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Urban mining of rare earth elements from rare earth magnets – alternate solvents for extraction

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LABORATORY PROJECT

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Statement of Authorship

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ABSTRACT

Neodymium (Nd) is a rare earth metal that exists in a mixture of iron (Fe) and boron (B) in permanent magnets used in many areas of modern technology. The increasing demand for neodymium magnets and the supply risk of Nd make end-of-life NdFeB magnets a feasible waste stream for the recovery of neodymium. The recycling method investigated in this project is hydrometallurgical processing.

The main impurity present in NdFeB end-of-life magnets is iron. Consequently, this research project aimed to measure the degree of extraction of Fe^{3+} ions from an aqueous nitric acid solution of varying concentrations (0.1, 0.5 and 0.9M), contacted with a 0.5M organic solvent containing HDEHP [(bis(2-ethylhexyl) phosphate)], diluted with n-dodecane, via an existing laboratory-scale, batch liquid-liquid extraction (LLE) set up. The aim was met via the execution of 4 experimental runs, that were repeated for reproducibility. The work was conducted at the Thermodynamics Research Unit, located at the University of KwaZulu-Natal.

Test system measurements were performed to measure the extraction of neodymium. Nd had the highest distribution coefficients of 9.63 and 10.67 at the lowest nitric acid feed concentration of 0.1M. The corresponding extraction efficiencies were 90.5% and 91.43%, respectively. The results obtained were comparable to the trends reported in literature.

The extraction of iron was thereafter measured in which a high reproducibility of results was obtained. The distribution ratios of iron were fairly constant over the nitric acid concentration range investigated.

The experiments investigating the effect of ionic liquid doping in the organic phase on separation efficiency were inconclusive due to phase splitting that occurred in both of the ionic liquids tested. These experiments were not pursued further.

The final set of extraction measurements tested a combined mixture of iron and neodymium. At 0.1M HNO_3, the distribution coefficient of Nd, of 926.65, was higher than the distribution coefficient of Fe, which on average was 14.14. This resulted in a high separation factor of 65.63 ($\beta_{Nd/Fe}$) and a desirable extraction efficiency of 99.89%. It was observed that the separation factor decreased significantly with increased nitric acid concentration.

It was concluded that the extraction of Nd from a mixture of Fe and Nd is possible with the use of dilute HNO_3 concentrations when HDEHP diluted with n-dodecane is the organic solution.

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF FIGURES

✓

LIST OF TABLES

1   INTRODUCTION

1.1   BACKGROUND

Rare earth elements (REEs), a group of 17 chemical elements, are of paramount importance in modern society due to their physical and chemical properties that have allowed for their integration into technological devices and advancements into a greener economy. The unique properties of rare earth metals (REMs) have resulted in their use in the manufacturing of catalysts, magnets and alloys (Ambaye, et al., 2020).

China is the primary supplier of the world's demand for REEs, justified by the supply trend shown in Figure 1-1 (Gergoric, et al., 2017). The figure illustrates the increasing global demand for REEs from which it can be seen that China also contributes significantly to the demand.
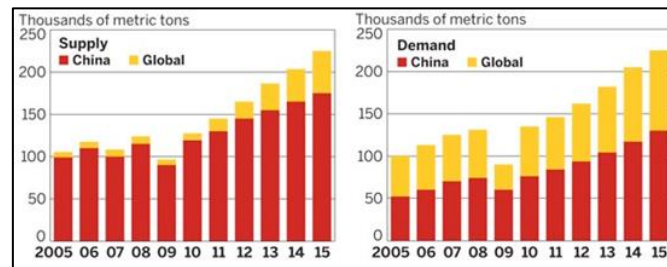
Figure 1-1: REMs supply and demand (Rutherford , 2015)

Due to the events that transpired during the rare-earth crisis of 2011, which led to increased REM prices when China decided to implement stringent exportation policies (Chen & Zheng, 2019), concerns regarding the vulnerability of supply disruptions have been raised in recent years. The increase in price, especially in neodymium, can be seen in Figure 1-2. Figure 1-1 justifies the aforementioned concern because after the financial crisis of 2011, there was an increased supply of REEs from alternative sources.
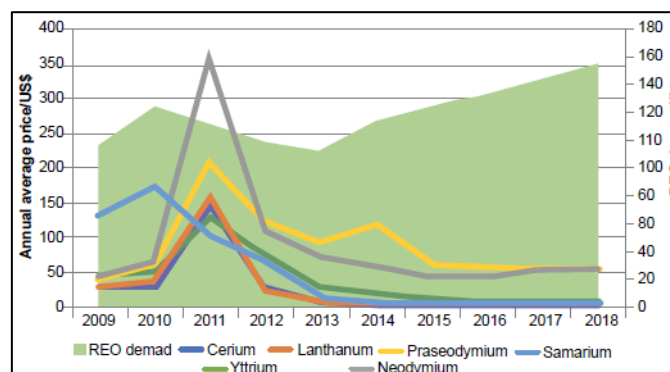
Figure 1-2: Price and demand development of REMs (Gao, et al., 2019)

Consequently, the decreasing supply of exploitable REM deposits and the factor of demand and supply has resulted in investigations being undertaken into secondary sources of REMs to reduce the dependence of the REM production industry on primary ore mining (Gergoric, et al., 2018). Additionally, the pending ban of waste electrical and electronic equipment (WEEE) from landfills in South Africa creates an urgency for the development of a suitable technology for REM extraction seeing as the WEEE has significant economic value.

Recycling of REMs from end-of-life electrical and electronic wastes is a prominent topic of interest as it will aid in reducing the demand from the primary ore reserves. It will also aim to promote independence away from China, the main supplier of REMs. According to Ambaye, et al. (2020), electrical and electronic waste is expected to constantly increase therefore the ability to recycle wastes will also reduce to impact that waste accumulation in landfills have with respect to environmental and social concerns.

Neodymium (Nd) is a rare earth metal that exists in a mixture of iron (Fe) and boron (B) to manufacture permanent magnets. NdFeB magnets are used in the manufacturing of hybrid/electric vehicles, hard disk drives, wind turbines, MRI scanners and many more important areas of modern society (Gergoric, et al., 2017). As such, the increasing demand for neodymium magnets and the supply risk of Nd make end-of-life NdFeB magnets a feasible waste stream for the recovery of neodymium (Gergoric, et al., 2018).

Conclusively, recycling of e-waste has the following advantages: environmental protection, job creation, promotes natural resource conservation by alleviating the shortage and saves energy (Kumar, et al., 2013).

This research project focuses on the recovery of neodymium from industrial waste NdFeB magnets, more particularly the solvent extraction step in the hydrometallurgical approach of recycling. However, neodymium magnets contain majority iron which can pose challenges in their ability to be recycled (Gergoric, et al., 2017). According to Gergoric, et al. (2017), the scarcity of data pertaining to the quantity of REM present in waste material has prevented the commercial application of an economically viable end-of-life recycling process. Additionally, the scarcity of solvent extraction data of Nd, Fe and B in an aqueous nitric acid solution has handicapped the progress of Nd recycling from NdFeB magnets seeing as nitric acid is a common leaching solution whilst scarce data has been published considering its use in context.

This project is being conducted in conjunction with a master student's study, (Bayeni, 2021), at the University of KwaZulu-Natal where the student has measured the distribution of

neodymium (III) oxide under a range of nitric acid and organic solvent concentrations. This laboratory project focuses on the generation of the extraction data for Fe^{+3} at concentrations that were deemed optimal by the master student's study. As such, the measurements from the Bayeni (2021) and this research project will be compared and contribute towards future developments of producing a commercial hydrometallurgical process for the beneficiation of NdFeB magnets.

1.2 AIM AND OBJECTIVES

This project aims to investigate the degree of extraction of Fe^{3+} ions from an aqueous nitric acid solution, contacted with a 0.5M organic solvent containing HDEHP [(bis(2-ethylhexyl) phosphate)], diluted with n-dodecane, via an existing bench-scale, batch liquid-liquid extraction (LLE) set up. The aim will be met through the execution of the following objectives:

i. Verify the existing experimental method by performing experiments with neodymium (III) oxide at 25°C as a test system.

ii. Measure the distribution ratio of Fe^{3+} ions at 25°C with varying nitric acid concentrations, using the above-mentioned organic solvent.

iii. Measure the distribution ratios of Fe^{3+} ions at 25°C with the above-mentioned organic solvent that is doped with an ionic liquid to investigate if enhanced separation is observed.

iv. Measure the distribution ratios of Nd and Fe ions in a combined neodymium (III) oxide and iron (III) oxide system to evaluate the separation factor.

v. Infer the feasibility of this separation method as a pilot- or commercial-scale process based on analysis of the results.

1.3 OVERVIEW

This report consists of 7 main chapters: Chapter 2 discusses an overview into the recycling of REEs, followed by the relevant theory associated with LLE measurements and the processing of the phase data measurements; Chapter 3 pertains to the experimental work conducted, the chemicals and apparatus used and the experimental procedure employed; Chapter 4 contains the results obtained from each of the 4 runs conducted; Chapter 5 details a discussion and analysis of the results obtained. Lastly, Chapters 6 and 7 contain the conclusions recommendations, respectively.

2 LITERATURE REVIEW

The following section contains an overview of the methods used for recycling rare earth metals, which will then be followed by the relevant theory associated with liquid-liquid-extraction (LLE) measurements. Lastly, the processing of the phase data measurements and the discussion of existing results from literature will be presented.

2.1 RECYCLING METHODS

According to Prodius, et al. (2020), recycling of neodymium from NdFeB magnets are typically undertaken using chemical recovery methods: pyrometallurgical or hydrometallurgical approaches. The former involves smelting the components using heat whereas the latter requires dissolving the components in an appropriate solvent or liquid (Ashiq, et al., 2019).

Table 2-1, adapted from Ashiq, et al. (2019) and Prodius, et al. (2020), summarizes the advantages and disadvantages of pyrometallurgical and hydrometallurgical processing in REE recycling, respectively.

The hydrometallurgical approach is the favourable chemical method to employ to recover neodymium. The process involves comminution of waste material, leaching the elements contained in the NdFeB magnets into an aqueous solution of desired concentration consisting mostly of strong acids (Gergoric, et al., 2018). Thereafter, the metal for recovery from the leachate will undergo a selective solvent extraction process and lastly stripping into a new aqueous solution for further processing (Gergoric, et al., 2018).

This research project focuses on metal recovery using solvent extraction via hydrometallurgical processing. This is due to the scarce data available in literature pertaining to the extraction data of neodymium and iron from a REE mixture or waste electronic equipment.

According to, Zhang, et al. (2020), NdFeB magnets contain a small amount of boron relative to iron and neodymium. The authors reported the typical composition of the NdFeB magnets as 70% iron and 30% neodymium (Zhang, et al., 2020).

Seeing as the future goal will be to design a commercial hydrometallurgical process for the beneficiation of NdFeB magnets to recover Nd, obtaining extraction data on the separation of Fe from Nd in a common aqueous nitric acid solution is crucial in designing the process efficiently.

Table 2-1: Comparison of pyrometallurgical and hydrometallurgical methods in REE recycling (Ashiq, et al., 2019) and (Prodius, et al., 2020)

Method	Advantages	Disadvantages
Pyrometallurgy	• Recovers REMs in the form of metals instead of oxides	• High energy demand and cost. • Metal recovery of individual species limited • Releases toxic chemicals during smelting/incineration operations.
Hydrometallurgy	• Environmentally friendly • Undertaken in controlled and moderate conditions • Economically viable • High REM recovery rate	• Waste generation • Does have environmental concerns if chemicals selected are not correctly – uses strong acids

2.2 SOLVENT EXTRACTION

Solvent extraction, or liquid-liquid extraction, is the process whereby the constituent target REM is separated by contact of a liquid solution with an insoluble organic solution (Ashiq, et al., 2019). According to Xie, et al. (2014), solvent extraction processes for the separation and purification of REMs are considered the most appropriate technology due to the need to process large volumes at a commercial scale and that extraction processes have high selectivity towards the target element.

Liquid-liquid extraction consists of two completely or partially immiscible phases. In the extraction of REMs, these two phases constitute as the organic and aqueous phases (Gergoric, et al., 2017).

The organic phase will consist of: the extracting agent which will form the complex with the metal ion from the aqueous solution and the diluent which aims to improve the organic phase properties for extraction (Gergoric, et al., 2017).

The aqueous phase contains the REM that needs to be extracted that is dissolved in a diluted aqueous solvent that serves as the leaching agent. The extraction is achieved by vigorous mixing and stage contacting of the organic and aqueous phases (Gergoric, et al., 2017).

Recovery of the metal ion and conclusions regarding the efficiency of the solvent extraction process are inferred by the calculation of the distribution coefficient (D) (Gergoric, et al., 2017):

$$D = \frac{[A]_{organic}}{[A]_{aqueous}} \qquad \text{(2-1)}$$

Where:

$[A]_{organic}$ is the REM equilibrium concentration in the organic phase

$[A]_{aqueous}$ is the REM equilibrium concentration in the aqueous phase

A large value of D indicates that the extraction of the solute into the organic phase is favoured.

Thereafter, the distribution coefficient can be used to calculate the separation factor ($\beta_{A/B}$) between two metals of comparable interest (Gergoric, et al., 2017) :

$$\beta_{A/B} = \frac{D_A}{D_B} \qquad \text{(2-2)}$$

Where:

D_A and D_B are the distribution ratios of metal A and B, respectively

The separation factor is indicative of the selectivity of the two metals after extraction (Nascimento, et al., 2015). A low value indicates difficulty in the separation of the two metals compared.

In the research project investigated, the organic solvent should have a high selectivity towards the metal ion thus large distribution coefficients are desirable for the neodymium test system, relative to iron. Should majority of the neodymium transfer into the organic phase, measurements pertaining to iron will be considered favourable if smaller distribution coefficients are achieved, relative to neodymium, as this would imply a higher separation factor between neodymium and iron achievable ($\beta_{Nd/Fe}$).

The extraction efficiency of the organic solvent at an equal volume of organic and aqueous phases can be calculated (Nascimento, et al., 2015) :

$$Extraction \% = \frac{[A]_{organic}}{[A]_0} \times 100 \qquad (2\text{-}3)$$

Where:

$[A]_{organic}$ is the REM equilibrium concentration in the organic phase

$[A]_0$ is the REM concentration in the aqueous phase initially

2.2.1 Organic phase

As mentioned previously, the organic phase consists of an extractant and a diluent. The organic extractant used in this research project was bis(2-ethylhexyl) phosphate) commonly known as HDEHP or DEHPA. The organic diluent that serves to increase the organic phase properties was n-dodecane.

2.2.1.1 Organic extractant:

There are three types of extractants for solvent extraction (Xie, et al., 2014): cation exchangers (acidic extractants), solvation extractants (neutral extractants) and anion exchangers (basic extractants).

HDEHP is a typical organophosphorus acidic extractant that is widely used for REM separation due to its high extraction efficiency, justified by Nascimento, et al. (2015) and Gergoric, et al. (2018). Additionally, it has shown good versatility in the extraction of REMs due to its chemical stability, good loading and stripping properties, good kinetics in extracting and its high availability in large quantities whilst being economically viable (Gergoric, et al., 2017). Consequently, HDEHP was chosen as the organic extractant in this research project because literature motivates its use in REM extraction.
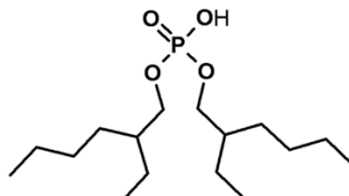
Figure 2-1: Molecular structure of HDEHP (Nayak, et al., 2014)

HDEHP is a cationic extract whereby the metal is exchanged by the hydrogen ion of its hydroxyl group (Xie, et al., 2014). The mechanism of an acidic extraction is shown in Equation 2-4. When the acidic extractant interacts with the aqueous phase via induction of vigorous mixing, for every trivalent metal ion transferred into the organic phase, $3H^+$ ions are discharged into the aqueous phase (Gergoric, et al., 2018).

$$Ln^{+3} + 3\overline{(HX)_2} \leftrightarrow \overline{LnX_3(HX)_3} + 3H^+ \qquad (2\text{-}4)$$

Where:

Ln^{+3} represents the REM lanthanide in solution

HX represents a molecule of HDEHP

The overbar symbolizes the organic solution

2.2.1.2 Organic diluent:

The organic phase requires an organic liquid that serves as a diluent because the organic extractant cannot be used in its pure form due to the following reasons (Regadio, et al., 2020): the density is close to that of the aqueous feed solutions, and it has a high viscosity.

Therefore, dilution decreases the viscosity and density of the organic extractant making the organic solution suitable for its use in solvent extraction. Additionally, the diluent allows for the manipulation of the organic phase concentration to desired ranges, which is necessary to achieve a specific metal loading of the extracted metal concentration (Regadio, et al., 2020).

In addition to being economically feasible and readily available, the following properties are crucial when selecting a suitable diluent for a specified extractant: high solvency for the extracted metal complex, low volatility, low solubility in the aqueous phase, low toxicity and viscosity (Regadio, et al., 2020).

The diluent employed plays a significant role in the formation of the complexes thus has a direct effect on the distribution coefficient obtained (Gergoric, et al., 2017). In this work, the organic liquid diluent selected was n-dodecane and Regadio et al. (2020) also justify the use of n-dodecane as a suitable organic diluent. Furthermore, Nayak, et al. (2014) performed LLE measurements using HDEHP diluted with n-dodecane. The authors obtained desirable results therefore n-dodecane is a suitable organic diluent for HDEHP.

Table 2-2: Properties of chemical compounds present in the organic phase (Bayeni, 2021)

Physical property	HDEHP	n-Dodecane
Boiling point	393°C	216.2°C
Density	0.968 g/cm^3	0.75 g/cm^3

2.2.2 Aqueous phase

The aqueous phase is the feed solution that contains the REM of interest for recovery. The aqueous solvent, solute and diluent were nitric acid, the respective metal oxide and deionised water, respectively.

In addition to the diluent, the acidic concentration in the aqueous phase also affects the extraction process. According to Gergoric, et al. (2018), the acidic concentration provides counter ions for the exchange mechanisms shown previously in Equation 2-4.

Nitric acid is a common leaching agent, however scarce data is present concerning its use in the combined system of interest. Neodymium extraction data from literature are limited to hydrochloric acid and sulphuric acid leaching solutions. Although the latter chemicals are more economical, they are stronger acids and therefore have increased health and safety concerns as well as adverse effects on process equipment.

Seeing as nitric acid is a suitable candidate for use in the hydrometallurgical processing of NdFeB magnets (Gergoric, et al., 2017), this research project utilizes nitric acid as the aqueous solvent to generate extraction data in the aforementioned system of interest.

Table 2-3: Chemical components present in the aqueous phase (Bayeni, 2021)

Physical property	Nd$_2$O$_3$	Fe$_2$O$_3$	Nitric acid	Deionised water
Density	7,42 g/cm^3	5,24 g/cm^3	1,51 g/cm^3	0,99 g/cm^3

To achieve a favourable extraction, the organic solvent should selectively attract the target compound and not the aqueous solvent. It has been established that HDEHP is a cationic extractant therefore it does not extract nitric acid. This was experimentally verified by Parcary, et al. (2012).

2.3   IONIC LIQUIDS

Several investigative research studies have been conducted into the use of ionic liquids in solvent extraction of REMs. Baba, et al. (2011) reports that some ionic liquid-based systems show better extraction and selectivity than the more traditional organic solvent extraction system. As such, the design of more efficient processes can only be commercially implemented should the solvent extraction data using laboratory-scale analysis prove desirable.

The advantages and disadvantages, obtained from Zhang, et al. (2020), of incorporating an ionic liquid into the organic phase solution are tabulated below.

Table 2-4: Advantages and disadvantages of using an ionic liquid in solvent extraction

Advantages	Disadvantages
Enables a high recovery of REM	High cost
Can obtain a high purity of a single REM	Difficult to prepare ionic liquid systems
Highly efficient	
Environmentally friendly	

Despite the advantages of ionic liquid incorporation into solvent extraction, the disadvantages pose severe limitations concerning commercial-scale implementation. However, the ability to generate the extraction data of the extraction of Nd and Fe using ionic liquids, in addition to the traditional organic solution, will enable comparable results to be obtained. This will allow for conclusions to be drawn regarding the feasibility of implementation on a commercial scale. Additionally, if the system can be synthesized with a cost-effective ionic liquid, which is also commonly referred to as a 'green solvent', it means a cleaner production process can be designed.

Consequently, to combat the aspect of a high cost, ionic liquid doping in the organic phase was investigated in this research study. Incorporating the ionic liquid into the system via doping of the organic phase implies a reduced quantity of the respective ionic liquid utilized. The cost-effective ionic liquids used in this study were tributylmethylphosphonium methyl sulfate and triisobutylmethylphosphonium tosylate due to it being available in the laboratory.

2.4   ANALYSIS TECHNIQUES

After extraction, the aqueous phase is withdrawn and diluted. The diluted sample is then analysed to determine the concentration of the target element remaining in the aqueous phase after extraction. By difference, the concentration of the REM that has been extracted by the organic extractant can be calculated. The analytical technique used to identify the metal concentration present in the sample is inductively coupled plasma optical emission spectrometry (ICP-OES). Analysis was also performed using a potentiometric titrator.

2.4.1   ICP-OES

ICP-OES is an analytical device that is used to determine the quantity of a specified component is present in a sample. The principle of operation was obtained from Boss & Fredeen (2004).

ICP-OES measures the quantity of an element present in a sample by subjecting the sample to high temperatures with the objective being to excite and energize the atoms to higher energy levels. The intensity of light emitted is measured when the atom drops to a lower energy level. Conclusively, this device measures the concentration of the target element present in the sample by relating it to the amount of electromagnetic radiation emitted and records the element present in the sample by relating it to the wavelength at which is the radiation is emitted (Boss & Fredeen, 2004).

Standard solutions are prepared by diluting high purity metals to obtain a set of desired concentrations. The standard solutions of known amounts of each element are measured by the ICP-OES to calibrate the measurement device thus producing a calibration curve (Boss & Fredeen, 2004).

2.4.2   Titration analysis

Titration measurements were performed to measure the concentration of H^+ ions in the aqueous phase after extraction. The reaction mechanism in Equation 2-4 predicts an increase in the nitric acid concentration after extraction.

A potentiometric titrator was used whereby the equivalence point of the titration is recorded with an indicator electrode. According to Hulanicki, et al. (2013), the indicator electrode in a potentiometric titrator records the change in potential as a function of the volume of titrant added of known concentration.

2.5   RESULTS FROM PREVIOUS STUDIES

In this research study, experimental measurements were performed to determine the distribution coefficient of neodymium (III) oxide and iron (III) oxide in an aqueous phase consisting of nitric acid and water, and an organic phase consisting of HDEHP and n-dodecane.

Thereafter, the separation factor of Nd and Fe was calculated using Equation 2-2. As mentioned previously, iron is the main impurity of NdFeB magnets and it is mentioned in literature that iron has been the main obstacle promoting the recycling of end-of-life NdFeB magnets commercially (Gergoric, et al., 2017).

Therefore, measurements from this research study are aimed to provide extraction data of iron, in the solvent extraction system investigated, that will enable future developments into the aforementioned commercial or pilot-scale process. There exists no measured data in literature regarding the system investigated in this research study, however, a brief overview concerning results from other REM and neodymium extraction systems will be discussed.

Figure 2-2 and 2-3, obtained from Nayak, et al. (2014), represents the extraction of Am(III) and Eu(III), respectively, using a similar solvent extraction system that this research study is investigating. The authors also experimentally verified the reaction mechanism shown in Equation 2-4.
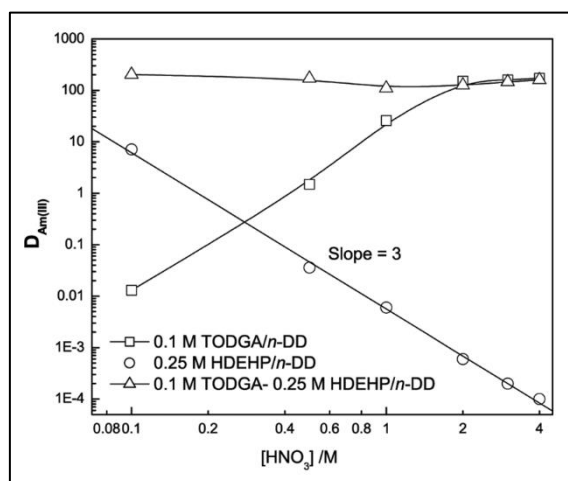
Figure 2-2: Distribution coefficient vs nitric acid concentration: Am (III)

(Nayak, et al., 2014)
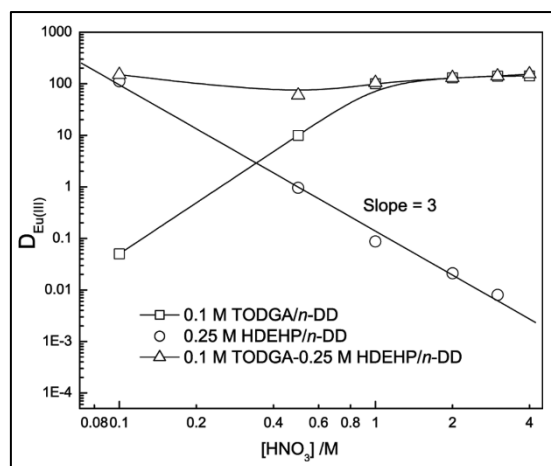
Figure 2-3: Distribution coefficient vs nitric acid concentration: Eu(III)

(Nayak, et al., 2014)

As stated in Chapter 1, this research study is being done in conjunction with a master's student study at the University of KwaZulu-Natal. Bayeni (2021) measured neodymium liquid-liquid extraction data therefore comparable results from the experimental work on the test system in this research study using Nd_2O_3 should be obtained seeing as the same solvent extraction system was used (organic solvent: 0.5M HDEHP diluted with n-dodecane).
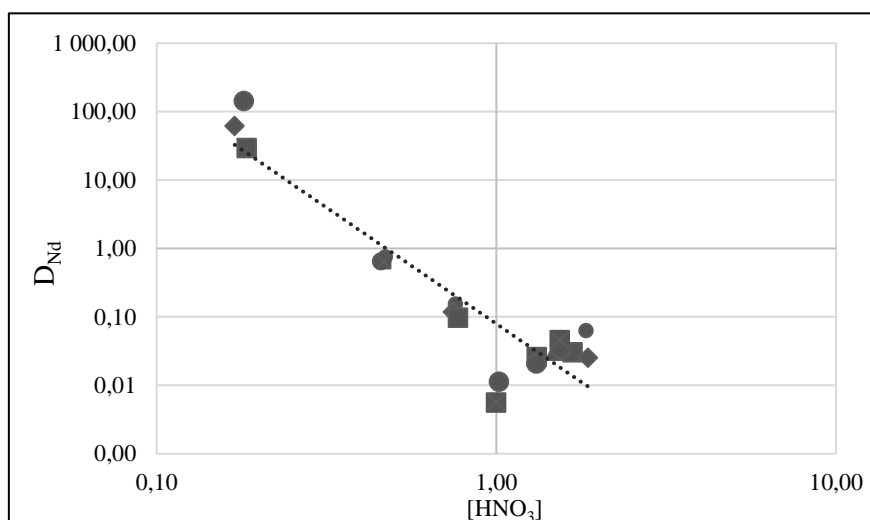
Figure 2-4: Distribution coefficient vs nitric acid concentration: Nd(III) *(Bayeni, 2021)*

In Figures 2-2 to 2-4, higher distribution coefficients were obtained at lower nitric acid concentrations. Seeing as both the sources, Nayak, et al. (2014) and Bayeni (2021), use the same solvent extraction system this research study is investigating, the same linear trend is anticipated to be observed in the neodymium and iron systems, respectively.

Gergoric, et al. (2018) generated distribution ratios for Nd and Fe in a solvent extraction system containing acetic and nitric acid in the aqueous phase and D2EHPA (HDEHP) diluted with Solvent 70 in the organic phase.

The following procedure was obtained from Gergoric, et al. (2018) and details the solvent extraction methodology employed by the authors: the experiments were performed on the IKA Vibrax Vxr basic shaking machine in 3.5mL glass vials that encountered vigorous shaking for 1 hour. The vials contained equal quantities of the aqueous and organic phases, respectively. After extraction, the aqueous phase was sampled and diluted in 1M HNO_3 and then the sample was measured using ICP-OES (Gergoric, et al., 2018).

The data obtained is displayed in Figure 2-5.
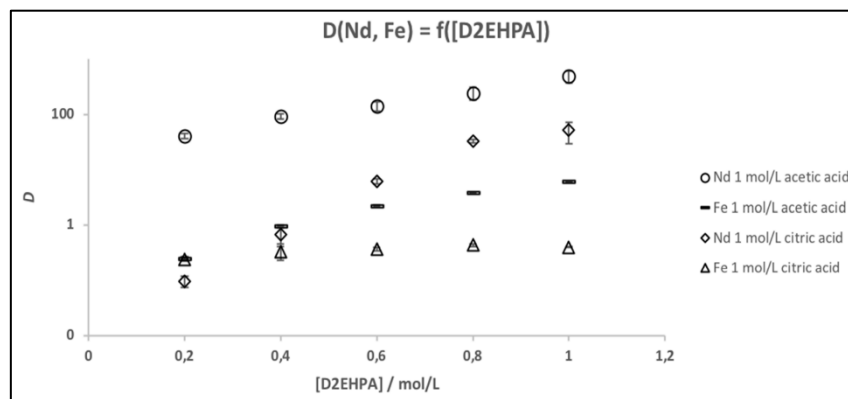
Figure 2-5: Distribution ratio vs D2EHPA concentration: Nd and Fe

(Gergoric, et al., 2018)

Figure 2-5 shows that high separation factors were achievable in the solvent extraction system seeing as Gergoric, et al. (2018) obtained lower distribution ratios of Fe when compared to Nd.

As mentioned previously, hydrochloric acid and sulphuric acid are the common acids employed in the extraction of REMs due to high extractions being obtained. Nitric acid is a weaker acid than the aforementioned acids. Seeing as acetic and citric acid are considered to be weaker acids than nitric acid, favourable results are expected to be obtained in the solvent extraction system being investigated, in comparison to the acetic and citric acid systems.

3 EXPERIMENTAL

The following section contains a detailed explanation of the experimental work conducted at the Thermodynamics Research Unit, the main apparatus used and the experimental procedure employed.

3.1 EXPERIMENTAL WORK CONDUCTED

The experimental work consisted of 4 runs and are summarised in Table 3-1. The effect of varying nitric acid concentration, on extraction potential, using 3 different concentrations (0.1, 0.5 and 0.9M) was investigated thus each run contained 3 cells. However, seeing as each student conducted each run independently to assess consistency, 6 cells were used which resulted in 6 measurements being obtained per run.

The following pertains to the components making up the aqueous phase in each of the respective runs:

- Run 1 was the test system: neodymium (III) oxide, 0.1, 0.5 and 0.9M nitric acid and deionised water.
- Run 2 and 3: iron (III) oxide, 0.1, 0.5 and 0.9M nitric acid and deionised water
- Run 4: a mixture of iron (III) oxide and neodymium (III) oxide in the mass ratio of 70:30 (Zhang, et al., 2020), 0.1, 0.5 and 0.9M nitric acid and deionised water.

In runs 1, 2 and 4, the organic phase consisted of 0.5M HDEHP diluted with n-dodecane. The effect of ionic liquid (IL) doping was investigated in run 3 therefore the organic phase consisted of tributylmethylphosphonium methyl sulfate, HDEHP and n-dodecane.

In each run, a metal loading of 2000mg/L was used.

Table 3-1: Experimental work conducted

Run number	Aqueous phase				Organic phase		
	HNO_3	H_2O	Nd_2O_3	Fe_2O_3	HDEHP	$C_{12}H_{26}$	IL
1	✓	✓	✓		✓	✓	
2	✓	✓		✓	✓	✓	
3	✓	✓		✓	✓	✓	✓
4	✓	✓	✓	✓	✓	✓	

3.2 CHEMICALS AND APPARATUS DETAILS

The chemicals and measurement devices used are tabulated below with their purities and associated uncertainties, respectively, as stated by the supplier. The chemicals were used as supplied by the manufacturer and distributor.

Table 3-2: Chemical inventory

Chemical name	Formula	CAS no.	Supplier	Purity
Bis(2-ethylhexyl) Phosphate (HDEHP)	$C_{16}H_{35}O_4P$	298-07-7	Merck	0.95[a]
n-Dodecane	$C_{12}H_{26}$	11-40-3	Merck	0.99[a]
Nitric acid	HNO_3	7697-37-2	Merck	0.55[b]
Deionised water	H_2O	7732-18-5	TRU Laboratory	[c]
Neodymium (III) oxide	Nd_2O_3	1313-97-9	Sigma Aldrich	0.99[b]
Iron (III) oxide	Fe_2O_3	1309-37-1	BDH	0.85[b]
tributylmethylphosphonium methyl sulfate	$C_{14}H_{33}O_4PS$	69056-62-8	Fluka Analytical	>0.95
triisobutylmethylphosphonium tosylate	$C_{20}H_{37}O_3PS$	344774-05-6	Iolitec	>0.95
Sodium hydroxide	$NaOH$	1310-73-2	Sigma Aldrich	0.98[b]

[a] – molar basis

[b] – mass basis

[c] – electrical resistivity (18MΩ·cm)

Table 3-3: Measurement devices with associated manufacturer uncertainty

Device	Manufacturer	Model	Manufacturer uncertainty	Readability
Mass balance	Ohaus	PA214	±0.0006g	0.00001g
Pt100 temperature sensor	TRU laboratory		±0.14°C	0.1°C
Micropipette (100 - 1000μL)	IsoLab	Non autoclavable 011.05.901	±0.02mL	-
Micropipette (1000 - 5000μL)	IsoLab	Non autoclavable 011.05.905	±0.02mL	-
Titration apparatus	Metrohm	888 Titrando	±0.0001mL	0.0001mL

Table 3-4: Additional glassware/apparatus

100mL volumetric flasks	Vials	Barometer
Measuring cylinders	Syringe with needle	Erlenmeyer flask
Dropper	Wash bottle with deionised water	
Spatula	Wash bottle with ethanol for cleaning	
Funnel	Centrifuge tubes	
Magnetic stirrer	Chiller and heater	

The main apparatus is a laboratory-scale liqud-liquid extraction apparatus shown in Figure 3-1.

It consists of a heater [2] and chiller [4] that controlled and monitored the temperature of the water bath. The latter was accomplished via a Pt100 temperature sensor [6] that was submerged into the water bath [7] during the allocated mixing and settling times.

Once the 6 vials were prepared with the respective aqueous phase concentration and organic phase, each test compartment was attached to the corresponding lid [17] present on the metallic frame. Each lid contained 2 ports: a sampling port that would be used to withdraw the separated aqueous layer after extraction and a port that served as an access point for the mixer shaft.

The main metallic framework fixes 6 mixers [10] that are connected to a motor [1]. The mixer facilitates vigorous mixing of each of the separate vials that is required for solvent extraction. The main metallic framework containing the attached test compartments is submerged into the water bath during operation to maintain isothermal conditions.
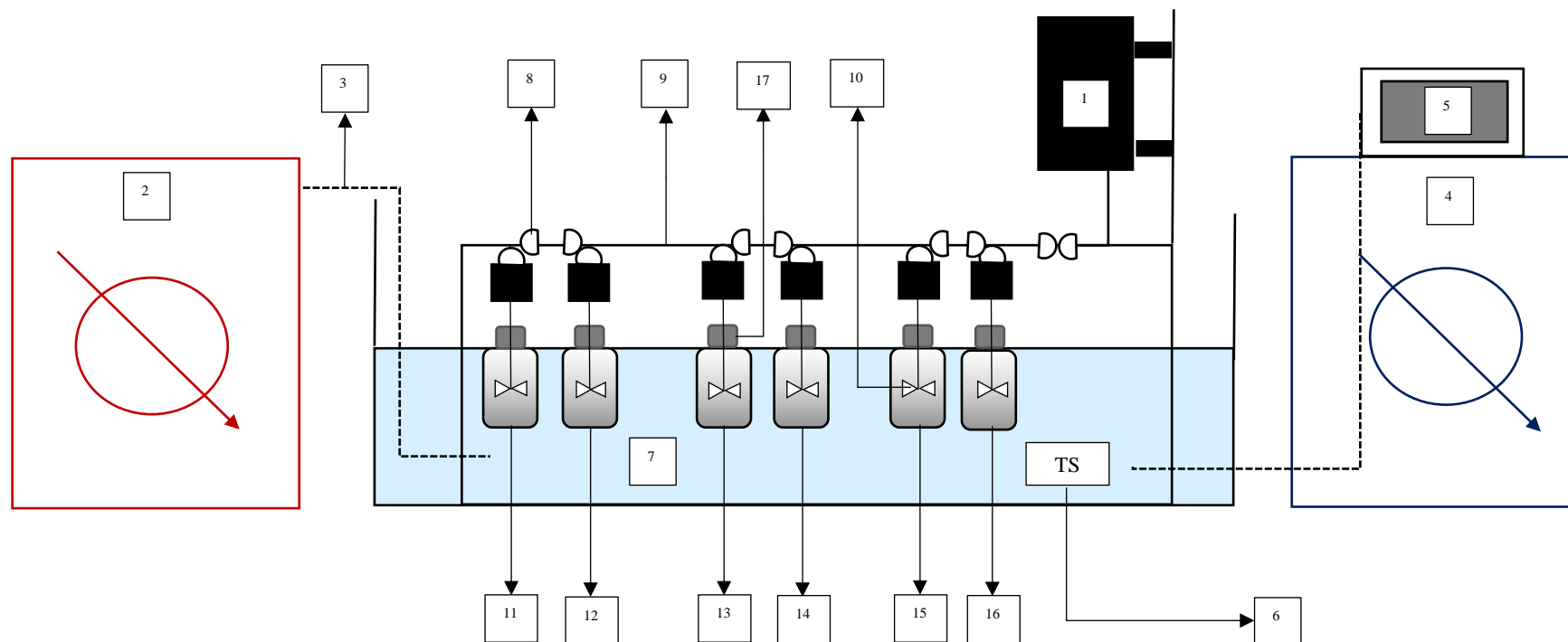
Figure 3-1: Schematic of LLE apparatus

1- Motor; 2-Heater; 3-Heating coil; 4- Chiller; 5-Temperature display; 6-Pt100 sensor; 7-Water bath; 8-Gears; 9- Metallic frame

10-Mixer; 11- Vial 1: Student 1 (0.1M HNO_3); 12- Vial 2: Student 1 (0.5M HNO_3); 13-Vial 3: Student 1 (0.9M HNO_3);

14-Vial 4: Student 2 (0.1M HNO_3); 15-Vial 5: Student 2 (0.5M HNO_3); 16-Vial 6: Student 2 (0.9M HNO_3); 17-Vial lid with sample hole

3.3   EXPERIMENTAL PROCEDURE

The following procedure was adapted from Bayeni (2021) and applies to the test system. This was modified accordingly to accommodate the variable tested in each of the experimental runs.

3.3.1   Stock solution preparation

The quantities required to make up the stock solutions were predetermined. Sample calculations are available in Appendix A.

1. The required glassware was washed 3 times with deionised water and twice with ethanol.
2. The aqueous phase consisted of neodymium (III) oxide, nitric acid and deionised water. Since the effect of varying nitric acid concentrations was being investigated, 3 aqueous stock solutions were made at 0.1, 0.5 and 0.9M, respectively.
   - 0.1M HNO_3 stock solution: Using the mass balance, 0.050 g Nd_2O_3, 24.549 g deionised water and 0.264 g HNO_3 were measured and placed into a 100mL volumetric flask.
   - 0.5M HNO_3 stock solution: Using the mass balance, 0.050 g Nd_2O_3, 23,974 g deionised water and 1,041 g HNO_3 were measured and placed into a 100mL volumetric flask.
   - 0.9M HNO_3 stock solution: Using the mass balance, 0.050 g Nd_2O_3, 23.400 g deionised water and 1.818 g HNO_3 were measured and placed into a 100mL volumetric flask.

A dropper, spatula and funnel were used when necessary.

3. The organic phase contained 0.5M HDEHP diluted with n-dodecane. 14.410 g and 56.260 g of HDEHP and n-dodecane, respectively, were measured using the mass balance and poured into a 100mL volumetric flask.
4. The aqueous and organic phase solutions were shaken well to allow for mixing.

3.3.2 LLE measurement procedure:

1. The temperature controllers for the bath and the chiller were switched on to ensure that the water bath temperature reading on the display read 25°C. The heater and water bath levels were filled with deionised water to the indicated levels.

2. The Pt100 sensor was placed in the water bath to monitor the temperature.

3. The barometric pressure in the room as well as the stabilized water bath temperature was recorded.

4. Each of the 6 vials was washed 3 times with deionised water and twice with ethanol. This was done in advance, if possible, to allow for complete drying of the vials before dispensing the solutions.

5. A micropipette was used to dispense 5mL of the aqueous phase and 5mL of the organic phase into each vial.

6. The vials were then attached to the preinstalled lids on the LLE bench-scale apparatus.

7. The timer was set to commence mixing for 12 hours.

8. Once mixing was completed, the agitated phases were allowed to settle for a further 8 hours.

The mixing and settling times were determined by previous LLE measurements (Bayeni, 2021) thus equilibrium was assumed to be reached within the specified time periods.

3.3.3 Sample extraction:

1. A syringe was used to withdraw the separated aqueous layer from each vial and transfer the withdrawn contents to a labelled centrifuge tube that indicated the nitric acid concentration.

2. The vials were removed from the LLE apparatus and cleaned 3 times with water and twice with ethanol.

3. The chiller and heater were switched off.

3.3.4 Sample dilution:

1. A sample of 1mL of the withdrawn aqueous phase was dispensed into a 100mL volumetric flask using a micropipette.

2. The contents in the volumetric flask were then diluted with water in the ratio of 1:100 on a volumetric basis.

3. Each flask was shaken well.

3.3.5 Analysis:

1. An amount of 15 mL of the diluted sample was poured into a centrifuge tube for ICP-OES analysis.

2. Thereafter, 25 mL of the diluted sample was poured into a centrifuge tube for titration analysis. Seeing as duplicate titration measurements were done, each sample was titrated twice therefore two 25 mL centrifuge tubes were prepared for titration analysis. The mass of each empty titration centrifuge tube and the mass of each tube filled with the diluted sample were recorded using the mass balance. By difference, the mass of the sample present was determined. The recorded masses can be found in Appendix B.

The ICP-OES analysis was conducted at the Department of Chemistry at the PMB campus. Calibration standards were made by diluting the extracted feed of high concentration (2000 ppm) with deionized water to lower concentrations (Boss & Fredeen, 2004). The range of concentrations made for ICP-OES calibration for the test system was: 100 ppm, 80 ppm, 50 ppm, 20 ppm, 9 ppm, 7 ppm, 5 ppm 3 ppm and 1 ppm (Bayeni, 2021).

Titration measurements were conducted using the Metrohm 888 Titrando Potentiometric Titrator and the following brief procedure was implemented on the graphical user interface when conducting titration measurements for the $0.1M$ HNO_3 samples:

1. Firstly, the titration software was opened
2. A magnetic stirrer was placed into the NaOH bottle.
3. Manual tab:
   - *Titration devices → Dosing device 1→ Prepare*
   - The burette was attached to the rod and placed in an Erlenmeyer flask
   - *Start* was selected
   - Once discharge was completed, the flask contents was discarded into a waste bottle
4. Configuration tab:
   - *'NaOH concentration'* was clicked → *Titer*
   - The diluted nitric acid concentration: $\frac{0.1M}{100}$ was entered
5. Method tab:
   - *'Open existing method'* was clicked → *'Thulani method'* (Bayeni, 2021)
   - *Workplace* was selected

- The sample mass measured previously, in step 2 of section 3.3.5, was entered in the respective block.
- A magnetic stirrer was placed into the centrifuge tube after agitation and the tube was placed on the titration apparatus
- The burette and probe were connected and placed into the sample tube.
- Once *start* was selected, NaOH was dispensed and the volume required to meet the equivalence point was displayed on the screen and recorded.

4   RESULTS

This chapter contains the results of the experimental work conducted. The measurements were conducted at a temperature of approximately 25°C and a pressure of 100 kPa. The operating conditions are tabulated in Table B-3 in Appendix B. The experiment to assess the effect of ionic liquid doping on the separation efficiency could not be evaluated. A discussion with justifications and recommendations for the aforementioned deviation from the work plan can be found in Chapter 5.

The results are inclusive of the combined standard uncertainty that was computed in Appendix C-1. The distribution coefficient and separation factor sample calculations can be found in Appendix C-4 and C-5, respectively.

As explained in the methodology section, 6 vials were used in each experimental run. Vials 1-3 were the author's measurements (highlighted in the tables below) whilst vials 4 – 6 were the author's partner repeat measurements (Sohana Bridgemohan).

Table 4-1:Distribution coefficients (D): Run 1 (Nd measurements) and Run 2 (Fe measurements) with organic solvent: 0.5M HDEHP diluted with n-dodecane

		Vial	Initial [HNO$_3$]	Final [HNO$_3$] (Calculated)	D$_{Nd}$	Extraction efficiency (%)
RUN 1	Nd measurements	1	0.1	0.097	9.63 ± 1.16	90.59
		2	0.5	0.500	0.57 ± 1.16	36.23
		3	0.9	0.896	0.06 ± 1.16	5.20
		4	0.1	0.097	10.67 ± 1.16	91.43
		5	0.5	0.500	3.99 ± 1.16	79.97
		6	0.9	0.896	1.07 ± 1.16	51.80
		Vial	Initial [HNO$_3$]	Final [HNO$_3$] (Calculated)	D$_{Fe}$	Extraction efficiency (%)
RUN 2	Fe measurements	1	0.1	0.105	20.35 ± 0.59	95.32
		2	0.5	0.512	21.87 ± 0.59	95.63
		3	0.9	0.918	19.98 ± 0.59	95.23
		4	0.1	0.105	20.37 ± 0.59	95.32
		5	0.5	0.512	21.92 ± 0.59	95.64
		6	0.9	0.918	15.31 ± 0.59	93.87

Table 4-2: Distribution coefficients (D) and separation factor ($\beta_{Nd/Fe}$): Run 4 (Fe and Nd measurements with organic solvent: 0.5M HDEHP diluted with n-dodecane)

Vial	Desired [HNO₃]	Actual [HNO₃]	D_{Nd}	Extraction efficiency - Nd (%)	D_{Fe}	Extraction efficiency – Fe (%)	$\beta_{Nd/Fe}$
1	0.1	0.106	926.65 ± 1.71	99.89	14.12 ± 1.81	93.39	65.63
2	0.5	0.507	1.32 ± 1.71	56.98	13.74 ± 1.81	93.22	0.10
3	0.9	0.904	0.65 ± 1.71	39.56	13.66 ± 1.81	93.18	0.05
4	0.1	0.106	N/A	N/A	14.16 ± 1.81	93.40	N/A
5	0.5	0.507	1.32 ± 1.71	56.92	13.73 ± 1.81	93.21	0.10
6	0.9	0.904	0.66 ± 1.71	39.61	13.64 ± 1.81	93.17	0.05

N/A indicates no result obtained from the ICP analyses
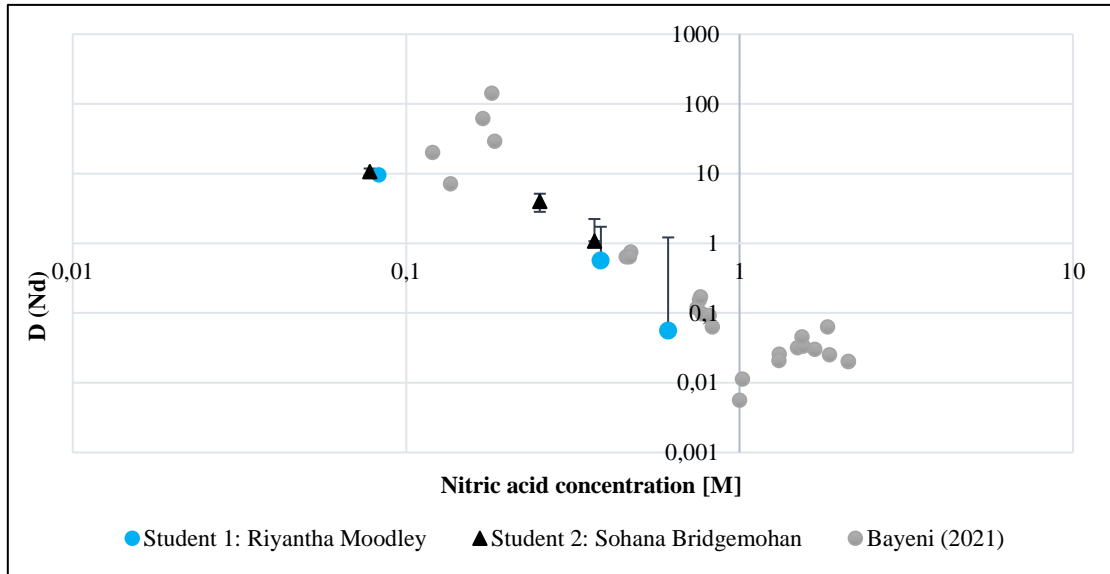
Figure 4-1: Log-scale graph of distribution coefficient (Nd) vs [HNO₃]: Run 1
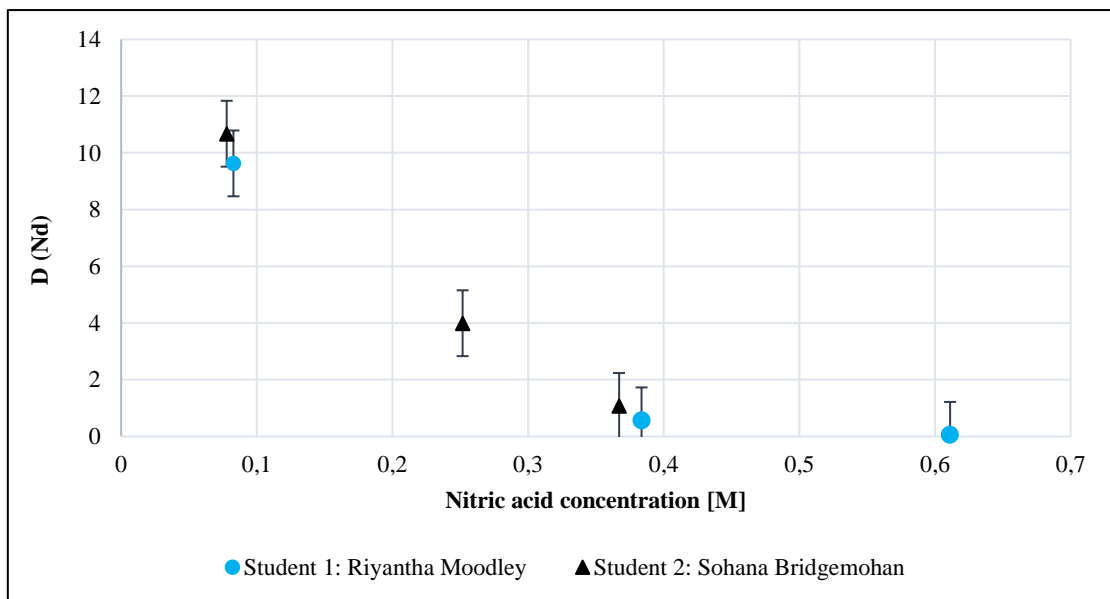
Figure 4-2: Distribution coefficient (Nd) vs [HNO₃]: Run 1
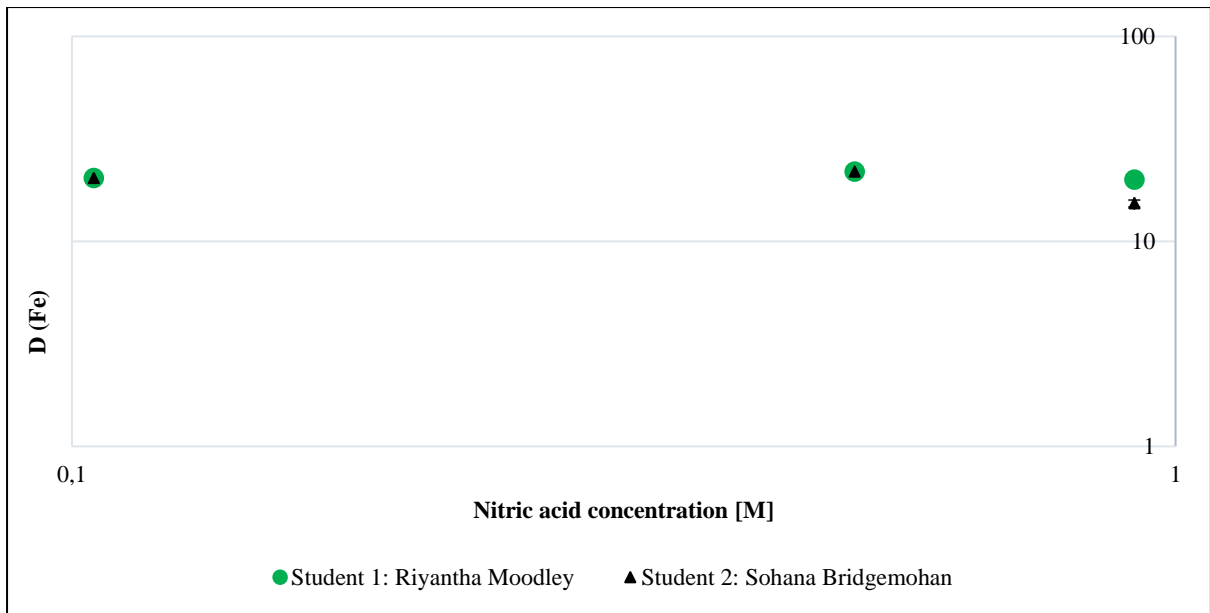
Figure 4-3: Log scale graph of distribution coefficient (Fe) vs [HNO₃]: Run 2
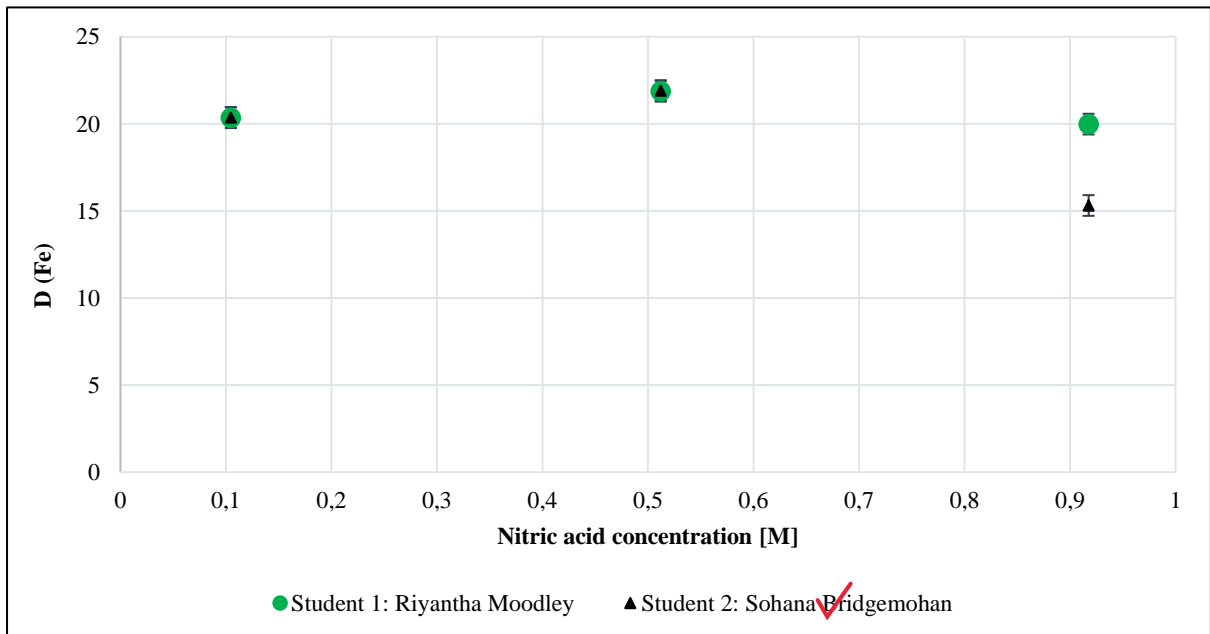
Figure 4-4: Distribution coefficient (Fe) vs [HNO₃]: Run 2
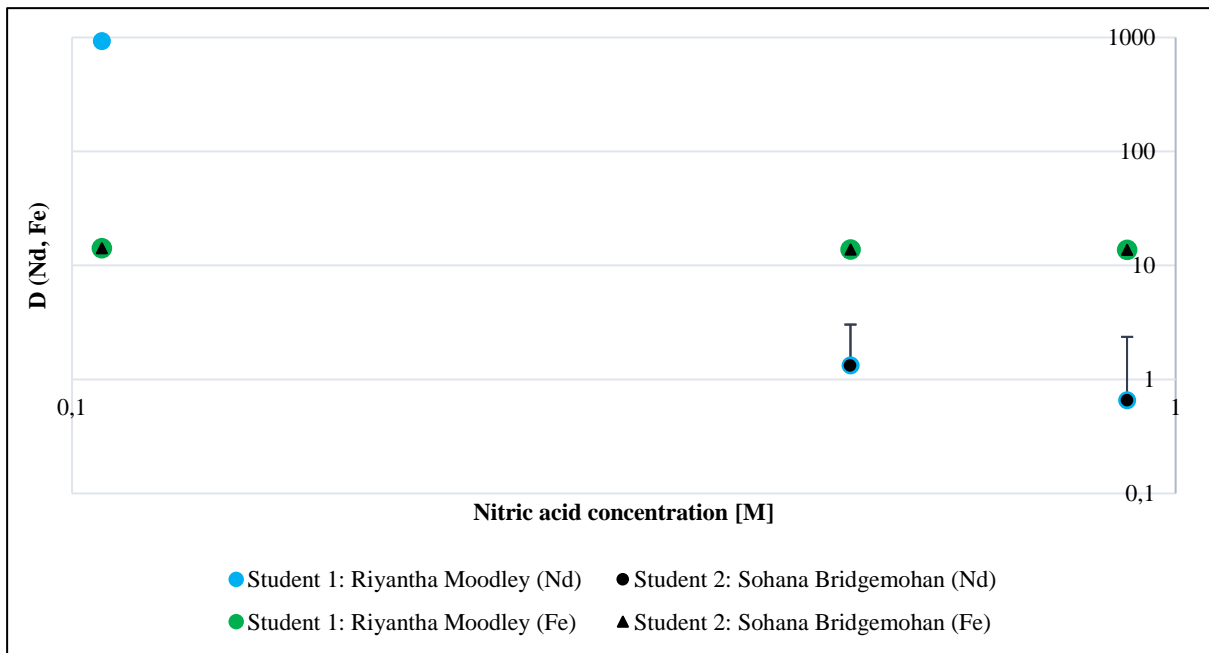
Figure 4-5: Log scale graph of distribution coefficient (Nd and Fe) vs [HNO₃]: Run 4
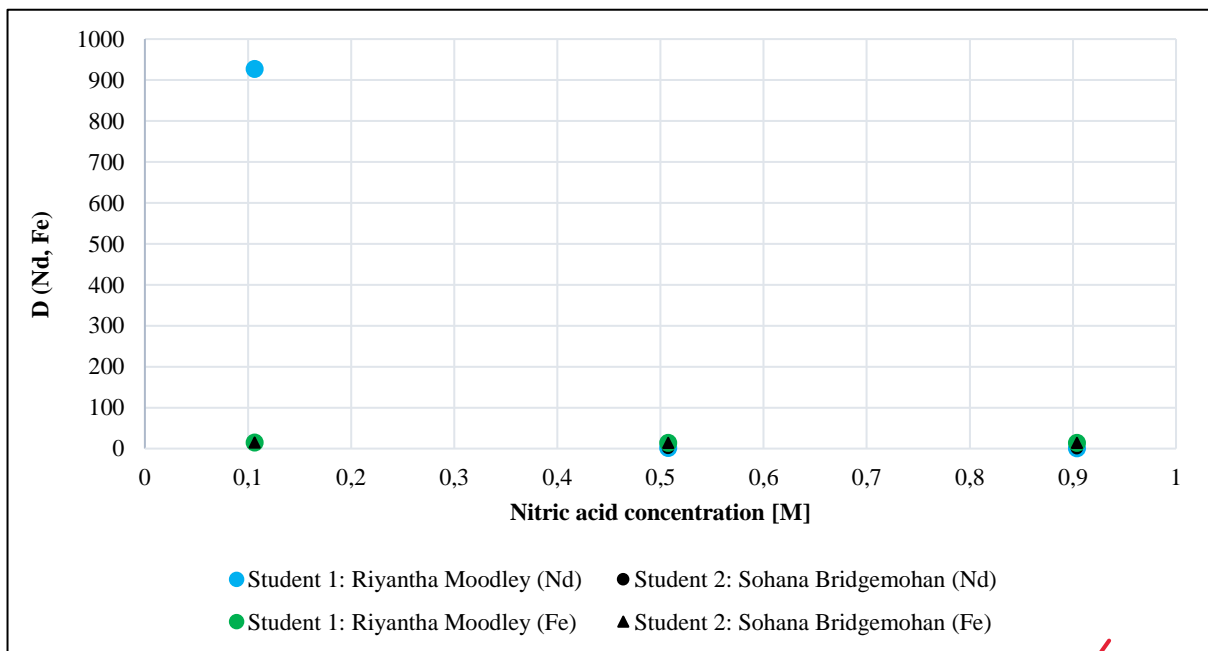
Figure 4-6: Distribution coefficient (Nd and Fe) vs [HNO₃]: Run 4

5   DISCUSSION

The following section contains a detailed discussion of the results presented in the previous chapter by comparing the observed trends to literature sources. Additionally, any observations made during the conduction of the experimental work will be presented and discussed.

The experimental work consisted of 4 experimental runs with the aim being to meet the previously mentioned objectives in Chapter 1.2.

The experimental method utilized in this research study was modified and developed by Bayeni (2021). The method was formulated in close adherence to literature concerning the conduction of solvent extraction measurements. A brief overview of a similar experimental method performed by Gergoric, et al. (2018) is provided in Chapter 2.5. The experimental method was verified via the conduction of run 1 which served as a test system with neodymium. Comparable results were obtained that abided by literature trends therefore the experimental method employed is acceptable.

The uncertainty due to the mass balance, Pt100 temperature sensor, micropipette and the titration apparatus were treated as type B uncertainties with a rectangular distribution (Kadis, 2000). The uncertainty due to the ICP-OES analytical device was evaluated as a RMSE (Chai & Draxler, 2014) using the calibration data provided by the ICP-OES technician. Thereafter the combined standard uncertainty was computed for accommodation into the results obtained (Farrance & Frenkel, 2012). Detailed sample calculations can be located in Appendix C-1.

5.1   TEST SYSTEM: NEODYMIUM DISTRIBUTION RATIOS (RUN 1)

Run 1 was the test system with neodymium (III) oxide. The organic and aqueous phases were colourless therefore no visible observations were made during the solvent extraction process. The results are plotted using a logscale graph as recommended by Nayak, et al. (2014), and a non-log scale axis. The resulting graphs are shown in Figures 4-1 and 4-2, respectively. Experimental run 1 had an associated combined standard uncertainty of 1.69 in the distribution coefficient measurements.

In Figure 4-1, the literature source used for comparison was the data of Bayeni (2021). The figure shows a good agreement between the data of Bayeni (2021) that was measured at different nitric acid concentrations and the data obtained in this experimental work at 0.1, 0.5 and 0.9M HNO_3. When comparing the measurements each student obtained in this

experimental work, it can be observed that for run 1, 4 out of the 6 measurements displayed excellent solvent extraction potential for HDEHP. The values for the distribution coefficients being greater than 1 were obtained for solutions of 0.1, 0.5 and 0.9M HNO_3 (vials 1, 4, 5 and 6). The solutions that were prepared using 0.1M HNO_3 (vials 1 and 4) boasted the highest distribution coefficient of 9.63 and 10.67, respectively. This shows great reproducibility in the results obtained.

The computation for the extraction efficiency can be found in Appendix C-5. The extraction efficiency for experimental run 1 falls within the range of 5.20 – 91.43 %. The acid concentration of 0.1M HNO_3 (vials 1 and 4) has extraction efficiencies of 90.59% and 91.43%, respectively. This further justifies 0.1M HNO_3 producing the highest extraction capabilities for Nd in HDEHP diluted with n-dodecane.

5.2   IRON DISTRIBUTION RATIOS (RUN 2)

The second set of experiments contained iron (III) oxide in the aqueous phase and the standard organic phase consisting of 0.5M HDEHP diluted with n-dodecane. It was observed that before extraction, the aqueous phase contained a reddish hue whereas the organic phase was colourless. Post-extraction, the organic phase contained the same reddish-hue that the aqueous phase contained initially whilst the aqueous phase was completely colourless. The reddish hue is most likely due to the Fe^{+3} ions and their distribution from the acid to the organic solvent phases. Figure D-1 contains a visual of the aforementioned observation.

Figures 4-3 and 4-4 depict the log-scale and non-log-scale representation of the results obtained, respectively, with the associated combined standard uncertainty of 0.59 in the distribution coefficient measurements.

It can be seen that the extraction of iron in HNO_3 using HDEHP as the cationic extractant diluted with n-dodecane produced a fairly constant linear trend over the entire concentration range investigated. Additionally, highly comparative results were obtained between the measurements each student conducted. In the nitric acid concentration range tested, the extraction of the solute into the organic phase was favoured. This was concluded by the relatively high distribution coefficients that were obtained, relative to run 1.

Using the constant distribution ratio over the entire acid concentration range, the average extraction efficiency for HDEHP in Fe extraction from HNO_3 over concentrations of 0.1, 0.5 and 0.9M was computed to be 95.17%. An important observation is that the iron (III) oxide

used reported a purity of 85%. Therefore, there could be a discrepancy in the analysis of the amount of metal ions transferred to the organic phase. This is likely due to the impurities, such as CaO and SiO_2 in the chemical. Such impurities would affect the distribution of the key components.

It has been established that there exists no published work in literature on the system of Fe extraction from a nitric acid leachate using 0.5M HDEHP diluted with n-dodecane. Consequently, a direct comparison of the results obtained with a literature source is not possible. indirect or similar element and compound comparisons?

Prediction of the solvent extraction behaviour in a combined iron and neodymium system can be established via the comparison of the results obtained in experimental runs 1 and 2. As mentioned in Chapter 2, the organic solvent should have a high selectivity towards the metal ion thus large distribution coefficients are desirable for the neodymium test system, relative to iron. Should majority of the neodymium transfer into the organic phase, measurements pertaining to iron will be considered favourable if smaller distribution coefficients are achieved, relative to neodymium, as this would imply a higher separation factor between neodymium and iron achievable ($\beta_{Nd/Fe}$).

It can be observed that what literature predicted to be favourable for REM extraction, did not occur in the system of interest when compared separately because both metal solutes favoured the extraction into the organic phase. Higher distribution coefficients were obtained for Fe when compared to Nd, seen in Table 5-1. This implies that very low separation factors ($\beta_{Nd/Fe}$) would be achieved.

5.3   IRON DISTRIBUTION RATIOS IN ORGANIC SOLVENT DOPED WITH AN IONIC LIQUID (RUN 3)

Run 3 consisted of iron (III) oxide in the aqueous phase whilst the standard organic phase was doped with an ionic liquid, tributylmethylphosphonium methyl sulfate. When preparing the organic phase stock solution, it was observed that phase splitting had occurred (Figure D-2) rendering the system not usable for solvent extraction measurements. To combat the aforementioned problem, a second ionic liquid (triisobutylmethylphosphonium tosylate) was used to dope the organic phase. Unfortunately, this attempt was unsuccessful seeing as phase splitting also occurred in the organic phase.

When performing solvent extraction measurements, the formation of a third phase is not uncommon because Nayak, et al. (2014) also experienced the formation of a third phase. Nayak, et al. (2014) reports that the third phase formation occurred in the organic phase of their experimental work due to the difference in the polarities of the extracted polar complex in n-dodecane (a non-polar diluent). ✓

To solve the problem of phase splitting, a phase modifier can be added to the organic phase, motivated by Gergoric, et al. (2017) & Nayak, et al. (2014). According to Nayak, et al. (2014), the phase modifier commonly used is another extractant (DHOA) or a polar diluent (1-octanol).

It is known that phase splitting does not occur between HDEHP and n-dodecane therefore the chemical/polarity differences that caused the phase splitting observed would have occurred between the ionic liquid tested and HDEHP or n-dodecane. ✓

Zhang, et al. (2020) conducted a review on the incorporation of ionic liquids in extraction processes. The authors acknowledge that ionic liquids contain physical properties that predict their ability to replace traditional organic solvents used in LLE processes. However, Zhang, et al.(2020) reiterates the fact that ionic liquids contain extraction mechanisms that are indefinite and this has hindered its application in solvent extraction of REMs.

5.4   IRON AND NEODYMIUM DISTRIBUTION RATIOS (RUN 4)

Due to phase splitting occurring in the organic phase that rendered run 3 inconclusive, a 4th experimental run was conducted. Run 4 compromised of the combined mixture of neodymium (III) oxide and iron (III) oxide.

The results for this system enable the prediction of the solvent extraction behaviour mentioned in Chapter 5.2 to be verified, which was concluded based on a comparison between the individual metal oxide distribution ratios. The experiments with the 'pure' metal oxides (runs 1 and 2) investigated how the individual metal oxides behave in the solvent extraction system of interest. Therefore, combining the metal oxides and measuring the extraction of neodymium and iron oxides is of crucial importance for designing a separation process efficiently.

The results obtained for the Nd and Fe mixtures are displayed in Figures 4-5 and 4-6. It can be seen that the reproducibility of the iron results from experimental run 2 was further justified in experimental run 4. The results from both students' measurements show nearly identical values for the distribution ratios of the components in the combined system with iron and neodymium. The reproducibility of the results obtained is also apparent in the neodymium extraction results.

Due to the ICP-OES device reporting the measurements conducted by student 2 for 0.1M HNO_3 (vial 4) as undervalue, the data point was omitted. However, due to the strong reproducibility of the other data points, it is expected that the omitted point would have a distribution coefficient close to the value of 926.65 obtained by the author for 0.1M HNO_3 (vial 1).

Figure 4-5 shows using a 0.1M HNO_3 solution, the distribution coefficient of Nd (926.65) was higher than the distribution coefficient of Fe (average of 14.14). Consequently, this resulted in a high separation factor of 65.63 ($\beta_{Nd/Fe}$) and a desirable extraction efficiency of 99.89%. In the higher nitric acid concentrations, the distribution coefficient of iron was higher than neodymium which meant iron had favoured extraction into the organic phase when compared to neodymium. This is the reason for the lower separation factors and decreasing extraction efficiencies for Nd shown in Table 4-2 at higher nitric acid concentrations.

The aforementioned conclusion regarding lower nitric acid concentrations producing desirable neodymium extraction results was further verified by Bayeni (2021). The concentration range chosen for this investigation was based on the observations made by Bayeni (2021) and that reported in literature for similar metals.

Bayeni (2021) investigated the extraction of Nd over a larger HNO_3 concentration range (feed basis): 0.1M – 2.9M HNO_3. It was observed that higher distribution ratios for Nd were obtained at lower nitric acid concentrations, as seen in his results in Figure 5-1. Therefore, this research study investigated a narrower concentration range of HNO_3 wherein higher distribution ratios for Nd were expected: 0.1, 0.5 and 0.9M.

The observations made in run 2 regarding the fairly constant distribution ratio of Fe obtained during the nitric acid concentrations investigated, was observed in run 4. This is further justified by the constant extraction efficiencies obtained for Fe shown in Table 4-2. Due to the lack of existing comparative data available in literature and seeing as this behaviour was observed twice, it can be proposed that iron produces constant distribution ratios over the range of nitric acid concentrations investigated using 0.5M HDEHP diluted with n-dodecane as the organic solvent. Verification can be conducted in the form of repeat runs using higher purity iron (III) oxide.

5.5   OVERVIEW

Chapter 2.5 contained figures from literature (Figures 2-2 to 2-4) wherein the respective authors, Nayak, et al. (2014) & Bayeni (2021), investigated the extraction of different REMs in the same solvent extraction system of interest. It was predicted in the aforementioned chapter that the trend the authors observed will be relevant to this study as well: the distribution ratios of the respective metal ion in HDEHP diluted with n-dodecane decreased with an increase in the concentration of nitric acid. The trend predicted from literature was observed in the results obtained in this research study and can be viewed distinctly in the test system results where Nd was extracted.

Titration measurements were performed to evaluate the equilibrium concentration of nitric acid. The cationic reaction mechanism shown in Equation 2-4 predicted that the HNO_3 concentration would increase after extraction due to the transfer of $3H^+$ ions. However, the results of the titration analysis, Appendix C-2, display a deviation from the expected trend seeing as the concentrations decreased after extraction. It was previously established that the Nd system behaved in the manner predicted by literature therefore it is assumed that the aforementioned deviation from the reaction mechanism is due to the concentration of the NaOH titrant. This is because an existing titrant solution was used in the analysis.

The extraction data obtained for Fe in HDEHP diluted with n-dodecane over the nitric acid concentration range investigated was fairly uniform and constant (Figures 4-3 and 4-5). This can be manipulated to generate a system that produces high separation factors for a Nd/Fe system. In other words, if the extraction of Fe is assumed to be constant over the nitric acid concentration range investigated, then a system with a nitric acid concentration that produces a distribution ratio of Nd higher than that of iron is recommended for a feasible and successful Nd extraction.

It was observed that the aforementioned requirement for a high separation factor was observed at 0.1M HNO_3. Therefore, to extract Nd from Fe, lower nitric acid concentrations should be used.

Nayak, et al. (2014) concluded extraction at higher acidities, if desired, can be investigated using TOGDA as the organic extractant. However, the goal in recycling end-of-life magnets via extraction of the REM is to design a feasible process. The chemicals used in this laboratory-scale investigation are feasible (TOGDA is more expensive and has limited availability when compared to HDEHP) therefore results obtained using the system investigated in this research

study will have promising future applications for pilot and/or commercial scale implementation.

This research project assessed the solvent extraction behaviour of Nd and Fe, individually and in a mixture. The next step after a successful extraction of Nd into the organic phase using HDEHP diluted with n-dodecane will be stripping of the metal out of the organic phase after solvent extraction to recover Nd (Gergoric, et al., 2017). Since HDEHP favourably extracted Nd at lower nitric acid concentrations, it is expected that the stripping of Nd from the organic phase will be achieved with a more acidic media (Gergoric, et al., 2017).

6   CONCLUSION

The extraction ability of Nd and Fe, separately, were evaluated using a laboratory-scale LLE apparatus shown in Figure 3-1. The extraction data were also measured for a mixture of Nd and Fe. The aforementioned measurements were conducted using varying nitric acid concentrations of 0.1M, 0.5M and 0.9M in 0.5M HDEHP diluted with n-dodecane as the organic solvent.

- Test system measurements with Nd (run 1) verified the experimental procedure employed. The reproducibility of the measurements was high and comparable to the data of Bayeni (2021). Nd had the highest distribution coefficients of 9.63 and 10.67 at the lowest nitric acid feed concentration of 0.1M HNO_3. The corresponding extraction efficiencies were 90.59% and 91.43%, respectively.

- For the distribution ratios of Fe in the solvent (run 2), results showed high reproducibility between the measurements each student conducted. The extraction of the solute into the organic phase was favoured, demonstrated by the high average extraction efficiency of 95.17%. The distribution ratios of iron were fairly constant and had a range of 15.31 – 21.87 over the nitric acid concentration range investigated of 0.1M, 0.5M and 0.9M.

- In the combined iron and neodymium system (run 4) at 0.1M HNO_3, the distribution coefficient of Nd, 926.65, was higher than the distribution coefficient of Fe, an average of 14.14. This resulted in a high separation factor of 65.63 ($\beta_{Nd/Fe}$) and a desirable extraction efficiency of 99.89%. The separation factor ($\beta_{Nd/Fe}$) decreased significantly with increased [HNO_3].

These laboratory-scale measurements show that the feasible beneficiation of Nd from a Nd-Fe mixture can be obtained successfully via solvent extraction of Nd at low nitric acid concentrations when utilizing 0.5M HDEHP diluted with n-dodecane as the organic solvent. There do exist limitations in the conclusions obtained due to the use Fe_2O_3 with a purity of 85%. However, this research project serves as the foundation for future developments.

7 RECOMMENDATIONS

The following are some recommendations for the work conducted in this research project and for future work.

- A data point had to be omitted in experimental run 4 due to the ICP-OES analytical device reporting an undervalue concentration. The ICP analysis method should be expanded to focus on the dilute range of 1-10 ppm. This will produce a calibration curve of higher accuracy thus reducing the production of undervalue results. By improving on this, the uncertainty in the reported distribution ratio will be reduced.

- The measurements for the Fe distribution will be repeated. Research investigation will be conducted with higher purity Fe_2O_3 (>85%) to verify the distribution results. The solution of 0.1M HNO_3 produced desirable results using 85% Fe_2O_3. Therefore, measurements with purer iron whilst investigating the effect of varying the organic extractant concentration with the HNO_3 concentration constant at 0.1M will allow for the optimal organic solvent concentration for extraction to be experimentally determined.

- For an improved design, more extraction data in the lower nitric acid concentration range (<0.1M) at 0.5M HDEHP diluted with n-dodecane should be measured. This is necessary to observe if the prediction of better extraction is achieved.

- Motivated by Zhang, et al. (2020): research should focus on understanding the extraction mechanisms of ionic liquids to design extraction systems efficiently. Once the mechanism is understood, ionic liquid doping in the organic phase can be investigated to prevent the wastage of expensive chemicals.

✓

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APPENDIX A: STOCK SOLUTION PREPARATION

The following section contains sample calculations pertaining to the test system (run 1) regarding the predetermined quantities required for stock solution preparation. The calculations were conducted under the guidance of Bayeni (2021).

Table A-1: Chemical properties

Chemical	Purity	Molar mass	Density
HDEHP	0.95	322.42	0.968
n-Dodecane	0.99	170.33	0.75
Nitric acid	0.55	63.01	1.51
Deionised water	1	18.015	0.99
Nd_2O_3	0.99	336.48	7.42

1. ORGANIC PHASE

One organic phase stock solution was prepared for runs 1 and 2 therefore a total volume of 90mL was prepared. Seeing as run 4 was not originally part of the project plan, a new stock solution was prepared for the aforementioned run.

Converged HDEHP mass = 14.41g

Converged n-Dodecane mass = 56.26g

$$\text{HDEHP moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{14.41}{322.42} = 0.045 \text{ moles}$$

$$\text{Actual HDEHP concentration} = \frac{\text{moles}}{\text{volume}} = \frac{0.045}{\frac{90}{1000}} = 0.5 \text{ M}$$

The required HDEHP concentration was 0.5, seeing as the actual concentration is 0.5, the mass of HDEHP and n-dodecane are correct.

$$\text{Volume HDEHP} = \frac{\text{mass}}{\text{density}} = \frac{14.41}{0.968} = 14.9885 \text{ mL}$$

$$\text{Volume n-Dodecane} = \frac{\text{mass}}{\text{density}} = \frac{56.26}{0.75} = 75.0115 \text{ mL}$$

2. AQUEOUS PHASE

As mentioned previously, 3 aqueous stock solutions were prepared at 0.1, 0.5 and 0.9M nitric acid concentration, respectively.

Each stock solution had a total volume of 25mL seeing as 5mL had to be dispensed into 2 vials. The metal loading was 2000 ppm.

The mass of neodymium (III) oxide for each stock solution was calculated to be:

$$\text{Metal loading} = \frac{\text{REM weight (mg)}}{\text{solution volume (L)}}$$

$$2000 = \frac{\text{REM weight}}{\frac{25}{1000}} \times 10^6$$

$\therefore$ REM weight = 50mg = 0.05 g

0.1M NITRIC ACID CONCENTRATION

REM mass and volume

Nd_2O_3 mass = 0.05 g ✓

$$\text{Volume } Nd_2O_3 = \frac{\text{mass}}{\text{density}} = \frac{0.05}{7.42} = 0{,}00674 \text{ mL}$$

$$Nd_2O_3 \text{ moles} = \frac{(0.99 \times 0.05)}{336.48} = 0{,}000149 \text{ moles}$$

Using equation $Nd_2O_3 \rightarrow 2Nd^{+3} + 3O^{-2}$

Nd moles = 2×Nd_2O_3 moles = 2 × 0,000149 = 0,000298 moles ✓

Nitric acid required for digestion

Using equation $Nd_2O_3 + 6HNO_3 \rightarrow 2Nd(NO_3)_3 + 3H_2O$

Moles of HNO_3 = 6×Nd_2O_3 moles = 6 × 0,000149 = 0,000891 moles

Mass of HNO_3 = 0,000891×63.01 = 0,0562 g

Mass of solution required

$$= HNO_3(g) \left(\frac{(\text{Purity } HNO_3 \times \text{Molar mass } HNO_3) + ((1 - \text{Purity } HNO_3) \times \text{Molar mass } H_2O))}{(\text{Purity } HNO_3 \times \text{Molar mass } HNO_3)} \right)$$

$$= 0.0562 \left(\frac{(0.55 \times 63.01) + ((1 - 0.55) \times 18.015)}{(0.55 \times 63.01)} \right) = 0{,}0693 \text{ g}$$

Volume of solution required using solution density of $1.34\text{g/cm}^3 = \frac{0.0693}{1.34} = 0.0517\text{mL}$

Solution density was provided by the manufacturer.

Nitric acid solution:

Converged mass of HNO_3 solution = 0.264 g

Volume of HNO_3 solution $= \frac{\text{mass}}{\text{density}} = \frac{0.264}{1.34} = 0.197$ mL

Moles of HNO_3 solution $= \frac{0.264}{(0.55\times63.01)+((1-0.55)\times18.015)}$

$$= 0{,}00617 \text{ moles}$$

Moles of $H^+ = 0.55\times0{,}00617 = 0.003391$ moles ✓

$\therefore H^+$ concentration $= \frac{0.003391}{\frac{0.197}{1000}} = 17.235$ M

Moles of H^+ after digestion = 0.003391 − 0,000891= 0.0025 moles

$\therefore H^+$ concentration $= \frac{0.0025}{\frac{0.197}{1000}} = 12.704$ M

Nitric acid dilution with deionised water:

Desired nitric acid concentration = 0.1 M

Deionised water required $= \frac{12.704\times0.197}{0.1} - 0.197 = 24.797$ mL

Mass of deionised water required $= 24.7965 \times 0.99 = 24.549$ g

Table A-2: Run 1 aqueous phase stock solution quantities for 0.1M nitric acid

Chemical	Mass [g]	Volume [mL]
Nd_2O_3	0.05	0.00674
HNO_3	0.264	0.197
Water	24.549	24.797
Total	**24.862**	**25**

0.5M NITRIC ACID CONCENTRATION

REM mass and volume

Nd_2O_3 mass = 0.05 g

Volume $Nd_2O_3 = \dfrac{mass}{density} = \dfrac{0.05}{7.42} = 0,00674$ mL

Nd_2O_3 moles $= \dfrac{(0.99 \times 0.05)}{336.48} = 0,000149$ moles

Using equation $Nd_2O_3 \rightarrow 2Nd^{+3} + 3O^{-2}$

Nd moles = 2×Nd_2O_3 moles = 2 × 0,000149 = 0,000298 moles

Nitric acid required for digestion

Using equation $Nd_2O_3 + 6HNO_3 \rightarrow 2Nd(NO_3)_3 + 3H_2O$

Moles of HNO_3 = 6×Nd_2O_3 moles = 6 × 0,000149 = 0,000891 moles

Mass of HNO_3 = 0,000891×63.01 = 0,0562 g

Mass of solution required ✓

$= HNO_3(g) \left(\dfrac{(\text{Purity } HNO_3 \times \text{Molar mass } HNO_3) + ((1 - \text{Purity } HNO_3) \times \text{Molar mass } H_2O))}{(\text{Purity } HNO_3 \times \text{Molar mass } HNO_3)} \right)$

$= 0.0562 \left(\dfrac{(0.55 \times 63.01) + ((1 - 0.55) \times 18.015)}{(0.55 \times 63.01)} \right)$

$= 0,0693$ g

Volume of solution required using solution density of $1.34 \text{g/cm}^3 = \dfrac{0.0693}{1.34} = 0.0517$ mL

Solution density was provided by the manufacturer.

Nitric acid solution:

Converged mass of HNO_3 solution = 1.0409g

Volume of HNO_3 solution $= \dfrac{mass}{density} = \dfrac{1.0409}{1.34} = 0.777$ mL

Moles of HNO_3 solution $= \dfrac{1.0409}{(0.55 \times 63.01) + ((1 - 0.55) \times 18.015)}$

$= 0.0243$ moles

Moles of H^+ = 0.55×0,0243 = 0.0134 moles

$\therefore$ H$^+$ concentration $= \dfrac{0.0134}{\frac{0.777}{1000}} = 17.235$ M

Moles of H$^+$ after digestion $= 0.0134 - 0,000891 = 0.0125$ moles

$\therefore$ H$^+$ concentration $= \dfrac{0.0125}{\frac{0.777}{1000}} = 16.087$ M

Nitric acid dilution with deionised water:

Desired nitric acid concentration $= 0.5$M

Deionised water required $= \dfrac{16.087 \times 0.777}{0.5} - 0.777 = 24.216$ mL

Mass of deionised water required $= 24.216 \times 0.99 = 23.974$ g

Table A-3: Run 1 aqueous phase stock solution quantities for 0.5M nitric acid

Chemical	Mass [g]	Volume [mL]
Nd$_2$O$_3$	0.05	0.00674
HNO$_3$	1.0409	0.777
Water	23.974	24.216
Total	**25.065**	**25**

0.9M NITRIC ACID CONCENTRATION

REM mass and volume

Nd_2O_3 mass = 0.05g

Volume $Nd_2O_3 = \frac{mass}{density} = \frac{0.05}{7.42} = 0,00674$ mL

Nd_2O_3 moles $= \frac{(0.99 \times 0.05)}{336.48} = 0,000149$ moles

Using equation $Nd_2O_3 \rightarrow 2Nd^{+3} + 3O^{-2}$

Nd moles = 2×Nd_2O_3 moles = 2 × 0,000149 = 0,000298 moles

Nitric acid required for digestion

Using equation $Nd_2O_3 + 6HNO_3 \rightarrow 2Nd(NO_3)_3 + 3H_2O$

Moles of HNO_3 = 6×Nd_2O_3 moles = 6 × 0,000149 = 0,000891 moles

Mass of HNO_3 = 0,000891×63.01 = 0,0562 g

Mass of solution required

$= HNO_3(g) \left(\frac{(\text{Purity } HNO_3 \times \text{Molar mass } HNO_3) + ((1 - \text{Purity } HNO_3) \times \text{Molar mass } H_2O))}{(\text{Purity } HNO_3 \times \text{Molar mass } HNO_3)} \right)$

$= 0.0562 \left(\frac{(0.55 \times 63.01) + ((1 - 0.55) \times 18.015)}{(0.55 \times 63.01)} \right)$

= 0,0693 g

Volume of solution required using solution density of 1.34g/cm^3 $= \frac{0.0693}{1.34} = 0.0517$mL Solution density was provided by the manufacturer.

Nitric acid solution:

Converged mass of HNO_3 solution = 1.818 g

Volume of HNO_3 solution $= \frac{mass}{density} = \frac{1.818}{1.34} = 1.357$ mL

Moles of HNO_3 solution $= \frac{1.818}{(0.55 \times 63.01) + ((1 - 0.55) \times 18.015)} = 0.0425$ moles

Moles of H^+ = 0.55×0,0425 = 0.0234 moles

$\therefore H^+$ concentration $= \dfrac{0.0234}{\frac{1.357}{1000}} = 17.235$ M

Moles of H^+ after digestion $= 0.0234 - 0,000891 = 0.00225$ moles

$\therefore H^+$ concentration $= \dfrac{0.00225}{\frac{1.357}{1000}} = 16.578$ M

Nitric acid dilution with deionised water:

Desired nitric acid concentration $= 0.9$ M

Deionised water required $= \dfrac{16.578 \times 1.357}{0.9} - 1.357 = 23.637$ mL

Mass of deionised water required $= 24.216 \times 0.99 = 23.40$ g

Table A-4: Run 1 aqueous phase stock solution quantities for 0.9M nitric acid

Chemical	Mass [g]	Volume [mL]
Nd_2O_3	0.05	0.00674
HNO_3	1.818	1.357
Water	23.40	23.637
Total	**25.065**	**25**

APPENDIX B: RAW DATA

The following section contains the measured masses when making the stock solutions, the mass dispensed into each of the vials for solvent extraction, the measured volumes and masses from titration analysis, and lastly the calibration values and measurements received from ICP-OES analysis.

1. STOCK SOLUTIONS

The calculated quantities to make the stock solutions were presented in Appendix A. The actual quantities measured are shown in Table B-1, which will be used in determining the associated uncertainties.

Table B-1: Aqueous phase actual stock solution masses

Run 1: Test System with neodymium				
[HNO3]	**Flask mass [g]**	**Nd_2O_3 mass [g]**	**HNO_3 mass [g]**	**H_2O mass [g]**
0.1	53.8096	0.0544	0.2638	24.5561
0.5	53.2889	0.0511	1.0429	23.9769
0.9	55.9431	0.0504	1.832	23.6932
Run 2: Iron				
[HNO3]	**Flask mass [g]**	**Fe_2O_3 mass [g]**	**HNO_3 mass [g]**	**H_2O mass [g]**
0.1	52.806	0.0713	0.462	34.3286
0.5	53.8426	0.0766	1.5846	33.5004
0.9	53.313	0.0703	2.673	32.697

Table B-1: Aqueous phase actual stock solution masses — continued

Run 4: Iron and neodymium					
[HNO3]	**Flask mass [g]**	**Nd_2O_3 mass [g]**	**Fe_2O_3 mass [g]**	**HNO_3 mass [g]**	**H_2O mass [g]**
0.1	53.1786	0.0221	0.0506	0.446	34.3425
0.5	56.4324	0.0210	0.0493	1.5343	33.5659
0.9	51.8778	0,0221	0.049	2.615	32.7648

Table B-2: Organic phase actual stock solution masses

RUN 1 AND 2			
[HDEHP]	Flask mass [g]	HDEHP mass [g]	n-Dodecane mass [g]
0.5	52.838	14.5867	56.3005
RUN 4			
[HDEHP]	Flask mass [g]	HDEHP mass [g]	n-Dodecane mass [g]
0.5	53.2969	7.2605	28.1412

2. LLE MEASUREMENT PREPARATION

Approximately 5mL of the aqueous and organic stock solutions were dispensed into the relevant vials which were then attached to the LLE apparatus for solvent extraction. The measured masses when dispensing the volumes into the vials were recorded and are shown in Table B-3 to Table B-6. These masses will also be used in the calculation of the uncertainty associated with the mass balance. It was explained in the experimental section that each run contained duplicate measurements.

Table B-3: Barometric pressure and water bath temperature

Run	Barometric pressure [kPa]	Temperature [°C]
1	100.09	25.2
2	100.305	24.55
4	99.605	21.45

Table B-4: Masses dispensed for LLE measurement preparation: Run 1

Vial number	[HNO3]	Vial mass [g]	Aqueous mass [g]	Organic mass [g]
1	0.1	18.7694	4.5868	3.623
2	0.5	18.1404	4.6264	3.6356
3	0.9	18.1839	4.673	3.6322
4	0.1	17.2695	4.6169	3.6039
5	0.5	18.638	4.6302	3.586
6	0.9	17.9431	4.6713	3.6341

Table B-5: Masses dispensed for LLE measurement preparation: Run 2

Vial number	[HNO3]	Vial mass [g]	Aqueous mass [g]	Organic mass [g]
1	0.1	18.7252	4.5937	3.651
2	0.5	18.1403	4.6468	3.6569
3	0.9	18.1829	4.6973	3.6723
4	0.1	17.2691	4.6304	3.629
5	0.5	18.5989	4.609	3.6208
6	0.9	17.9429	4.6717	3.6105

Table B-6: Masses dispensed for LLE measurement preparation: Run 4

Vial number	[HNO3]	Vial mass [g]	Aqueous mass [g]	Organic mass [g]
1	0.1	18.8123	4.5947	3.6782
2	0.5	18.138	4.7144	3.5852
3	0.9	18.1813	4.7409	3.5747
4	0.1	17.7148	4.6066	3.6081
5	0.5	18.7015	4.6659	3.6335
6	0.9	17.9408	4.676	3.6178

3. TITRATION ANALYSIS

Tables B-7 to B-9 displays the data measured when conducting the titration analysis using the Metrohm 888 Titrando Potentiometric Titrator. The mass of the diluted sample that was representative of approximately 25mL was calculated by difference. This was done by subtracting the mass of the empty centrifuge tube from the mass of the centrifuge tube inclusive of the sample. Seeing as each sample was diluted twice, 12 titrations were conducted per run.

All titrations were performed using an average NaOH concentration of 0.029615M.

Table B-7: Titration analysis: Raw data: Run 1

Vial	Tube mass [g]	Tube + sample [g]	Sample mass [g]	Sample volume [mL]	Volume delivered [mL]
1	12.634	39.0412	26.4072	26	0.6132
	12.5446	37.5779	25.0333	25	0.8079
2	12.6424	38.2957	25.6533	25.5	3.2454
	12.5908	36.9043	24.3135	24	3.1632
3	12.6649	38.2483	25.5834	25.5	5.2991
	12.5563	37.7496	25.1933	25	5.1211
4	12.7286	37.9871	25.2585	25	0.5736
	12.532	38.283	25.751	26	0.7685
5	12.7539	39.1811	26.4272	26	2.5044
	12.7271	37.9006	25.1735	25	1.8419
6	12.5753	39.0127	26.4374	26	3.2059
	12.7914	38.5656	25.7742	25.5	3.1756

Table B-8: Titration analysis: Raw data: Run 2

Vial	Tube mass [g]	Tube + sample [g]	Sample mass [g]	Sample volume [mL]	Volume delivered [mL]
1	12.8218	37.8851	25.0633	25	0.6978
	12.8322	36.4126	23.5804	24	0.5078
2	12.7238	38.4341	25.7103	26	3.359
	12.6663	38.4121	25.7458	26	3.6261
3	12.7536	37.1871	24.4335	24	5.7397
	12.9627	38.0802	25.1175	25	6.0055
4	12.7518	39.3457	26.5939	27	1.3674
	12.4059	37.7289	25.323	25	1.1764
5	12.5633	37.5041	24.9408	25	3.4018
	12.5565	38.067	25.5105	26	3.4129
6	12.3778	39.4278	27.05	27	3.2059
	12.5608	38.5383	25.9775	26	3.1756

Table B-9: Titration analysis: Raw data: Run 4

Vial	Tube mass [g]	Tube + sample [g]	Sample mass [g]	Sample volume [mL]	Volume delivered [mL]
1	12.9595	38.0594	25.0999	25	0.9168
	12.8515	37.3866	24.5351	25	1.2952
2	12.8576	38.775	25.9174	26	3.4392
	12.8238	37.8293	25.0055	25	3.3123
3	12.4724	37.0507	24.5783	25	5.1625
	12.7616	37.4296	24.668	25	5.4718
4	12.7076	37.2274	24.5198	25	1.0423
	12.899	37.1593	24.2603	24	0.8409
5	12.7115	38.7582	26.0467	26	3.2294
	12.7781	37.9497	25.1716	25	3.3147
6	12.7577	36.9072	24.1495	24	5.2987
	12.6548	37.8766	25.2218	25	5.5363

4. ICP-OES ANALYSIS

As mentioned previously, analysis using ICP-OES was conducted at the Department of Chemistry located at the PMB campus. The concentration of the REM present in the extracted sample that was diluted is shown in Table B-10 to B-12. An average of the 3 measurements obtained for neodymium was taken and used in future calculations.

The standard solutions that were prepared and sent with the samples for ICP-OES analysis were used in calibrating the device. The result of the calibration was used in determining the uncertainty contribution of the analytical device for each run. Table B-13 to B-16 contains the calibration results for each of the experimental runs. The resulting calibrating plots from ICP-OES measurements are strictly linear.

Table B-10: ICP-OES results: Run 1

Vial	[HNO₃]	Nd 401,224 [mg/L]	Nd 406,108 [mg/L]	Nd 410.945 [mg/L]	Average diluted metal concentration [mg/L]
1	0.1	2.03	2.06	2.05	2.0467
2	0.5	13	13.2	12.9	13.033
3	0.9	18.7	19.2	18.7	18.867
4	0.1	1.86	1.88	1.85	1.863
5	0.5	4.09	4.1	4.09	4.093
6	0.9	9.59	9.6	9.61	9.6

Table B-11: ICP-OES results: Run 2

Vial	[HNO₃]	Diluted metal concentration [mg/L
1	0.1	0.953
2	0.5	0.956
3	0.9	0.956
4	0.1	0.952
5	0.5	0.954
6	0.9	1.230

Table B-12: ICP-OES results: Run 4

Vial	[HNO₃]	Nd 401,224 [mg/L]	Nd 406,108 [mg/L]	Nd 410.945 [mg/L]	Average Nd concentration [mg/L]	Fe Diluted concentration [mg/L]
1	0.1	u/v	u/v	0.0068	0.0099	0.955
2	0.5	2.51	2.63	2.59	2.5767	0.954
3	0.9	3.78	3,93	3.72	3.81	0.954
4	0.1	u/v	u/v	u/v	N/A	0.953
5	0.5	2.54	2.65	2.55	2.58	0.955
6	0.9	3.76	3.9	3.76	3.81	0.954

Table B-13: ICP-OES calibration results: Run 1

Nd 401.224 Calibration (mg/L) on Apr 20 2021, 09:18:13 am			
Standard	**Flags**	**Int (c/s)**	**Std Conc**
Blank	---	245.4	0
Standard 1	e	0	0.97
Standard 2	---	10881.5	2.91
Standard 3	---	12444.7	4.85
Standard 4	---	21649.1	6.79
Standard 5	---	37611.6	9.7
Standard 6	---	106598.8	19.4
Standard 7	---	264641.2	48.5
Standard 8	e	0	97
Correlation Coefficient	0.997283		
Status	Calibrated.		
Curve Type	Linear		
Curve Coefficient 1:	-9463.102		
Curve Coefficient 2:	5646.38		
Blank Offset	-9463.1		
Nd 406.108 Calibration (mg/L) on Apr 20 2021, 09:18:13 am			
Standard	**Flags**	**Int (c/s)**	**Std Conc**
Blank	---	109.9	0
Standard 1	e	0	0.97
Standard 2	---	11122.2	2.91
Standard 3	---	13020	4.85
Standard 4	---	22841.7	6.79
Standard 5	---	39783.6	9.7
Standard 6	---	116240	19.4
Standard 7	---	290053.9	48.5
Standard 8	e	0	97
Correlation Coefficient	0.99708		

Status	Calibrated.		
Curve Type	Linear		
Curve Coefficient 1:	-11190.137		
Curve Coefficient 2:	6201.87		
Blank Offset	-11190.1		
Nd 410.945 Calibration (mg/L) on Apr 20 2021, 09:18:13 am			
Standard	**Flags**	**Int (c/s)**	**Std Conc**
Blank	---	146.1	0
Standard 1	e	0	0.97
Standard 2	---	12153	2.91
Standard 3	---	14031.5	4.85
Standard 4	---	24416.4	6.79
Standard 5	---	41942.5	9.7
Standard 6	---	119946.3	19.4
Standard 7	---	298854.1	48.5
Standard 8	e	0	97
Correlation Coefficient	0.997285		
Status	Calibrated.		
Curve Type	Linear		
Curve Coefficient 1:	-10890.599		
Curve Coefficient 2:	6377.906		
Blank Offset	-10890.6		

Table B-14: ICP-OES calibration results: Run 2

Fe 259.940 Calibration (mg/L) on May 11 2021, 08:45:44 am			
Standard	**Flags**	**Int (c/s)**	**Std Conc**
Blank	---	631.1	0
Standard 1	---	1827.1	1
Standard 2	---	9971.8	3
Standard 3	---	19046.3	5
Standard 4	---	32928.5	7

Standard	Flags	Int (c/s)	Std Conc
Standard 5	---	45080.2	9
Standard 6	---	114224.8	20
Correlation Coefficient	0.995555		
Status	Calibrated.		
Curve Type	Linear		
Curve Coefficient 1:	-5569.952		
Curve Coefficient 2:	5837.768		
Blank Offset	-5570		

Table B-15: ICP-OES calibration results: Run 4 (iron)

Fe 259.940 Calibration (mg/L) on May 18 2021, 09:43:29 am			
Standard	**Flags**	**Int (c/s)**	**Std Conc** **Calc Conc**
Blank	---	753.5	0
Standard 1	---	117425.2	20
Standard 2	---	275220	50
Standard 3	---	439941.4	80
Standard 4	---	563551.2	100
Standard 5	---	800927.8	150
Correlation Coefficient	0.999353		
Status	Calibrated.		
Curve Type	Linear		
Curve Coefficient 1:	8251.027		
Curve Coefficient 2:	5370.782		
Blank Offset	8251		

Table B-16: ICP-OES calibration results: Run 4 (neodymium)

Nd 401.224 Calibration (mg/L) on May 18 2021, 09:49:50 am			
Standard	**Flags**	**Int (c/s)**	**Std Conc**
Blank	---	303.4	0
Standard 6	e	0	20
Standard 7	---	231571	50
Standard 8	---	388486.8	80
Standard 9	---	480631.6	100
Standard 10	---	692354.9	150
Correlation Coefficient	0.999255		
Status	Calibrated.		
Curve Type	Linear		
Curve Coefficient 1:	4896.465		
Curve Coefficient 2:	4654.909		
Blank Offset	4896.5		
Nd 406.108 Calibration (mg/L) on May 18 2021, 09:49:50 am			
Standard	**Flags**	**Int (c/s)**	**Std Conc**
Blank	---	145.7	0
Standard 6	e	0	20
Standard 7	---	248438.3	50
Standard 8	---	420913.5	80
Standard 9	---	513293.6	100
Standard 10	---	761062	150
Correlation Coefficient	0.999648		
Status	Calibrated.		
Curve Type	Linear		
Curve Coefficient 1:	1177.821		
Curve Coefficient 2:	5099.905		
Blank Offset	1177.8		

Nd 410.945 Calibration (mg/L) on May 18 2021, 09:49:50 am			
Standard	**Flags**	**Int (c/s)**	**Std Conc**
Blank	---	286.5	0
Standard 6	e	0	20
Standard 7	---	239410.5	50
Standard 8	---	401614	80
Standard 9	---	498268.6	100
Standard 10	---	718253	150
Correlation Coefficient	0.999303		
Status	Calibrated.		
Curve Type	Linear		
Curve Coefficient 1:	4501.221		
Curve Coefficient 2:	4829.807		
Blank Offset	4501.2		

APPENDIX C: SAMPLE CALCULATION OF RESULTS

The following section contains sample calculations for the results present in Chapter 4. The sample calculations will pertain to the test system using neodymium (run 1).

1. UNCERTAINTY CALCULATION

Type B uncertainties are the preferred analysis 'by other means' when statistical analysis is not appropriate (Kadis, 2000). The uncertainty due to the mass balance, Pt100 temperature sensor, micropipette and the titration apparatus were treated as type B uncertainties with a rectangular distribution. The following formula applied (Kadis, 2000) :

$$\mathbf{u_i(\theta) = \frac{b}{\sqrt{3}}} \qquad \textbf{(C-1)}$$

The error due to the ICP-OES calibration was evaluated using the root mean square error (RMSE) approach to establish the uncertainty in the result (Chai & Draxler, 2014) :

$$\mathbf{RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(error)^2}} \qquad \textbf{(C-2)}$$

To account for the uncertainty in the results, the combined standard uncertainty was computed using Equation 11-3 (Farrance & Frenkel, 2012) :

$$\mathbf{u_C(\theta) = \pm\sqrt{\sum_i u_i(\theta)^2}} \qquad \textbf{(C-3)}$$

To compute $u_i(\theta)$ for the mass balance, Pt100 temperature sensor, micropipette and the titration apparatus, an average of all measured values, present in Tables B-1 to B-9, during each of the runs were taken. The results of computing the averages are shown in Table C-1.

Table C-1: Results of computing the average of the measurements recorded

Run	Description	Average measurement
1	Organic phase mass	41.24 g
	Deionised water mass	24.08 g
	Nitric acid mass	1.05 g
	Nd_2O_3 mass	0.05 g
	Flask mass	54.35 g
	Aqueous phase in vial	4.63 g
	Organic phase in vial	3.62 g
	Vial mass	18.16 g
	Centrifuge tube	12.65 g
	Centrifuge tube + sample	38.23 g
	TOTAL AVERAGE	19.80 g
	Titration: Volume delivered	2.52 mL
	Micropipette (100-1000μL)	1 mL
	Micropipette (1000-5000μL)	5 mL
2	Deionised water mass	33.51 g
	Nitric acid mass	1.57 g
	Fe_2O_3 mass	0.073 g
	Flask mass	53.32 g
	Aqueous phase in vial	4.64 g
	Organic phase in vial	3.64 g
	Vial mass	18.14 g
	Centrifuge tube	12.65 g
	Centrifuge tube + sample	38.09 g
	TOTAL AVERAGE	18.41 g
	Titration: Volume delivered	2.97 mL
	Micropipette (100-1000μL)	1 mL
	Micropipette (1000-5000μL)	5 mL
4	Organic phase mass	29.57 g
	Deionised water mass	33.56 g

Nitric acid mass	1.53 g
Nd_2O_3 mass	0.022 g
Fe_2O_3 mass	0.050 g
Flask mass	53.83 g
Aqueous phase in vial	4.67 g
Organic phase in vial	3.62 g
Vial mass	18.25 g
Centrifuge tube	12.77 g
Centrifuge tube + sample	38.70 g
TOTAL AVERAGE	17.78 g
Titration: Volume delivered	3.24 mL
Micropipette (100-1000µL)	1 mL
Micropipette (1000-5000µL)	5 mL

Thereafter, an average of the total averages obtained in each run was taken.

Table C-2: Total average measurement for each measurement device

Device	Manufacturer uncertainty	Total average measurement
Mass balance	± 0.0006 g	18.66
Pt100 T sensor	± 0.14 °C	23.73
Micropipette	± 0.02 mL	5
Micropipette	± 0.02 mL	1
Titration apparatus	± 0.0001 mL	2.91

The quantities in Table C-2 were used to compute $u_i(\theta)$, using Equation C-1 for each measurement device. A sample calculation is shown for the mass balance:

$$u_i(\theta) = \frac{\frac{0.0006}{18.67}}{\sqrt{3}} = 1.86 \times 10^{-5}$$

Table C-3: Calculated type B uncertainties

Device	$u_i(\theta)$	$u_i^2(\theta)$
Mass balance	1.86×10^{-5}	3.44×10^{-10}
Pt100 T sensor	0.0034	1.16×10^{-5}
Micropipette	0.0023	5.33×10^{-6}
Micropipette	0.0115	0.000133
Titration apparatus	1.98×10^{-5}	3.90×10^{-10}

To evaluate the combined uncertainty associated with each run, the uncertainty due to the ICP-calibration needs to be computed.

For run 1, the calibration equation (of form y =mx+c) recorded in Table B-13 was used to calculate the concentration (x) using the reported ICP-OES intensities (y).

The error was then determined using the calculated concentration and the reported standard concentration in Table B-13.

Thereafter, each calculated error was squared and an average was taken after which the square root of the calculated average was computed.

Lastly, an average of each of the previously mentioned quantity was calculated to produce the $u_i(\theta)$ for the respective run.

A similar procedure was applied to the other runs.

The aforementioned procedure describes the approach used to calculate the RMSE shown in Equation C-2.

A sample calculation will be provided for run 1, Nd 401.224. The standards that were 'flagged' in Table B-13 with error 'e' were not used in the calibration.

Table C-4: ICP-OES uncertainty calculation: Run 1

Nd 401.224 Calibration (mg/L) on Apr 20 2021, 09:18:13 am					
Calibration equation: y = 5646.38x - 9463.10					
Standard	**Intensity (c/s)** y	**Standard concentration [M]** 1	**Calculated concentration [M]** x	**Error** $1 - x$	**Error^2** $(1 - x)^2$
Blank	245.4	0	245.4 = 5646.38x - 9463.10 $\therefore x = 1.72$	0-1.72 = -1.72	2.96
Standard 2	10881.5	2.91	10 881.5 = 5646.38x - 9463.10 $\therefore x = 3.60$	2.91-3.6 = -0.69	0.48
Standard 3	12444.7	4.85	12 444.7 = 5646.38x - 9463.10 $\therefore x = 3.88$	4.85 – 3.88 = 0.97	0.94
Standard 4	21649.1	6.79	21 649.1 = 5646.38x - 9463.10 $\therefore x = 5.51$	6.79-5.51 = 1.28	1.64
Standard 5	37611.6	9.7	37 611.6 = 5646.38x - 9463.10 $\therefore x = 8.34$	9.7-8.34 = 1.36	1.86
Standard 6	106598.8	19.4	245.4 = 5646.38x - 9463.10 $\therefore x = 20.56$	19.4-20.56 = -1.16	1.33
Standard 7	264641.2	48.5	245.4 = 5646.38x - 9463.10 $\therefore x = 48.55$	48.5-48.55 = -0.045	0.002
Average (Error^2) = 1.32					
$\sqrt{\textbf{Average (Error}^2)}$ = RMSE = 1.147					
Nd 406.108 Calibration (mg/L) on Apr 20 2021, 09:18:13 am					
Calibration equation: y = 6201.87x - 11 190					
Standard	**Intensity (c/s)**	**Standard concentration [M]**	**Calculated concentration [M]**	**Error**	**Error^2**

Blank	109.9	0	1.82	-1.82	3.32
Standard 2	11122.2	2,91	3.60	-0.69	0.43
Standard 3	13020	4,85	3.90	0.95	0.90
Standard 4	22841.7	6,79	5.49	1.30	1.70
Standard 5	39783.6	9,7	8.22	1.48	2.19
Standard 6	116240	19,4	20.55	-1.15	1.32
Standard 7	290053.9	48,5	48.57	-0.07	0.0053

$$\text{Average (Error}^2) = 1.41$$

$$\sqrt{\textbf{Average (Error}^2)} = \textbf{RMSE} = 1.189$$

Nd 410.945 Calibration (mg/L) on Apr 20 2021, 09:18:13 am

Calibration equation: y = 6377.91 -10 891

Standard	Intensity (c/s)	Standard concentration [M]	Calculated concentration [M]	Error	Error^2
Blank	245.4	0	1.73	-1.73	0.49
Standard 2	10881.5	2.91	3.61	-0.70	0.89
Standard 3	12444.7	4.85	3.91	0.94	1.57
Standard 4	21649.1	6.79	5.54	1.25	2.01
Standard 5	37611.6	9.7	8.28	1.42	1.24
Standard 6	106598.8	19.4	20.51	-1.12	0.004
Standard 7	264641.2	48.5	48.57	-0.0652	0.49

$$\text{Average (Error}^2) = 1.31$$

$$\sqrt{\textbf{Average (Error}^2)} = \textbf{RMSE} = 1.146$$

AVERAGE ICP MEASUREMENT UNCERTAINTY: $\frac{1.147+1.189+1.146}{3} = \mathbf{1.16}$

Similarly, the uncertainty due to the ICP-calibration for runs 2 and 4 was computed.

Table C-5: ICP-OES calibration uncertainty: Run 2 and 4

Run	$u_i(\theta) = RMSE$
2	0.59
4: Neodymium	1.71
4: Iron	1.81

Equation C-3 was then used to compute the combined standard uncertainty for each run. The sample calculation for run 1 using the values in Tables C-3 and C-4 is shown:

$$u_C(\theta) = \pm\sqrt{\sum_i u_i(\theta)^2}$$

$$= \pm\sqrt{3{,}44\times10^{-10} + 1{,}16\times10^{-5} + 5.33\times10^{-6} + 0.000133 + 4.66\times10^{-10} + 1.16^2}$$

$$= 1.16$$

Similarly, the combined standard uncertainty for runs 2 and 4 was computed. These are the tabulated values that appear in Chapter 4.

Table C-6: Combined standard uncertainty: Runs 2 and 4

Run	$u_i(\theta)$
2	0.59
4: Neodymium	1.71
4: Iron	1.81

2. TITRATION CALCULATIONS

The following formula was used for calculating the concentration of nitric acid using the values from the titration measurements:

$$C_1V_1 = C_2V_2 \qquad (C\text{-}4)$$

where C_1 is the nitric acid concentration

V_1 is the volume of sample titrated

C_2 is the NaOH concentration

V_2 is the volume delivered

Using the data in Table B-7 to demonstrate a sample calculation for C_1:

$$C_1 = \frac{C_2V_2}{V_1} = \frac{0.029615 \times 0.6132}{26} = 0.0006985 \text{ M}$$

Seeing as the extracted aqueous sample was diluted with deionised water in a ratio of 1:100 (volume basis), the actual nitric acid concentration is: $0.0006985 \times 100 = 0.06985$ M

The above calculation was repeated for each run using the values tabulated in Tables B-7 to B-9.

Table C-7: Titration feed concentration: Runs 1

Vial	V_1 [mL]	V_2 [mL]	Actual C_1 [M]	Average C_1 [M]
1	26	0.6132	0.0699	0.083
	25	0.8079	0.0957	
2	25.5	3.2454	0,3760	0.384
	24	3.1632	0.3903	
3	25.5	5.2991	0.6154	0.611
	25	5.1211	0.6066	
4	25	0.5736	0.0679	0.078
	26	0.7685	0.0875	
5	26	2.5044	0.2852	0.252
	25	1.8419	0.2181	
6	26	3.2059	0.3651	0.367
	25.5	3.1756	0.3688	

Table C-8: Titration feed concentrations: Run 2

Vial	V_1 [mL]	V_2 [mL]	Actual C_1 [M]	Average C_1 [M]
1	25	0.6978	0.0826	0.073
	24	0.5078	0.0626	
2	26	3.3590	0.3826	0.398
	26	3.6261	0.4130	
3	24	5.7397	0.7082	0.710
	25	6.0055	0.7114	
4	27	1.3674	0.1499	0.145
	25	1.1764	0.1393	
5	25	3.4018	0.4029	0.396
	26	3.4129	0.3887	
6	27	3.2059	0.3516	0.357
	26	3.1756	0.3617	

Table C-9: Titration feed concentration: Run 4

Vial	V_1 [mL]	V_2 [mL]	Actual C_1 [M]	Average C_1 [M]
1	25	0.9168	0.1086	0.131
	25	1.2952	0.1534	
2	26	3.4392	0.3917	0.392
	25	3.3123	0.3923	
3	25	5.1625	0.6115	0.630
	25	5.4718	0.6481	
4	25	1.0423	0.1235	0.114
	24	0.8409	0.1037	
5	26	3.2294	0.3678	0.380
	25	3.3147	0.3926	
6	24	5.2987	0.6538	0.655
	25	5.5363	0.6558	

3. RECALCULATING FEED CONCENTRATION AND METAL LOADING

The equations and method employed in Appendix A to determine the quantities required to make up the stock solution were used to determine the actual metal loading (stock solutions were prepared using a metal loading of 2000ppm) and final nitric acid feed concentration. This was done using the masses recorded in Table B-1. The final values from the computation for each run are tabulated below.

Table C-10: Actual metal oxide loading and final nitric acid feed concentration: Run 1

Initial [HNO$_3$]	Final [HNO$_3$]	% Difference	Actual metal loading [mg/L]
0.1	0.097	3.08	2175.27
0.5	0.500	0.03	2043.65
0.9	0.896	0.46	1991.58

Table C-11: Actual metal oxide loading and final nitric acid feed concentration: Run 2

Initial [HNO$_3$]	Final [HNO$_3$]	% Difference	Actual metal loading [mg/L]
0.1	0.105	4.66	2035.18
0.5	0.512	2.42	2186.33
0.9	0.918	1.95	2006.54

Table C-12: Actual metal oxide loading and final nitric acid feed concentration: Run 4

Initial [HNO$_3$]	Final [HNO$_3$]	% Difference	Nd metal loading [mg/L]	Fe metal loading [mg/L]	Total metal loading [mg/L]
0.1	0.106	6.40	630.80	1444.28	2075.08
0.5	0.507	1.48	598.94	1406.07	2005.01
0.9	0.904	0.42	630.36	1397.62	2027.98

4. ICP-OES RESULTS CALCULATIONS

The extracted aqueous phase that was withdrawn, was diluted with deionised water before sending the samples for ICP-OES analysis. Therefore, the actual concentration was calculated in the same manner that the concentration was computed in Appendix C-2 using the average diluted concentrations present in Tables B-10 to B-12. The distribution coefficient was defined in Equation 2-1.

The concentration of the metal ion in the aqueous phase is the actual concentration obtained from the ICP-OES analysis. The concentration of the metal ion in the organic phase is calculated by subtracting the concentration of the metal ion in the aqueous phase from the total metal loading computed in Appendix C-3. Thereafter, the concentration of the metal ion in the aqueous and organic phases, respectively, are substituted into Equation 2-1 to determine the distribution coefficient.

Following is a sample calculation for the aforementioned calculation procedure using vial 1 from run 1:

The average diluted concentration of Nd in the aqueous phase after extraction: 2,0467 mg/L

Actual concentration of Nd in aqueous phase after extraction: 2,0467 M × 100 = 204.67 mg/L

Recall from Equation 2-1: $D = \dfrac{[A]_{organic}}{[A]_{aqueous}}$

$\therefore [A]_{aqueous} = 204.67$ M

Vial 1 was synthesized to contain the 0.1M desired nitric acid concentration $\therefore$ from Table 11-10, the actual metal loading was 2175,27M.

$\therefore [A]_{organic} = 2175,27M - 204.67$ M $= 1970,61$ M

Therefore, $D_{Nd} = \dfrac{[Nd]_{organic}}{[Nd]_{aqueous}} = \dfrac{1970,61\ M}{204.67\ M} = 9.63$

A similar calculation procedure was applied to the remainder of the runs. The results of the computation are tabulated below.

For run 4, the separation factor was computed using Equation 2-2. A sample calculation for vial 1 is shown:

$\beta_{A/B} = \dfrac{D_A}{D_B} \therefore \beta_{Nd/Fe} = \dfrac{D_{Nd}}{D_{Fe}} = \dfrac{926.65}{14.16} = 65.63$

Table C-13: Distribution coefficient - Run 1

Vial	Desired [HNO3]	[Nd]$_{aqueous}$	[Nd]$_{organic}$	D$_{Nd}$
1	0.1	204.67	1970.61	9.63
2	0.5	1303.33	740.32	0.57
3	0.9	1886.67	104.92	0.06
4	0.1	186.33	1988.94	10.67
5	0.5	409.33	1634.32	3.99
6	0.9	960	1031.58	1.07

Table C-14: Distribution coefficient - Run 2

Vial	Desired [HNO3]	[Fe]$_{aqueous}$	[Fe]$_{organic}$	D$_{Fe}$
1	0.1	95.32	1939.86	20.35
2	0.5	95.60	2090.73	21.87
3	0.9	95.62	1910.92	19.98
4	0.1	95.23	1939.95	20.37
5	0.5	95.41	2090.92	21.92
6	0.9	123	1883.54	15.31

Table C-15: Distribution coefficient and separation factor - Run 4 ✓

Vial	Desired [HNO3]	[Nd]$_{aqueous}$	[Nd]$_{organic}$	D$_{Nd}$	[Fe]$_{aqueous}$	[Fe]$_{organic}$	D$_{Fe}$	$\beta_{Nd/Fe}$
1	0.1	0.68	630.12	926.65	95.53	1348.75	14.12	65.63
2	0.5	257.67	341.27	1.32	95.38	1310.69	13.74	0.01
3	0.9	381	249.36	0.65	95.36	1302.26	13.66	0.05
4	0.1	N/A	N/A	N/A	95.26	1349.02	14.16	N/A
5	0.5	258	340.94	1.32	95.48	1310.59	13.73	0.01
6	0.9	380.67	249.69	0.66	95.44	1302.18	13.64	0.05

5. EXTRACTION EFFICIENCY

The extraction efficiency was computed using Equation 2-3.

$$\text{Recall: Extraction } \% = \frac{[A]_{organic}}{[A]_0} \times 100$$

$[A]_{organic}$ was obtained in the previous section and the results are tabulated in Tables C-13 to C-15.

$[A]_0$ refers to the re-calculated metal loading initially constituting the aqueous phase tabulated in Tables C-10 to C-12.

Sample calculation for run 1, vial 1:

$$\text{Extraction efficiency } \% = \frac{1970.61}{2175.27} \times 100 = 90.59\%$$

Similarly, the extraction efficiency % of the remaining vials in run 1 and runs 2 and 4 were computed. The final results are tabulated below.

Table C-16: Extraction efficiency %: Run 1, 2 and 4

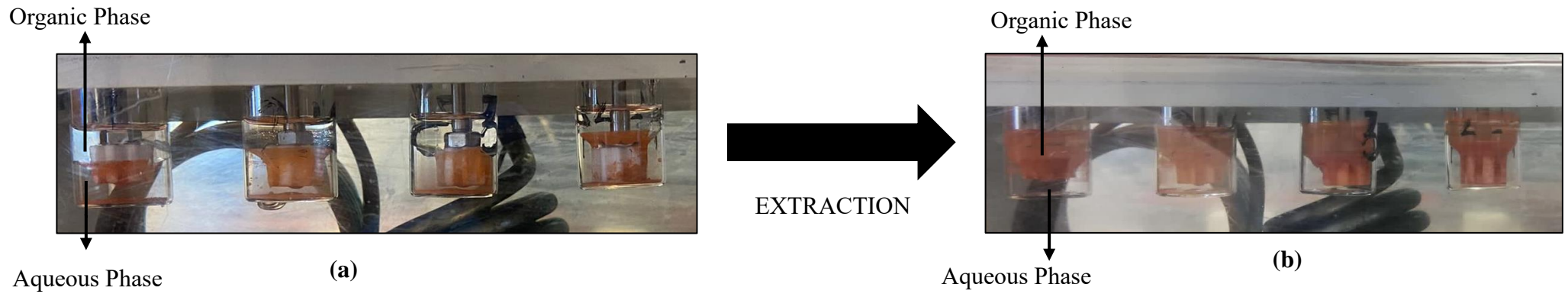| Vial number	Run 1	Run 2	Run 4	
			Iron	Neodymium
1	90.59 %	95.32 %	93,39 %	99.89 %
2	36.23 %	95.63 %	93,22 %	56.98 %
3	5.27 %	95.23 %	93,18 %	39.56 %
4	91.43 %	95.32 %	93,40 %	N/A
5	79.97 %	95.64 %	93,21 %	56.92 %
6	51.80 %	93.87 %	93,17 %	39.61 %

Figure D-1: Pre-extraction (a) and post-extraction (b) for Run 2
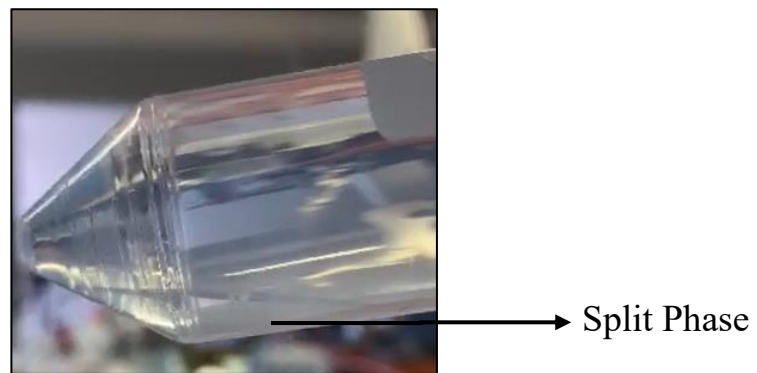

Figure D-2: Phase splitting in Run 3

APPENDIX A: RESEARCH PROPOSAL

School of Engineering
University of KwaZulu-Natal
ENCH4LA Laboratory Project Proposal Template

Name of student: Riyantha Moodley   **Student no.** 218009136
Name of student: Sohana Bridgemohan   **Student no.** 218010264

Topic 22: Urban Mining of Rare Earth Elements from Rare Earth Magnets – Alternate Solvents for Extraction

Supervisor/s: Prof P Naidoo, Dr Williams-Wynn and Dr K Moodley

a) Problem Identification:

Iron (Fe) and boron (B) exist in a leaching solution with neodymium (Nd), a rare earth element (REE). The inability of sending waste electrical and electronic (WEEE) materials to landfills has increased research into recovery of REE's from WEEE to promote recycling. However, there lacks data in literature reporting on the separation of Fe from an aqueous HNO_3 solution via an HDEHP-based solvent, in the context of Nd recovery from waste NdFeB magnets. As such, this research study investigates the effect of the aforementioned extent of Fe separation as well as whether the separation is improved by ionic liquid doping.

b) Rationale and Motivation:

Rare earth metals (REM's), a group of 17 chemical elements, are important in today's society due to their properties that have enabled their contribution into many areas of technological advancements (Gergoric, et al., 2017).With the high demand for electronic and electrical equipment, it has been established that the REM's are crucial components in the manufacturing of the aforementioned devices. Nd has a wide variety of uses: the manufacturing of powerful magnets and computer hard drives. Nd magnets (NdFeB) are crucial components required in the production of wind turbines and hybrid cars; given the global shift in interest towards these green technologies, there is a high demand for these NdFeB magnets. Thus, the focus of this research proposal is neodymium, particularly NdFeB magnets.

Recycling of REM's found in WEEE is a prominent topic of interest. Scarcity of economically viable REM deposits with concerns of insufficient energy resources compromises run-of-mine extraction. Thus, there exists a need for REM recovery from secondary sources. Additionally, the pending ban of WEEE from landfills in South Africa creates an urgency for the development of a suitable technology for REM extraction. The recycling of e-wastes has the following advantages: alleviating the shortage, energy savings in mining and processing; resource conservation and reduction in pollution and greenhouse emissions.

According to (Prodius, et al., 2019), recycling of REM's via chemical recovery methods involves either pyrometallurgical or hydrometallurgical approaches. Hydrometallurgical processing of WEEE materials is considered a traditional approach to extract REM's. It is preferred over pyrometallurgical approaches since large amounts of solid wastes are generated and the process can be quite energy-consuming. Additionally, hydrometallurgical processing enables higher recovery rates of REM's.

Consequently, this research study focuses on hydrometallurgical processing. It involves comminution of waste material, leaching of the chemical constituents and separation of the individual elements via solvent extraction (Wang, et al., 2017). Solvent extraction is the separation of the constituent target REE by contact of a liquid with an insoluble organic solution (Ashiq, et al., 2019).

Due to the lack of availability of existing solvent extraction data of Nd, Fe, B (within the aqueous-organic system of interest) respectively, there exists a need to experimentally measure the extraction of each of these components within this system. The extraction data of these individual components in solution is necessary to enable future studies into the extraction from a real leachate solution containing all 3 elements. Ultimately, this would form the basis of future developments of a potentially commercial hydrometallurgical process for the beneficiation of NdFeB magnets.

This research project contributes towards the aforementioned future work, by generating the solvent extraction data of Fe. Nayak, et al. (2014) reported on the equivalent exchange of hydrogen ions from HDEHP with Am(III) ions in nitric acid; thus, it is expected that Fe^{3+} ions bound to nitrate ions in the aqueous phase will be absorbed into the organic phase through a similar mechanism.

c) Research Aims & Objectives:

The aim of this research project is to investigate the degree of extraction of Fe^{3+} ions from an aqueous nitric acid solution, contacted with an organic solvent (bis(2-ethylhexyl) phosphate, "HDEHP", diluted with n-dodecane), via an existing bench-scale, batch LLE set up. This aim will be met through the execution of the following objectives:

i. Verify the existing experimental method by performing experiments with Nd.
ii. Measurement of the distribution ratio of Fe^{3+} ions with varying nitric acid concentrations at 25°C, to establish the optimal aqueous acid concentration for Fe^{3+} recovery, using the above-mentioned organic solvent.
iii. Measurement of the distribution ratios of Fe^{3+} ions with the above-mentioned organic solvent that is doped with an ionic liquid (tributylmethylphosphonium methyl sulfate) at varying concentrations (0.01M, 0.1M and 0.25M, respectively).
iv. Infer the feasibility of this separation method as a pilot- or commercial-scale process based on analysis of the results.

d) Work plan – Research Activities:

Activity	Purpose	Timeframe
Literature Review	Report existing theory regarding the REE recovery, solvent selection and known extraction mechanisms	Ongoing (08/03/2021 – 18/05/2021)
Experimental Work: Test system (Nd_2O_3 extraction) New system (Fe_2O_3 extraction) Repeat new system with ionic liquid Analysis (ICP-OES)	Collect experimental data to: Verify experimental method, obtain new data (with and without ionic liquid) and determine distribution coefficients of Fe^{3+}	4- 5 weeks (Based on laboratory schedule)
Oral presentation of research project	Critical assessment	1 day (04/05/2021)
Submission of research project report	Critical assessment to present findings and display results and conclusions	Work will be ongoing Submission = 1day (18/05/2021)

e) Resources:

The following equipment will be used:
- LLE apparatus (Thermodynamics Research Unit)
- Mass balance (TRU)
- Wet chemistry glassware (titrations for pH determination) (TRU)
- ICP-OES Spectrophotometer (PMB Chemistry)
- Sample containers and vials

In addition, the following chemicals will be utilized:

- Nitric acid, Nd_2O_3, Fe_2O_3 powder, HDEHP, n-dodecane and ionic liquid (tributylmethylphosphonium methyl sulphate)

f) References

Ashiq, A., Kulkarni, J. & Vithanage, M., 2019. *Hydrometallurgical Recovery of Metals From E-waste*, Sri Lanka: Elsevier Inc.

Gergoric, M.; Ekberg, C.; Foreman, M.R.S.J.; Steenari1, B.M. & Retegan, T., 2017. *Characterization and Leaching of Neodymium Magnet Waste and Solvent Extraction of the Rare-Earth Elements Using TODGA*, Europe : Springer.

Nayak, P.K.; Kumaresan, R.; Venkatesan, K.A.; Antony, M.P.; Vasuveda Rao, P.R. 2014. Extraction Bheaviour of Am(III) and Eu(III) from Nitric Acid Medium in Tetraoctyldiglycomide-Bis(2-Ethylhexyl)Phospohoric Acid Solution. *Separation Science Technology*, 49(8), pp. 1186-1191.

Prodius, D., Gandha, K., Mudring, A. V. & Nlebedim, I. C., 2019. *Sustainable Urban Mining of Critical Elements from Magnet and Electronic Wastes*, United States: ACS Publications.

Wang, M., Tan, Q., Chiang, J. & Li, J.F., 2017. Recovery of rare and precious metals from urban mines - A review. *Frontiers of Environmental Science & Engineering*, 11(5), pp. 1-17.

Safety evaluation

Hazards – Equipment:

Exercise caution when working with the experimental apparatus to ensure no water comes into contact with any electrical cables or power sockets.

Hazards – chemicals:

- Nitric acid: Causes severe skin burns (requires nitrile gloves and proper storage) and eye damage, acute inhalation toxicity (mists), requires inhalation protection.
- Fe_2O_3: Use with adequate ventilation.
- HDEHP: Mildly flammable and toxic; harmful in contact with the skin; inhalation may cause irritation of lungs/throat, use in a well-ventilated area, with respirator.
- n-Dodecane: Flammable and inhalation hazard, requires respiration protection.
- Nd_2O_3: Handle with nitrile gloves
- Tributylmethylphosphonium methyl sulphate: Do not inhale fumes (acute oral toxicity).

PPE: Lab coat, safety mask (A-P Filter), tight-sealing safety goggles, protective gloves (nitrile) and safety shoes.

We, the students have read the MSDS for all chemicals to be used, and are aware of the health and safety rules when working in the laboratories.

Yes ☒   No ☐

Note: Any student/s caught in contravention of the health and safety rules of the School will face disciplinary action.

Signature of candidates: *[signatures]*   **Date:** 24/03/2021

I (we), …Paramespri Naidoo, the supervisor(s) of the student project have checked all possible hazards from the equipment, procedures and materials used in the project, and have instructed the students about safe working practice. *[This will be done once the students are allowed in the laboratory; students have been through the equipment via a video call with the MSc.Eng. student, Thulani Bayeni]*

Signature of Main Supervisor: *[signature]*   **25 March 2021**

TOPIC 22: GANTT CHART

PROJECT MEMBERS: RIYANTHA MOODLEY (218009136)

SOHANA BRIDGEMOHAN (218010264)

SUPERVISORS: Prof P Naidoo

Dr M Williams-Wyn

Dr K Moodley

				8/3/2021 START DATE						18/5/2021 END DATE			
Task ID	Task Name	Start Week	End Week	WK01	WK02	WK03	WK04	WK05	WK06	WK07	WK08	WK09	WK10	WK11	WK12
1	Deliverable: Safety forms	WK01	WK01	■											
2	Deliverable: Research proposal and MOU	WK01	WK02	■	■										
3	Deliverable: Gantt chart	WK01	WK02	■	■										
4	Literature review	WK01	WK12	■	■	■	■	■	■	■	■	■	■	■	■
5	Progress assessment with supervisor	WK01	WK12	■	■	■	■	■	■	■	■	■	■	■	■
6	Experimental work	WK03	WK03			■									
6.1	Perform a test run (Neodymium extraction)	WK03	WK03			■									
6.2	Solvent extraction measurements	WK04	WK05				■	■							
6.3	Solvent extraction measurements (with IL doping)	WK05	WK06					■	■						
6.4	ICP-OES sample analysis (PMB Chemistry)	WK07	WK07							■					
6.5	Analysis & discussion of results	WK07	WK12							■	■	■	■	■	■
7	Presentation	WK03	WK09			■	■	■	■	■	■	■			
7.1	Presentation preparation	WK03	WK09			■	■	■	■	■	■	■			
7.2	Presentation slides	WK07	WK09							■	■	■			
7.3	Deliverable: Presentation	WK09	WK09									■			
8	Final report	WK01	WK12	■	■	■	■	■	■	■	■	■	■	■	■
8.1	Final report writing	WK01	WK12	■	■	■	■	■	■	■	■	■	■	■	■
8.2	Deliverable: Final report	WK12	WK12												■

CHEMICAL ENGINEERING

ENCH4LA – LABORATORY PROJECT

Memorandum of Understanding

This memorandum sets out the responsibilities of the undergraduate student, the supervisor(s), and the cluster/discipline to one another and asks each party to sign (at the end of the document) and thereby acknowledge the importance of these responsibilities.

A) Details of Student, Supervisors, and Project

Student Names: Riyantha Moodley and Sohana Bridgemohan

Student Numbers: 218009136 and 218010264

Supervisor(s): Prof P Naidoo, Dr Williams-Wynn and Dr K Moodley

Research Topic: Topic 22: Urban Mining of Rare Earth Elements from Rare Earth Magnets - Alternate Solvents for Extraction

B) Duties and Responsibilities of the Undergraduate Student

A Student's training consists mainly of the following activities performed under the guidance of the supervisor:
a) Reading books/scientific articles and possibly attending lectures/meetings to obtain the necessary background for successful research in the chosen field.
b) Research (depending on the discipline this can be field work, laboratory work, computer work, or pencil and paper research).
c) Regular meetings with the supervisor to discuss and plan the research, and to report on progress,
d) Collection of the research data – to maintain a logbook which must be presented at all meetings and discussions with the supervisor
e) Presentation of the results and conclusions in a scholarly written manuscript (which typically becomes a chapter of the final report).

While initially the student performs these activities following detailed instructions by the supervisor, it is expected that the student, as work progresses, gains increasing independence, in particular with regard to a), b), d), and e).

Student and supervisor should keep a copy of the proposal, as it might serve as an indicator of how much work has to be done to complete the project.

If requested by the supervisor, students must lodge a backup of all data, results and notes with the Supervisor or ensure that they regularly update their notes and results to an appropriate format.

C) Responsibilities of the Supervisor

As mentioned under B), one of the key activities during laboratory project study is regular meetings between student and supervisor. A supervisor has to make himself/herself available for such meetings. If the supervisor is absent from UKZN for an extended period of time, he/she has to make provisions for either a co-supervisor or a colleague to assist the student, or continual contact by email.

The role of the supervisor is not to provide help with the collection of actual research results. The supervisor should provide guidance to the student, such as giving advice as to which scientific literature is likely to be relevant for the project, which scientific methods and techniques are appropriate and perhaps demonstrating

1

such techniques, and what kind of equipment is available. The supervisor should also give guidance as to how information should be collected and later, in the writing up of the report, how results are analysed and presented in a scholarly way.

Field trips that are essential for the project are to be arranged by the supervisor.

The supervisor has to submit a Supervisor's report on the student's progress and contribution to the project. This must be submitted by the due date of the final laboratory project report.

Should the project require ethical clearance from the university or any other kind of permit (for example for collecting indigenous plants), then it is the supervisor's responsibility to obtain these. However, the student has to assist in preparing the necessary documentation.

The supervisor/technician has to bring the relevant safety rules to the student's attention and it is the responsibility of the student to abide by the rules of the discipline, School and University in terms of code of conduct and, health and safety regulations.

The supervisor should also clarify co-authorship of papers with the student and co-supervisors.

D)   Final report

Students are advised to write up their results as their research progresses, typically in the form of chapters of the final report. The supervisor will advise on how to go about the writing-up. The supervisor will read chapters handed in by the student and give feedback within a reasonable time, if such an agreement is made. It is, however, not the supervisor's job to proofread chapters.

The decision on the format of the report is made by the supervisor in consultation with the student.

The university rules for plagiarism apply.

Should parts of the report be published, then the supervisor in consultation with the student will decide which authors appear on the paper, and in which order. In this decision, the supervisor will take into account the contributions of the co-supervisor, student, and possibly third parties, to the part of the project that is to be published. A supervisor may publish results obtained by a undergraduate student without consulting the student if within one year of submission of the report no attempt has been made by the student to publish the results or to extend the research leading to these results.

If the student is bound by a confidentiality agreement, for example with a sponsor, then it is the student's and Supervisor's responsibility to make sure that the agreement is honoured.

Legal opinion must be sought regarding the matter of intellectual property, particularly in terms of Supervisors who are funded by external Organisations but have a student needing to withdraw.

E)   Running and Travel Expenses

Should the project require use of expensive chemicals, samples, or equipment, costs of fieldtrips, travel and any other expenses, all this must be specified on a separate sheet and presented to the Academic Leader. Such expenses must be discussed and payment confirmed; responsibility for these expenses made clear before the presentation of topics to the students. The discipline/cluster operates on a strict allowance per project and any additional expenses must be covered by the supervisor.

F)   Collegiality

Student and supervisor should treat each other with respect and dignity. In the interest of the research project, student and supervisor should keep each other informed about any activity relating to or relevant for the project. It is unacceptable for either party to submit results of the research project for publication or to present

2

them at a conference without prior consultation with the other party.

G)   Time Frames

Student and supervisor should agree on time frames for different phases of the project, these time frames should be reviewed at least annually.

H)   Conflict Resolution

Should there be a conflict or disagreement between supervisor and student which cannot be resolved by the parties involved, then either party can approach the Academic Leader of the Discipline or Dean and Head of School about the conflict. The Academic Leader of the Discipline or Dean and Head of School will then either arbitrate or choose a senior academic of the School not involved in the conflict to arbitrate. The arbitrator's decision is final and cannot be appealed.

Signatures:

Student .....Riyantha Moodley: .... Sohana Bridgemohan: ....

Date   ...24/03/2021...

Supervisor.......(*P Naidoo signs on behalf of all supervisors*)......

Date   ....26-March-2021...

Note
Copies of this must be attached to your laboratory project proposal document.