species need to be chemically modified to be make them hydrophobic and soluble in the organic phase. The organic molecular species that are involved in this process are called extractants and, depending on the mechanism of the extraction of the metal from the aqueous into the organic phase, they can be classified in three main groups: [42]

- ACIDIC: the organic acid dissociates and its conjugated base reacts with the cation to form a neutral complex according to the following equation 3: [7]

$$\mathrm{Ln^{3+}} + \overline{\mathrm{m(HR)_2}} \rightleftarrows \overline{\mathrm{LnR_3(HR)_{2m-3}}} + 3\,\mathrm{H^+} \tag{3}$$

where HR represents the associated acidic extractant molecules and Ln^{3+} the REE ion in the solution.

- BASIC / ION PAIR: the organic specie forms an ion pair with the negatively charged metal complex in the aqueous phase according to the following equations 4 and 5:

$$2\overline{\mathrm{RNH_2}} + 2\mathrm{H_2SO_4} \rightleftarrows 2\overline{\mathrm{(RNH_3)_2SO_4}} \tag{4}$$

$$2\mathrm{Ln(SO_4)_3^{3-}} + 3\overline{\mathrm{(RNH_3)_2SO_4}} \rightleftarrows 2\,\overline{\mathrm{(RNH_3)_3\,Ln(SO_4)_3}} + 3\mathrm{SO_4^{2-}} \tag{5}$$

where RNH_2 represents the tri-alky methylamine and Ln^{3+} represents the REE ion in the aqueous solution. This extraction mechanism is only possible in the presence of strong anionic ligands.

- SOLVATING: the hydrating water in the inner sphere of the metal atom are replaced with the organic species according to the following equation 6:

$$\mathrm{Ln^{3+}} + 3\mathrm{NO_3^-} + 3\overline{\mathrm{TBP}} \rightleftarrows \overline{\mathrm{LnTBP_3(NO_3^-)_3}} \tag{6}$$

TBP represents tributyl phosphate, a common solvating extractant, and Ln^{3+} the REE ion in the aqueous solution.

Solvent extraction has a wide range of applications, which include nuclear reprocessing, metal recovery from aqueous solutions and production of organic compounds. [11]

When considering the use of a certain extracting agent, some key properties need to be taken into consideration prior to the application: [42, 43]

- Reasonable cost of production
- Chemical and photochemical stability
- Very low solubility in aqueous solutions
- Soluble in organic diluents
- Selectivity towards the solute to be extracted
- Extraction occurs without the addition of modifiers
- Efficient function of the extractant-diluent mixture with the proposed feed and strip solution in terms of rates of operations and degradation stability

3.1.1. Solvent extraction using the acidic extractant D2EHPA

Di-(2-ethylhexyl)phosphoric acid is an organophosphorous compound, which is primarily used in the solvent extraction of uranium and REEs. It has shown good versatility as an extractant for lanthanide separations due to its chemical stability, good kinetics in extraction, good loading and stripping properties and availability in commercial quantities.[44] Many authors [45, 46] have reported that the extraction of REEs with D2EHPA (here called HR) occurs according to the reaction path described in equation 7,

$$\mathrm{M^{3+}} + \overline{\mathrm{m(HR)_2}} \rightleftarrows \overline{\mathrm{MR_3(HR)_{2m-3}}} + 3\,\mathrm{H^+} \tag{7}$$

where M^{3+} is the lanthanide ion in the solution, HR is the organophosphorous extractant in the organic phase occurring as a dimer $(HR)_2$ and as $MR_3(HR)_{2m-3}$ in the complex formed, soluble only in the organic phase.

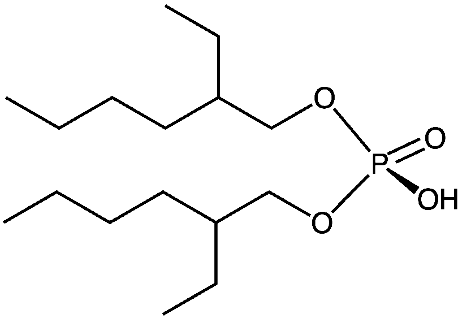


Figure 5. Structural formula of D2EHPA (di-(2ethylhexyl)phosphoric acid)

3.1.2. Solvent extraction using the solvating extractant TODGA

N, N, N′,N′-tetraoctyl-diglycolamide is a solvating extractant, which creates strong tridentate complexes with metal ions, and has shown particularly good extraction properties for REEs ions in terms of selectivity in comparison to other ions in the aqueous solution. [32] This extractant has shown good stability at room temperature and mutual miscibility with the commonly used diluents. The only setback for large industrial use is currently the price.

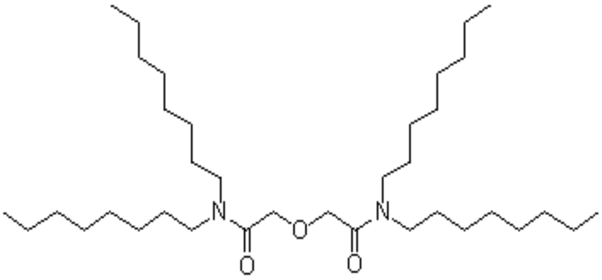


Figure 6. Structural formula of TODGA (N, N, N′, N′-tetraoctyl-diglycolamide)

The solvating mechanism is assumed for all the complexation reactions with TODGA. The slope can then be calculated from equation (9), m that is, which represents the number of ligand molecules that is used in the forming of the complex.

$$\mathrm{M^{n+}} + \mathrm{nNO_3^-} + \overline{\mathrm{mTODGA}} \rightleftarrows \overline{\mathrm{M(NO_3)_nTODGA}} \qquad \mathrm{K_{ex}} = \frac{[\overline{\mathrm{M(NO_3)_nL_m}}]}{[\mathrm{M^{n+}}][\mathrm{NO_3^-}]^{\mathrm{n}}[\overline{\mathrm{L}}]^{\mathrm{m}}} \qquad (8)$$

$$\log D = m \log[\overline{L}] + n \log[NO_3^-] + \log K_{ex} \qquad D = \frac{\overline{[(M(NO_3)_n L_m)]}}{[M^{n+}]} \tag{9}$$

The concentration represented in the equations is the equilibrium concentration in the organic phase after extraction, and the distribution ratio the equilibrium concentration of metals in the solution.

3.1.3. Diluents in solvent extraction

A diluent is a liquid or homogenous mixture of liquids in which extracting agent(s) and modifier(s) can be dissolved to form the solvent phase. [47] Solvent should be not used as a term since it is a broad term in the solvent extraction field. The term solvent in solvent extraction represents the mixture of the extractant and diluent. The diluent itself does not extract the solute significantly.

An array of methods for classifying diluents have been proposed as well as finding a perfect way of predicting the outcome of an extraction. This was based on the solubility parameters, connectivity, dielectric constant, but no original way has been found. [48]

Diluents can be classified according to their chemical and physical properties such as the ability to form ordered networks. They can be divided into following groups [11]:

1) Liquids capable of forming three-dimensional networks of strong hydrogen bonds, e.g. water, hydroxy acids, polyols and other.

2) Liquids containing both active hydrogen atoms and donor atoms (O, N, F) but do not form three-dimensional networks, but instead form chainlike oligomers, e.g. primary alcohols, carboxylic acids primary amines and other.

3) Liquids containing donor atoms but no active hydrogen atoms, e.g. ketones, ethers, aldehydes and other.

4) Liquids containing active hydrogen atoms but no donor atoms, e.g. chloroform and some other aliphatic halides.

5) Liquids with no active hydrogen atoms and no donor atoms, e. g. hydrocarbons, carbon disulfide, carbon tetrachloride and other.

The diverse properties of the diluents in a solvent extraction system lead to differences in distribution ratios of the solute and the overall extraction process. The diluents in group 3 often have the ability to extract the solute without further addition of the extractant. The liquids from groups 4 and 5 do not dissolve salt without the addition of the extractant and are often used as diluents in a solvent extraction system. The liquids from group 1 are easily soluble in water and are impractical from a solvent extraction point of view.[11] Water belongs to this group and it is usually used as a second phase. The polarity of the diluent can also significantly affect the extraction process since the solubility of the neutral complex in the organic phase is inversely proportional to the polarity of the organic diluent. [49] The polarity of the diluent can be expressed with the dielectric constant, also called the relative static permittivity (ε) which is a measure of chemical polarity. The values of dielectric constants for the diluents used in this work are shown in table 3:

Table 3. The values of the dielectric constant for solvent 70, hexane, octane, cyclohexanone, 1-octanol, chloroform and toluene. [50]

Diluent	Dielectric constant
Solvent 70	1.8
Hexane	1.88
Octane	2
Cyclohexanone	18.3
1-Octanol	10.3
Chloroform	4.81
Toluene	2.38

The ability of the organic diluent to form hydrogen bonds can significantly affect the extraction process. For example, alcohols have both active hydrogen atoms and donor atoms for hydrogen bonds forming. This can affect the solubility of the extractant in the diluent and thus lead to lower distribution ratios. Thus, the interactions between the diluent and the complex formed in the organic phase will depend on the properties of the diluents and the nature of the complex formed.

Water solubility is an important parameter for the organic diluents, since it will affect the phase ratio change, and it is known that the organic solvent should be as water-immiscible as possible. The water solubility of the diluents used in this work, expressed as S/mass % at 25 °C are as follows: solvent 70 (traces), hexane (0.0011), octane(0.000071), cyclohexanone(8.8), 1-octanol (0.054), toluene (0.0531) and chloroform (0.80). [51]

Along with the extractants, the diluents play a pivotal role in the extraction process a need for introducing the demands for the diluents was needed. Some of the general demands for the diluents are:[52]

- Low density
- Low water solubility
- High flash point
- High boiling point and low freezing point
- Low chemical transformation rate with water or reagents
- No third phase formation under loading conditions

4. EXPERIMENTAL

The research carried out in this work has been the investigation of the diluent effect on the solvent extraction of the REEs out of the leachate obtained by dissolution of the neodymium magnet waste. Two routes were followed for the experimental part. They can be divided into the following:

1) Leaching of the magnet powder with HNO_3 followed by solvent extraction of the REEs with TODGA diluted in various diluents. The experiments carried out in this section have focused on the characterization of the hydrogen decrepitated neodymium magnet, leaching of the waste using HNO_3, investigation of the effect of HNO_3 concentration on the solvent extraction process, investigation of the effect of diluent on the solvent extraction process and stripping of the REEs out of the organic phase.

Figure 7. Flow sheet for the leaching of the REEs out of hydrogen decrepitated neodymium magnet in HNO_3 followed by the solvent extraction with TODGA in various diluents

2) Solvent extraction of the REEs with D2EHPA, in various diluents, from a provided leachate. The experiments carried out in this section have focused on determining the composition of the aqueous phase (provided leachate), investigation of the kinetics of solvent extraction, investigation of the effect of the diluent on the solvent extraction, effect of the equilibrium pH on the solvent extraction process and stripping of the REEs out of the organic phase.

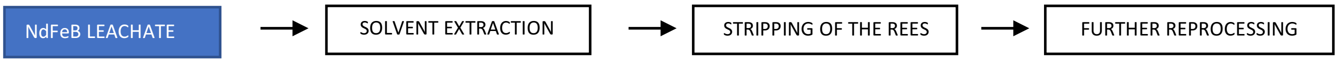


Figure 8. Flow sheet for the solvent extraction and stripping of the REES out of a leachate obtained by sulfonation roasting (sulfate media)

4.1. LEACHING OF THE MAGNET POWDER FOLLOWED BY SOLVENT EXTRACTION OF THE REES WITH TODGA

4.1.1. Determination of the composition of the magnet material

The hydrogen decrepitated neodymium magnet material was obtained by the University of Birmingham in a powder form. The particle size was 50 – 100 μm. The composition of the hydrogen decrepitated neodymium magnet material was determined after total dissolution in aqua regia at 80 ± 1 ° C. The experiments were done in triplicates which were then used for estimation of the uncertainty of a particular experiment.

Aqua regia was prepared by mixing concentrated nitric (70 %, ACS reagent, Sigma Aldrich) and hydrochloric acid (37 %, ACS reagent, Sigma Aldrich) in volume ratios of 1 : 3, accordingly. Approximately 1 g of the hydrogen decrepitated material was totally dissolved in 10 mL *aqua regia*, 10 % w/V ratio. The samples were treated for 1 hour on a heating plate. Samples obtained were left to cool for 2 hours and then filtered through polypropylene filters (0.45 μm VWR) and further diluted with 0.5 M HNO_3 (65%, suprapur®, Merck) for measurement with ICP-OES (ppm scale). No residues were observed on the filter paper.

4.1.2. Preparation of the leachate

The leachate of the NdFeB powder was prepared by dissolving roughly 1 g of the powder in 50 mL 4 M HNO_3 (70 %, ACS reagent, Sigma Aldrich). The powder leaching was carried out for 24 hours at the temperature of 25 ± 1 °C on a magnetic stirrer. The leaching experiments were done in triplicates in polypropylene bottles secured with lids. Residues were noticed at the bottom of the vial after the leaching experiment. The residue was filtered through a polypropylene filter (0.45 μm, VWR) and further dissolved in aqua regia at 80 ± 1 ° C for 1 hour on a heating plate. The dissolved residue was the diluted with 0.5 M HNO_3 (65 %, suprapur®, Merck) and the solution content was determined by the ICP-OES, and showed that only Ni was present in the residue, the element used in the coating of the magnet. The filtered leachate was also further diluted with 0.5 M HNO_3 (65 %, suprapur®, Merck) and analyzed with the ICP-OES.

4.1.3. Model solution testing

A preliminary experiment was done with the model solution representing the leachate. The model solution was prepared out of standard solutions of Nd, Dy and Fe (LGC Standards, 1000 mg/L). The model solution contained 21.49 mM Fe, 3.46 mM Nd and 0.62 mM Dy in 0.1, 1, 2, 3, 4, 5, 6 M HNO_3, to test the nitric acid concentration effect on the solvent extraction. The concentration of the nitric acid in the aqueous solution was determined by titrating with NaOH (0.1 M NaOH, FIXANAL). The aqueous phases were put in contact with 0,1 M TODGA (>97 % synthesized at Chalmers University of Technology and 2.0 g obtained by the Institut für Nukleare Entsorgung, Karsruhe Institute of Technology) in Solvent 70. The organic to aqueous phase ratio was $\Theta = 1$. The vials were shaken for 50 minutes, which was enough to achieve equilibrium [32], at the temperature of 25 ± 1 °C using a shaking machine (IKA Vibrax VXR Basic) with an adjacent thermostatic bath. Shaking speed was 1 750 vibrations per minute. The phases were put in contact in 3.5 mL glass vials (46 x 13 x 0.8 mm) with polypropylene lids. All the experiments were done in triplicates and were centrifuged at rotation speed 2 000 rpm for 1 minute before sampling. The sampled aqueous solution was diluted with 0.5 M HNO_3 and analyzed using the ICP-OES.

4.1.4. The effect of the concentration of TODGA and the diluent on solvent extraction

The filtered leachate obtained in section 4.1.2. was diluted with 3 M HNO_3 to achieve 4 000 mgL^{-1} of the totally dissolved powder in the solution, and was used in the solvent extraction experiments. The concentration of HNO_3 after the dilution was determined by titration with NaOH (0.1 M NaOH, FIXANAL), and was determined to be 3.1 M. The concentrations of TODGA used were 0.01, 0.05, 0.1, 0.2 and 0.4 M. Solvent 70 (hydrocarbons C11-C14, ≤ aromatics, Statoil, Sweden), hexane (95 %, anhydrous, Sigma Aldrich), toluene (99,8 %, anhydrous, Sigma Aldrich), cyclohexanone (≥ 99 %, ACS reagent, Sigma Aldrich) and 1-octanol (≥ 99 %, ACS reagent, Sigma Aldrich) were used as diluents for determining the optimal extraction conditions. All the organic phases were pre-equilibrated with an equal amount of 3.1 M HNO_3. Pre-equilibration was done in order to minimize the phase ratio change, since some diluents are soluble in water. It is done also to minimize the effect another species in the solution, i.e. in extractants which extract acids. [47] The phases were put in contact in 3.5 mL glass vials and were shaken using a shaking machine with an adjacent thermostatic bath. Shaking speed was 1750 rotations per minute. All the vials were shaken for 50 minutes to assure equilibrium during the extraction experiments. The experiments were performed in triplicates and the uncertainties were expressed as $\pm 1\ \sigma$. All the extraction experiments were performed at the temperature of 25 ± 1 °C. In all the performed experiments the organic to aqueous volume ratio was $\Theta = 1$. Before sampling of the aqueous phase, the vials were centrifuged at rotation speed of 2 000 rpm for 1 minute. The sampled aqueous solutions were diluted with 0.5 M HNO_3 and analyzed using ICP-OES. The distribution ratios were calculated as mass balance, the concentration of the elements in the aqueous solution before and after the extraction.

4.1.5. Stripping

Stripping (back-extraction) was performed by using 0.01, 0.1 M HNO_3 (70 %, ACS reagent, Sigma Aldrich) and MQ water as aqueous phases. The organic phase after the extraction was separated from the metal-depleted aqueous phase and put in contact with the stripping aqueous phase. This was done by putting 5 mL of each of the phases into contact over 20 minutes by manual shaking in a 20 mL glass vials. The loaded organic phases used for stripping were 0.01 M TODGA in Solvent 70 and 0.1 M TODGA in hexane after extraction. A temperature of 25 ± 1 °C was used as well as the $\Theta = 1$. All the stripping experiments were done in triplicates. The pH of the stripping solution was measured before and after the stripping experiments. The sampled aqueous phases were diluted with 0.5 M HNO_3 and measured using ICP-OES. Since the HNO_3 acid extracted by TODGA was expected to be stripped back into the aqueous solution the equilibrium pH was measured before and after the stripping.

4.2. SOLVENT EXTRACTION OF THE REES WITH D2EHPA FROM A LEACHATE OBTAINED BY SELECTIVE LEACHING

The neodymium magnet leachate was produced by Önal and co-workers using sulfation, selective roasting and water leaching. [25] The neodymium magnet leachate composition was measured using ICP-OES by diluting the sampled leachate with 0.5 M HNO_3 (65 %, suprapur®, Merck) and then performing the measurement. The experiment was done in triplicates. The pH value of the solution was measured with MeterLab^{TM} PHM 240 pH/Ion Meter pH electrode, taking into account the ionic strength of the leachate. The sulfate ion concentration needed to be determined. This was done by precipitation of $BaSO_4$ using $BaCl_2$ (99,999 % trace metal basis, Sigma Aldrich) dissolved in MQ water. The obtained precipitate was filtered through a polypropylene filter paper (0.45 μm, VWR), washed with 20 mL MQ water and then dried over 48 hours in the fume hood under normal ventilation conditions at the temperature 25 ± 1 °C. The mass difference between the dried filter paper containing the precipitate and the mass of filter paper before filtration was used as the mass of $BaSO_4$.

4.2.1. Investigation of the kinetics of solvent extraction

The study on the kinetics of the solvent extraction was done to determine the contact time needed between the two phases to achieve equilibrium and to see how the equilibrium time changes with each diluent.

During the investigation of the extraction kinetics the mixing time was varied from 1 to 20 minutes. The organic phases used were 0,6 M D2EHPA (97 %, Sigma Aldrich) diluted in in

Solvent 70 (hydrocarbons C11-C14, ≤ aromatics, Statoil, Sweden), hexane (95 %, anhydrous, Sigma Aldrich), Octane (98 %, reagent grade), toluene (99,8 %, anhydrous, Sigma Aldrich), cyclohexanone (≥ 99 %, ACS reagent, Sigma Aldrich), 1-octanol (≥ 99 %, ACS reagent, Sigma Aldrich) and chloroform (≥ 99,9 %, contains amylenes as stabilizer, Sigma Aldrich). All the organic phases were pre-equilibrated with the equal amount of MQ water. The experiments were performed in 3.5 mL glass vials at 25 ± 1 °C, aqueous to organic phase ratio Θ = 1. All the experiments were done in triplicates. The vials before each sampling were centrifuged at rotation speed of 2 000 rpm for 1 minute. The sampled aqueous phases, as well as the aqueous phases before extraction were diluted with 0.5 M HNO_3 and analyzed using the ICP-OES. The distribution ratios were calculated as mass balance of these measurements.

4.2.2. The effect of the concentration of D2EHPA and the diluent on solvent extraction

The effect of the concentration of D2EHPA and diluent on the solvent extraction of the REEs out of the leachate was investigated in order to determine the optimal organic phase composition for the solvent extraction process.

The extractant, D2EHPA (97 %, Sigma Aldrich), was used in concentrations 0.3, 0.6, 0.9 and 1.2 M diluted in Solvent 70 (hydrocarbons C11-C14, ≤ aromatics, Statoil, Sweden), hexane (95 %, anhydrous, Sigma Aldrich), Octane (98 %, reagent grade), toluene (99,8 %, anhydrous, Sigma Aldrich), cyclohexanone (≥ 99 %, ACS reagent, Sigma Aldrich), 1-octanol (≥ 99 %, ACS reagent, Sigma Aldrich) and chloroform (≥ 99,9 %, contains amylenes as stabilizer, Sigma Aldrich). All the organic phases used in this work were pre-equilibrated with MQ water before performing the experiments. The aqueous phase used for the kinetics experiments was the obtained leachate without dilution. Ika Vibrax Vxr basic shaking machine (shaking speed 1750 vibrations per minute) with an adjacent thermostatic water bath was used for the shaking experiments. All the extraction experiments were performed in 3.5 mL shaking vials (46 x 13 x 0.8 mm) made of glass. The temperature was kept at 25 ± 1 ° C and the organic to aqueous phase ratio Θ = 1. The experiments were performed in triplicates and the uncertainties were expressed as ± 1 σ. The vials before sampling were centrifuged at a rotation speed of 2 000 rpm, and the sampled aqueous phases were diluted with 0.5 M HNO_3 and analyzed using the ICP-OES with the same method as outlined above.

4.2.3. Investigation of the pH effect on extraction

Extraction with D2EHPA is pH dependent. [7] The pH of the leachate was varied in order to determine the effect of the pH on the extraction of the metals out of the aqueous phase, and to determine the possibilities of achieving higher selectivity among the elements present. The organic phase used was 0.3 M D2EHPA in Solvent 70. The equilibrium pH after extraction with no modification was 1. The pH of the aqueous phase was adjusted by adding small amounts of 0.1 M or 3 M NaOH to increase the pH or konc. H_2SO_4 to lower the pH. A certain amount of the organic phase was added to the extraction system which corresponded to the amount of the $NaOH_{aq}$ or konc. H_2SO_4 added. The equilibration was performed for 20 minutes by manual shaking before sampling to ensure re-equilibration. The sampled aqueous phases were diluted with 0.5 M HNO_3 and analyzed using the ICP-OES. The reported pH values are the measured proton activities at the specific ionic strength of each solution.

4.2.4. Stripping

After determining the optimal extraction conditions, the metals need to be stripped into the new aqueous phase for further reprocessing.

Stripping was performed by putting the organic phase from extraction into contact with 0.5, 1, 1.5, 2, 2.5 and 3 M HCl hydrochloric acid (37%, puriss, Sigma-Aldrich). The organic phase after the extraction was separated from the metal-depleted aqueous phase and put in contact with the stripping aqueous phase. The volume of 5 mL of each of the phases was put in contact in a 20 mL vial and shaken manually for 20 minutes at the temperature of 25 ± 1 ° C and a phase ratio of $\Theta = 1$. After the stripping the stripping aqueous phases were sampled and diluted with 0.5 M HNO_3 before the analysis with the ICP-OES.

5. RESULTS AND DISCUSSION

5.1. LEACHING OF THE MAGNET POWDER FOLLOWED BY SOLVENT EXTRACTION OF THE REES WITH TODGA

5.1.1. Determination of the composition of the magnet material

The results of the total dissolution analysis are shown in Table 4. The sum is lower than 100 % (around 95 – 97 %) mostly due to the probable experimental error and the inability to measure elements like O and N which also make a certain percentage of the composition of the NdFeB magnet. The results were in accordance to the literature values of the percentage of elements present in the neodymium magnet. [3]

Table 4. The composition of the obtained material with elements shown in mass percentages. The material was totally dissolved in aqua regia and diluted with 0.5 M HNO_3. The measurement was performed with the ICP-OES iCAP 6500, Thermo Fisher (ppm scale).

element	mass %
Al	0.95 ± 0.16
B	1.00 ± 0.02
Co	1.42 ± 0.07
Cu	0.22 ± 0.05
Dy	1,08 ± 0.27
Fe	61.09 ± 1.04
Mn	0.15 ± 0.01
Nd	25.38 ± 0.66
Ni	2.03 ± 0.23
Pr	2.62 ± 0.17
Si	0.02 ± 0.02

5.1.2. Model solution testing

A model solution containing 21.49 mM Fe, 3.46 mM Nd and 0.62 mM Dy in various nitric acid concentration was tested. The nitric acid concentrations were 0.1, 1, 2, 3, 4, 5 and 6 M HNO_3. The results are shown in Figure 9.

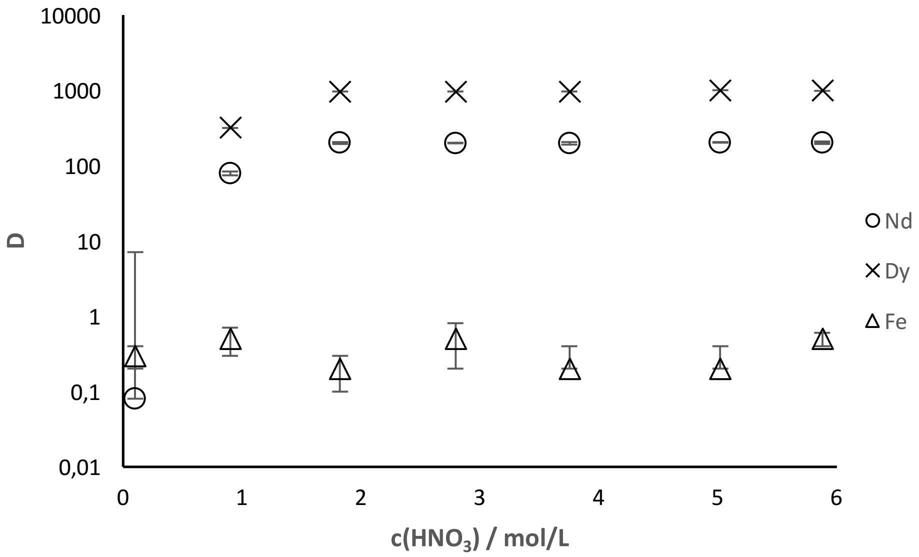
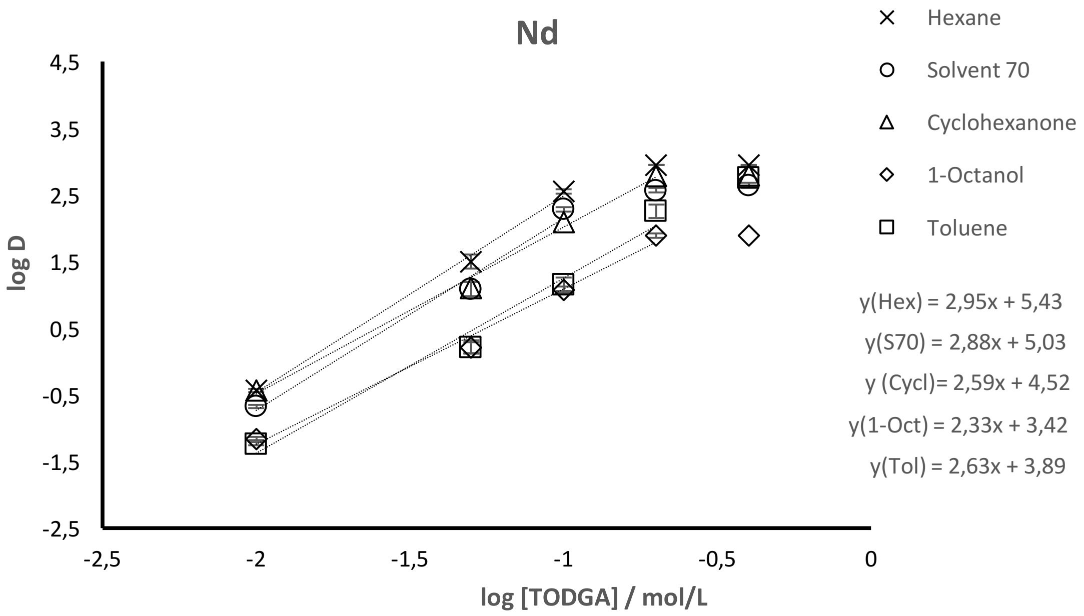


Figure 9. The dependence of the distribution ratios of Fe, Nd and Dy in 0.1 M TODGA in Solvent 70 on initial HNO_3 concentrations of 0.1, 1, 2, 3, 4, 5 and 6 M in the aqueous phase. The temperature was kept at 25 ± 1 ° C and the organic to aqueous ratio at 1 : 1.

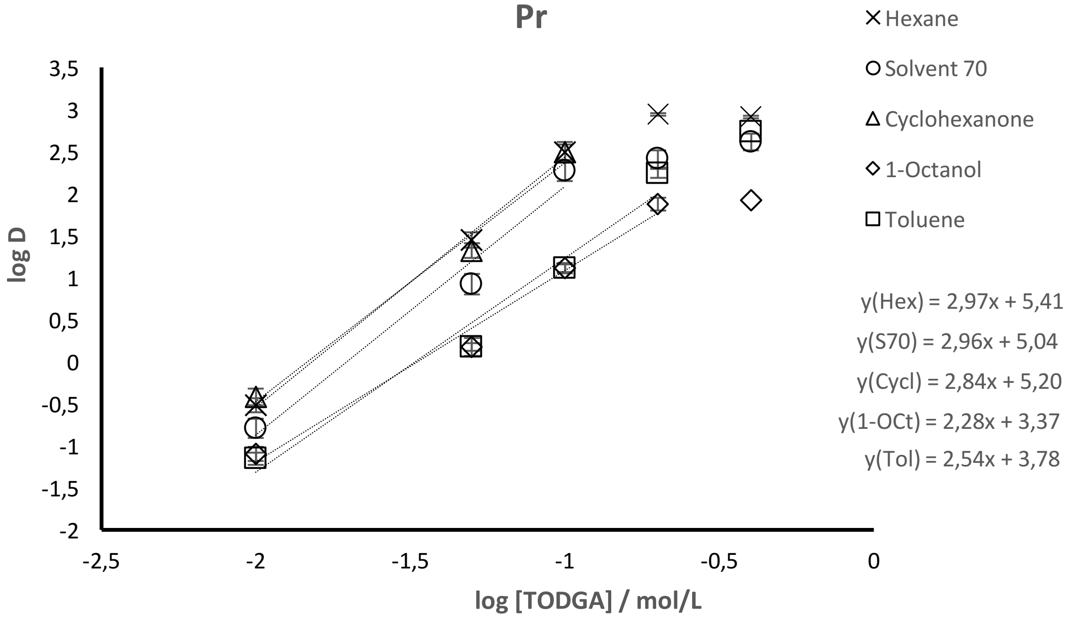
It can be observed from Figure 9 that no extraction is obtained at 0.1 M HNO_3. With the increasing nitric acid concentration to 1 M the distribution ratios for Nd and Dy increase dramatically, while the distribution ratios of Fe stay low. When the HNO_3 concentration is increased to 2 M the equilibrium distribution ration values are reached for Nd and Dy and they remain unchanged with increasing of the NO_3^- concentration. The distribution ratios for Fe stay low throughout the whole range of nitric acid concentration and do not exceed 0.4. Thus, the extraction with TODGA will be further carried on at nitric acid concentration of around 3 M HNO_3 to ensure enough NO_3^- counter ions for the efficient formation of the complex in the organic phase. From equation 3 it is clear that with increasing the NO_3^- concentration, the equilibrium will be shifted to the right hand side.

5.1.3. The effect of the concentration of TODGA and the diluent on solvent extraction

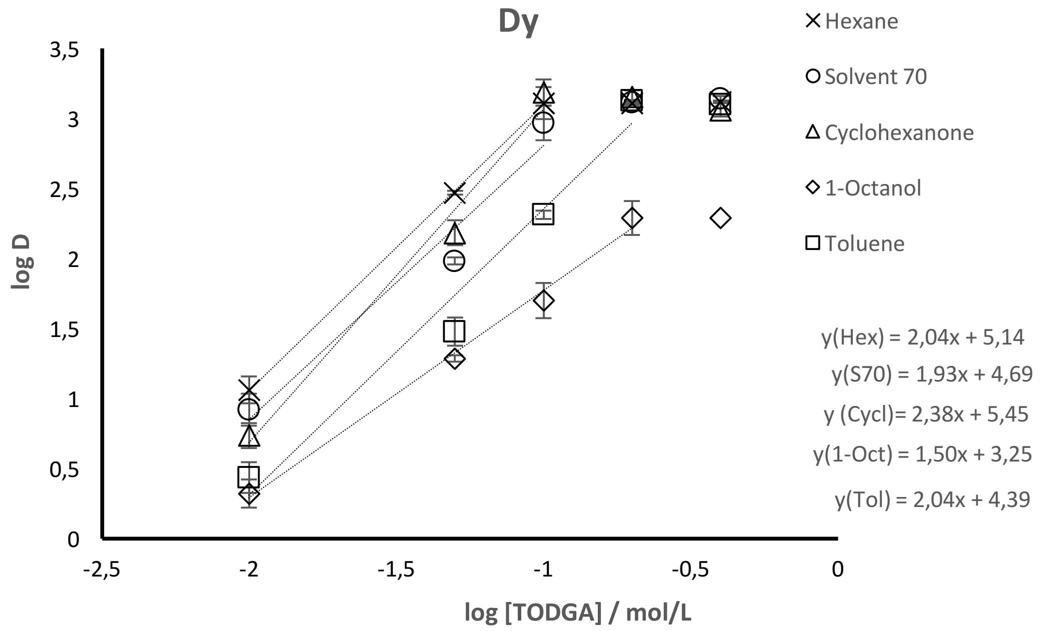
The diluent effect on extraction of the elements from a 3 M HNO_3 solution was investigated. The diluents used were Solvent 70, hexane, toluene, cyclohexanone and 1-octanol. The concentrations of the extracting agent TODGA were 0.01, 0.05, 0.1, 0.2 and 0.4 M in the listed diluents.


Nd
Hexane
Solvent 70
Cyclohexanone
1-Octanol
Toluene
y(Hex) = 2,95x + 5,43
y(S70) = 2,88x + 5,03
y (Cycl)= 2,59x + 4,52
y(1-Oct) = 2,33x + 3,42
y(Tol) = 2,63x + 3,89
log D
4,5
3,5
2,5
1,5
0,5
-0,5
-1,5
-2,5
-2,5
-2
-1,5
-1
-0,5
0
log [TODGA] / mol/L

a)


Pr
Hexane
Solvent 70
Cyclohexanone
1-Octanol
Toluene
y(Hex) = 2,97x + 5,41
y(S70) = 2,96x + 5,04
y(Cycl) = 2,84x + 5,20
y(1-OCt) = 2,28x + 3,37
y(Tol) = 2,54x + 3,78
log D
3,5
3
2,5
2
1,5
1
0,5
0
-0,5
-1
-1,5
-2
-2,5
-2
-1,5
-1
-0,5
0
log [TODGA] / mol/L

b)



c)

Figure 10. The dependence of the distribution ratios of Dy, Nd and Pr after extraction on TODGA concentration Solvent 70, hexane, 1-octanol, cyclohexanone and toluene. The organic to aqueous ratio was kept at 1 : 1 and the temperature at 25 ± 1 ° C. The aqueous phase used was 4 000 mg / L of the magnet leached in 3 M HNO_3.

It is noticed that the distribution ratios for Nd, Pr and Dy increase with the TODGA concentration. Distribution ratios of the REEs increase with the concentration of TODGA in all the diluents, reaching values up to 1000 at highest concentrations. The distribution ratios of the REEs in certain diluents decrease in the following order: hexane > cyclohexanone > solvent 70 > toluene > 1-octanol. It can be concluded that the distribution ratios for extractable species decrease with the polarity of the diluents, with the exception of cyclohexanone, which has an active oxygen donor atom which has the ability to form complexes soluble in the organic phase. [53] This, most probably, led to higher distribution ratios in this particular diluent. TODGA showed high selectivity of extraction of the REEs. It was observed that the distribution ratios for the heavy REE Dy are higher than those for light REEs, which can be attributed to higher charge density of the heavy REEs, due to smaller ionic radii, which facilitates the complex formation. The very high distribution ratios for REEs can be attributed to the strong oxygen donor atoms in the TODGA molecule. The distribution ratios of other elements in the leachate reach values less than 0.1. The highest distribution ratios were registered for B and Al in cyclohexanone which reach 0.5, but these higher values could be attributed to the ability of cyclohexanone to extract these ions out of the solution by itself.[54] The greatest advantage of TODGA in recycling of the NdFeB magnets is the inability of the molecules to extract Fe, which is the element making up around 60 % of the magnet as previously mentioned, and it is not interested from a recycling perspective. In a study by Zhu et al. [32] it was shown that divalent ions with ionic radii smaller than 80 pm and trivalent ions with ionic radii smaller than 70 pm show very weak extraction with TODGA in n-dodecane which is in accordance with this study. The ionic radius thus plays a role in solvent extraction with TODGA, with REEs, having larger ionic radii being prioritized in the extraction process.

5.1.4. Slope analysis (stoichiometry)

When logD vs. logc(TODGA) is plotted, the slopes, m (equation 4), for Pr, Nd and Dy, indicate the number of ligand molecules involved in the extraction process per single REE ion. The slopes are nonintegral indicating that more than one specie of the complexes of REE : TODGA is created. The slopes for Nd and Pr in the non-polar diluents are very close to 3, which indicates that the majority of the species formed were Nd(Pr) $(NO_3^-)_n$ $TODGA_3$. It can be observed that the slopes decrease with the polarity of the used diluents. The slopes for toluene are close to 2.5 indicating that species Nd(Pr) $(NO_3^-)_n$ $TODGA_2$ and Nd(Pr) $(NO_3^-)_n$ $TODGA_3$ were formed. The lowest slopes values closing in on the value of 2 were obtained for 1-octanol. Since the solubility of the the extractant in the diluent plays a pivotal role in the extraction process, the polarity of the diluent in this case could have contributed to the number of TODGA molecules used in the complex formation.[29] This is probably due to the interaction between the donor atoms in the DGA (diglycolamide) group and the aromatic and other donor atoms (oxygen) in the polar diluents. As for Dy, the slopes are very close to the value of 2 in all the diluents, meaning that the species $Dy(NO_3^-)_n(TODGA)_2$ are formed, with the same polarity vs. slope trend. However, due to the limited knowledge about the activity of the extractant in the organic phase the method has limitations.

The complexes as such should be analyzed by XAFS since the slope analysis method gives only a rough idea about the structure.

The main conclusion is that roughly 2-3 molecules of TODGA are involved with the complex formation with REEs ions, which is in accordance with previous studies. [29, 31]

5.1.5. Separation factors

The separation factors between REEs and other elements were not calculated because none of the distribution ratios of the elements except REEs reach a value above 0.1 (except in cyclohexanone). The focus was on the extraction of the REEs from one another. The separation factors between Dy (HREE) and Nd and Pr (LREE) were calculated, since Nd and Pr showed similar distribution ratios and Dy showed higher distribution ratios (gets extracted better) from the solution. The separation factors are shown in Table 5. The highest separation factors between Dy and and light REE were reached in 0.01 M TODGA in Solvent 70, at which

Dy gets extracted selectively from other elements and the light REE. Very good separation between Dy and other elements is reached at 0.01 M TODGA in hexane and 1-octanol, but reach values as high as 14 in other diluents as well. A general conclusion would be:

1) Very good separation factors for Dy at 0,01 M TODGA Solvent 70
2) REEs extracted selectively and completely as a group at 0,1 M TODGA in all the diluents

Table 5. Separation factor for the REEs and other elements at extraction with 0.01, 0.05 and 0.1 M TODGA in Solvent 70, hexane, 1-octanol, cyclohexanone and toluene. The organic to aqueous ratio was kept at 1 : 1 and the temperature at 25 ± 1 ° C. The aqueous phase used was 4 000 mg / L of the magnet leached in 3 M HNO_3

SOLVENT 70	c(TODGA) / M	$\alpha_{Dy/Nd}$	$\alpha_{Dy/Pr}$
	0.01	39.0 ± 1.1	51.7 ± 2.1
	0.05	6.2 ± 0.6	9.0 ± 0.7
	0.1	4.8 ± 0.4	5.0 ± 0.3
	0.2	4.4 ± 0.6	5.0 ± 0.2
	0.4	2.5 ± 0.4	2.7 ± 0.3

HEXANE	c(TODGA) / M	$\alpha_{Dy/Nd}$	$\alpha_{Dy/Pr}$
	0.01	30.8 ± 0.5	37.7 ± 0.3
	0.05	9.2 ± 0.2	10.4 ± 0.7
	0.1	3.6 ± 0.5	4.2 ± 0.6
	0.2	1.4 ± 0.1	1.5 ± 0.3
	0.4	1.5 ± 0.2	1.6 ± 0.3

CYCLOHEXANONE	c(TODGA) / M	$\alpha_{Dy/Nd}$	$\alpha_{Dy/Pr}$
	0.01	14.4 ± 0.6	14.2 ± 0.7
	0.05	11.8 ± 0.3	7.3 ± 0.9
	0.1	12.1 ± 0.6	4.9 ± 0.5
	0.2	3.8 ± 0.5	1.8 ± 0.6
	0.4	1.8 ± 0.2	1.4 ± 0.4

1-OCTANOL	c(TODGA) / M	$\alpha_{Dy/Nd}$	$\alpha_{Dy/Pr}$
	0.01	30.0 ± 1.5	26.3 ± 0.9
	0.05	11.7 ± 0.3	12.9 ± 0.6
	0.1	4.2 ± 0.5	3.9 ± 0.1
	0.2	2.5 ± 0.3	2.6 ± 0.2
	0.4	2.5 ± 0.4	2.3 ± 0.2

TOLUENE	c(TODGA) / M	$\alpha_{Dy/Nd}$	$\alpha_{Dy/Pr}$
	0.01	14.0 ± 0.7	13.2 ± 0.4
	0.05	18.4 ± 0.3	20.0 ± 0.8
	0.1	14.2 ± 0.2	15.8 ± 0.6
	0.2	7.4 ± 0.4	7.7 ± 0.1
	0.4	2.2 ± 0.2	2.3 ± 0.6

5.1.6. Stripping

The stripping was conducted with 0.01, 0.1 M HNO_3 and MQ water. The organic phases chosen for the stripping were 0.01 M TODGA in Solvent 70 after extraction for the recovery of Dy that was selectively extracted from the leachate, and 0.1 M TODGA in hexane where Nd, Pr and Dy were extracted as a group. The organic phase was taken after the extraction and put in contact after the extraction with the equal amount of the aqueous phase 1 : 1 for 50 minutes at 1300 shakes per minute at room temperature 25 ± 1 °C. The results of the stripping are giving in % metal stripped.

Table 6. Stripping of Dy out of 0.01 M TODGA in Solvent 70 with 0.01 M, 0.1 M HNO_3 and MQ water after shaking 50 minutes. A : O kept at 1 : 1 for 50 minutes at 1300 shakes per minute at room temperature 25 ± 1 °C.

Stripping aq phase	Dy stripping efficiency / %
MQ water	97.1 ± 0.9
0.01 M HNO_3	91.3 ±0.8
0.1 M HNO_3	56.2 ± 1.3

Table 7. Stripping of Nd, Pr and Dy out of 0.1 M TODGA in hexane with 0.01, 0.1 M HNO_3 and MQ water after shaking 50 minutes. A : O kept at 1 : 1 for 50 minutes at 1300 shakes per minute at room temperature 25 ± 1 °C.

Stripping aq phase	Dy stripping efficiency / %	Nd stripping efficiency / %	Pr stripping efficiency / %
MQ water	96.1 ± 0.9	97.2 ± 0.8	97.0 ± 1.2
0.01 M HNO_3	91.3 ±0.8	89.1 ± 1.3	91.6 ± 0.9
0.1 M HNO_3	56.2 ± 1.3	49.2 ± 0.9	48. 2 ± 0.9

The stripping of the metals out of the solution after solvent extraction is crucial for the recovery of the metals of interest. Since TODGA extracts with higher distribution ratios in higher nitric acid concentrations, it is expected that the stripping will be feasible with less acidic media or even MQ water. Thus the stripping was conducted with 0.01, 0.1 M HNO_3 and MQ water. The recovery of the metals was not 100 %, but it reached almost 100 % in MQ water for Nd, Pr and Dy. 0.1 M HNO_3 preformed really bad with only 50 % of metals stripped Incomplete recovery was achieved with 0.01 M HNO_3. It was showed that using only MQ water with no NO_3^- couter-ions was enough to break the complex from the organic phase and achieve high stripping efficiency.
A significant drop of pH of the stripping agents to the value of around 1 and less was observed. This indicates that the HNO_3 extracted with the solvent extraction with TODGA was stripped using these stripping agents. No precipitation was observed in the aqueous phase after stripping.

5.2. SOLVENT EXTRACTION OF THE REES WITH D2EHPA FROM A LEACHATE OBTAINED BY SELECTIVE LEACHING

5.2.1 Determination of the composition of the leachate

The measurable/detectable concentrations of Nd, Dy, Pr, Gd, Co and B in the leachate are given in Table 8.

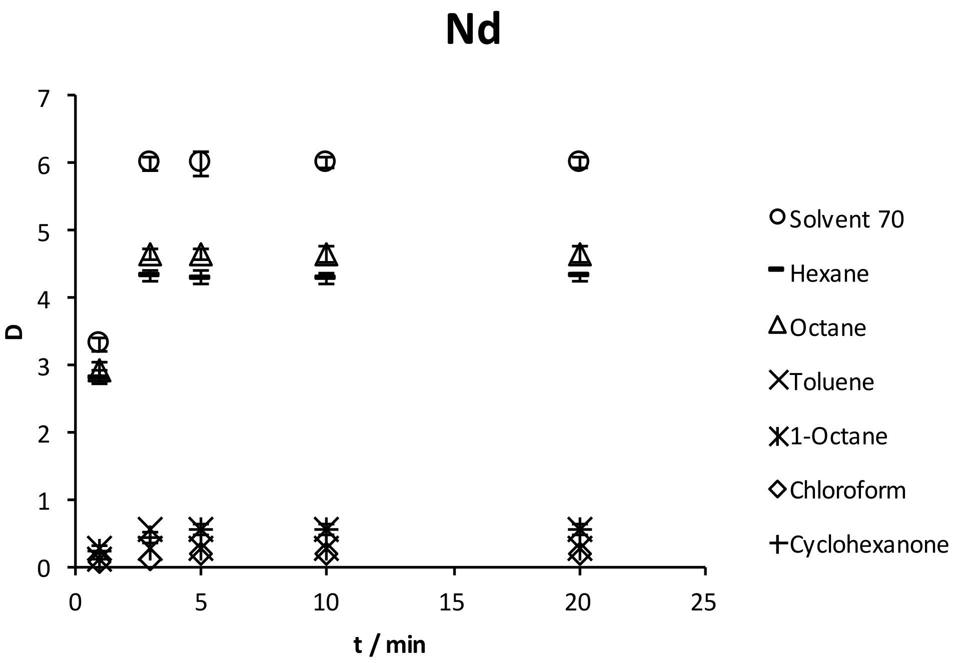
Table 8. Concentrations of the metals of interest in the leachate measured with the ICP-OES. The measurement was performed with the ICP-OES after diluting the obtained leachate with 0.5 M HNO_3

Element	Concentration / mM
Nd	9.1 ± 0.9
Dy	2.7 ± 0.6
Pr	3.2 ± 0.4
Gd	0.69 ± 0.16
Co	0.17± 0.09
B	0.55± 0.14
other	below detection limit

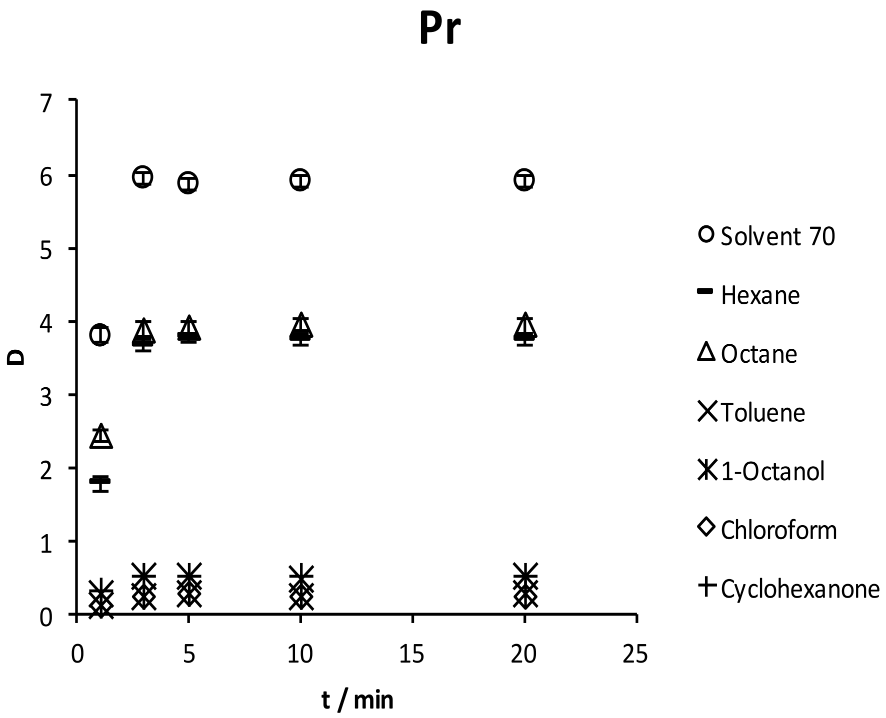
The ionic strength of the solution was determined to be I = 0.12 M. The pH value of the solution was measured with MeterLab^{TM} PHM 240 pH/Ion Meter pH electrode and it was determined to be around 5. The concentration of the sulfate ion was determined after the precipitation of the sulfate ion using a $BaCl_2$ solution, and was determined to be $[SO_4^{2-}]$ = 22.62 ± 1.23 mM and was kept constant throughout this research.

5.2.2. Investigation of the kinetics of solvent extraction

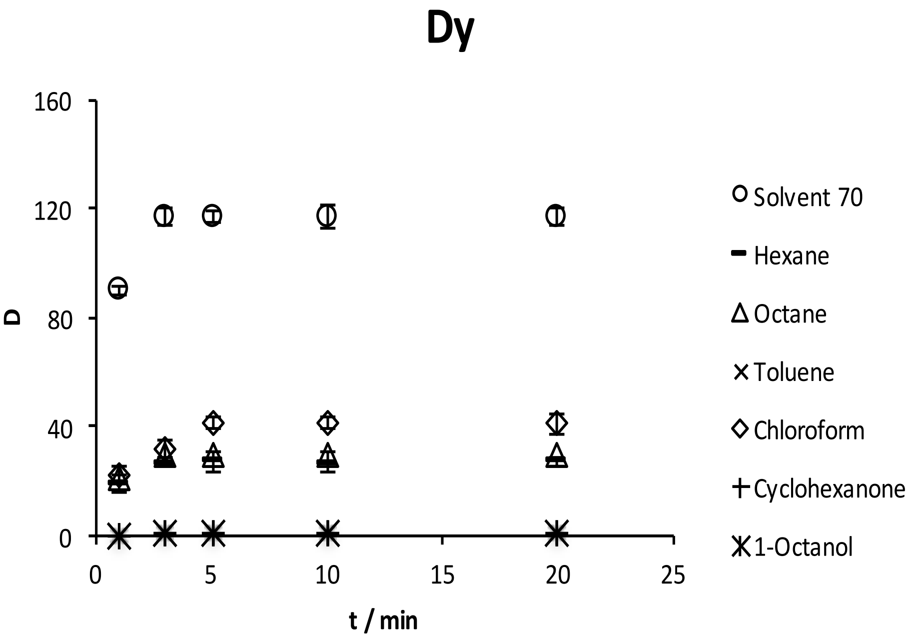
The investigation of the extraction kinetics was performed with the aforementioned leachate. The organic phase was 0.6 M D2EHPA in Solvent 70, hexane, octane, cyclohexane, 1-octanol, toluene and chloroform. From Figure 11 it can be seen that the time required for the distribution ratios for the REEs (Nd, Pr, Gd and Dy) between the organic and aqueous phase is reached within 3 minutes in Solvent 70, hexane, octane, toluene and 1-octanol, while in cyclohexanone and chloroform it took 5 minutes for the equilibrium to be reached. No extraction of cobalt whatsoever was observed at any of the conditions, which shows that REEs can be extracted selectively without any cobalt transfer into the organic phase. Boron distribution ratios reach a mere 0.1 in Solvent 70 after 5 minutes, and some minor extraction in 1-Octanol while no other extraction was registered in other diluents. A conclusion can be drawn that D2EHPA at these conditions shows good selectivity between REEs and the B and Co.


Nd
D
7
6
5
4
3
2
1
0
0
5
10
15
20
25
t / min
○ Solvent 70
▬ Hexane
△ Octane
✕ Toluene
✳ 1-Octane
◇ Chloroform
+ Cyclohexanone

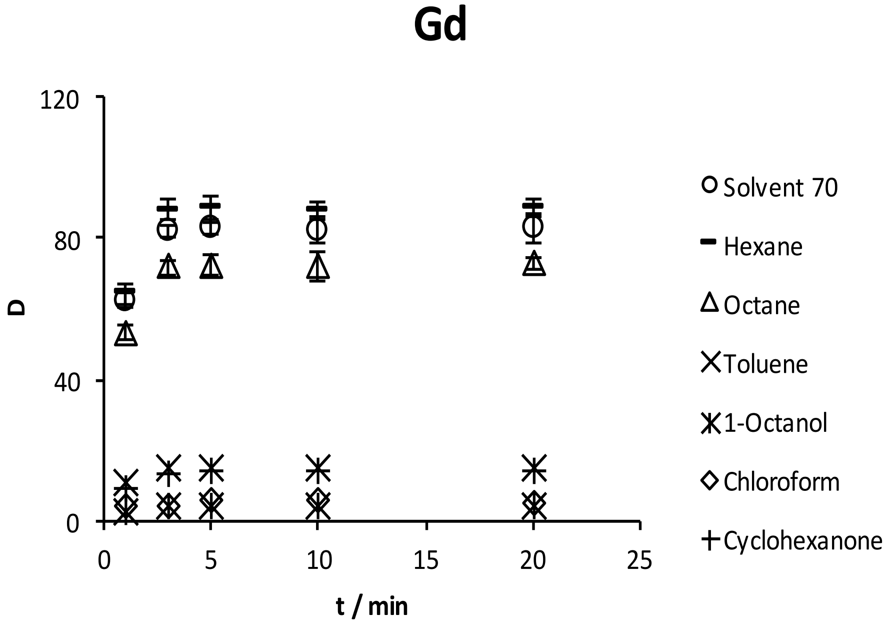
a)


Pr
D
7
6
5
4
3
2
1
0
0
5
10
15
20
25
t / min
○ Solvent 70
▬ Hexane
△ Octane
✕ Toluene
✳ 1-Octanol
◇ Chloroform
+ Cyclohexanone

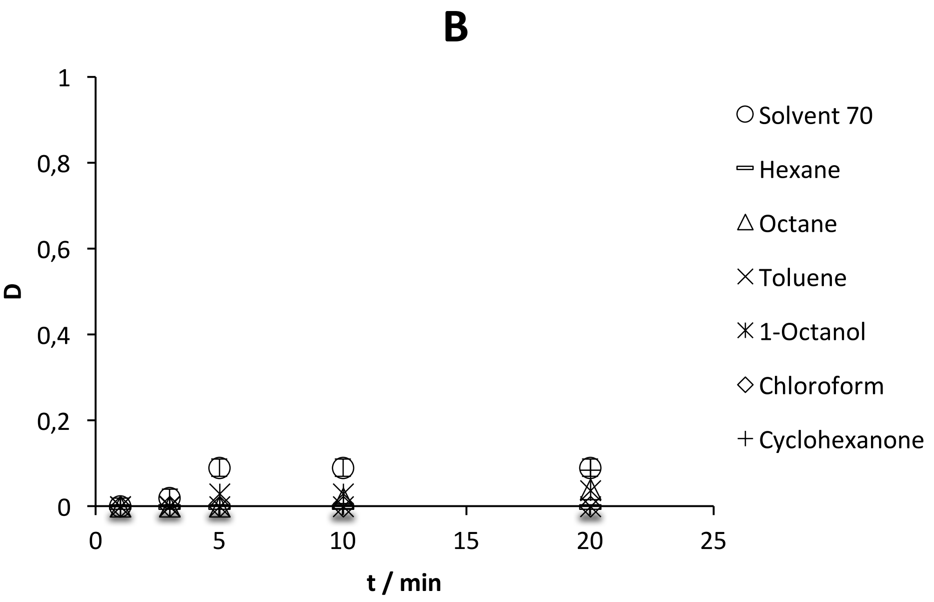
b)


Dy
160
120
80
40
0
D
0
5
10
15
20
25
t / min
○ Solvent 70
▬ Hexane
Δ Octane
× Toluene
◇ Chloroform
+ Cyclohexanone
⋇ 1-Octanol

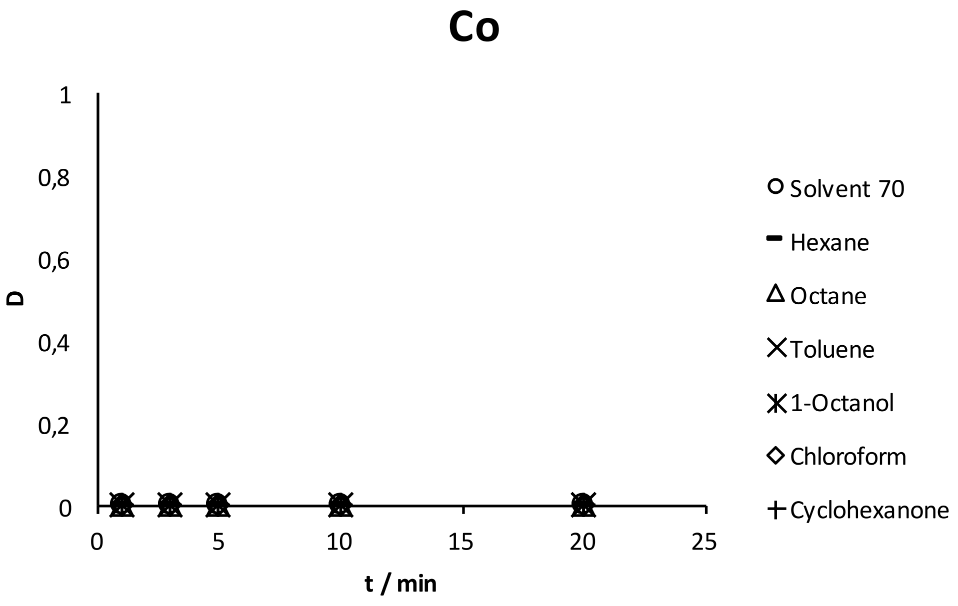
c)


Gd
120
80
40
0
D
0
5
10
15
20
25
t / min
○ Solvent 70
▬ Hexane
Δ Octane
× Toluene
⋇ 1-Octanol
◇ Chloroform
+ Cyclohexanone

d)



e)

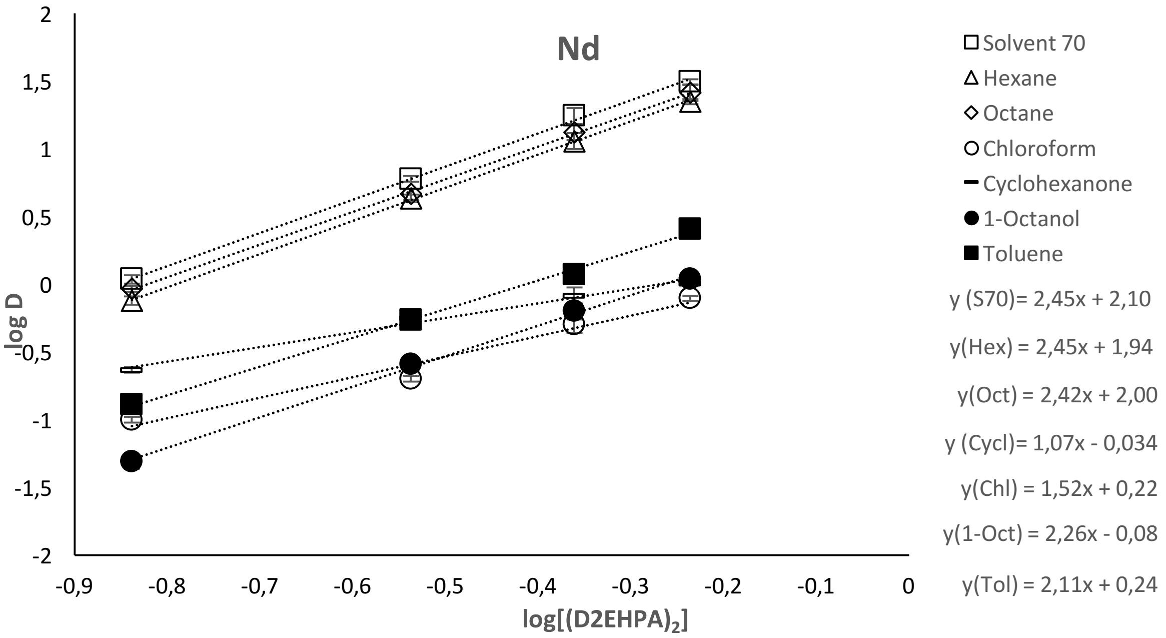


f)

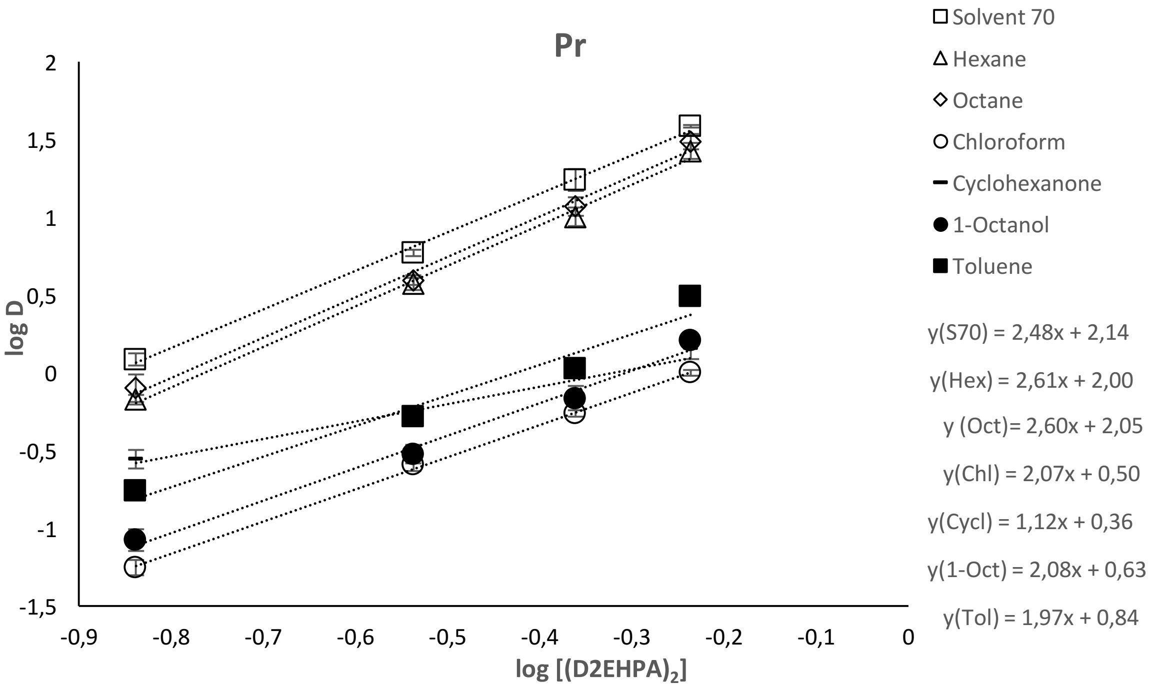
Figure 11. Distribution ratios of Nd, Pr, Dy, Gd, Co and B in the leachate solution plotted as a function of time which was varied between 1 and 20 minutes. The organic phases were 0.6 M D2EHPA in Solvent 70, hexane, octane, toluene, 1-octanol, cyclohexanone and chloroform. The extraction conditions were 25 ± 1 ° C and Θ = 1 The uncertainty bars represent the standard deviation of a triplicate test.

5.2.3. The effect of the concentration of D2EHPA and the diluent on solvent extraction

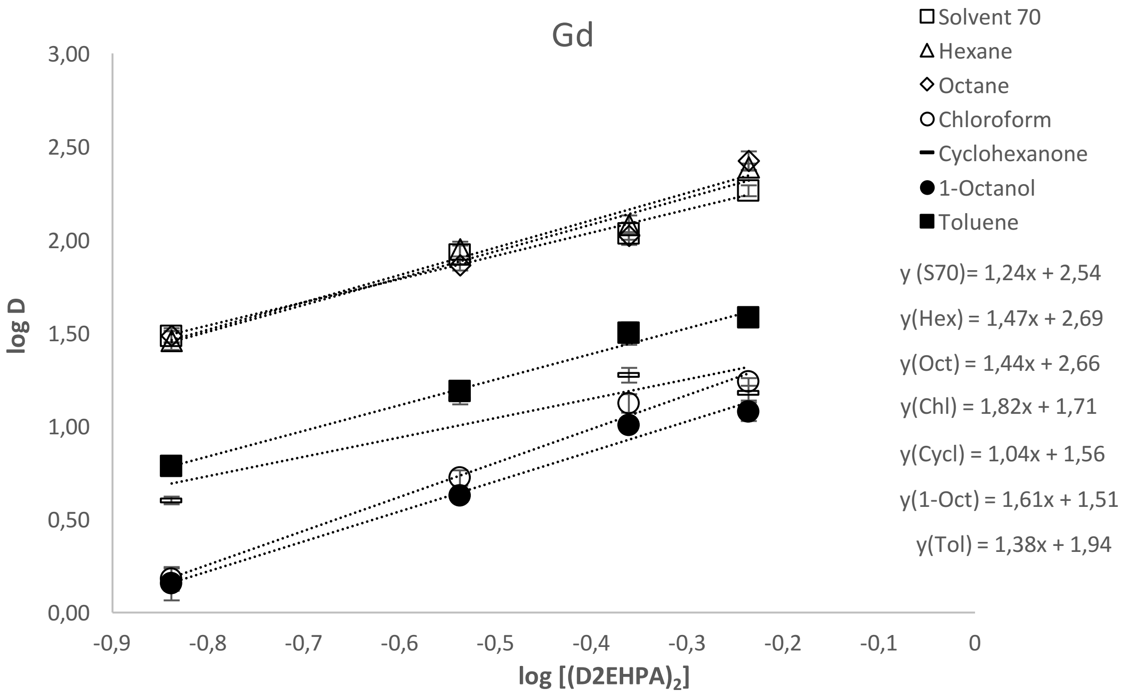
The influence of D2EHPA concentration on the extraction of Nd, Pr, Dy in various diluents is shown in Figure 12.



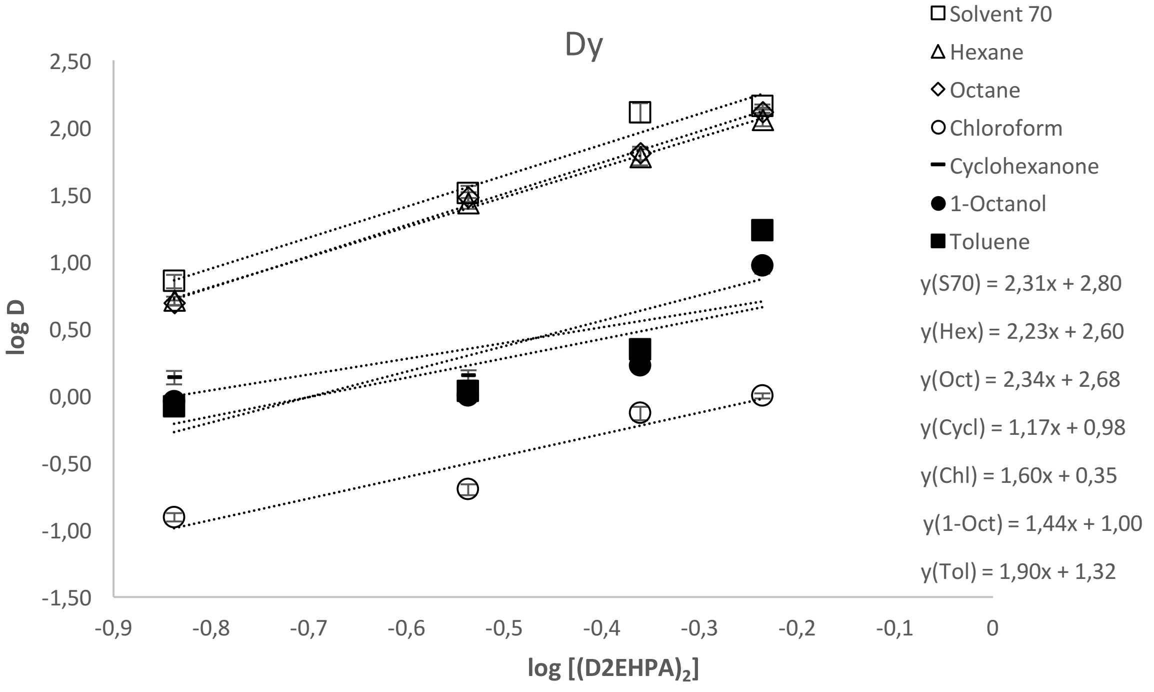
a)



b)



c)



d)

Figure 12. The influence of D2EHPA concentration on the extraction of Nd, Pr, Gd and Dy from the aqueous consisting of 9.11mm Nd, 2.71 mM Dy, 3.16 mm Pr, 0.69 mM Gd 0.17 mM Co 0.55 mM B. using different concentration of 0.3, 0.6, 0.9 and 1.2 M D2EHPA in Solvent 70, hexane, octane, toluene, cyclohexanone, chloroform and 1-octanol. The temperature was kept at 25 ±

1 ° C and the organic to aqueous phase ratio Θ = 1. The error bars represent the standard deviation of a triplicate test.

The distribution ratios of the REEs increases with the increase of the concentration of D2EHPA in all the diluents. The extractant clearly shows higher efficiency for heavy REEs (Dy and Gd) over the light REEs (Nd and Pr) in all the diluents. Similar trends were previously observed in a study by Mohammadi et al.[39] The distribution ratios are higher in the aliphatic diluents (hexane, octane, solvent 70), followed by toluene and showing the lowest efficiency in the polar diluents (cyclohexanone, 1-octanol and chloroform). Cobalt does not get extracted at any of the investigated conditions and the distribution ratios remained around 0. The distribution ratios for B are low at all concentrations and diluents. It gets extracted up to 10 % in cyclohexanone and 1-octanol. This can be attributed to the carbonyl group in cyclohexanone and the hydroxyl group in 1-octanol that could actually allow the diluent molecules to form complexes with B soluble in the organic phase. It is observed that at 0.9 and 1.2 M D2EHPA in hexane and octane 100 % of all the REEs get transferred into the organic phase, while no Co and B get co-extracted.

As mentioned before, the distribution ratios are higher for the heavy REEs than the light REEs which corresponds to the deceasing ionic radii of these elements. The ionic radii of hydrolyzed Pr^{3+}, Nd^{3+}, Gd^{3+} and Dy^{3+} are, accordingly: 0.99 Å, 0.983 Å, 0.938 Å and 0.912 Å [10]. The outcome will be increased charge density with the decreasing ion radius. The smaller ion can contribute to the REE^{3+} binding to the D2EHPA molecule, which works on a cation-exchange mechanism, favoring the extraction of the heavy REEs over the light REEs. According to the HSAB theory, which divides the acids and bases on hard and soft [11], Co^{2+} is a borderline acid, meaning it can act as a soft or hard acid, and it is thus difficult to predict it's behavior since it can be influenced by various factors, like removal of hydrate water, steric effects etc. In this case Co^{2+} was as soft acid which did not form a complex with the D2EHPA from the organic phase.

To get a clearer picture of how diluents affect the extraction of different REEs, a graph showing the distribution ratios of Nd in 0.9 M D2EHPA was made vs. the dielectric constants (ε) of the diluent (Figure 13).

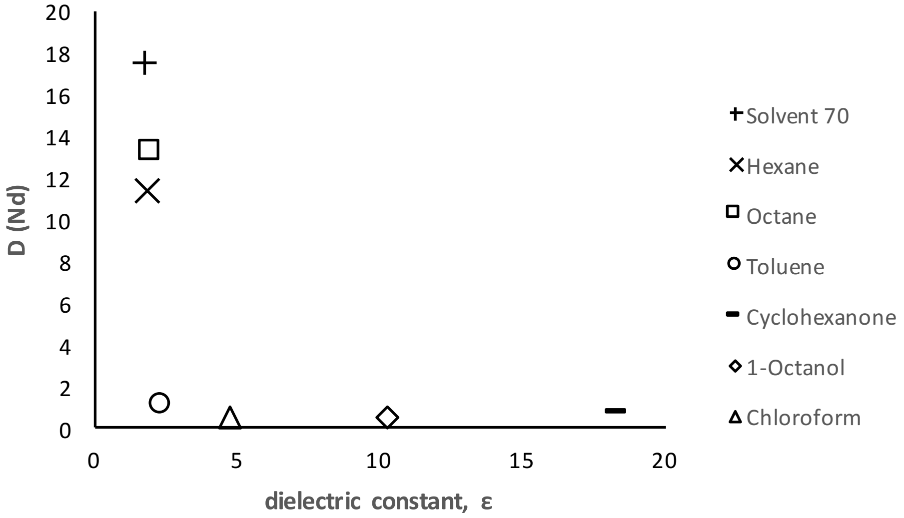


Figure 13. Distribution ratio of Nd plotted as the function of the dielectric constants of the diluents. The organic phase used was 0.9 M D2EHPA diluted in Solvent 70, hexane, octane, toluene, cyclohexanone, chloroform and 1-octanol. The aqueous phase consisted of 9.11mm Nd, 2.71 mM Dy, 3.16 mm Pr, 0.69 mM Gd 0.17 mM Co 0.55 mM B. The extraction conditions were 25 ± 1 °C and Θ = 1.

The distribution ratios of Nd in 0.9 M D2EHPA diluted in various solvents are depicted in Figure 13. The distribution ratios of Nd show a regular trend, decreasing with the polarity of the diluent in the order Solvent 70 > octane > hexane >toluene > cyclohexanone > 1-octanol > chloroform. The distribution ratios are one order higher in the aliphatic non-polar diluents (Solvent 70, hexane, octane) than in aromatic and polar ones (toluene, cyclohexanone, 1-octanol and chloroform). Considering the D2EHPA being a relatively non-polar molecule, owing it to the 2-ethylhexyl chains, could explain good solubility of the D2EHPA extractant in the aliphatic non-polar diluents. thus leading to less aggregation of the extractant molecules and consequently leading to higher distribution ratio for Nd. This explanation could not be used for D2EHPA diluted with cyclohexanone, which gives distribution ratios for Nd higher than other polar diluents (1-octanol and chloroform) even though it has the largest dielectric constant (18.3). Nonetheless, this extraction-enhancing phenomenon was expected, since cyclohexanone is a molecule with a donor atom, oxygen, for hydrogen bonding, but no active hydrogen atoms. This could cause it to form complexes with the REE ions in the solution, which could be then transferred into the organic phase. [54] This phenomenon could also explain the extraction of boron into the organic phase seen in Figure 11 e).

5.2.4. Stoichiometry

The stoichiometric ratios between REEs and the extractant were determined by plotting the log*D* vs. log $[(D2EHPA)_2]$ and then doing the linear regression to determine the stoichiometric ratio between the element and the extractant. The results are shown in Figure 12. It can be observed from the graphs that for Nd, Pr and Dy in hexane, octane and solvent 70 the slopes show values of around 2.5. This means that D2EHPA will form complexes with 2 and 3 D2EHPA dimers, meaning the complexes will look like $MR_3(HR)_3$ and $MR_3(HR)$, where M represents the lanthanide ion. In the toluene case the slopes for Nd, Pr and Dy are approaching 2, which indicates the formation of a complex $MR_3(HR)$. As for Gd, the slopes for the aliphatic diluents graphs are close to the value of 1.5, indicating the complexation of these REEs with 1 and 2 dimers of the D2EHPA molecules. In 1-Octanol 1-2 molecules. Gd forms complexes with around 1 dimer of D2EHPA. The complexes of REEs in cyclohexanone seem to form complexes with one D2EHPA dimer. And 1-2 in chloroform. It is observed that the number of molecules needed to form a complex decrease with the increased polarity of the diluent, which can be due to the interaction of the active groups with the oxygen in the phosphoric acid group in D2EHPA. [29]

5.2.5. Investigation of the pH effect on extraction

As expected, the increase of pH (lower proton concentration) led to higher metal extraction. This is a typical behavior for acidic extractants like D2EHPA and it can also be seen in equation 4 that lower pH values will shift the equilibrium to the left hand side. On the other hand, the increase in proton concentration will favor the stripping reaction. It was observed that by increasing the pH values Dy and Gd get extracted first, followed by Nd and Pr. At pH around 1 no extraction of Co and B whatsoever can be observed, while when increasing the pH value to the value of 2 around 10 % of B is extracted and around 20 % of Co is extracted, so to avoid the co-extraction of the exogenes with the REEs as much as possible the equilibrium pH should be kept at or below the value of 1. The results also show that the light REEs (Nd and Pr) will be co-extracted with the heavy REEs in the first step of any method used with the ratios around 100 % : 50 % = heavy : light. Increasing the equilibrium pH up to 2 will lead to complete extraction of the REEs in the solution into the organic phase, but with the disadvantage of the increased co-extraction of Co and B in minor percentages. This could lead to more extraction stages in a, for example, mixer-settler.

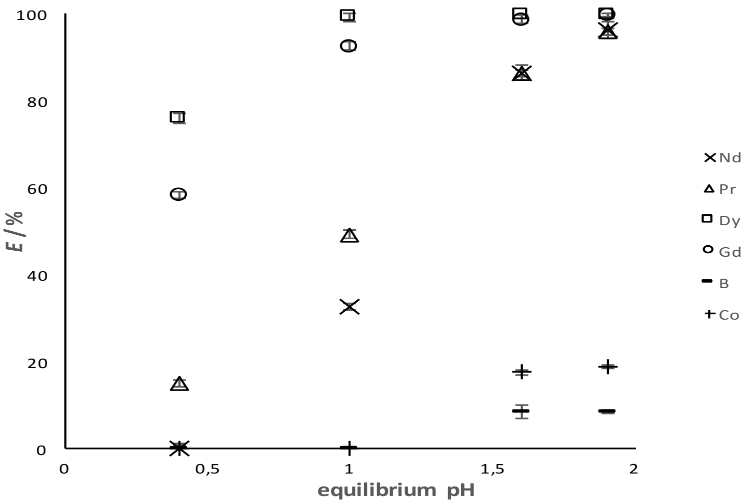


Figure 14. Percentage of the Nd, Pr, Dy, Gd, Co and B extracted from the neodymium magnet leachate consisting of 9.11mm Nd, 2.71 mM Dy, 3.16 mm Pr, 0.69 mM Gd 0.17 mM Co 0.55 mM B with varied equilibrium pH. The extraction conditions were 25 ± 1 °C and Θ = 1. The organic phase used was 0.3 M D2EHPA in Solvent 70.

5.2.6. Separation factors between heavy and light REEs

To further investigate the selectivity between light and the heavy REE of these extractions, the separation factors were calculated. The calculated separation factors are shown numerically in Table 9.

Table 9. Separation factors between the heavy and the light REE after extraction. The concentrations of D2EHPA were 0.3, 0.6, 0.9 and 1.2 mol/L in Solvent 70, hexane, octane, toluene, cyclohexanone, chloroform and 1-octanol. The aqueous phase consisted of 9.11mm Nd, 2.71 mM Dy, 3.16 mm Pr, 0.69 mM Gd 0.17 mM Co 0.55 mM B. The temperature was kept at 25 ± 1 ° C and the organic to aqueous phase ratio Θ = 1.

SOLVENT 70	c(D2EHPA) / M	$\alpha_{Dy/Nd}$	$\alpha_{Dy/Pr}$	$\alpha_{Gd/Nd}$	$\alpha_{Gd/Pr}$
	0.3	6.55 ± 3.2	5.85 ± 3.1	27.7 ± 1.2	24.8 ± 0.9
	0.6	5.34 ± 0.7	5.43 ± 0.5	13.7 ± 0.2	14.0 ± 0.3
	0.9	7.3 ± 0.1	7.4 ± 0.2	6.1 ± 0.6	6.2 ± 0.2
	1.2	4.6 ± 0.4	3.8± 0.5	5.8 ± 0.5	4.7 ± 0.4

HEXANE	c(D2EHPA) / M	$\alpha_{Dy/Nd}$	$\alpha_{Dy/Pr}$	$\alpha_{Gd/Nd}$	$\alpha_{Gd/Pr}$
	0.3	6.8 ± 0.6	7.6 ± 0.8	37.7 ± 1.2	42.4 ± 1.6
	0.6	6.3 ± 0.7	7.27 ± 0.4	20.6 ± 0.9	23.7 ± 1.2
	0.9	5.3 ± 0.6	5.94 ± 0.3	10.5 ± 0.7	11.9 ±0.5
	1.2	5.1 ± 0.3	4.28 ± 0.6	10.9 ± 0.5	9.2 ± 0.4

OCTANE	c(D2EHPA) / M	$\alpha_{Dy/Nd}$	$\alpha_{Dy/Pr}$	$\alpha_{Gd/Nd}$	$\alpha_{Gd/Pr}$
	0.3	5.8 ± 0.2	6.1 ± 0.4	33.1 ± 1.2	38.3 ± 0.9
	0.6	6.5 ± 0.4	7.6 ± 0.3	15.7 ± 0.9	18.5 ± 0.7
	0.9	4.8 ± 0.3	5.4 ± 0.7	7.9 ± 0.6	8.9 ± 0.5
	1.2	5.0 ± 0.3	4.2 ± 0.6	10.2 ± 0.9	8.6 ± 0.4

TOLUENE	c(D2EHPA) / M	$\alpha_{Dy/Nd}$	$\alpha_{Dy/ Pr}$	$\alpha_{Gd/Nd}$	$\alpha_{Gd/Pr}$
	0.3	6.5 ± 0.7	4.8 ± 0.9	36.8 ± 0.9	34.5 ± 0.7
	0.6	2.0 ±0.4	2.1 ± 0.1	27.9 ± 0.6	29.3 ± 0.5
	0.9	1.9 ± 0.3	2.1 ± 0.3	26.7 ± 0.9	29.5 ± 0.5
	1.2	6.7 ± 0.4	5.5 ± 0.8	14.8 ± 0.6	12.2 ± 0.7

CYCLOHEXANONE	c(D2EHPA) / M	$\alpha_{Dy/Nd}$	$\alpha_{Dy/ Pr}$	$\alpha_{Gd/Nd}$	$\alpha_{Gd/Pr}$
	0.3	5.9 ± 0.3	4.9 ± 0.3	17.0 ± 0.9	14.3 ± 0.7
	0.6	2.5 ± 0.4	2.6 ± 0.1	25.1 ± 0.7	25.8 ± 0.2
	0.9	2.7 ± 0.2	3.0 ± 0.3	22.7 ± 0.2	24.4 ± 0.4
	1.2	9.0 ± 0.6	6.3 ± 0.5	14.8 ± 1.2	10.4 ± 0.9

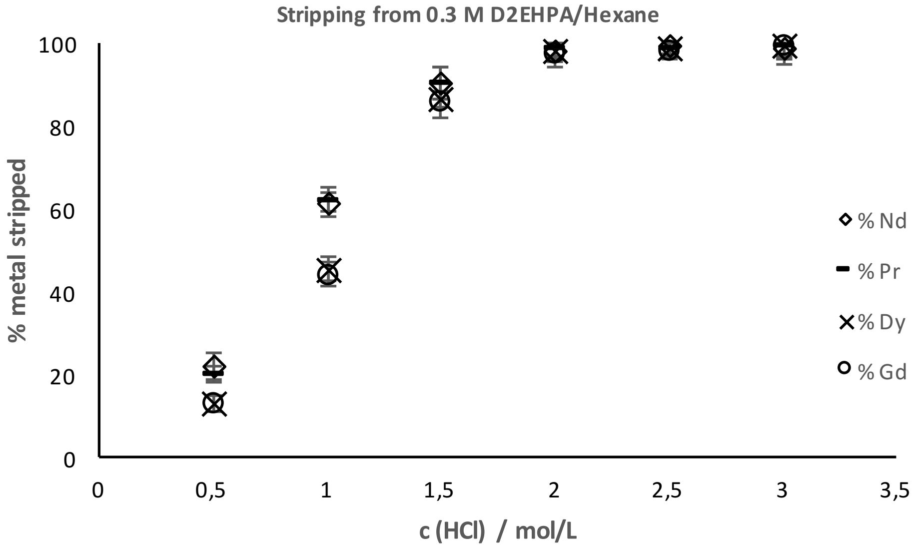
CHLOROFORM	c(D2EHPA) / M	$\alpha_{Dy/Nd}$	$\alpha_{Dy/ Pr}$	$\alpha_{Gd/Nd}$	$\alpha_{Gd/Pr}$
	0.3	5.2 ± 0.5	6.0 ± 0.1	25.0 ± 0.2	26.8 ± 0.4
	0.6	3.5 ± 0.4	2.7 ± 0.5	26.2 ± 0.9	20.5 ± 0.4
	0.9	1.5 ± 0.1	1.4 ± 0.3	26.1 ± 0.6	24.1 ± 0.5
	1.2	0.9 ± 0.3	0.9 ± 0.1	17.0 ± 0.3	17.2 ± 0.3

1-OCTANOL	c(D2EHPA) / M	$\alpha_{Dy/Nd}$	$\alpha_{Dy/Pr}$	$\alpha_{Gd/Nd}$	$\alpha_{Gd/Pr}$
	0.3	4.9 ± 0.6	5.1 ± 0.8	29.0 ± 1.2	26.9 ± 0.8
	0.6	3.9 ± 0.4	3.3 ± 0.1	16.3 ± 0.7	14.0 ± 0.9
	0.9	2.7 ± 0.3	2.5 ± 0.6	15.9 ± 0.5	14.8 ± 0.8
	1.2	8.5 ± 0.9	5.8 ± 0.8	10.9 ± 1.0	7.34 ± 0.9

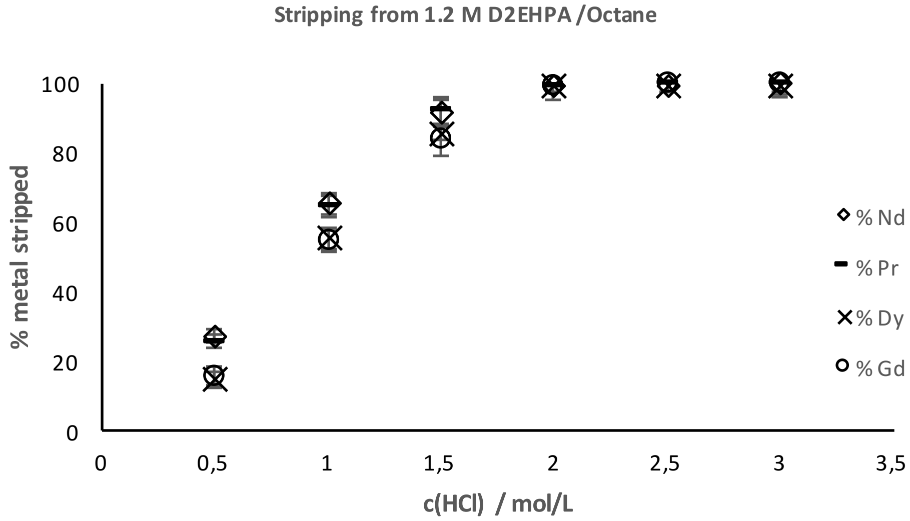
The highest separation factors between Dy and Nd were achieved at 0.3 % D2EHPA in hexane. In these conditions around 50 % of Nd and Pr got extracted, and around 99 % of Dy and Gd extraction was registered. The α Dy / (Nd & Pr) keeps decreasing with the increasing concentration of D2EHPA for Solvent 70, while it stays below 10 for other concentrations of D2EHPA for all the other diluents. As for Gd/Nd, and Gd/Pr the best separation factor was found to be also in 0.3 M hexane. It can be noticed that the separation factors between Dy and other light REEs are one order lower than those of Gd and other light REEs. Even though it is expected for Dy and Gd to have similar distribution ratios, but as it can be seen from Table 9., the concentration of Dy is four times higher than that of Gd in the leachate. This concentration difference might have led to the much higher distribution ratios for Gd than those of Dy, leading consequently to these results. Since Dy is present in a much higher concentration and its current price is currently around 10 times higher than that of Gd, the organic phase consisting of 0.3 M D2EHPA diluted in hexane was chosen as the best organic phase from separation Dy and Gd from other light REEs, especially considering the small amounts of B and Co being extracted. Future work on the scale-up process in a mixer settler is proposed.

5.2.7. Stripping

The stripping experiments were conducted for the organic phases after extraction with 0.3 M D2EHPA in Solvent 70 and 1.2 M D2EHPA in octane. At 0.3 M D2EHPA in Solvent 70 the highest separation factors between the heavy and the light REEs was achieved and at 1.2 M D2EHPA the REEs were completely extracted out of the leachate as a group leaving the exogen metals (Co, B) in the solution, so these two cases showed to be the most interesting for future process developments if needed. The elements were stripped back into the new aqueous phase using hydrochloric acid, at concentration 0.5, 1, 1.5, 2, 2.5 and 3 M for 5 minutes. The organic phase after extraction was put in contact with the hydrochloric acid in the above listed concentrations and shaken with Ika Vibrax Vxr shaking machine temperature of 25 ± 1 ° C with the O : A = 1 : 1. The results of the stripping are shown in Figure 15.



a)



b)

Figure 15. The stripping of the REEs back in the aqueous solution from 0.3 M D2EHPA in hexane and 1.2 M D2EHPA in octane after extraction. The stripping agents used were aqueous solutions of 0.5, 1, 1.5, 2, 2.5 and 3 M hydrochloric acid. The stripping conditions were the temperature of 25 ± 1 ° C and the organic to aqueous phase ratio Θ = 1. Shaking time was 20 minutes.

The metals are stripped at 100 % efficiency at 2 M HCl or higher, which is in accordance with equation 3, meaning that increasing the concentration of H^+ ions in the aqueous solution, the reaction will be shifted to the left hand side.

These were the observations made on a small (3.5 mL) scale and for further developing the process larger amounts of the leachate are required and mixer settler studies are recommended with 0.3 M D2EHPA in hexane and 1.2 M of D2EHPA in octane to develop a large scale process in the future.

6. CONCLUSIONS

The goal of this work was to determine the feasibility of the use of TODGA and D2EHPA for the selective extraction of REEs out of real leachates obtained by dissolving the neodymium magnet waste. The focus was on the effect of the composition of the organic phase on the selective extraction of the REEs out of the leachates and from each other.

TODGA in various diluents was used for the extraction of the REEs out of the neodymium magnet leachate obtained by dissolving the magnet waste in nitric acid. This study was focused on selective extraction of REEs from other elements to achieve the best recovery possible. The separation factors between the REEs were also calculated. It was found that the nitric acid concentration over 2 M HNO_3 was needed for achieving the highest distribution ratios for the REEs. As expected the distribution ratios of the REEs increase with the concentration of TODGA in all the diluents. Highest separation factors for Dy were observed at 0,01 M TODGA in Solvent 70. REEs were extracted selectively as a group at 0,1 M TODGA in hexane, solvent 70 and cyclohexanone with the other elements not exceeding distribution ratios over 0.1, except for cyclohexanone where the distribution ratios reach up to 0.5. The stripping of these elements was efficient with MQ water out of the organic phase. Two to three TODGA molecules were used for the formation of the complex with REEs according to the slope analysis study.

D2EHPA was used for the extraction of the REEs from a real leachate obtained from the neodymium magnet leachate in sulfuric acid media, and find most suitable separation conditions between them. The general extraction order is HREEs > LREEs which was expected. The distribution ratios increased with the D2EHPA concentration and the lowering of acidity. The kinetics of the extraction was monitored for 0.6 M D2EHPA in Solvent 70, hexane, octane, chloroform, cyclohexanone, 1-octanol and toluene. It was shown that the equilibrium is reached within 3 minutes for all the diluents except for cyclohexanone and 1-octanol, in which the equilibrium is reached within 5 minutes.

It was concluded that the most suitable diluents for the solvent extraction of REEs with D2EHPA were hexane, octane and Solvent 70. The slightly polar ones, cyclohexanone, chloroform and 1-octanol showed the lowest distribution ratios for the extracted REEs Toluene lays somewhere in between of the 2 groups previously mentioned according to the obtained distribution ratios of the REEs. It has also been shown that at 0.9 M and 1.2 M D2EHPA concentration in hexane and octane the REEs are completely extracted out of the leachate solution as a group leaving the exogenes (Co and B) in the solution. Concerning the separation between the heavy and the light REEs, the best separation factors factors were obtained at extraction with 0.3 M D2EHPA in hexane. At such conditions almost all the Dy and

Gd were extracted from the solution, while around half of the amount (50 %) of the present light REEs were extracted. The stripping studies were performed from the organic phases after the extraction with 0.3 M D2EHPA in hexane and 1.2 M D2EHPA in octane. It has been shown that the complete stripping of the elements back into the aqueous phase is achieved at 2 M HCl or higher.

These were the observations made on a small (3.5 mL) scale and for further developing the process larger amounts of the leachate are required and mixer settler studies are needed to develop a large scale process in the future.

7. FUTURE WORK

A few paths could be followed for future research depending on the area of interest. These can be summed up into the following.

The scaling up of the process using solvent extraction equipment like mixer settlers. There different parameters like flows, phase contact time and mixing and organic to aqueous phase ratios could be altered in order to tailor the separation between the elements in the leachate.

Further small-scale studies could be done where the interfacial tension between the solvent and the aqueous phase and the density of the solvent effect on the extraction could be monitored in order to determine the effect of changing these parameters on the outcome of the process.

XAFS measurements for the determination of the complex structure and detailed modelling of the complexes formed in the organic phase.

Thermodynamics of the extraction.

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APPENDIX

ICP-OES (Inductively coupled plasma – Optical Emmission Spectrometer)

A thermo iCAP 6500 ICP-OES was used to measure the elemental composition of the aqueous solutions after leaching and solvent extraction. ICP-OES is a method commonly used for the analysis of trace metals. The machine is made up of two parts, the ICP and the optical spectrometer. It works on the principle of plasma excitation of the atoms and the detection of emitted light from the relaxation of the excited atoms. Every element has a unique set of spectral lines and can be detected individually in a sample.