

HYDROMETALLURGICAL PROCESSING OF RARE EARTH ELEMENTS FROM ION ADSORPTION CLAYS

BY

EDDY MIIRO

In fulfilment of the requirements for the degree:

Master of Science in Chemical Engineering

Faculty of Engineering and Built Environment



Supervisor: Prof. Jochen Petersen

Date: January 31, 2023

The copyright of this thesis vests in the author. No quotation from it or information derived from it is to be published without full acknowledgement of the source. The thesis is to be used for private study or non-commercial research purposes only.

Published by the University of Cape Town (UCT) in terms of the non-exclusive license granted to UCT by the author.

DECLARATION

I, Eddy Miuro, know the meaning of plagiarism and declare that all the work in this document, save for that which is properly acknowledged, is my own. This thesis/dissertation has been submitted to the Turnitin module and I confirm that my supervisor has seen my report and that any concerns revealed by such have been resolved with my supervisor.

Signed by candidate

Signature

January 31, 2023

Date

ACKNOWLEDGEMENTS

I would like to acknowledge the following individuals from the University of Cape Town, who assisted me during the MSc project journey:

- Prof. Jochen Petersen for allowing me to undertake the MSc in Chemical Engineering project under his supervision and for the support and mentorship beyond a supervisor.
- Associate Prof. Megan Becker for the collaboration and advice throughout the Master project.
- Ms. Mymoena Shaik for the financial and administrative support throughout the Master project.
- Dr Kathija Shaik for the laboratory work and support beyond the laboratory work throughout 2021 and 2022.
- Chad Naude for sharing ideas and working together on the same research project.
- Jemitias Chivavava for sharing ideas and working together on the same research project.

The project is based on research supported by the Government of Uganda. I would like to thank everyone from the following organisations/initiatives

- Hydromet research group for being a family away from home.
- Minerals to Metals initiative for giving me a platform to represent the research project and engage with exceptional individuals through forums and seminars.

I would like to extend warm gratitude to my mother, Mrs. Sarah Mubiru, brothers Mr. John Mubiru and Lt. Richard Mutebi, and my family, my wife Mrs. Aidah Nakasi Miiro, daughter Sera Edrinah Miiro, and son Joel Elvis Miiro.

ABSTRACT

The surface mining and heap leaching of China's ion-adsorption rare-earth resources have caused severe environmental damage, there is a need to better understand Rare Earth leaching from Clay ore with the use of agglomerates that improve the permeability of the ore during heap leaching operation. The practice of in-situ leaching has also revealed serious environmental problems including underground contamination, mine collapses, and landslides.

The performance of lixiviants in extracting Rare Earth has been compared in many studies however this has been carried out in agitated systems and the heap leach scenario is different from agitated systems. This limits the understanding of poor heap permeability and post-closure stability whereas un-agitated leaching of Rare Earth from Clay agglomerates gives a better understanding of diffusion, heap permeability, and material balance to mimic the heap leach scenario. A comprehensive understanding of the leaching mechanism is crucial for achieving high extraction efficiency with low cost and less environmental impact.

A series of inorganic salts with different concentrations were employed to leach the Ion-adsorption rare earth agglomerates, and the relationship between the leaching efficiency of rare earth and reagent type was investigated in unagitated systems. This study showed that ammonium sulfate extracts less aluminum content than magnesium chloride. Even when magnesium sulfate (hydrate) extracts less aluminum (impurity in Pregnant Leach Solution) content than the other lixiviants used in the study, magnesium sulfate extracts less Rare Earth Elements (REE) compared to the other lixiviants in the same leaching time, this was an unexpected result when magnesium sulfate hydrate was used instead of anhydrous magnesium sulfate that was much more expensive (per mass) compared to the prices of the other leaching reagents. Therefore the lixiviant of preference in terms of REE extraction from ion adsorption clays in un-agitated systems is in the order $(\text{NH}_4)_2\text{SO}_4 > \text{MgCl}_2 \cdot 6\text{H}_2\text{O} > \text{NaCl} > \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

NOMENCLATURE

Notations

A	Area (m ²)
g, kg	grams, kilograms
H	height
K	permeability
M	molarity
m, cm, mm	meter, centi-meter, milli-meter
rpm	revolutions per minute
s	second
t	time
T	tonne
v	velocity
V	Volume

Symbols

φ	Rare earth leached efficiency
ε_0	the total amount of the ion-exchangeable phase rare earth in the original ore sample
ε_V	the total amount of rare earth in leaching solution at volume V
ε_t	the total amount of rare earth in leaching solution at time t
β	packed porosity

Abbreviations

BTPIT 1153	Madagascan sample	IUPAC	International Union of Pure and Applied Chemistry
RRMDT C1-10	Ugandan sample		
ABT	Agitated batch test	L:S	Liquid to solid ratio
AR	Aqua regia	La	Lanthanum
AS	Ammonium sulfate	LREEs	Light Rare Earth Elements
Au	Gold	Lu	Lutetium
Ce	Cerium	MS	Magnesium sulfate
CET	Column elution test	Nd	Neodymium
Cl ⁻	Chloride	O	oxygen/oxide
DI	De-ionised water	Pm	Promethium
Dy	Dysprosium	ppm	parts per million
Er	Erbium	Pr	Praseodymium
Eu	Europium	PLS	Pregnant leach solution
Gd	Gadolinium	PSD	particle size distribution
Ho	Holmium	QEMSCAN	Quantitative Evaluation of Materials by Scanning Electron Microscopy
HREEs	Heavy Rare Earth Elements	RE	Rare Earth
HL	Heap leaching	REE	Rare Earth Elements
IAC	Ion-Adsorption Clays	REO	Rare Earth Oxide
ICP-MS	Inductively Coupled Plasma Mass Spectrometry	SBT	Stagnant bed test
ISL, ISR	In-situ	Sc	Scandium
leaching/recovery		SEM	ScanningElectron Microscope

Si	Silicon		Tm	Thulium
Sm	Samarium		TREEs	Total Rare Earth Elements
SSE	Sum of square errors		U	Uranium
Tb	Terbium		wt%	weight percent
TEM	Transmission Microscopy	Electron	XRF	X-ray fluorescence
			Y	Yttrium
Th	Thorium		Yb	Ytterbium

Table of Contents

DECLARATION	i
ACKNOWLEDGEMENTS	ii
ABSTRACT	iii
NOMENCLATURE	iv
Table of Contents	vii
List of Tables	x
List of Figures	xi
1 INTRODUCTION	1
1.1 Background	1
1.2 Problem statement and Research Questions.....	3
1.3 Research Objectives	5
2 LITERATURE REVIEW	6
2.1 Introduction to REEs.....	6
2.2 Rare Earth Elements (REE) ores.....	6
2.2.1 Carbonate and phosphate ores	7
2.2.2 Ion Adsorption Clays	7
2.3 Characteristics of Ion Adsorption Clays	8
2.4 Processing of REEs from Ion Adsorption Clays.....	9
2.4.1 Process chemistry of clays	9
2.4.2 Industrial recovery of REEs from IAC.....	11
2.4.3 Heap leaching (HL).....	13
2.4.4 In-situ leaching (ISL).....	15
2.4.5 Ore agglomeration	16

2.4.6	Environmental issues associated with the use of ammonium sulfate in heap/in-situ leaching.....	17
2.5	Agitated tests for IAC ores and their scale-up limitations to un-agitated REE leaching processes.....	17
2.5.1	Agitated leach tests	17
2.5.2	Un-agitated leach test.....	19
2.6	Discussion of literature review.....	22
3	MATERIALS AND METHODS.....	24
3.1	Materials.....	25
3.1.1	Ion-Adsorption Clays (IACs).....	25
3.1.2	Reagents.....	28
3.2	Equipment	29
3.2.1	Column reactors	29
3.2.2	Suspended ball reactors.....	31
3.2.3	Agitated batch reactors	32
3.3	Methods.....	33
3.3.1	Phase 1: Test work on Madagascan ore.....	33
3.3.2	Phase 2: Test work on Ugandan ore	33
3.3.3	Elemental analysis of solutions.....	36
4	RESULTS AND DISCUSSION.....	37
4.1	Test work on the Madagascan ore.....	37
4.1.1	Effect of sulfate system on leaching of REE from Madagascan IAC.....	37
4.1.2	Effect of chloride system on leaching of REE from Madagascan IAC	39
4.2	Test work on Ugandan ore	40
4.2.1	Effect of Reagent flow-rate on column leaching	41
4.2.2	Effect of agglomerate size on column/suspended agglomerate leaching	43

4.2.3	Effect of reagent type and concentration the three different reactor setups: stirred batch reactor, column reactor and suspended ball reactor.....	46
4.2.4	Reactor comparison	68
5	CONCLUSIONS AND RECOMMENDATIONS	71
6	REFERENCES	74
7	APPENDICES	77

List of Tables

Table 1: Results of REE analysis for Madagascan (Ram et al., 2019), and Ugandan ore samples	26
Table 2: Major element oxides determined by XRF for Ugandan ore sample RRMDT C1-10 and Madagascan Sample (Ram et al. 2019).....	27
Table 3: Quantitative analysis of whole rock mineralogy from powder XRD using the Rietveld Method (wt %) (Ram et al., 2019)	28
Table 4: Reagents used in the preparation of lixivants:.....	29
Table 5: Experimental matrix for test work on Ugandan sample	34
Table 6: Comparison of the different leaching reagents in column leaching	60

List of Figures

Figure 1: Kaolinite atomic structure (Deng et al., 2002)	8
Figure 2: Mechanism for REE desorption from Ion adsorption clays with monovalent cations proposed by (Moldoveanu & Papangelakis, 2012).....	10
Figure 3: Summary diagram of the salt treatment processing of REEs from Ion Adsorption Ore (adopted from Vahindi et al., 2016).....	13
Figure 4: Generic block flow diagram of copper heap leaching. Adapted from van Staden, Naseri & Petersen (2017c)	14
Figure 5: Typical heap bioleach flow diagram for copper adapted from (Ghorbani et al., 2016)	15
Figure 6: Schematic diagram of inter-particle and intra-particle solution diffusion in heap operation adapted from (Ghorbani et al., 2016).....	15
Figure 7: Schematic diagram of In-situ Leaching (adapted from Zou, 2012)	16
Figure 8: Agitated batch setup adapted from Mkhize (2020)	18
Figure 9: Light REE, Heavy REE, and Total REE extraction efficiency of ammonium sulfate at different concentration of 0.05M, 0.1M, 0.25M, 0.5M and 1.0M adapted from Mkhize (2020).	19
Figure 10: Stagnant bed test setup adapted from Mkhize (2020)	20
Figure 11: REE Extraction efficiency of Ammonium sulfate in Stagnant Bed test (adapted from Mkhize, 2020).....	20
Figure 12: Schematic column leaching setup (Mkhize, 2020)	21
Figure 13: REE extraction efficiency of Ammonium sulfate in column setup adapted from Mkhize (2020).....	22
Figure 14: Flowsheet to show the overall experimental approach for agglomerate column leaching	24
Figure 15: (a) Dickie and Stockler (Pty) 10-way splitter, (b) 10kg rotary splitter, and (c) 1kg Rotary Micro Riffler	26
Figure 16: Schematic of column setup.....	30
Figure 17: Air drying of the agglomerated clay balls	31
Figure 18: Schematic of Suspended agglomerate reactor	32
Figure 19: REE extraction efficiency of 0.5M ammonium sulfate at 3L/day flowrate, 298K, and pH 3-4	38

Figure 20: REE extraction efficiency of 0.25M magnesium chloride at 3L/day flowrate, 298K, and pH 3-4	40
Figure 21: REE extraction efficiency of 0.75M ammonium sulfate at different flowrates of (a) 0.5L/day, (b) 3L/day, and (c) 5L/day.....	42
Figure 22: REE extraction efficiency of 0.75M ammonium sulfate at different agglomerate sizes of (a) 2.5cm, (b) 3.0cm, and (c) 3.5cm in the suspended ball reactor setup and operating conditions were: 0.5L/day flowrate, pH 3-4, and temperature maintained at 298K	45
Figure 23: REE extraction efficiency of 0.75M ammonium sulphate in stirred batch reactor	48
Figure 24: REE extraction efficiency of 0.75M magnesium sulphate in stirred batch reactor.....	48
Figure 25: REE extraction efficiency of 1.5M sodium chloride in stirred batch reactor.....	49
Figure 26: REE extraction efficiency of 0.75M magnesium chloride in stirred batch reactor	49
Figure 27: Maximum REE extraction of 1.5M ammonium sulfate (AS), 1.5M magnesium sulfate (MS), 1.5M magnesium chloride (MC), and 3.0M sodium chloride (NC) in stirred batch reactors	50
Figure 28: REE extraction efficiency of columns (a) 0.75M ammonium sulfate and (b) 1.5M ammonium sulfate.....	53
Figure 29: REE extraction efficiency of columns (c) 0.75M magnesium chloride and (d) 1.5M magnesium chloride	54
Figure 30: REE extraction efficiency of columns (e) 1.5M sodium chloride and (f) 3.0M sodium chloride	55
Figure 31: REE extraction efficiency of columns (g) 0.75M magnesium sulfate and (h) 1.5M magnesium sulfate	56
Figure 32: Maximum REE extraction of 0.75M and 1.5M ammonium sulfate (AS), 0.75M and 1.5M magnesium sulfate (MS), 0.75M and 1.5M magnesium chloride (MC), 1.5M and 3.0M sodium chloride (NC) in column reactors.....	57
Figure 33: REE percentage extraction of 0.75M ammonium sulfate compared to de-ionised (DI) water leaching when agglomerated with ammonium sulfate at the same concentration of 0.75M and same PLS volume of 500mL.....	58
Figure 34: REE extraction of (a) 0.75M ammonium sulfate and (b) 1.5M ammonium sulfate from 2.5cm agglomerates suspended in two different suspended ball reactors	63

Figure 35: REE extraction of (c) 0.75M magnesium sulfate and (d) 1.5M magnesium sulfate from 2.5cm agglomerates suspended in two different suspended ball reactors	64
Figure 36: REE extraction of (e) 1.5M sodium chloride and (f) 3.0M sodium chloride from 2.5cm agglomerates suspended in two different suspended ball reactors	65
Figure 37: REE extraction of (g) 0.75M magnesium chloride and (h) 1.5M magnesium chloride from 2.5cm agglomerates suspended in two different suspended ball reactors.....	66
Figure 38: Maximum REE extraction of 0.75M and 1.5M ammonium sulfate (AS), 0.75M and 1.5M magnesium sulfate (MS), 0.75M and 1.5M magnesium chloride (MC), 1.5M and 3.0M sodium chloride (NC) in suspended ball reactors	67
Figure 39: Comparison of REE extraction efficiency of 0.75M ammonium sulfate in different reactors (a) stirred batch reactor, (b) column reactor, and (c) suspended ball reactor.....	70

1 INTRODUCTION

1.1 Background

Rare earth elements (REEs) comprise 15 lanthanides (atomic numbers between 57 and 71), scandium (atomic number 21), and yttrium (atomic number 39) (Balaram, 2019). The light REEs (La, Ce, Pr, Nd) are more abundant and concentrated than medium and heavy REEs (from Sm to Lu plus Sc and Y) and usually make up about 80-99% of a total deposit. Based on properties, Sc is considered similar to light REEs (LREEs), while Y is similar to heavy REEs (HREEs). However, medium and heavy REEs have more applications and are of higher value than light REEs (Yang et al., 2013). REEs have become vital and indispensable components of many high-tech products, devices, and technologies, including clean energy, for example magnets used in wind turbines (Chakhmouradian & Wall, 2012). About 200 rare earth minerals are distributed in a wide variety of mineral classes, such as halides, carbonates, oxides, phosphates, silicates, etc. Rare earth ore deposits have relatively low concentrations ranging from 10 to a few hundred parts per million by weight, making them difficult to mine economically (Jordens et al., 2013) and only a few mineral species, such as bastnaesite $(\text{Ce, La})(\text{CO}_3)\text{F}$, monazite $(\text{Ce, La})\text{PO}_4$, xenotime YPO_4 , and REE-bearing ion adsorption clay (IAC) have been recovered for commercial production (Kanazawa & Kamitani, 2006).

The IAC rare earth deposits were formed by chemical weathering decomposition and dissolution of granite porphyry (containing a relatively high abundance of rare earth elements) and subsequent adsorption and enrichment on clay minerals during the migration and penetration process of solutions rich in dissolved RE ions (Dushyantha et al., 2020). The minerals are therefore also called weathered crust elution-deposited rare earths (Yang et al., 2013). The weathered residual deposits have been formed under tropical and sub-tropical climates and the weathering processes concentrate REEs in a particular clay mineral layer in the weathered crusts whose sources were originally REE-rich rocks like granite and carbonatite (Kanazawa & Kamitani, 2006). Despite an extremely low ratio of ion-adsorption rare earth reserves, this type of rare earth accounted for 26% of China's total rare earth production between 1988 and 2007 (Yang et al., 2013) and reached 35% in 2009.

However, the surface mining and heap leaching of China's unique IAC rare earth resources, largely by artisanal mining, have caused severe environmental damage (Malhotra et al., 2020); it is estimated that for the production of 1 of ton Rare Earth Oxide (REO) from IAC rare earth ores, 300m² vegetation and topsoil are removed, 2000 tons residue tailings are disposed into adjacent valleys and streams, and 1000 tons of wastewater containing high concentrations of ammonium sulfate and heavy metals is produced (Kanazawa & Kamitani, 2006; Yang et al., 2013). The in-situ leaching technology is advantageous in terms of not needing clearing of surface vegetation and soil excavation (Yan et al., 2018). However, the enforcement of in-situ leaching to tackle environmental problems associated with rare earth mining and extraction remains highly contentious (Yanfei et al., 2015) since the practice of in-situ leaching technology has subsequently revealed serious environmental problems including underground water contamination, mine collapses, and landslides (Yang et al., 2013). Furthermore, capillary forces surrounding the injection wells attract high concentrations of leaching solution back to the topsoil layer, destroying surface vegetation and plants and making rehabilitation more difficult.

The production of rare earth elements has been increasing in recent years (Goodenough et al., 2018), however the chemical process of REEs extraction is still faced with environmental problems (Yanfei et al., 2015). For example, ammonium sulfate contamination of 3500-4000 mg/L has been observed in the groundwater, as have elevated pH in the soil matrix and increased concentrations of ammonium, rare earths (80-160 mg/L ammonium and 20 mg/L REEs) in surface waters.

The leaching efficiency of various salts at lower concentrations (0.25 – 0.5M) was investigated by Moldoveanu & Papangelakis (2012) in stirred batch reactors at the laboratory scale, and different monovalent cation types and salt system (sulfates vs chlorides) were used; the leaching efficiency in terms of %REE extracted decreased in the order $\text{Cs}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{Li}^+$ from 90% to approximately 60%, respectively, with sulfates extracting approximately 10% more than chlorides. The differences in rare earth metal desorption capability were explained in terms of the difference in cation hydration energies, and species with low hydration energy extract to a lesser degree compared to species with high hydration energy (higher affinity for water) (Moldoveanu & Papangelakis, 2012; Xu et al., 2019). A standardized desorption procedure was established to systematically investigate the influence of leaching conditions such as lixiviant concentration,

temperature, pH, and agitation rate (Moldoveanu & Papangelakis, 2013) on desorption kinetics and REEs extraction levels. It was determined that only sufficient stirring to ensure complete slurry suspension for effective mass transfer was required and extraction kinetics were found to be very fast, with less than 5 min to achieve complete extraction (Moldoveanu & Papangelakis, 2012, 2013), and independent of lixiviant concentration, pH, temperature, and agitation speed. The use of magnesium sulfate instead of ammonium sulfate was investigated by Yanfei et al. (2015) to solve the problem of ammonia-nitrogen pollution during the recovery of rare earth elements. 93% total rare earth leaching efficiency and around 50% aluminum leaching efficiency suggesting that magnesium sulfate was capable of producing identical recovery efficiency as ammonium sulfate and reducing aluminum leaching efficiency at the same time. (Xu et al., 2019) investigated the relationship between the leaching efficiency of rare earth and the zeta potential of clay particles, and a series of inorganic monovalent electrolytes at different concentrations were employed to leach the IAC-bound rare earths. A linear relationship between the leaching efficiency and zeta potential of clay particles was observed for every electrolyte and the linear relationship greatly depends on the type of the cations (Moldoveanu & Papangelakis, 2012). The dependence of zeta potential on the leaching efficiency and the residual ion concentration in rinsing solutions is considered to be the main factor influencing the environment of the mine district (Xu et al., 2019); thereby estimating the environmental impact of remaining electrolytes in mine tailing. Heap leaching technology is finding increasingly widespread applications to recover values from low-grade ores (Petersen, 2016), especially in the gold and copper industry. The particular attractiveness of the process is the relatively low-cost recovery of the target metal at the site without the need for energy-intensive comminution (Ghorbani et al., 2016). However, this is contrasted with often slow and inefficient recovery, and technical issues such as poor heap permeability and post-closure stability (Petersen, 2016). A comprehensive understanding of the leaching mechanism is crucial for achieving high extraction efficiency with low-cost heap leaching and less environmental impact.

1.2 Problem statement and Research Questions

As was outlined above, the heap/in-situ leaching of rare earth bearing IACs using ammonium sulfate as lixiviant has caused severe environmental impact in China, having lead to the search for alternative reagents and optimised processes. The performance of various lixiviants in extracting rare earths from such ores has been compared in many studies (Moldoveanu & Papangelakis, 2012, 2013; Su et al., 2019; Xu et al., 2019). However there is limited literature about agglomeration of clay ore as a way to improve permeability of the heap when extracting REE from Ion Adsorption Clay because most of the work has been carried out in agitated systems, and the heap leach scenario is different from agitated systems. This limits the applicability of the leach results to understanding aspects such as predicting extraction efficiency, poor heap permeability and post-closure stability.

While the chemical ion exchange reaction proceeds rapidly, the kinetics in heap leaching are determined by the rate of diffusion of reagents and reaction products in and out of the larger clay agglomerates. There is a very limited understanding of the kinetics in the context of heap leaching of Rare Earth clays. Studying the un-agitated leaching of Rare Earth from clay ore agglomerates is therefore postulated to give a better understanding of reaction-diffusion within the agglomerates, heap permeability, and material balance to mimic the heap leach scenario.

Based on an understanding of conventional heap leaching (HL) is therefore postulated that the overall rate of extraction is determined by diffusion through clumps/agglomerates of clay and potentially also the reduced extent of extraction. Therefore agglomerate size should be a significant factor that needs to be investigated in this context. Further, overall heap permeability is maintained by ensuring stability of the agglomerate, potentially through modest irrigation rates. Consequently, the following key questions are put forward:

- 1) How do different leaching agents compare in the leaching of Rare Earth Elements from Ion Adsorption Clays in un-agitated systems, for example column reactor?
- 2) How to improve heap permeability of clay ore?
- 3) How to achieve permeability of clay ores beds, even at laboratory-scale when leaching clay ore in column reactor?
- 4) When clay ore agglomerates are packed in a laboratory column reactor, does this prevent the column reactor from overflowing with leaching reagent?
- 5) Does the size of the agglomerates affect the REEs leaching efficiency?

- 6) As a very slow irrigation rate limits the breakdown of agglomerate stability and also improves the residential time of leaching agent in the heap, so do different flow rates affect the REEs leaching efficiency?

1.3 Research Objectives

The research presented in this study followed the following objectives:

- Evaluate IAC materials (Madagascan and Ugandan samples) with respect to agglomerate heap leaching, varying both particle size and lixiviant.
- Investigate the REEs leaching from agglomerate particles of clay in small-scale column apparatus, a ‘suspended ball reactor’ developed for this project, and benchmark against insights from a stirred batch reactor.
- Evaluate the effect of reagent type, reagent concentration, and agglomeration size on the Rare Earth Elements leaching from Ion-adsorption clays

The research project contributes to solving challenges related to the Sustainable Development Goal (SDG) 7 ensuring access to affordable, reliable, sustainable, and modern energy for all in the application of Rare Earth Elements (REEs) in green energy production for example REEs used in the manufacture of wind turbines, manufacture of permanent magnets used in electric cars; SDG 8 target 8.4 improve global resource efficiency in consumption and production endeavor to decouple economic growth from environmental degradation; SDG 9 foster innovation, the innovation is not only downstream in the REEs application but also upstream in the hydrometallurgical processing of REEs from Clays to further ease downstream processing and application of REEs.

2 LITERATURE REVIEW

2.1 Introduction to REEs

According to the International Union of Pure and Applied Chemistry (IUPAC), Rare earth elements (REE) are 17 transition metals part of group 3 in the periodic table and these include: Scandium (Sc), Yttrium (Y), and 15 Lanthanides in the order of increasing atomic number Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium (Nd), Promethium (Pm), Samarium (Sm), Europium (Eu), Gadolinium (Gd), Terbium (Tb), Dysprosium (Dy), Holmium (Ho), Erbium (Er), Thulium (Tm), Ytterbium (Yb), and Lutetium (Lu) (Balaram, 2019). REE are commonly grouped by their atomic number as Light REE (La, Ce, Pr, Nd) and Heavy REE (Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y) (Yang et al., 2013). REE are used in the high technology industry for example in the manufacture of optical devices, laser, chemical catalysts, and permanent magnets that take approximately 25% of REE market share. (Balaram, 2019; Chakhmouradian & Wall, 2012).

2.2 Rare Earth Elements (REE) ores

The main sources of REE are bastnaesite, monazite, and ion-adsorption clays (IAC) (Jordens et al., 2013). Bastnaesite $(\text{Ce, La})(\text{CO}_3)\text{F}$ is a carbonate ore and contains 65-75 wt% REO, monazite $(\text{Ce, La})\text{PO}_4$, and xenotime YPO_4 are phosphate ores (Kanazawa & Kamitani, 2006). Monazite contains 55-65 wt% REO, and xenotime contains 25-60 wt% Y_2O_3 (Kanazawa & Kamitani, 2006). Ion Adsorption Clays (IAC) are aluminosilicate weathered crust elution deposited ores that contain 0.05-0.3 wt% REE, IAC have been recovered for commercial production (Kanazawa & Kamitani, 2006).

2.2.1 Carbonate and phosphate ores

Bastnaesite (with a formula of $(\text{Ce},\text{La})\text{CO}_3(\text{F},\text{OH})$), monazite (with a formula of $(\text{Ce},\text{La})\text{PO}_4$), and xenotime (with a formula of YPO_4) ores are far more complicated and costly to extract than ion-adsorption clays (Kanazawa & Kamitani, 2006). Carbonate and phosphate (i.e. bastnaesite, monazite, and xenotime) ores are first ground to (50 μm -1mm) and beneficiated by physical processes, for example, flotation or magnetic separation, to obtain a concentrate (Jordens et al., 2013). A typical bastnaesite concentrate containing about 70% REO is acid digested with 30% w/w HCl to produce $\text{REECl}_2 \cdot 6\text{H}_2\text{O}$ that is taken for further REEs separation processes whereas monazite concentrate, in the ratio of 1:1 w/w, is alkali digested in 50-75% w/w hot NaOH and then leached in either HCl or HNO_3 to form intermediate products for further REEs separation (Silva et al., 2018) however acid baking with 98% w/w H_2SO_4 for monazite concentrate is no longer in use because of impure products.

2.2.2 Ion Adsorption Clays

The ion-adsorption rare earth deposits were formed by chemical weathering decomposition and dissolution of granite porphyry (containing a relatively high abundance of rare earth elements) and subsequent adsorption and enrichment on clay minerals during the migration and penetration process of solutions rich in dissolved RE ions (Dushyantha et al., 2020) the minerals are therefore also called weathered crust elution-deposited rare earths (Yang et al., 2013). The weathered residual deposits have been formed under tropical and sub-tropical climates and the weathering processes concentrate REEs in a particular clay mineral layer in the weathered crusts whose sources were originally REE-rich rocks like granite and carbonatite (Kanazawa & Kamitani, 2006). Although Ion Adsorption Clays (IAC) deposits are substantial of lower grade than other lanthanide sources, they are much easier to mine (Chen et al., 2022; Ram et al., 2019) by salt treatment without any beneficiation (Banerjee et al., 2021), therefore have low processing costs. Ion Adsorption ores have a low content of radioactive elements that would have required further processing to remove them from the REE concentrate (Arshi et al., 2018; Kanazawa & Kamitani, 2006).

2.3 Characteristics of Ion Adsorption Clays

IAC are mainly characterized by laterite formation that reflects in-situ weathering controlled by the solubility of the different components of the source rock, resulting in the enrichment of poorly soluble components (AL, Fe) and depletion in soluble components (Ram et al., 2019).

Mineral clays are crystalloid minerals mostly composed of silicon (Si^{4+}), oxygen (O^{2-}) see Figure 1, and other metallic elements (Al^{3+} , Mg^{2+}) bonded to the hydroxyl group (OH^-) (Ram et al., 2019). The structure of phyllosilicate minerals, one of the biggest groups of mineral clays, is made up of tetrahedron-bonded silicate sheets and octahedron-bonded metallic hydroxyl (Me-OH) sheets (Mkhize, 2020; Ram et al., 2019). The packing can be either 1:1 (kaolinite) or 2:1 (montmorillonite) whereas, in the 2:1 packing, the octahedron sheet is sandwiched between two tetrahedron sheets (Deng et al., 2002)

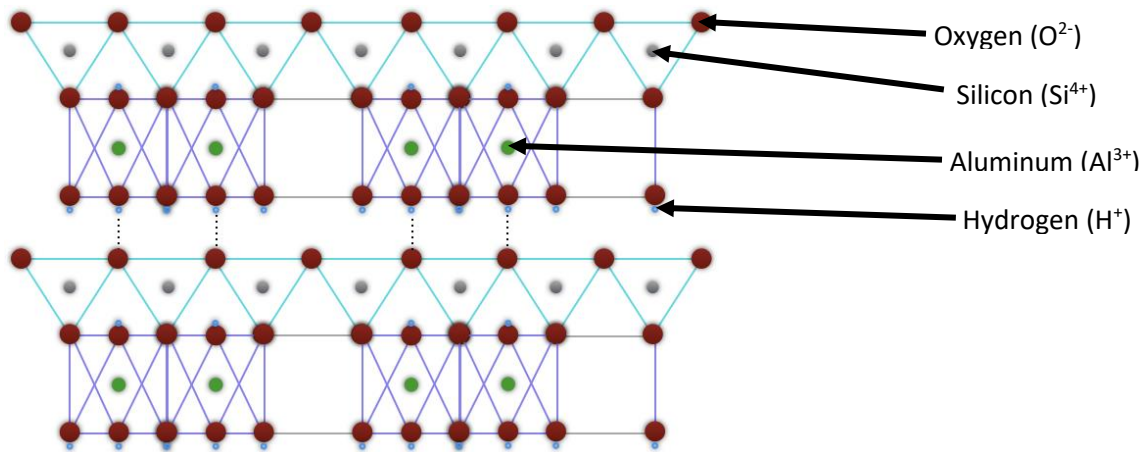


Figure 1: Kaolinite atomic structure (Deng et al., 2002)

The phyllosilicate group of mineral clays is characterized by small particle sizes, high surface areas, and unique exchange properties; the latter is the measure of available ions that can be substituted (Ram et al., 2019). Phyllosilicate minerals tend to have a negative surface charge where for example montmorillonite is naturally found to be negatively charged because of Al^{3+} that can substitute Si^{4+} , resulting in charge imbalance in the structure that facilitates (REE cations) ion-

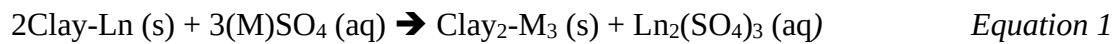
adsorption on the clays (Moldoveanu & Papangelakis, 2012, 2013), and this driving force is also used in the leaching of elements from the clay.

2.4 Processing of REEs from Ion Adsorption Clays

Direct chemical leaching is the only method for extraction of REE from the Ion Adsorption Clays (IAC) since the usual physical processing methods such as flotation, magnetic, gravity and electrostatic technology can not enrich IACs (Chi and Tian, 2012).

Although Ion Adsorption Clays (IAC) deposits are substantial of lower grade than other lanthanide sources, they are easily mined by use of salt lixiviants without any beneficiation therefore low processing costs (Yanfei et al., 2015). Ion Adsorption ores have a low content of radioactive elements (Kanazawa & Kamitani, 2006) that would have been harmful to workers, and require further processing to remove radioactive elements from the REE concentrate.

The REEs physisorbed on IAC are easily and selectively desorbed and substituted on the substrate by the monovalent/divalent ions followed by transfer into solution as soluble REE sulfates, nitrates, or chlorides (Xiao et al., 2016; Yanfei et al., 2015).



where Ln is the Lanthanide element, M is a divalent cation, and (s) and (aq) represent the solid phase and aqueous phase respectively.

2.4.1 Process chemistry of clays

Ion Adsorption Clays (IAC) are Alumino-silicate minerals (Kanazawa & Kamitani, 2006; Moldoveanu & Papangelakis, 2012; Ram et al., 2019) such as kaolinite, muscovite, and halloysite. IAC has physisorbed ions that ion-exchange by isomorphous substitution of one cation with another of similar size but with lesser charge (for example Al^{3+} for Si^{4+} or Mg^{2+} for Al^{3+}) which

leads to a charge imbalance that accounts for the permanent negative charge on clay particles and consequently the ability of clays to attract cations for this case REEs to the surface (Moldoveanu & Papangelakis, 2013; Xiao et al., 2016; Xu et al., 2019).

REE from (Sc to La) are d-transition elements and from (Ce to Lu) are f-transition elements therefore all Lanthanide (Ln^{3+}) compounds have great similarity to each other as well as to Y^{3+} , La^{3+} , and a limited similarity extends to Sc^{3+} (Jordens et al., 2013; Moldoveanu & Papangelakis, 2012; Yan et al., 2018).

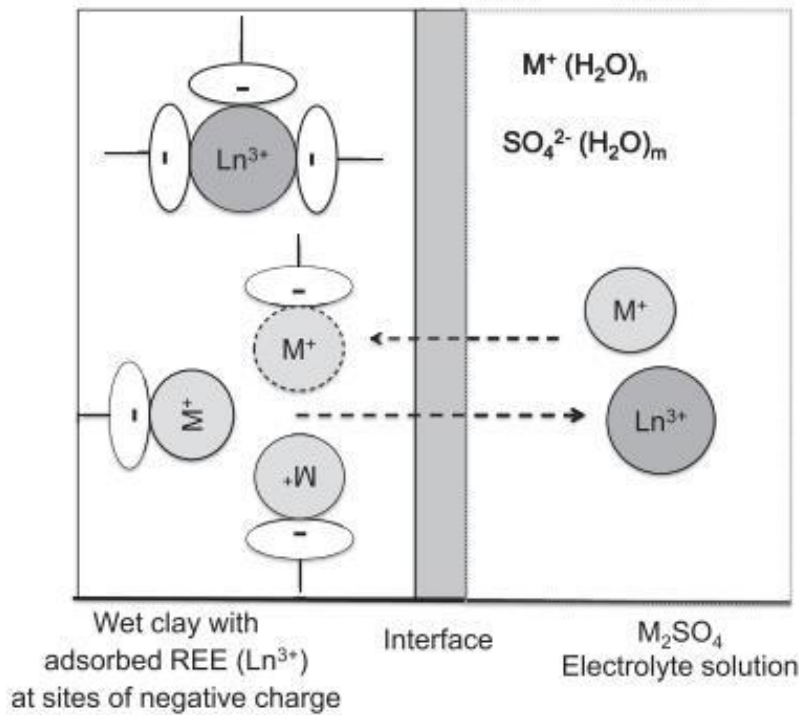


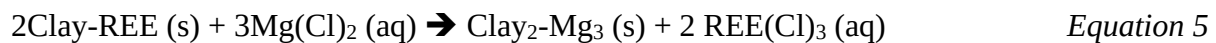
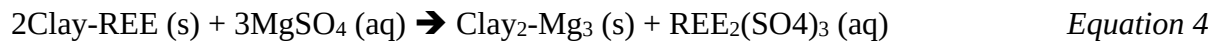
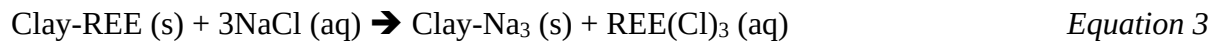
Figure 2: Mechanism for REE desorption from Ion adsorption clays with monovalent cations proposed by (Moldoveanu & Papangelakis, 2012)

Stoichiometry and chemical reaction equations of leaching REE from IAC

The RE ions would be exchanged when the IAC is eluted by leaching reagents, for example $(\text{NH}_4)_2\text{SO}_4$ or NaCl , similar to the ion-exchange process (Chi and Tian, 2012). The ion-exchange reaction proceeds between the clay minerals, called the immobile phase, and the leaching reagent,

called mobile phase; the leaching reagent in the solution is adsorbed and the RE ions are desorbed (see Figure 2). The ion-exchange reaction is a reversible reaction and reaches an equilibrium (Moldoveanu & Papangelakis, 2013, Chi and Tian, 2012)

For the different leaching reagents that were used in the study, ammonium sulfate would react with rare earth clay at a molar ratio of 2:3 of Clay-REE to ammonium sulfate and the same molar ratio of 2:3 applied for Clay-REE to magnesium sulfate and Clay-REE to magnesium chloride (see equation 2, 4, and 5) whereas the molar ratio of Clay-REE to sodium chloride is 1:3 (see equation 3), this means that twice the molar concentration of sodium chloride was required to compare it to ammonium sulfate chemical reaction with Clay-REE (Moldoveanu & Papangelakis, 2013).



2.4.2 Industrial recovery of REEs from IAC

The industrial recovery of REEs from IAC ores has involved over three generations of leaching technology, which are:

First generation leaching technology

In the early 1970s, vat leaching was carried out using 1M sodium chloride to extract REEs from IACs. The REEs were leached in barrels with 1M NaCl and precipitated with oxalic acid (Chi et

al., 2012) However vat leaching was limited by low yield product and the use of high concentration of lixiviant (Moldoveanu & Papangelakis, 2016).

Second generation leaching technology

In 1980s, heap leaching using 0.3M ammonium sulfate solution was developed and this replaced vat leaching with 1M NaCl (Chi et al., 2012). The IACs were mined and piled up on a leak-proof layer and $(\text{NH}_4)_2\text{SO}_4$ solution was irrigated on the of heap then pregnant leach solution (PLS) was collected at the bottom of the heap. Due to stronger stronger desorption capability of NH_4^+ compared with Na^+ (Moldoveanu & Papangelakis, 2012; 2013), the technology produced a higher quality product and a reduction in lixiviant consumption.

Third generation leaching technology

The intense use of vat and heap leaching posed a devastating effect to the environment in southern China (Moldoveanu & Papangelakis, 2016). The Chinese government banned vat and heap leaching and implemented the use of in-situ leaching technology. There is limited vegetation clearing and no surface mining of IACs when using in-situ leaching technology, vertical leaching holes are drilled to reach the top of the REE-enriched layer to allow injection of pressurized 0.3M $(\text{NH}_4)_2\text{SO}_4$ as leaching reagent and the PLS is collected by recovery ponds at the bottom of the orebody (Chi et al., 2012).

The recovery of REEs from the PLS, regardless of leach process, is by salt treatment (Moldoveanu & Papangelakis, 2012, 2013). A typically 0.1% REE IAC ore is leached with 0.5M salt (M_2SO_4 / MCl) where M is Na^+ / NH_4^+ at 25°C and pH of (3-5) to produce an impure pregnant leach solution (PLS) that is either treated with oxalic acid $\text{H}_2\text{C}_2\text{O}_4$ or carbonation with ammonium carbonate to precipitate out $\text{REE}_2(\text{C}_2\text{O}_4)_3$ or $\text{REE}_2(\text{CO}_3)_3$ and by calcination, REE_2O_3 is formed (see Figure 3) which is shipped for further REEs separation processes in a centralized refinery (Vahidi et al., 2016).

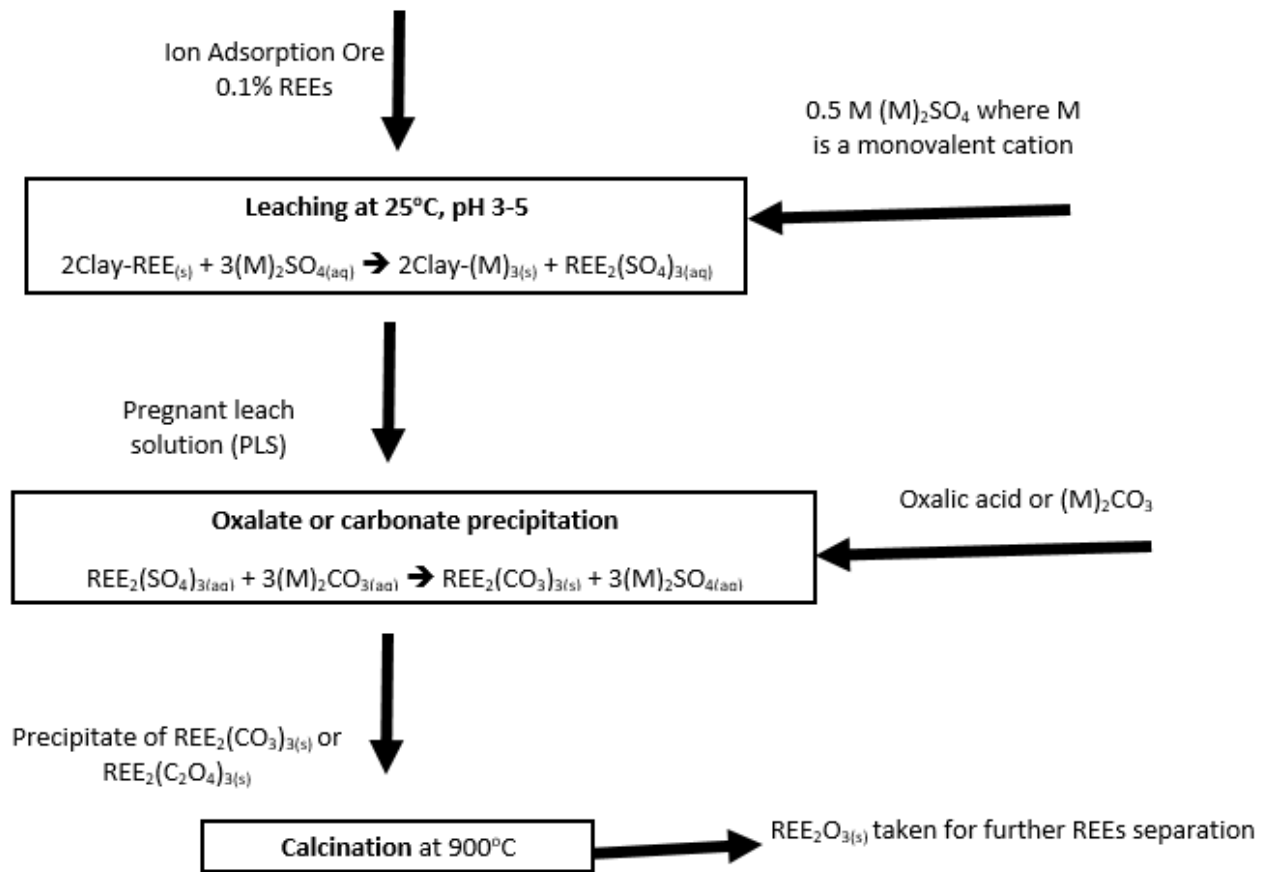


Figure 3: Summary diagram of the salt treatment processing of REEs from Ion Adsorption Ore (adopted from Vahindi et al., 2016)

2.4.3 Heap leaching (HL)

REEs from IACs are processed by vat/heap leaching (see Figure 5) and in-situ leaching (see Figure 7) methods that enable the economical processing of low-grade ores which could not otherwise be exploited (Petersen, 2016). In copper heap leaching, the ore is agglomerated (see Figure 4) into larger macro-particles that facilitate solution flow through the bed (Ghorbani et al., 2016; Wassink et al., 2013). Agglomeration and heap leaching finds application mostly in copper heap leaching (Ghorbani et al., 2016) where crushed and agglomerated ore is stacked in heaps on an impermeable pad and the leaching solution is irrigated from the top of the ore bed and intermediate leach solution

(ILS) from ‘older’ ore is used to irrigate ‘fresher’ ore, pregnant leach solution (PLS) is collected by a drainage system at the base of the pile and channeled to the PLS pond, which proceeds to copper recovery by solvent extraction (SX) and electro-winning (EW).

For REE leaching from IAC, the processes for separating individual rare earth elements (REE) after leaching utilize the small differences in basicity resulting from the decrease in ionic radius (Panias, 2021). The basicity differences affect the solubility of salts, the hydrolysis of ions, and the complex species formation, and these pave the basis of separation procedures by ion exchange, and solvent extraction of REE.

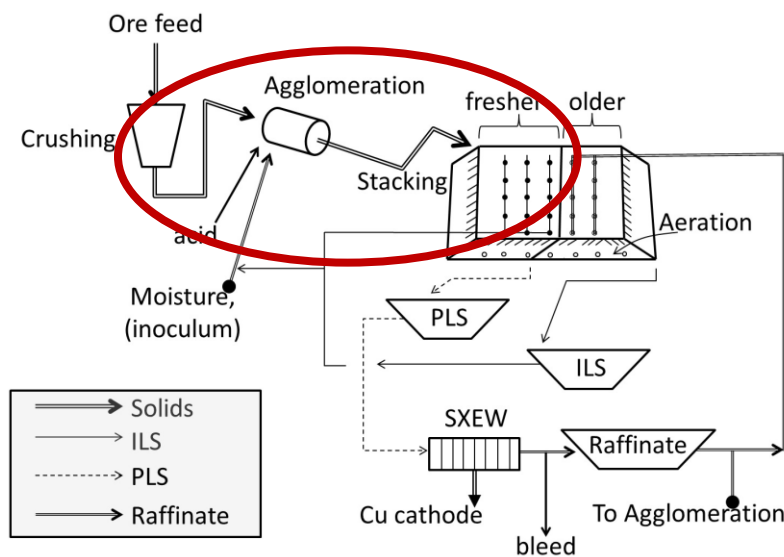


Figure 4: Generic block flow diagram of copper heap leaching. Adapted from van Staden, Naseri & Petersen (2017c)

However, as all percolation leach processes, the heap leaching of REEs from Ion Adsorption ores has ‘speed limits’, for example poor heap permeability and diffusion constraints of reactants in and products out of the clay particles (see Figure 6 for solution flow in inter-particle and intra-particle case scenario) that increases of the time required for maximum recovery of REE from ore, This results in higher operational costs, for example, continuing heap operation for a longer time, use of much higher volumes of leaching reagent, and generating a large amount of effluent that affects the environment and yet with limited recovery of REEs (Kanazawa & Kamitani, 2006; Petersen, 2016; Vahidi et al., 2016).

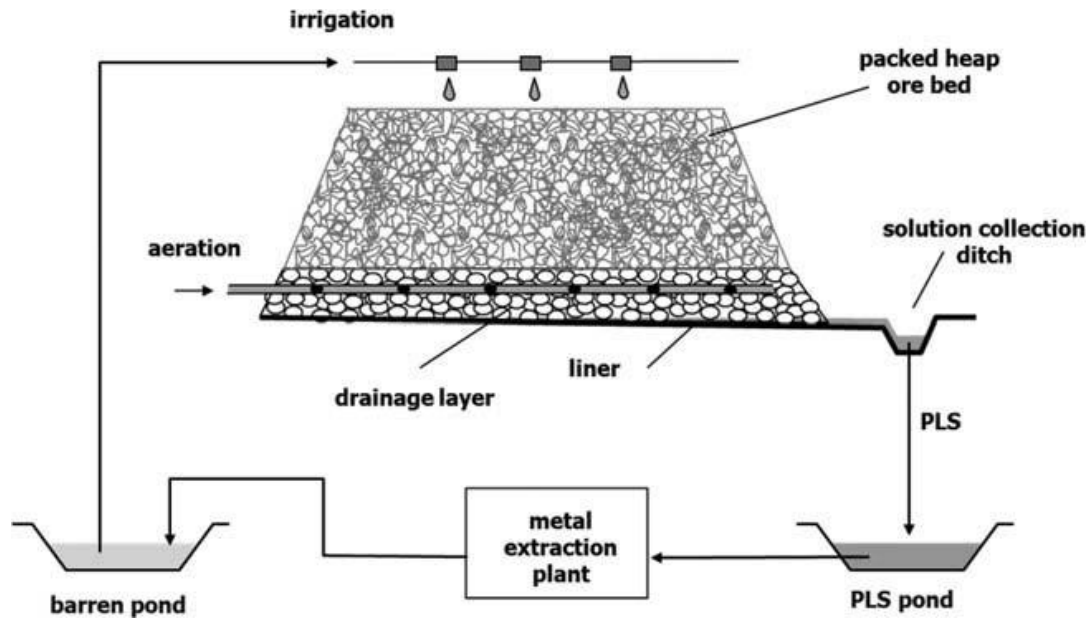


Figure 5: Typical heap bioleach flow diagram for copper adapted from (Ghorbani et al., 2016)

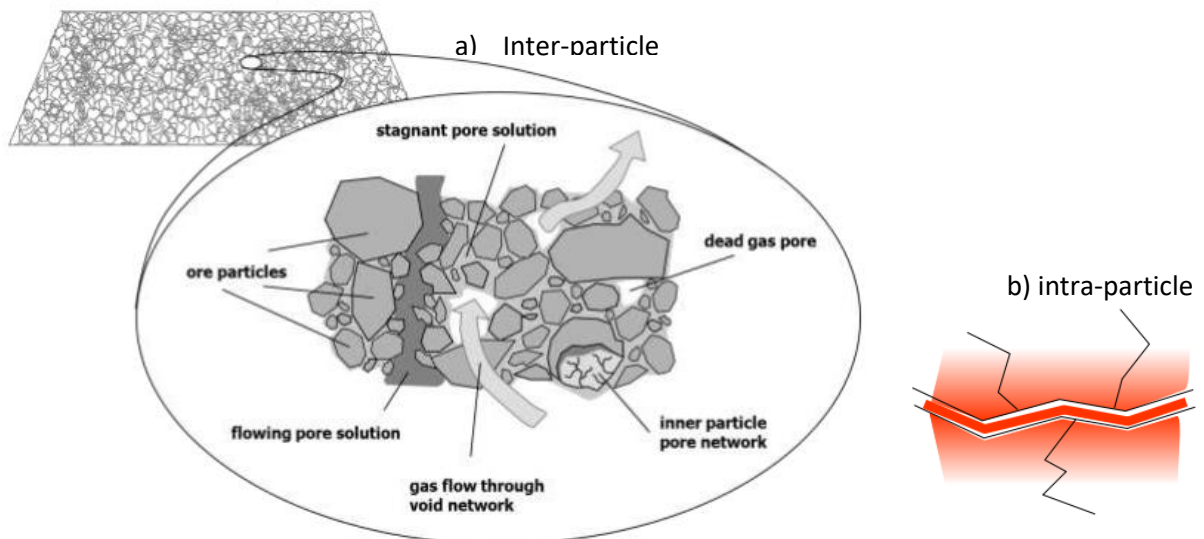


Figure 6: Schematic diagram of inter-particle and intra-particle solution diffusion in heap operation adapted from (Ghorbani et al., 2016)

2.4.4 In-situ leaching (ISL)

During in-situ leaching, the lixiviant is supplied to a certain layer of the unmined clay deposit by injection pipes (Arshi et al., 2018; Vahidi et al., 2016). It seeps through the pores and diffuses through the clay bed then penetrates further through the aggregates to the particles and by

substitution with cations of the lixiviant, the REEs are desorbed from the clay ore to the pregnant leach solution (PLS) that is either pumped back to the surface, or, for deposits in a hill, collected through drainage channels at the base of the deposit for further processing (Vahidi et al., 2016). In-situ leaching is location-specific where a feasible location must have a bedrock to ensure the lixiviant and other reagents do not mix with the underground water (Kanazawa & Kamitani, 2006).

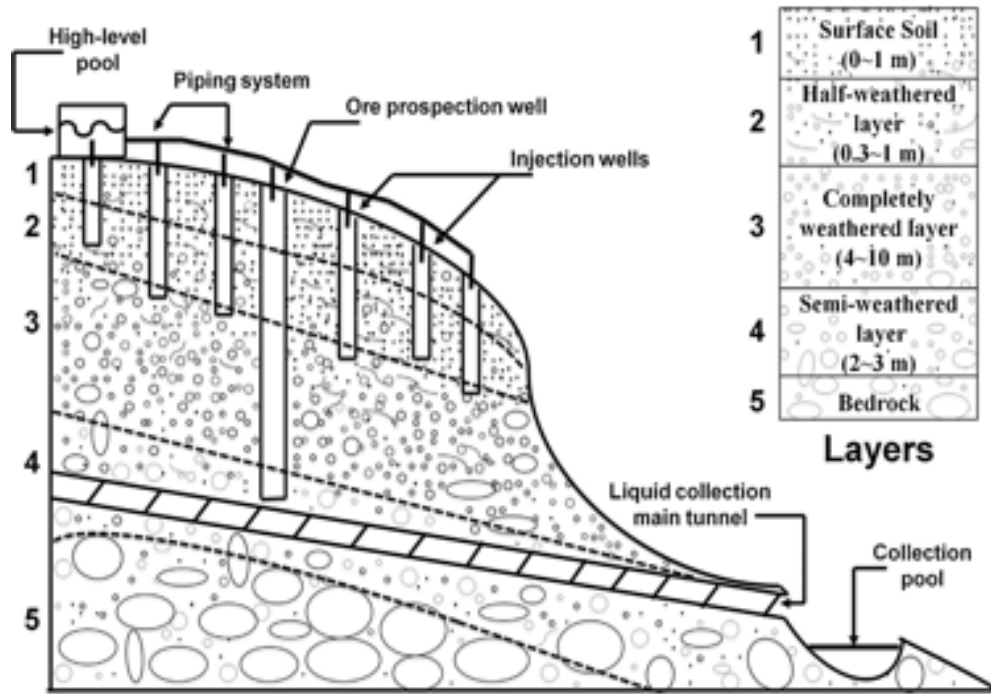


Figure 7: Schematic diagram of In-situ Leaching (adapted from Zou, 2012)

2.4.5 Ore agglomeration

The nonuniform percolation of solution throughout the heap is a common problem caused by the presence of fines (Ghorbani et al., 2016). The solution chooses the path of least resistance called channeling and if enough fines have built up, the solution may not be able to flow to the bottom of the heap this causes clogging in the heap, the solution to this problem agglomeration heap as applied in both gold and copper heap leaching (Ghorbani et al., 2016). Agglomeration helps percolation and reduces the gradual clogging of the heap by fines. Additional additives (binders)

for example cement, and lime, are needed to prevent agglomerates from breaking up as leaching solution percolates through the heap, Garcia and Jorgensen (1997) recommended agglomeration of ore with binder if the ore contains more than 10-15% of fines.

2.4.6 Environmental issues associated with the use of ammonium sulfate in heap/in-situ leaching

The application of ammonium sulfate has serious environmental problems (Kanazawa & Kamitani, 2006) such as ammonia-nitrogen pollution when leaching solution seeps back to the surface effecting vegetation cover, in water bodies when leaching solution gets into the ground water and this can cause further problems for example plant growth difficulties that negatively impact communities living nearby and therefore the need to investigate the use of different lixiviant compositions (Su et al., 2019; Yanfei et al., 2015) for example magnesium sulfate (MgSO_4), aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$), and others instead of $(\text{NH}_4)_2\text{SO}_4$ as lixiviant in the recovery of REEs.

2.5 Agitated tests for IAC ores and their scale-up limitations to un-agitated REE leaching processes

2.5.1 Agitated leach tests

The conventional approach to investigating the solubilization of REEs from IAC materials is through agitated batch leaching tests with lixiviants such as sodium chloride and ammonium sulfate are used to determine the leaching kinetics (Moldoveanu & Papangelakis, 2012; Yanfei et al., 2015) of REE from ion adsorption clays (IAC). The tests were run for 30 minutes even though equilibrium conditions were achieved after 15 minutes however this is still carried out in stirred reactors (Moldoveanu & Papangelakis, 2012, 2013) that have no relationship with the heap leach scenario (Petersen, 2016).

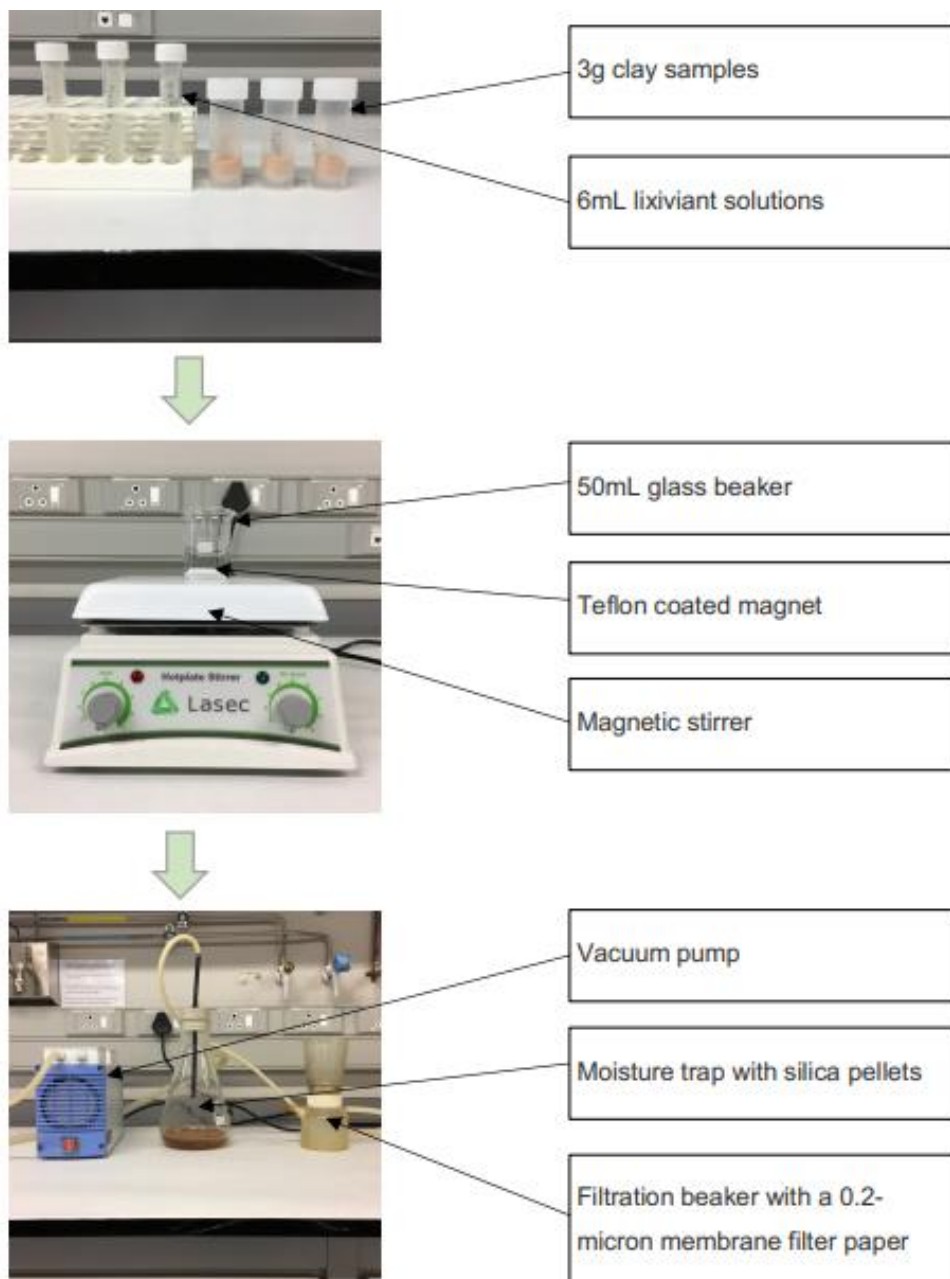


Figure 8: Agitated batch setup adapted from Mkhize (2020)

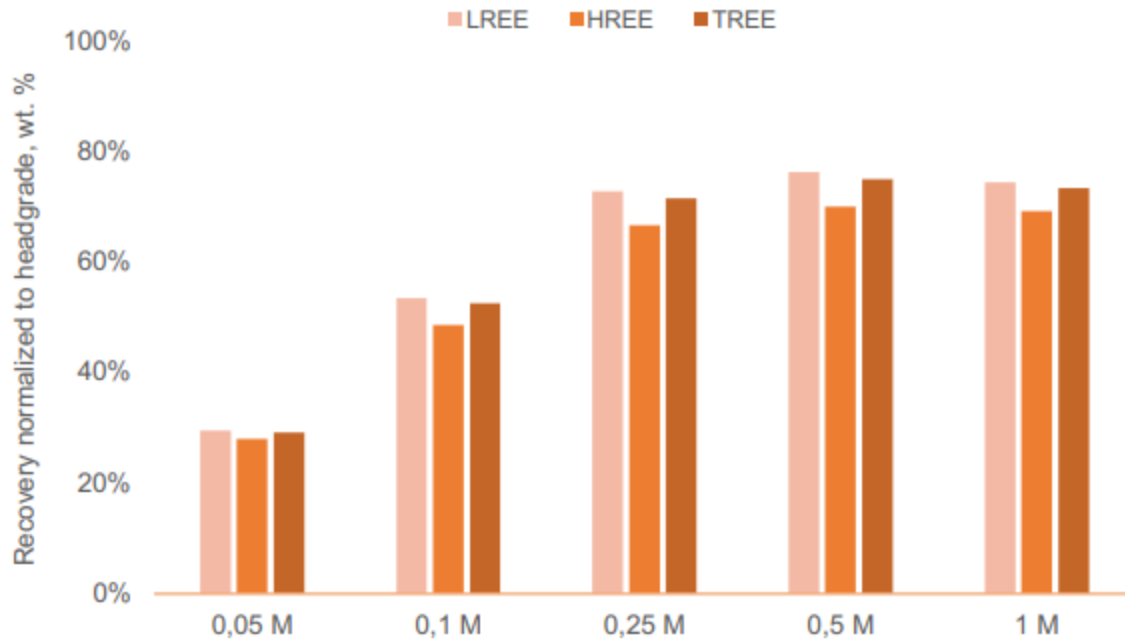


Figure 9: Light REE, Heavy REE, and Total REE extraction efficiency of ammonium sulfate at different concentration of 0.05M, 0.1M, 0.25M, 0.5M and 1.0M adapted from Mkhize (2020)

Mkhize (2020) also investigated the effect of concentration of ammonium sulfate on extent of REE extraction in agitated systems that showed higher concentrations of ammonium sulfate 0.25M, 0.5M, and 1.0M extracted more or less the same percentage of REE.

2.5.2 Un-agitated leach test

Mkhize (2020) carried out diffusion test experiment of REE leaching from IAC when he manually layered a clay ore bed into the bottom of the beaker and observed leaching from this bed into a gently agitated leach solution place above the layer (see Figure 10 and 11).

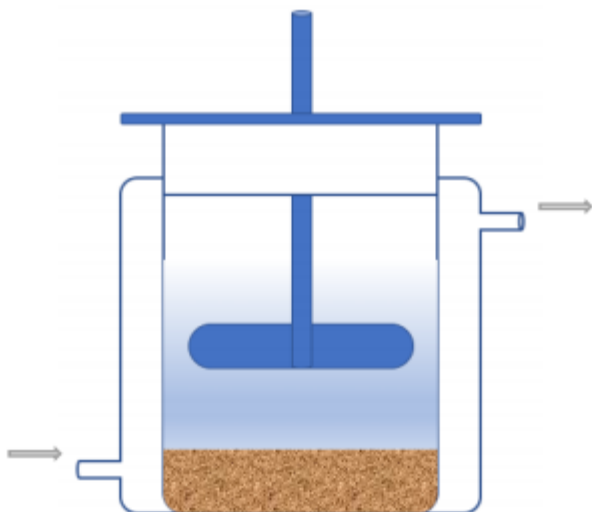


Figure 10: Stagnant bed test setup adapted from Mkhize (2020)

The duration of the diffusion tests was 16 days and the extraction curve levels-off after 12 days of leaching with extent of REE leaching <50%, this setup clearly showed the effect of diffusion constraints on leaching kinetics (see Figure 11)

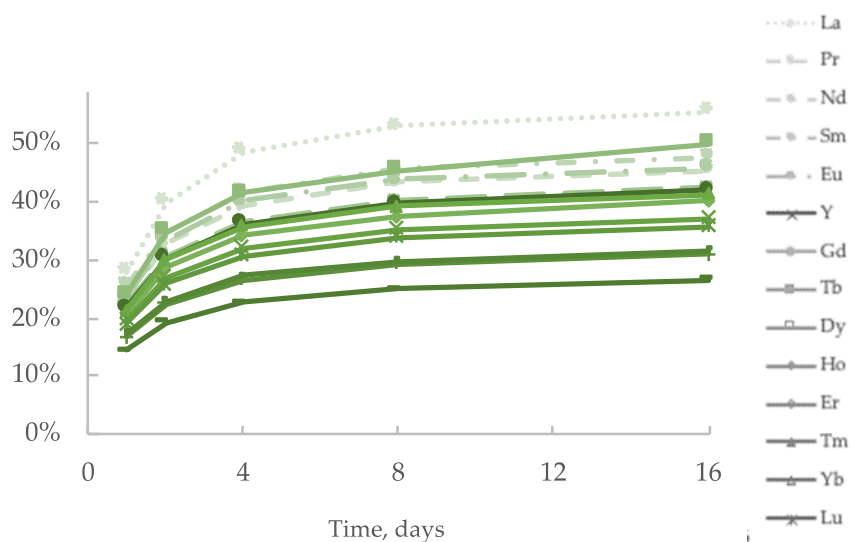


Figure 11: REE Extraction efficiency of Ammonium sulfate in Stagnant Bed test (adapted from Mkhize, 2020)

2.5.3 Column leach tests

Mkhize (2020) also conducted conventional column leaching tests, as illustrated in Figure 12, one of the methods used to investigate the desorption of REE from IAC to mimic solution flow through a bed of such material as it would occur in a heap or in-situ leaching (Ghorbani et al., 2016; Petersen, 2016; Xiao et al., 2016). However, it was found that the percolation through the clay material was very slow and this in cases caused the laboratory column to overflow if the solution could not find a preferential channel through the packed bed (which depended on the quality of the packing).

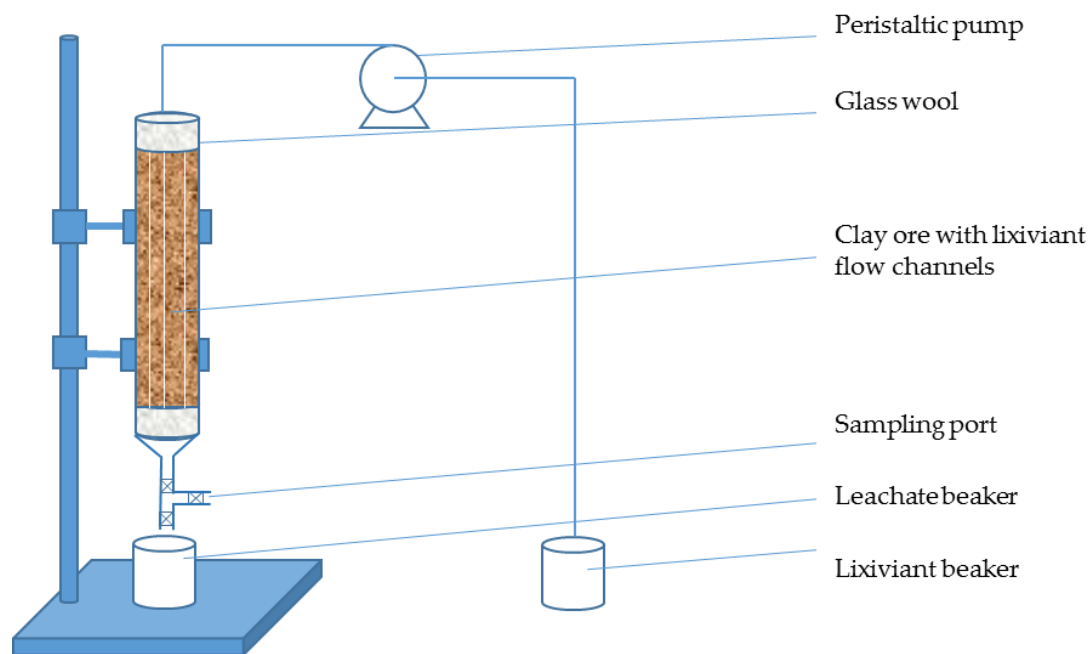


Figure 12: Schematic column leaching setup (Mkhize, 2020)

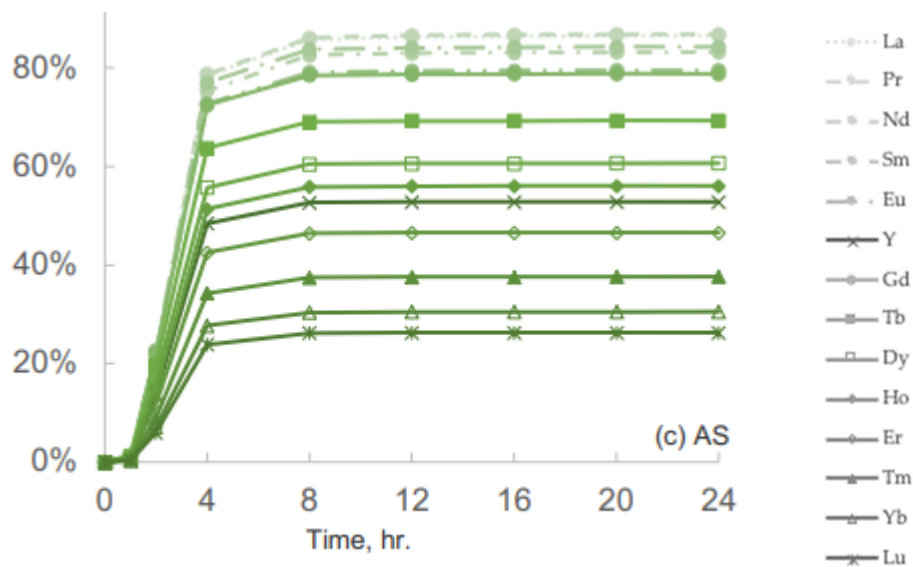


Figure 13: REE extraction efficiency of Ammonium sulfate in column setup adapted from Mkhize (2020)

The extent of REE leaching in small laboratory column was rapid and reached above 80% extraction for highest extracted REE but this test was mainly affected by poor permeability of clay ore and leaching reagent overflow in the laboratory column test.

2.6 Discussion of literature review

Sodium chloride (NaCl) was used historically as a lixiviant to leach REE from IAC however due to lower concentrations required to recover REE from IAC, ammonium sulfate ((NH₄)₂SO₄) was considered a better lixiviant (Moldoveanu & Papangelakis, 2012, 2013). In the leaching process of IAC, the leaching efficiency of REE is expected to be high and the leaching efficiency of impurities to be low, especially the aluminum ions (Yanfei et al., 2015) that interfere with REE recovery during the REE recovery process and high consumption of precipitant. Thus there is a need to make a comparison of the leaching reagent type and varied leaching concentration in an un-agitated system with suitably designed tests.

The poor permeability of clay ore is disadvantageous at the laboratory scale as this causes packed ore columns to overflow or even burst due to pressure differences, unless the lixiviant can flow

through a particular channel induced by packing the micron-sized clay particles that are not agglomerated. There is a need to create numerous independent flow channels by agglomeration of the clay ore to macro-size clay agglomerates and when packed in a column they leave various voids in the clay bed that will prevent lixiviant overflow of the column to enable the continuous leaching of IAC at a constant flowrate as it would have been in a conventional heap leach scenario. Therefore a set of suitable tests need to be developed that allow the determination of the likely kinetic leach behaviour of REE IACs in a n agglomerated heap leach scenario.

3 MATERIALS AND METHODS

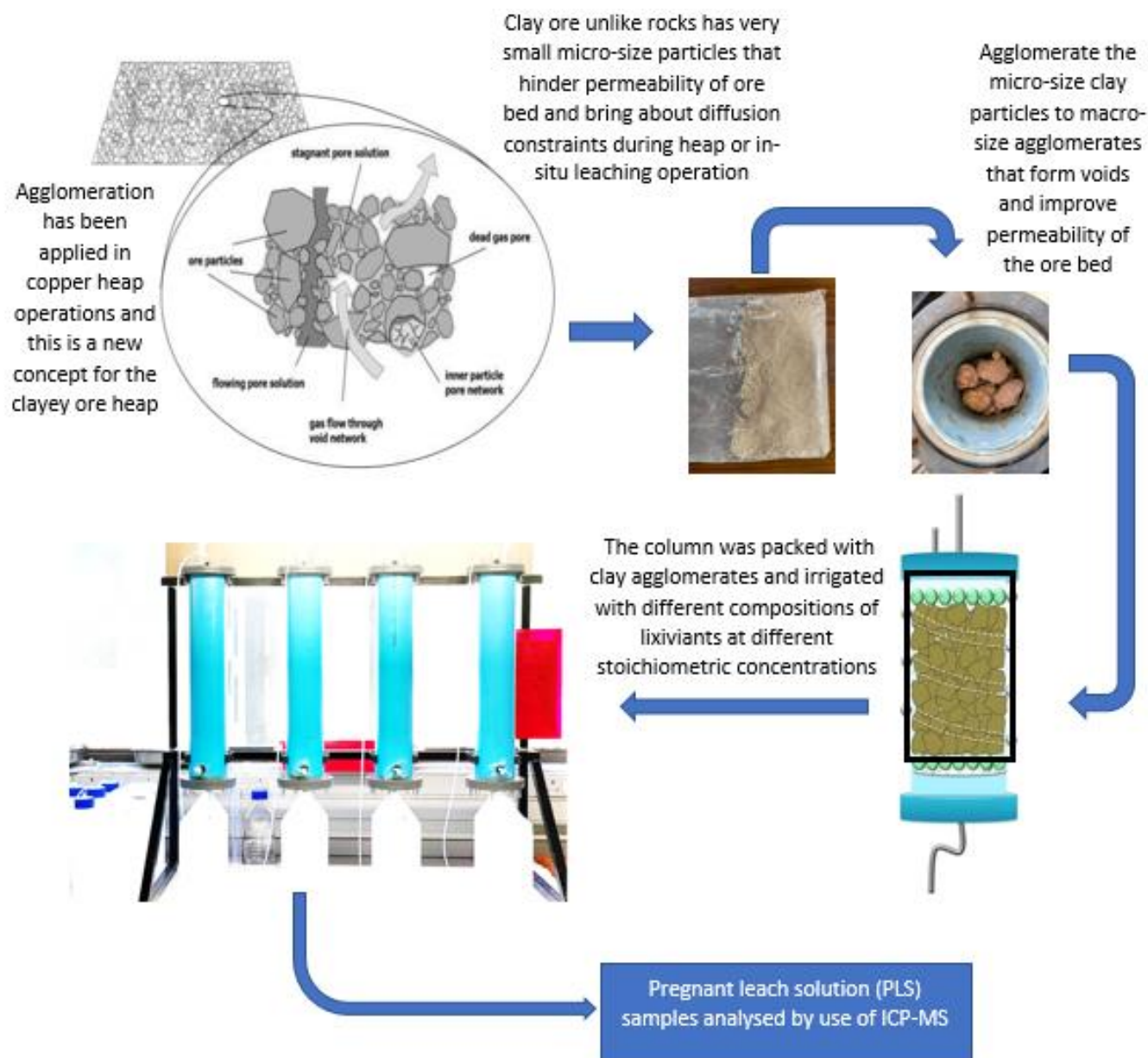


Figure 14: Flowsheet to show the overall experimental approach for agglomerate column leaching

3.1 Materials

3.1.1 Ion-Adsorption Clays (IACs)

Two bulk samples from Madagascar and Uganda were used in the study. The Madagascan ore was previously characterized by (Ram et al., 2019), and sample BTPIT1153 was used in the preliminary study. The characterization of the Ugandan ore was done in context of the present study at the University of Cape Town, and bulk sample RRMDT C1-10 was used in the final study.

Sample preparation

80kg bulk sample was first dried for 24 hours. To attain a representative sample for analysis, the bulk sample was mixed and divided by coning and quartering, then crushed and screened to an under-size of 0.5mm. The crushed sample was split by the 10-way Dickie and Stockler splitter to attain 8kg samples that were further split by the 10-way-1 kg rotary splitter to attain 800g samples that were pulverized to $<1\mu\text{m}$ size and split by a rotary micro riffler to attain 10g samples that were taken for XRD, XRF, and acid digestion combined with ICP-MS analysis.

Acid digestion method

A 50mg homogenized sample was added to 5mL of HF (48% w/w) with 1mL Aqua Regia (1 HNO₃(70% w/w): 3 HCl (37% w/w)) and digested for 5 hours (Ram et al., 2019). The resultant solution was analyzed using a Thermo-Fisher X-series II quadrupole ICP-MS system.

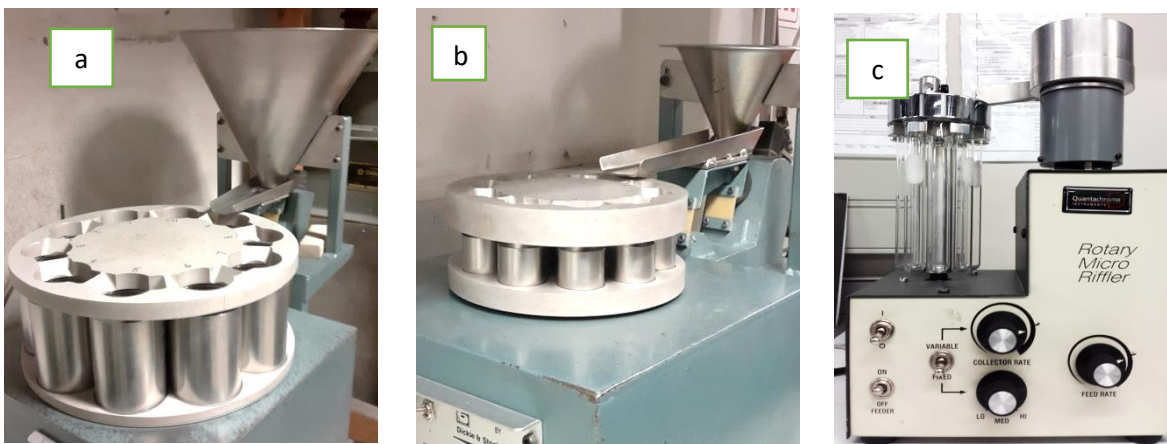


Figure 15: (a) Dickie and Stockler (Pty) 10-way splitter, (b) 10kg rotary splitter, and (c) 1kg Rotary Micro Riffler

The ICP-MS results for the digestion analysis of the two different samples are detailed in the Table 1 below.

Table 1: Results of REE analysis for Madagascan (Ram et al., 2019), and Ugandan ore samples

REE	REE concentration (ppm) of BTPIT1153 (Madagascan ore sample)	REE concentration (ppm) of RRMDT C1-10 (Ugandan ore representative sample)
La	3033	118.7
Ce	458.7	226.2
Pr	557.1	26.25
Nd	1488	85.74
Sm	194.4	16.44
Eu	20.12	3.038
Tb	146.1	2.159
Gd	25.07	14.40
Dy	130.5	11.56
Ho	32.07	2.330

Er	95.83	6.800
Tm	14.56	0.989
Yb	75.92	6.402
Lu	15.09	0.962
Sc	0.0	23.26
Y	922.6	63.48
Total Rare Earth Elements (TREEs)	7209.06	608.71

The XRF results of major oxides of the two samples are in the Table 2 below:

Table 2: Major element oxides determined by XRF for Ugandan ore sample RRMDT C1-10 and Madagascan Sample (Ram et al. 2019)

Major element oxides (wt %)	Sample: F-1153 (Madagascan ore sample)	Sample: RRMDT C1-10 (Uganda ore representative sample)
SiO ₂	45.79	42.74
Al ₂ O ₃	31.44	27.04
Fe ₂ O ₃	4.67	13.92
MnO	0.34	0.13
MgO	Below detection limit	0.56
K ₂ O	1.83	1.44
TiO ₂	0.03	1.25
Na ₂ O	0.44	<0.01
Cr ₂ O ₃	3.37	0.03
V ₂ O ₅	-	0.06
CaO	-	0.30
P ₂ O ₅	-	0.13
H ₂ O	3.37	-

Loss on ignition (wt %)	10.92	11.09
-------------------------	-------	-------

XRD analysis of the Madagascan ore sample was performed by Council for Geoscience in South Africa, to determine whole rock mineralogy is reflected in Table 3 (Ram et al., 2019; Burcher-Jones et al., 2018). Similar analysis for the Ugandan ore was not available at the time of writing.

Table 3: Quantitative analysis of whole rock mineralogy from powder XRD using the Rietveld Method (wt %) (Ram et al., 2019)

Mineral	Sample: F-1153
Kaolinite	68.8
Halloysite-7	18.6
K-feldspar	10.4
Gibbsite	2.2
Hematite	Trace
Quartz	Trace

3.1.2 Reagents

The reagents that were used in the preparation of lixiviants included magnesium chloride hexahydrate, sodium chloride, ammonium sulfate, magnesium sulfate (hydrate), sodium sulfate, and aluminum sulfate supplied by Merck Life Science (Pty) Ltd. Sodium sulfate has unusual solubility characteristics in water causing it to initially harden instead of dissolving; this gave an inaccurate concentration of solution at room temperature. The aluminum sulfate leach product contained a high concentration of aluminum because the aluminum was already present in the leaching reagent, therefore, making the recovery of REE from the solution more difficult because of the presence of aluminum as an impurity in high concentration. Therefore sodium sulfate and aluminum sulfate were excluded from the final test work. The magnesium chloride (hydrate) and magnesium sulfate (hydrate) were considered for reagent preparation because they were less expensive compared to chloride and sulfate counterparts without the hydrate.

Table 4: Reagents used in the preparation of lixivants:-

Reagent	Chemical formula
Sodium chloride	NaCl
Ammonium sulfate	(NH ₄) ₂ SO ₄
Magnesium chloride hexahydrate	MgCl ₂ .6H ₂ O
Magnesium sulfate heptahydrate	MgSO ₄ .7H ₂ O

3.2 Equipment

3.2.1 Column reactors

Column reactors were used to leach REE from clay agglomerates with the use of different leaching reagents (lixivants) in the different columns. The advantage of using column reactors was to mimic the heap leach scenario of REE heap leaching from ion adsorption clays (IAC). The columns that were used in the study were 50cm in height and 9cm in diameter. The column leaching of REE from ion adsorption clays was carried out at a room temperature of 298K. Leaching reagent was pumped into the column via a peristaltic pump at varied flowrates of 0.5L/day, 3L/day, and 5L/day depending on the test experiment as shown in the experimental matrix table. The out-flowing stream of the pregnant leach solution (PLS) was collected in a plastic container. A representation of the column setup is in Figure 16 below.

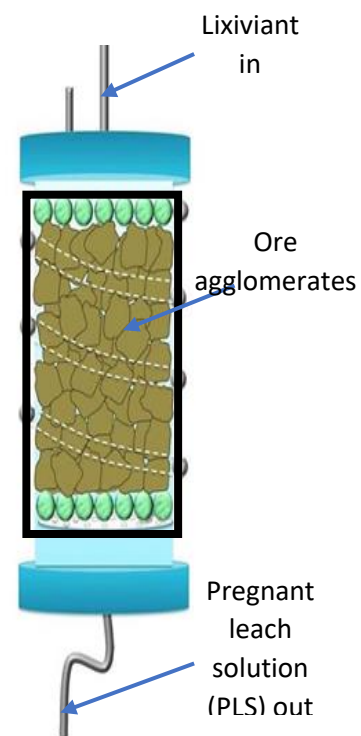
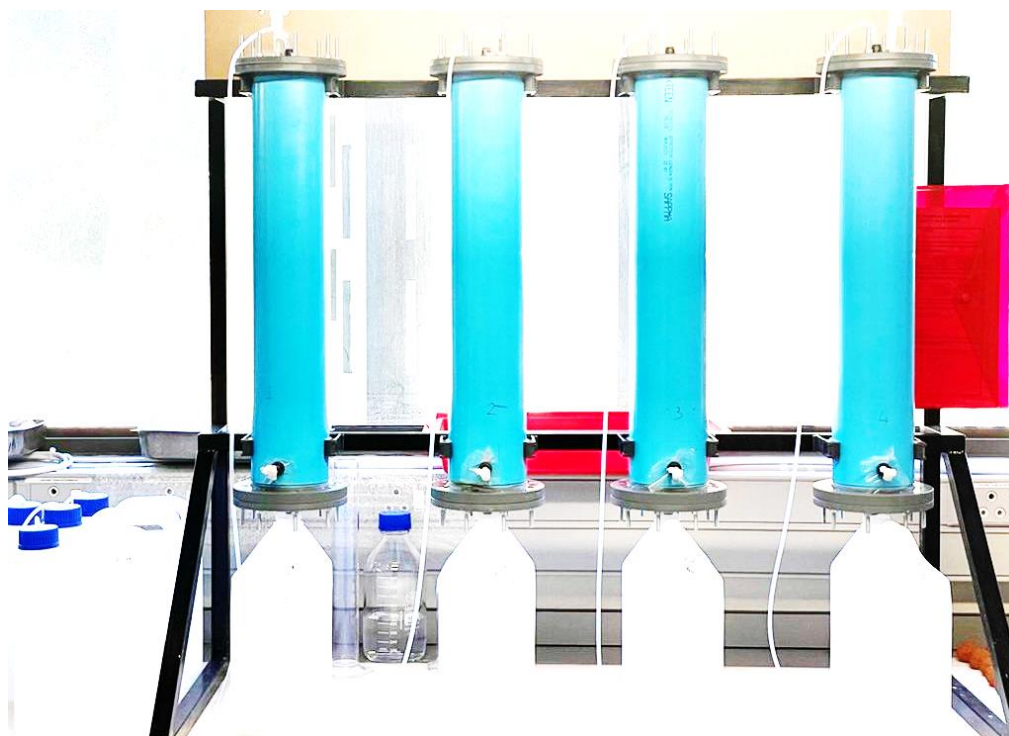


Figure 16: Schematic of column setup

Agglomerate preparation

Before packing the column, approximately 1.8kg of ion adsorption clay was mixed with deionized water to form a slurry with a solid-to-liquid ratio of 3:2. The slurry was rolled into uniform balls of sizes in the range of (2.5-3.5cm). The agglomeration procedure was highly manual by hand and it was not possible to attain one particular size of agglomerate but rather in a range of (2.5-3.5cm). The agglomerate balls were dried for 24 hours at 298K (see Figure 17) and then packed in the column.



Figure 17: Air drying of the agglomerated clay balls

3.2.2 Suspended ball reactors

Suspended ball reactors were used to test the effect of agglomerate size on the REE leaching from ion adsorption clays (IAC). In this reactor, as shown in Figure 18, an individual agglomerate ball is suspended in a closed glass vessel through using Nylon stocking material. The Nylon webbing also ensure the physical integrity of the agglomerate was maintained. The reactors were equipped with a leaching reagent (lixiviant) in-flow stream which dripped onto the ball and pregnant leach solution (PLS) out-flow stream from the bottom of the vessel via a peristaltic pump. In addition, the vessel was sitting on a magnetic stirrer to keep the pregnant leach solution (PLS) that collected at the bottom uniformly stirred before it is withdrawn from the reactor. The set-up is intended to allow leaching from the inside of ball to proceed via diffusion in and out of the solution flowing on the outside. The test was carried out at a room temperature of 298K and the was scaled down from 3L/day to 0.5L/day because the column cross-section area was 15times larger than the agglomerate ball (i.e the ratio of the cross-sectional area of the ball relative to the cross sectional area of the column) therefore the need to reduce the flow-rate in the suspended ball reactors and

0.5L/day was least possible flow-rate that was achieved for this suspended ball reactor setup (see Appendix A).

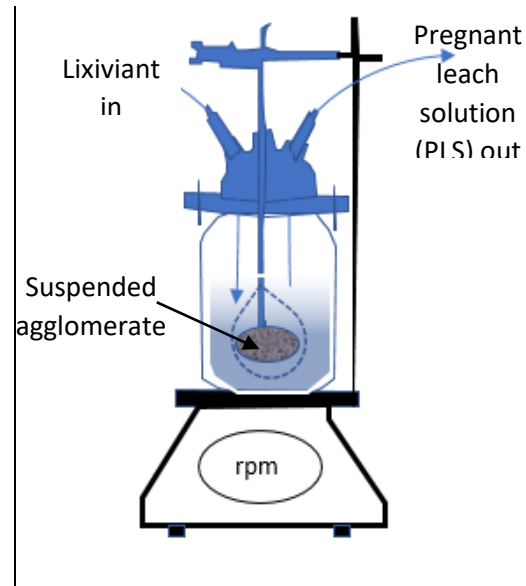


Figure 18: Schematic of Suspended agglomerate reactor

3.2.3 Agitated batch reactors

The agitated batch reactor or stirred batch reactor was a glass beaker of 100ml placed on a magnetic stirrer and the magnetic stirrer was set at 1100rpm the highest speed for stable stirring without risking damage to the glassware of the reactor setup. The stirred test was carried out at a room temperature of 298K and the lixiviant was added to the 30g clay in the reactor at a solid-to-liquid ratio of 1:2. The PLS samples were collected off at 0.5, 1, 2, 4, 8, 24, 60 minutes leaching times. A centrifuge was used for solid-liquid separation and the solution was taken for ICP-MS analysis.

3.3 Methods

3.3.1 Phase 1: Test work on Madagascan ore

Agglomerate column leaching of Madagascan IAC at 5L/day flowrate, pH 3-4 and 298K operating conditions. The pH was closely monitored by measuring each time before taking a sample and was found to be between 3 to 4 and on a rare occasion it would reach 5 but on average pH 3-4.

The leaching reagents that were used in the test work on the Madagascan ore were ammonium sulfate and magnesium chloride at 0.5M and 0.25M, respectively. 0.5M ammonium sulfate was used to test for maximum extraction of REE from ion adsorption clay agglomerates.

0.25M MgCl_2 and 0.5M $(\text{NH}_4)_2\text{SO}_4$ cannot be directly compared because they differ in terms of the concentration of positive charges. 0.25M MgCl_2 contributes 0.5M Mg^{2+} , and 0.5M $(\text{NH}_4)_2\text{SO}_4$ contributes 1M NH_4^+ .

0.25M magnesium chloride is concentrated enough in the given context to extract REE to a sufficient degree from ion adsorption clays.

The test work on the Madagascan IAC was carried out while awaiting the Ugandan bulk sample.

3.3.2 Phase 2: Test work on Ugandan ore

The leaching reagents that were used in the final test work on the Ugandan ore were ammonium sulfate, sodium chloride, magnesium chloride, and magnesium sulfate. The operating conditions were 298K, and pH 3-4. The pH was closely monitored by measuring each time before taking a sample and was found to be between 3 to 4 and on a rare occasion it would reach 5 but on average pH 3-4. The full test work experimental plan is detailed in Table 5 below overleaf.

Table 5: Experimental matrix for test work on Ugandan sample

Column reactors	Flowrate (L/day)	0.5	0.5	0.5	0.5	3	5	0.5
	Size range of agglomerates (cm)	2.5-3.5	2.5-3.5-3.5	2.5-3.5	2.5-3.5	2.5-3.5	2.5-3.5	2.5-3.5
	Lixiviant type	NaCl	(NH ₄) ₂ SO ₄	Mg(Cl) ₂	MgSO ₄	(NH ₄) ₂ SO ₄	(NH ₄) ₂ SO ₄	(NH ₄) ₂ SO ₄
	Agglomerate with	DI water	DI water	DI water	DI water	DI water	DI water	(NH ₄) ₂ SO ₄
	Rinse with	NaCl	(NH ₄) ₂ SO ₄	Mg(Cl) ₂	MgSO ₄	(NH ₄) ₂ SO ₄	(NH ₄) ₂ SO ₄	DI water
Lixiviant concentration (M)	0.5 (half strength)	1.5	0.75	0.75	0.75	0.75	0.75	0.75
	1.0 (full strength)	3	1.5	1.5	1.5			
Suspended ball reactor (SBR)	Flowrate (L/day)	0.5	0.5	0.5	0.5	0.5	0.5	
	Size of agglomerate (cm)	3.0	3.0	3.0	3.0	2.5	3.5	
Lixiviant concentration (M)	0.5 (half strength)	1.5	0.75	0.75	0.75	0.75	0.75	
	1.0 (full strength)	3	1.5	1.5	1.5			

Agitated batch reactor	Agitation rate (rpm)	1100	1100	1100	1100			
	Size of agglomerate (mm)	<1mm	<1mm	<1mm	<1mm			
Lixiviant concentration (M)	0.5 (half strength)	1.5	0.75	0.75	0.75			
	1.0 (full strength)	3	1.5	1.5	1.5			

3.3.3 Elemental analysis of solutions

The REE composition of the pregnant leach solution (PLS) was analyzed by ICP-MS at the Central Analytical Facilities at Stellenbosch University.

The REE extraction of lixivants was determined by use of the equation 6 below:

$$\varphi = \frac{\varepsilon_V}{\varepsilon_O} \quad \text{Equation 6}$$

Where φ is REE extraction, ε_O is the total amount of the ion-adsorption rare earth in the original ore sample, ε_V is the total amount of rare earth in leaching solution at volume V

4 RESULTS AND DISCUSSION

4.1 Test work on the Madagascan ore

4.1.1 Effect of sulfate system on leaching of REE from Madagascan IAC

The operating conditions of agglomerate column leaching of Madagascan IAC when using 0.5M ammonium sulfate as the leaching agent were 5L/day flowrate, pH 3-4, and temperature maintained at 298K.

The agglomerate size varied from 2.5cm to 3.5cm and all these sizes of agglomerates were packed together in the column. The reason is because the agglomeration process was highly manual and the sizes of agglomerates were not uniform but in a range of 2.5cm to 3.5cm.

0.5M ammonium sulfate was used to leach rare earth elements from ion-adsorption clay in the agglomerate column leaching of the Madagascan sample that was well characterized (Ram et al., 2019). The preliminary test work was done on the Madagascan ion adsorption clay while awaiting the Ugandan ion adsorption clay bulk sample for more test work. From the literature, higher concentrations above 0.5M ammonium sulfate extract approximately the same percentage of REE from ion-adsorption clay (Mkhize, 2020; Moldoveanu & Papangelakis, 2013). Therefore there was no need for testing for lower concentrations of ammonium sulfate.

0.5M $(\text{NH}_4)_2\text{SO}_4$ contributes 1M NH_4^+ that is concentrated enough to extract of REE to a sufficient degree from the Madagascan ore.

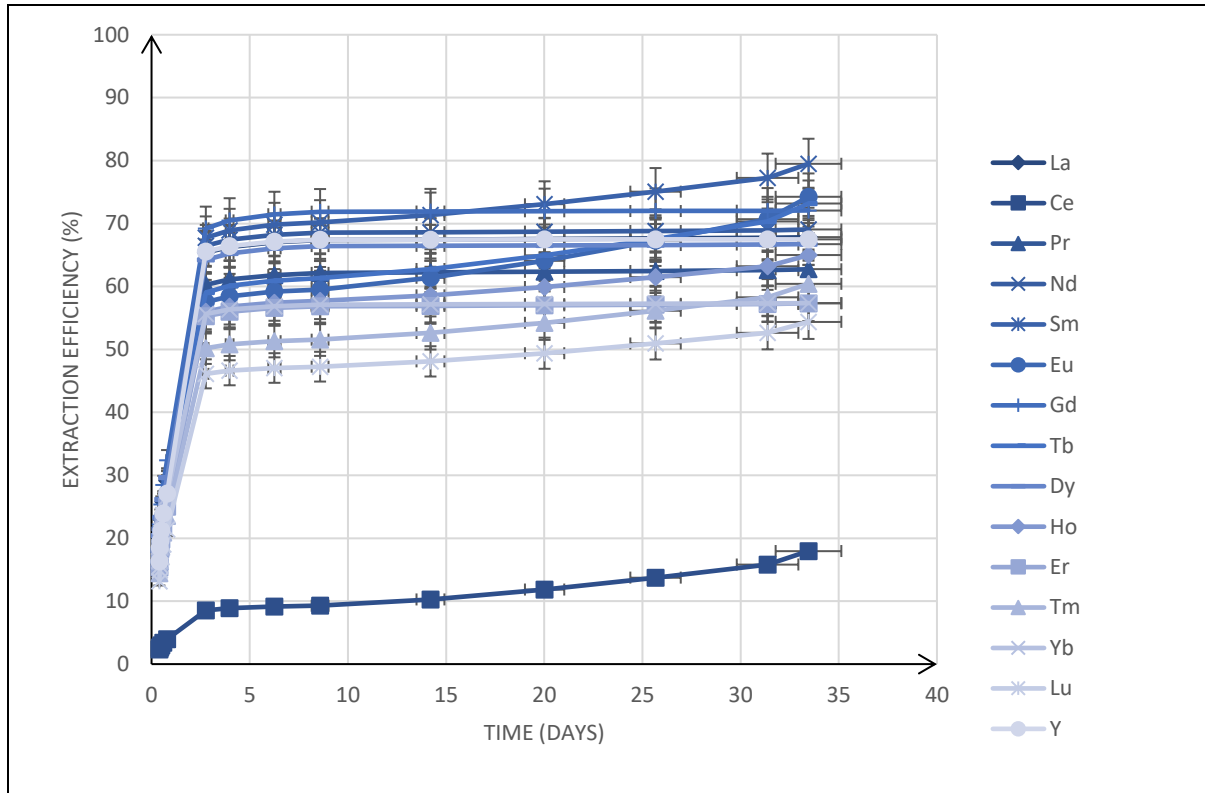


Figure 19: REE extraction efficiency of 0.5M ammonium sulfate at 3L/day flowrate, 298K, and pH 3-4

The extraction curve of 0.5M ammonium sulfate (see Figure 19) shows rapid extraction within the first three days leaching time to reach over 70% for the highest extracted REE, Gd, and then levels off for the next ten days. The PLS was collected daily in 5L plastic container and this was later transferred to 20L plastic containers and this meant that beyond 12 days of leaching, there was over 20L of pregnant leach solution (PLS) and yet less extraction was taking place therefore a more dilute PLS product maybe got after 12 days of leaching. The extraction curve of 0.5M ammonium sulfate in agglomerate column leaching setup is significantly different where REE extractions are above 50% compared to the extraction curve of the stagnant batch leach test in Figure 11 where REE extractions are below 50%. This was attributed to the independent lixiviant flow channels created when agglomerates are packed in a column compared to when fine clay particles are layered in a bed and the lixiviant has to force itself to flow through a certain channel that may not uniformly distribute the leaching agent throughout the whole clay sample being leached.

4.1.2 Effect of chloride system on leaching of REE from Madagascan IAC

From literature (see Figure 9), 0.25M and 0.5M of the ammonium sulfate system leach approximately the same REE percentage extractions (Mkhize, 2020; Moldoveanu & Papangelakis, 2012) however this was done in agitated systems and not in un-agitated systems, 0.25M Magnesium chloride is concentrated enough in the given context to extract REE to a sufficient degree.

The operating conditions for agglomerate column leaching of Madagascan IAC when using 0.25M magnesium chloride as the leaching agent are 5L/day flowrate, pH 3-4, and temperature maintained at 298K.

The agglomerate size varied from 2.5cm to 3.5cm and all these sizes of agglomerates were packed together in the column. The reason is because the agglomeration process was highly manual and the sizes of agglomerates were not uniform but in a range of 2.5cm to 3.5cm.

The extraction curve of magnesium chloride system (see Figure 20) is different from the ammonium sulfate system, here the curve increases gradually for 10 days before levelling off and does so at much lower extraction levels.

Extraction of REE from ion-adsorption clays is rapid as over 45% of highest extracted REE, Gd, is reached within 10 days of leaching and only 5% is extracted for the next 20 days to reach a maximum extraction of 50% for Gd whereas Lu only reached a maximum extraction of 10%.

Because of less Madagascan IAC sample provided, test works of this sample were few and this was one of the reasons that more test work was done on the bulk Ugandan IAC sample.

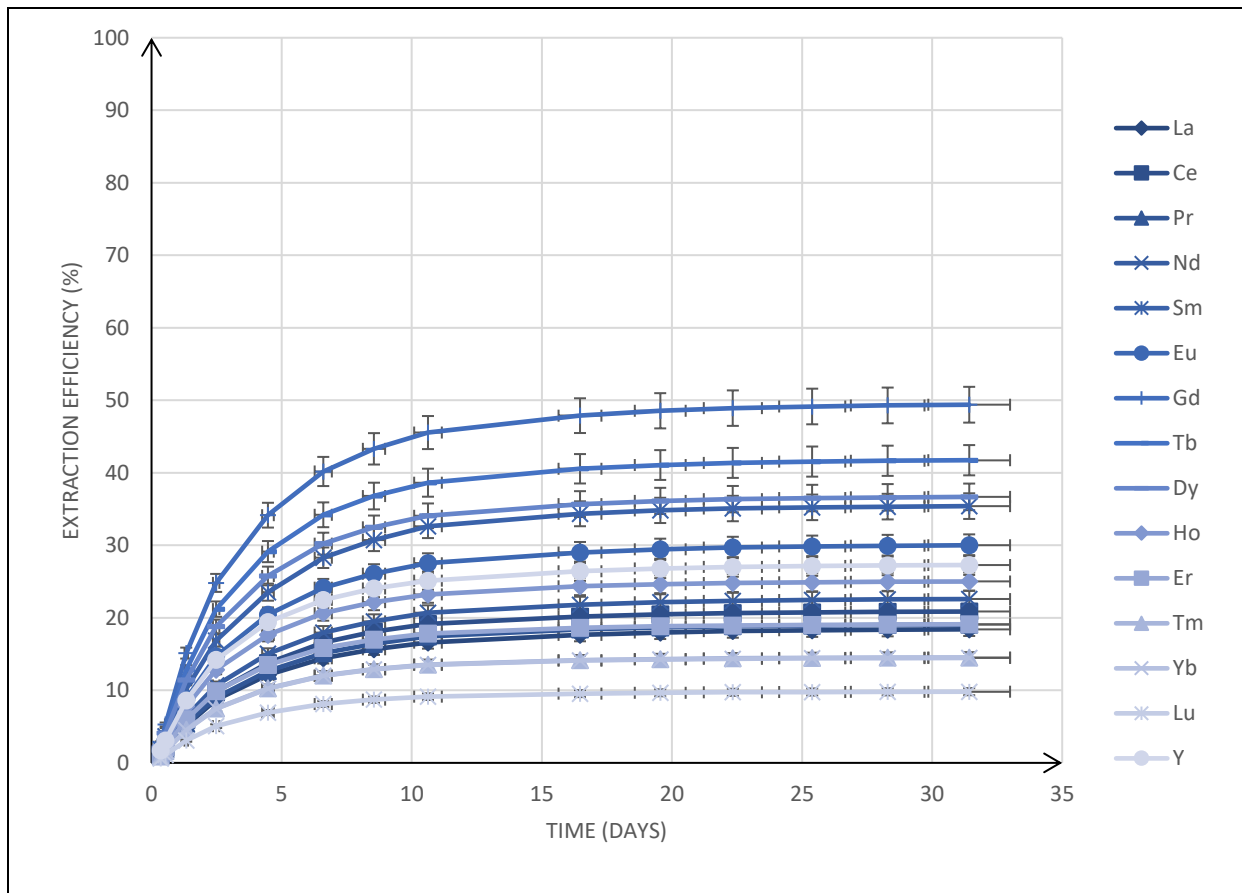


Figure 20: REE extraction efficiency of 0.25M magnesium chloride at 3L/day flowrate, 298K, and pH 3-4

4.2 Test work on Ugandan ore

From the graphs illustrated below, the column leaching time was reduced to a maximum of 12 days because a steady state was reached between 10 to 15 days from the test work done on the Madagascan ore, and therefore around 12 leaching days were used during the test work on the Ugandan ore.

A comparison of these reagents at a low concentration below 0.5M was already done in previous literature (Moldoveanu & Papangelakis, 2012), so the present test work was done at a slightly higher concentration of 0.75M or more.

4.2.1 Effect of Reagent flow-rate on column leaching

The flow-rate experiment was carried out to test for effect of leaching reagent flowrate on agglomerate column leaching. Three different columns were setup at different flow-rates of 0.5L/day, 3L/day, and 5L/day. This meant that it takes about 10 days to collect 5L PLS when using 0.5L/day whereas it takes 1 day to collect 5L PLS when using 5L/day flowrate, and there was need to compare percentage REE extractions at approximately the same volume of PLS collected that is 5L volume of plastic container used.

The operating conditions for agglomerate column leaching of Ugandan IAC when using 0.75M ammonium sulfate as the leaching agent to test for effect of flow-rate on agglomerate column leaching are flowrate 0.5L/day, 3L/day, 5L/day varied in three different columns and all the three columns were maintained at pH 3-4, and temperature at 298K.

The agglomerate size varied from 2.5cm to 3.5cm and all these sizes of agglomerates were packed together in the column. The reason is because the agglomeration process was highly manual and the sizes of agglomerates were not uniform but in a range of 2.5cm to 3.5cm.

From Figure 21 below, the 3L/day and 5L/day flow-rates yielded very similar results however the very slow flow rate of 0.5L/day yielded lower percentage extraction of REE even after 10 days of leaching and yet at increased flow rates of 5L/day and 3L/day, 40% extraction of Yttrium (as the highest extracted REE) was reached in less than one day of leaching. 0.5L/day only reached 10% extraction of Yttrium in 1 day and 34% extraction of Yttrium in 5 days. A steady state was reached within 24 hours when using a 3L/day flow rate whereas a 5L/day flow rate showed higher extraction of 43% Yttrium compared to a 40% Yttrium extraction that leveled off in 24 hours at a 3L/day flow rate.

The higher flow rates of 5L/day and 3L/day extracted more REE compared to 0.5L/day. The problem is at higher flow rates there is the risk of overflowing the column with the leaching reagent this is because the stability of ore agglomerates packed in the column reduces faster with the increase in the flow rate of leaching reagent.

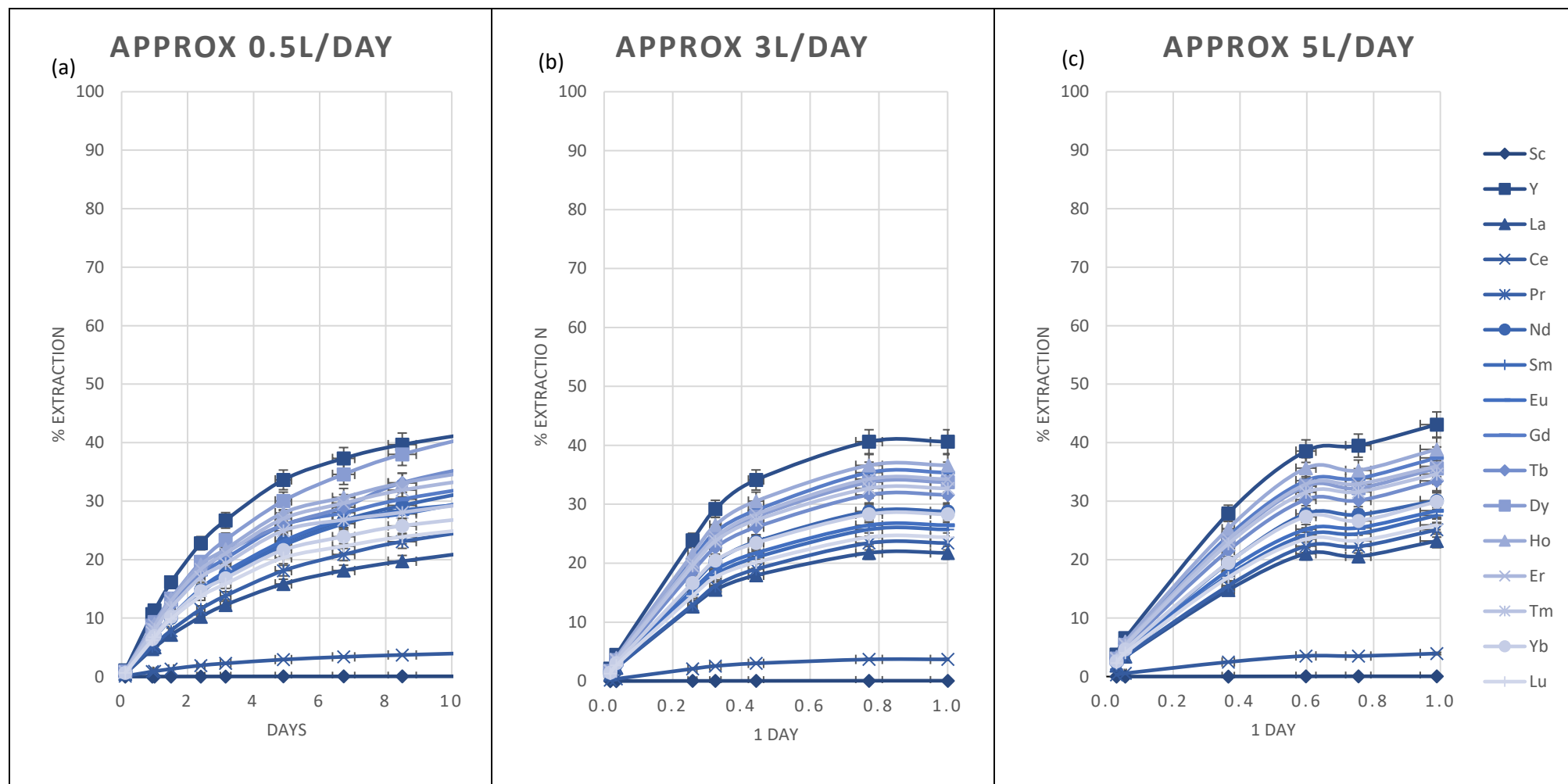


Figure 21: REE extraction efficiency of 0.75M ammonium sulfate at different flow rates of (a) 0.5L/day, (b) 3L/day, and (c) 5L/day

4.2.2 Effect of agglomerate size on column/suspended agglomerate leaching

The agglomerate size was varied in this experiment to test for effect of agglomerate size on column/suspended agglomerate leaching. Three different columns and three different suspended ball reactors were setup and each pair of column and suspended ball reactor was to have a particular size of agglomerate for example column 1 and suspended ball reactor 1 to have 2.5cm agglomerate size, column 2 and suspended ball reactor 2 to have 3.0cm agglomerate size, and column 3 and suspended ball reactor 3 to have 3.5cm agglomerate size. However, the agglomeration of clay particles was highly a manual process and the sizes of agglomerates were not uniform but rather in a range of 2.5cm to 3.5cm, this meant that manually agglomerating over 100 clay balls to one particular size for example 2.5cm that fill-up a column when the agglomeration process is not mechanized was nearly a impossible task. Still the experiment was conducted but instead of manually agglomerating over 100 clay balls of one particular size , only one agglomerate for example 2.5cm was manually made for one suspended ball reactor, this meant that only three balls (clay agglomerates) at different sizes (2.5cm, 3.0cm, and 3.5cm) were made and the three different ball sizes were used in only three different suspended ball reactors.

The effect of agglomerate size on column leaching was not done in the columns setup but this effect of agglomerate size was tested in suspended ball reactors and the reason was because the agglomeration process was highly manual and the sizes of agglomerates were not uniform but in a range of 2.5cm to 3.5cm and only one agglomerate ball at a particular size was used in the suspended ball reactor.

The agglomerate balls weighed averagely 20g and a solid to liquid ratio of 1:2 was used this meant that twice the volume occupied by the agglomerate was the amount of leaching reagent added to the reactor, the PLS is collected off at 0.5h, 1h, 2h, 4h, 6h, 12h, 24h, 48h, 72h, 120h, and 216h. A small amount of leaching reagent was topped-up during PLS collection to maintain the 1:2 solid to liquid ratio.

The operating conditions for the suspended ball agglomerate leaching of Ugandan IAC when using 0.75M ammonium sulfate as the leaching agent to test for effect of agglomerate size on column/suspended agglomerate leaching are agglomerate sizes: 2.5cm, 3.0cm, 3.5cm varied in

three different suspended ball reactors and all the three suspended ball reactors were maintained at pH 3-4, and temperature at 298K.

From Figure 22 below, the different agglomerate sizes (2.5cm, 3.0cm, 3.5cm) were leached at flowrate of 0.5L/day to increase residence time and also because the suspended ball reactor is a small setup there was need to minimize the effect of a higher flowrates when leaching one clay ball (agglomerate) instead of over 100 clay balls in a column reactor, the suspended ball setup was run for 5 days at 0.5L/day flow-rate and after 5 days of leaching there was excessive evaporation of PLS from the reactor and disintegration of agglomerate balls therefore inaccurate extractions obtained beyond 5 days leaching time. The 2.5cm agglomerate size only extracted slightly above 20% Yttrium however the 3.0cm agglomerate size showed higher percentage extraction at 54% Yttrium (as the highest extracted REE) and 50% Yttrium extraction obtained when using 3.5cm agglomerate size, this showed that moderately larger agglomerate sizes of ore leach better than smaller agglomerate sizes, this is attributed to less surface area that limits diffusion of leaching reagent into the agglomerate.

The suspended ball experiments still proceeded substantially faster than the stagnant bed experiments by Mkhize (2020), although these beds were quite shallow (10mm) they took in the order of 30 days to achieve equilibrium extraction and could be modelled as diffusion only. Hence it needs to be assumed that in the irrigated agglomerate there is a degree of flow through the agglomerate, at least near the surface, and so the leaching mechanism may be driven by combination of diffusion and permeation.

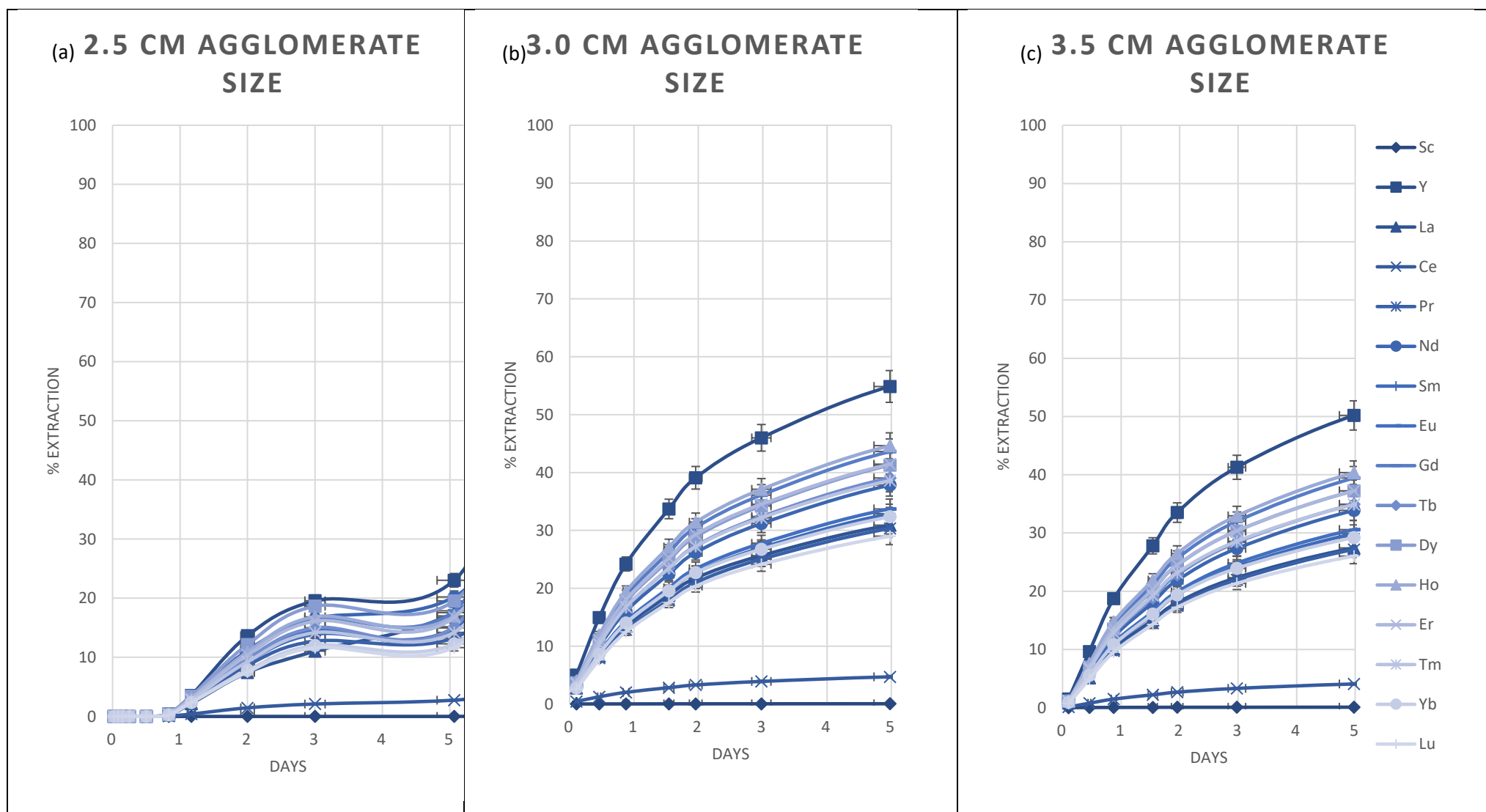


Figure 22: REE extraction efficiency of 0.75M ammonium sulfate at different agglomerate sizes of (a) 2.5cm, (b) 3.0cm, and (c) 3.5cm in the suspended ball reactor setup and operating conditions were: 0.5L/day flowrate, pH 3-4, and temperature maintained at 298K

4.2.3 Effect of reagent type and concentration the three different reactor setups: stirred batch reactor, column reactor and suspended ball reactor.

As stated in Section 6.1.2 Chi and Tian (2012) the Rare Earth (RE) leaching efficiency depends on the electrolyte property; that is to say the different leaching reagents have different leaching ability.

The different reagents that were used in the test work on the Ugandan ore included: ammonium sulfate (AS), magnesium sulfate (MS), sodium chloride (NC), and magnesium chloride (MC).

The difference between the total concentration of charge in cations NH_4^+ , Na^+ , and Mg^{2+} in the lixiviant and the actual salt concentration is significant for example in 0.75M $(\text{NH}_4)_2\text{SO}_4$ there are 1.5 moles NH_4^+ (double the concentration of the salt), 1.5M NaCl there are 1.5 moles of Na^+ , and 0.75M MgSO_4 there are 0.75 moles of Mg^{2+} but this brings twice as much charge concentration as 0.75M NaCl and is similar to 0.75M $(\text{NH}_4)_2\text{SO}_4$.

The various reagents were tested in stirred batch reactor, suspended ball reactor and column reactors as detailed in the following.

4.2.3.1 Stirred batch reactor extractions

The stirred batch reactor setup was used to test for effect of reagent type and reagent concentration on REE leaching in agitated systems in comparison with un-agitated systems. Eight different stirred batch reactors were setup at the same agitation rate of 1100rpm, different reagents ($(\text{NH}_4)_2\text{SO}_4$, NaCl, MgCl_2 , and MgSO_4) were varied in pairs of four stirred reactors to make the total of eight stirred reactors, and the reagent concentration was increased from 0.5 (half concentration strength) to 1.0 (full concentration strength) in all the eight reactors, this meant that the first four reactors were ran as a single batch at 0.5 (half concentration strength) (see Figures 23-26) and more four reactors were ran in the second batch at 1.0 (full concentration strength) (see Figure 27) to make a total of eight stirred batch reactors for this test.

This meant that $(\text{NH}_4)_2\text{SO}_4$ was used in two different stirred reactors at two different concentrations 0.75M and 1.5M, NaCl was also used in two different stirred reactors at two different concentrations 1.5M and 3.0M, MgCl_2 was as well used in two different stirred reactors at two different concentration 0.75M and 1.5M, MgSO_4 was also used in two different stirred reactors at two different concentrations 0.75M and 1.5M.

The operating conditions for stirred batch leaching of Ugandan IAC when using $((\text{NH}_4)_2\text{SO}_4$, NaCl, MgCl_2 , and MgSO_4) as different leaching reagents at different concentrations ($(\text{NH}_4)_2\text{SO}_4$ at two concentrations 0.75M and 1.5M, NaCl at two concentrations 1.5M and 3.0M, MgCl_2 at two concentrations 0.75M and 1.5M, and MgSO_4 at two concentrations 0.75M and 1.5M) to test for effect of reagent type and reagent concentration on stirred batch leaching in comparison of REE leaching in agitated systems and REE leaching in un-agitated systems was done in eight stirred batch reactors maintained at pH 3-4, 0.5L/day flowrate, <1mm particle size and temperature at 298K. The stirred batch reactor extraction curves were later compared to column reactor extraction curves and suspended ball (agglomerate) reactor extraction curves.

The leaching curves of $(\text{NH}_4)_2\text{SO}_4$, NaCl, MgCl_2 are fairly similar after 12 to 15 minutes leaching time in stirred batch reactors apart from MgSO_4 whose extent of REE leaching is relatively slow. The extent of leaching-of $0.75\text{M } (\text{NH}_4)_2\text{SO}_4 > 0.75\text{M } \text{MgSO}_4 > 0.75\text{M } \text{MgCl}_2 > 1.5\text{M } \text{NaCl}$. $0.75\text{M } (\text{NH}_4)_2\text{SO}_4$ extracted 55% Y, $0.75\text{M } \text{MgSO}_4$ extracted 52% Y, $0.75\text{M } \text{MgCl}_2$ extracted 51% Y, , and $1.5\text{M } \text{NaCl}$ extracted 47% Y. Given this, the experiments at the higher salt concentrations were limited to 15 minutes. The maximum REE extractions at the higher salt concentrations are in the order of $3.0\text{M } \text{NaCl} > 1.5\text{M } \text{MgCl}_2 > 1.5\text{M } (\text{NH}_4)_2\text{SO}_4 > 1.5\text{M } \text{MgSO}_4$. $1.5\text{M } (\text{NH}_4)_2\text{SO}_4$ extracted 67% Y, $1.5\text{M } \text{MgSO}_4$ extracted 65% Y, $1.5\text{M } \text{MgCl}_2$ extracted 76% Y, , and $3.0\text{M } \text{NaCl}$ extracted 80% Y. For Figure 28, the Y extraction increases significantly for 3M NaCl, but that of the other species change only marginally.

The extent of REE extraction increases with an increase of lixiviant concentration. When the lixiviant concentration is doubled for $(\text{NH}_4)_2\text{SO}_4$, NaCl, MgCl_2 , and MgSO_4 , the REE extraction increases within the same leaching time.

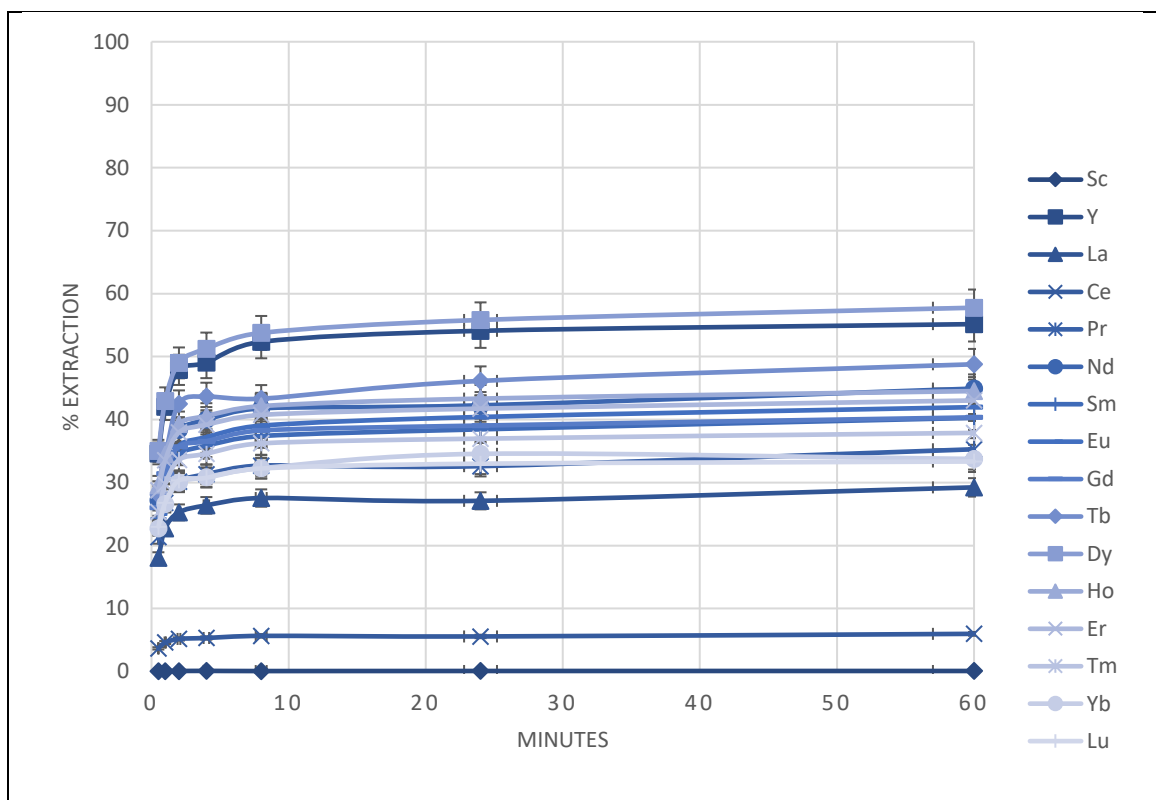


Figure 23: REE extraction efficiency of 0.75M ammonium sulphate in stirred batch reactor

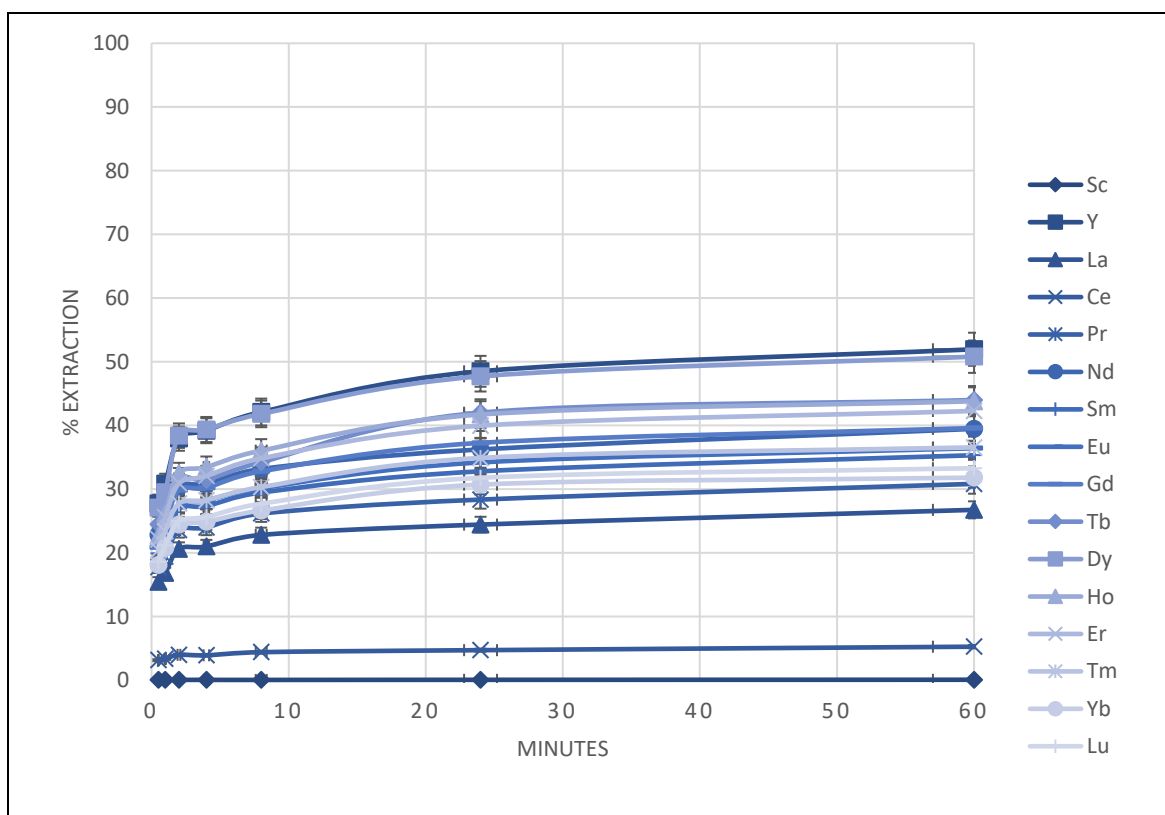


Figure 24: REE extraction efficiency of 0.75M magnesium sulphate in stirred batch reactor

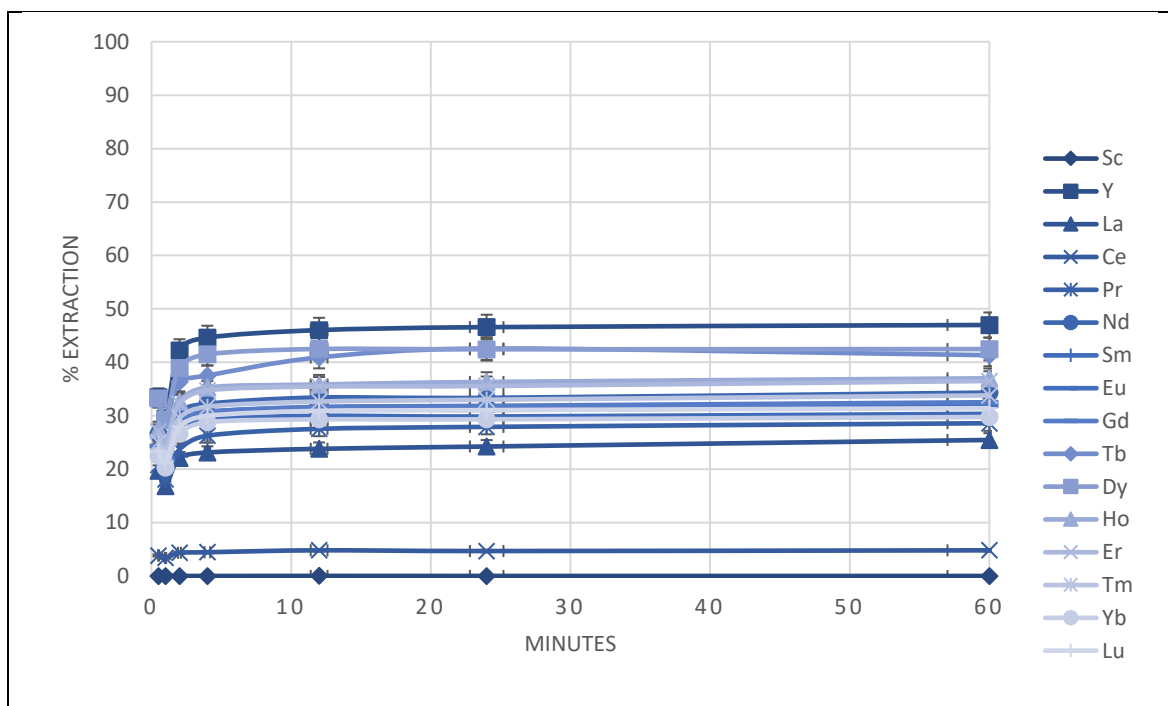


Figure 25: REE extraction efficiency of 1.5M sodium chloride in stirred batch reactor

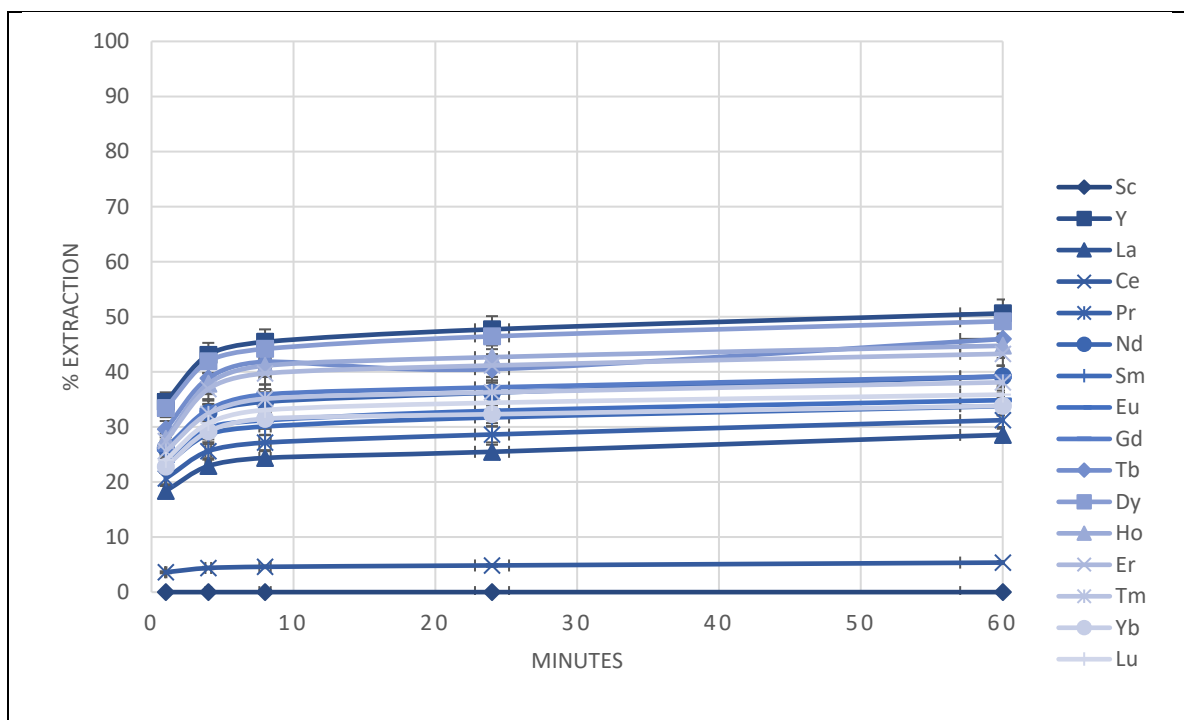


Figure 26: REE extraction efficiency of 0.75M magnesium chloride in stirred batch reactor

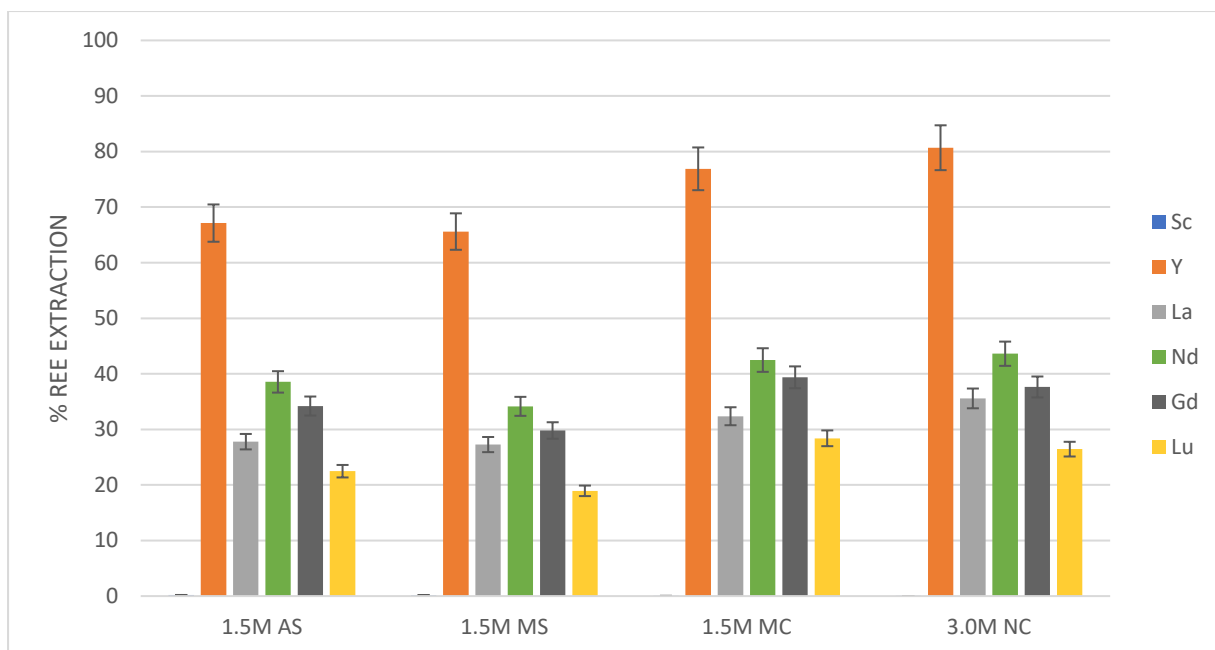


Figure 27: Maximum REE extraction of 1.5M ammonium sulfate (AS), 1.5M magnesium sulfate (MS), 1.5M magnesium chloride (MC), and 3.0M sodium chloride (NC) in stirred batch reactors

4.2.3.2 Column reactor extractions

The column reactor setup was used to test for effect of reagent type and reagent concentration on REE leaching in un-agitated systems in comparison with agitated systems. Eight different column reactors were setup at the same flow-rate of 0.5L/day, different reagents ($(\text{NH}_4)_2\text{SO}_4$, NaCl, MgCl_2 , and MgSO_4) were varied in pairs of four column reactors to make the total of eight column reactors, and the reagent concentration was increased from 0.5 (half concentration strength) to 1.0 (full concentration strength) in all the eight reactors, this meant that the first four reactors were ran as a single batch at 0.5 (half concentration strength) and more four reactors were ran in the second batch at 1.0 (full concentration strength) to make a total of eight column reactors for this test.

This meant that $(\text{NH}_4)_2\text{SO}_4$ was used in two different column reactors at two different concentrations 0.75M and 1.5M, NaCl was also used in two different column reactors at two different concentrations 1.5M and 3.0M, MgCl_2 was as well used in two different column reactors at two different concentration 0.75M and 1.5M, MgSO_4 was also used in two different column reactors at two different concentrations 0.75M and 1.5M.

The operating conditions for agglomerate column leaching of Ugandan IAC when using different leaching reagents ($(\text{NH}_4)_2\text{SO}_4$, NaCl, MgCl_2 , and MgSO_4) are: different reagent concentrations ($(\text{NH}_4)_2\text{SO}_4$ at two concentrations 0.75M and 1.5M, NaCl at two concentrations 1.5M and 3.0M, MgCl_2 at two concentrations 0.75M and 1.5M, and MgSO_4 at two concentrations 0.75M and 1.5M) to test for effect of reagent type and reagent concentration on agglomerate column leaching in comparison of REE leaching in un-agitated systems and REE leaching in agitated systems, the eight column reactors maintained at pH 3-4, 0.5L/day flowrate, agglomerate sizes in range (2.5cm – 3.5cm) and temperature at 298K.

The agglomerate size varied from 2.5cm to 3.5cm and all these sizes of agglomerates were packed together in the column. The reason is because the agglomeration process was highly manual and the sizes of agglomerates were not uniform but in a range of 2.5cm to 3.5cm.

The column reactor extraction curves were later compared to stirred batch reactor extraction curves and suspended ball (agglomerate) reactor extraction curves.

The leaching curves of $(\text{NH}_4)_2\text{SO}_4$, NaCl , MgCl_2 , and MgSO_4 are significantly different (see Figures 28-31). The different lixivants at the low concentrations have approximately the same percentage of extractions in 12 days. 0.75M ammonium sulfate, 0.75M magnesium chloride, and 1.5M sodium chloride with 43%, 46%, and 45% Yttrium (Y) respectively as the highest percentage extraction compared to the other Rare Earth Elements and Scandium (Sc) was the least extracted with less than 0.1%. However, the curves at higher concentrations for the different lixivants have a completely different profile, with 1.5M ammonium sulfate at 69% Y extraction, 1.5M magnesium chloride at 72% Y extraction, 3.0M sodium chloride at 74% Y extraction, and magnesium sulfate at both concentrations 0.75M and 1.5M performed worse extracting only 37% Y and 40% Y respectively.

Magnesium sulfate reached steady state extraction much faster at 9 days, 37% Y was extracted for 0.75M, followed by 0.75M magnesium chloride at 11 days 46% Y was extracted. 0.75M ammonium sulfate and 1.5M sodium chloride showed they were still extracting even at 12 days. Ammonium sulfate at 1.5M reached an extraction peak at 69% Y on day 12 and fewer percentage extractions were realized after day 12. The same extraction peak at 72% Y was obtained for 1.5M magnesium chloride on day 8 and fewer percentage extractions were realized after day 8 however 3.0M sodium chloride showed it was still extracting even at 14 days reaching 74% Y this was attributed to the higher concentration used for sodium chloride so higher concentrations of lixivants perform better reaching above 70% for the most extracted

As seen in Figure 32, the extent of leaching in order of $0.75\text{M MgCl}_2 > 1.5\text{M NaCl} > 0.75\text{M } (\text{NH}_4)_2\text{SO}_4 > 0.75\text{M MgSO}_4$ and this is not consistent at higher concentrations, with the extent of leaching in order of $3.0\text{M NaCl} > 1.5\text{M MgCl}_2 > 1.5\text{M } (\text{NH}_4)_2\text{SO}_4 > 1.5\text{M MgSO}_4$ in terms of the highest leached REE. The RE leaching rate increases with the increase of lixiviant concentration. When the lixiviant concentration is doubled for $(\text{NH}_4)_2\text{SO}_4$, NaCl , MgCl_2 , and MgSO_4 , the REE extraction increases within the same leaching time. When aluminum content as an impurity in PLS product is considered as well as other variables (see Table 6) the preference of lixiviant in un-agitated systems is in order of $(\text{NH}_4)_2\text{SO}_4 > \text{MgCl}_2 > \text{NaCl} > \text{MgSO}_4$.

There was the need to carry out more tests and explain results in terms of the physical properties for example difference in density and viscosity of the various lixivants but not much was done in this line so this was made a recommendation to further investigate the dependence of REE leaching on the permeation and difference in physical properties of the lixivants.

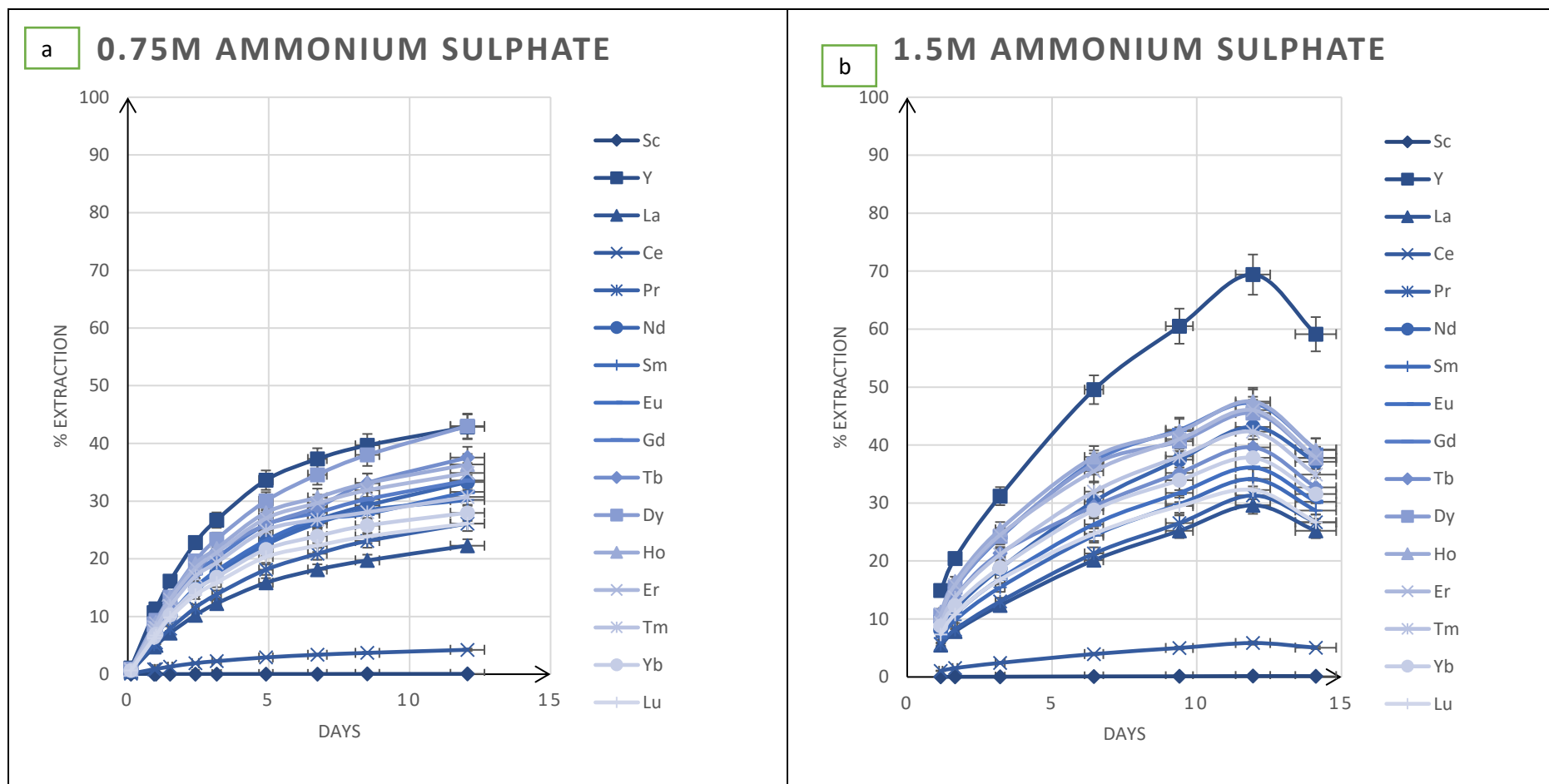


Figure 28: REE extraction efficiency of columns (a) 0.75M ammonium sulfate and (b) 1.5M ammonium sulfate

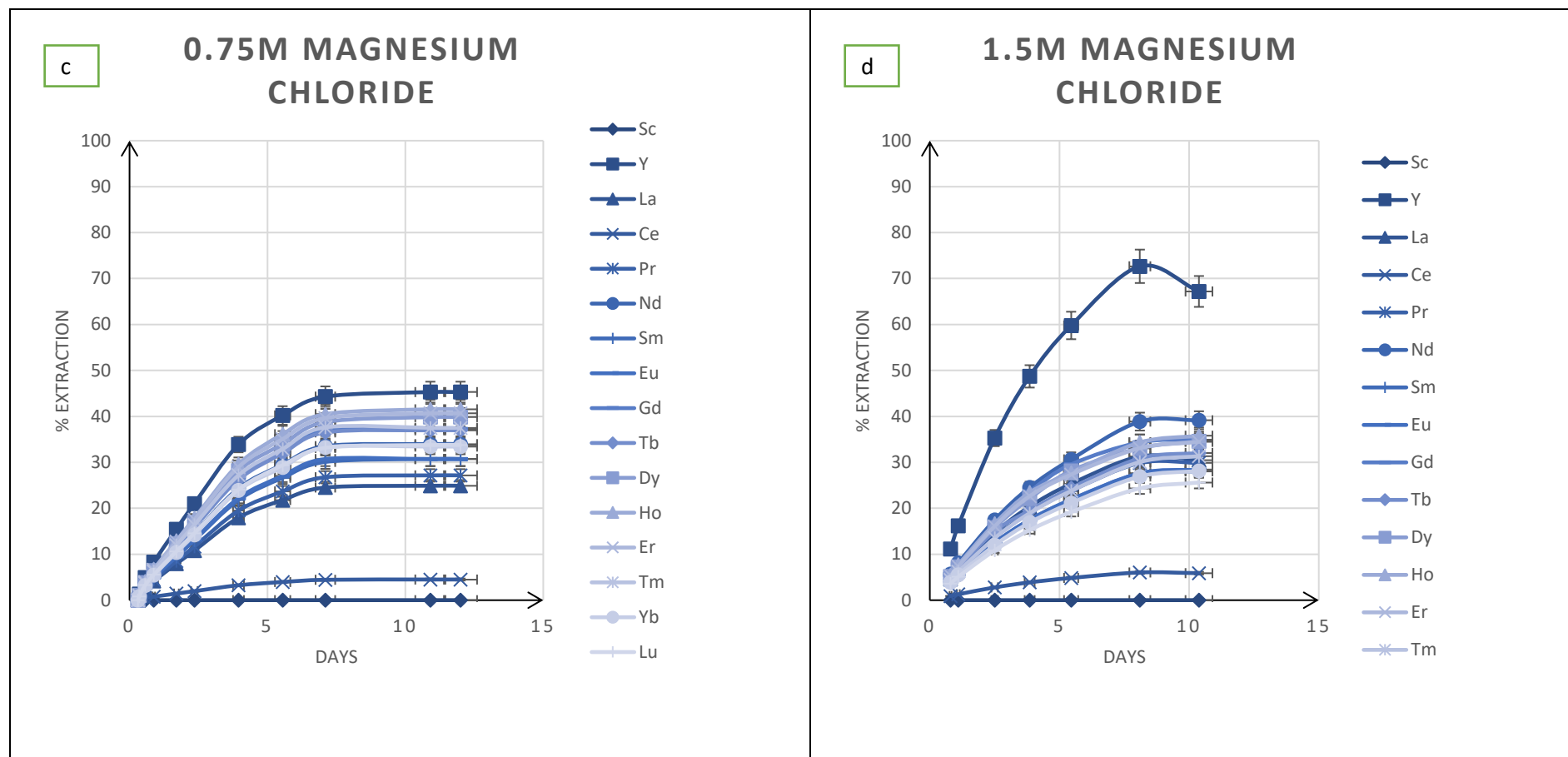


Figure 29: REE extraction efficiency of columns (c) 0.75M magnesium chloride and (d) 1.5M magnesium chloride

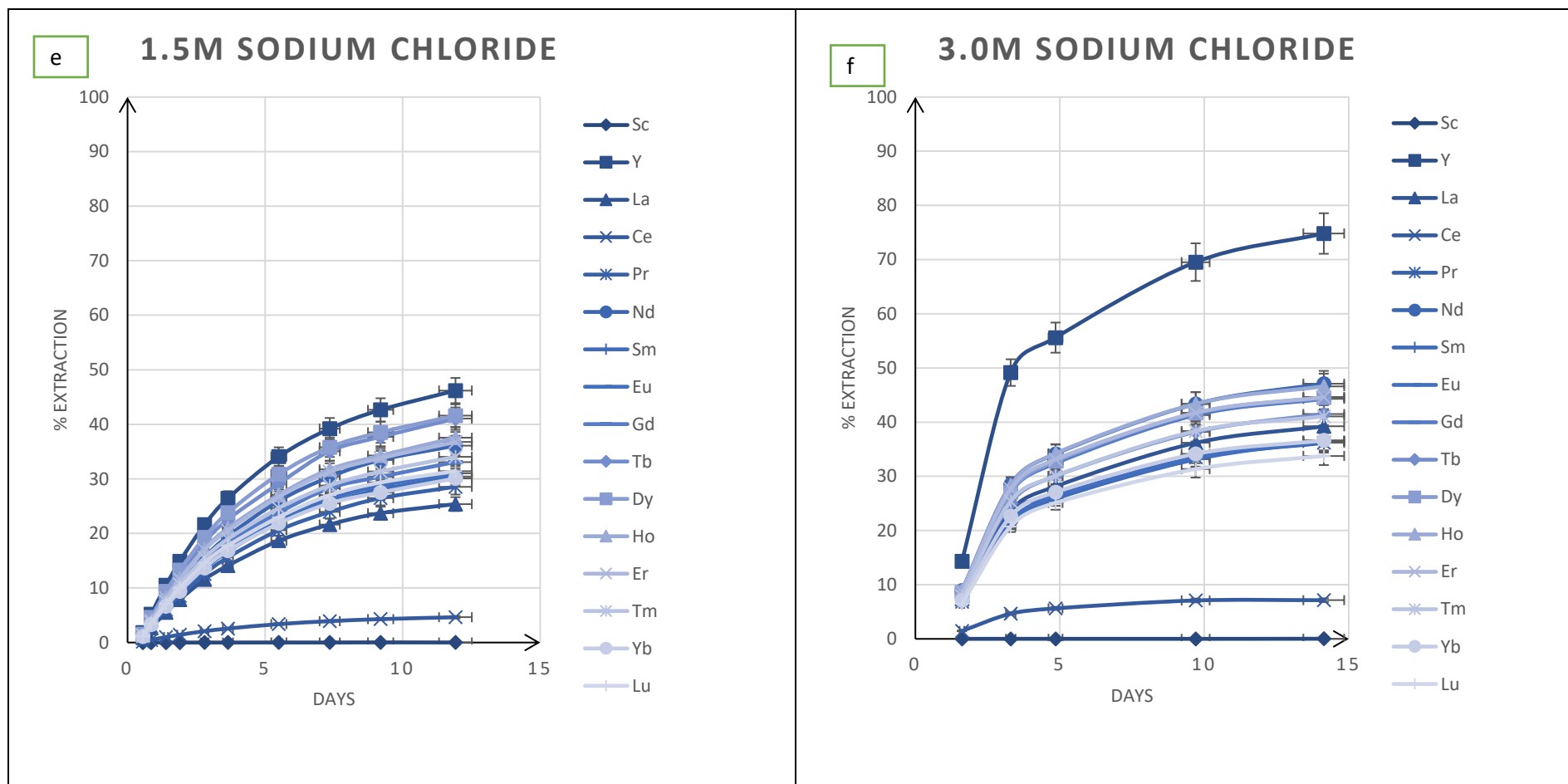


Figure 30: REE extraction efficiency of columns (e) 1.5M sodium chloride and (f) 3.0M sodium chloride

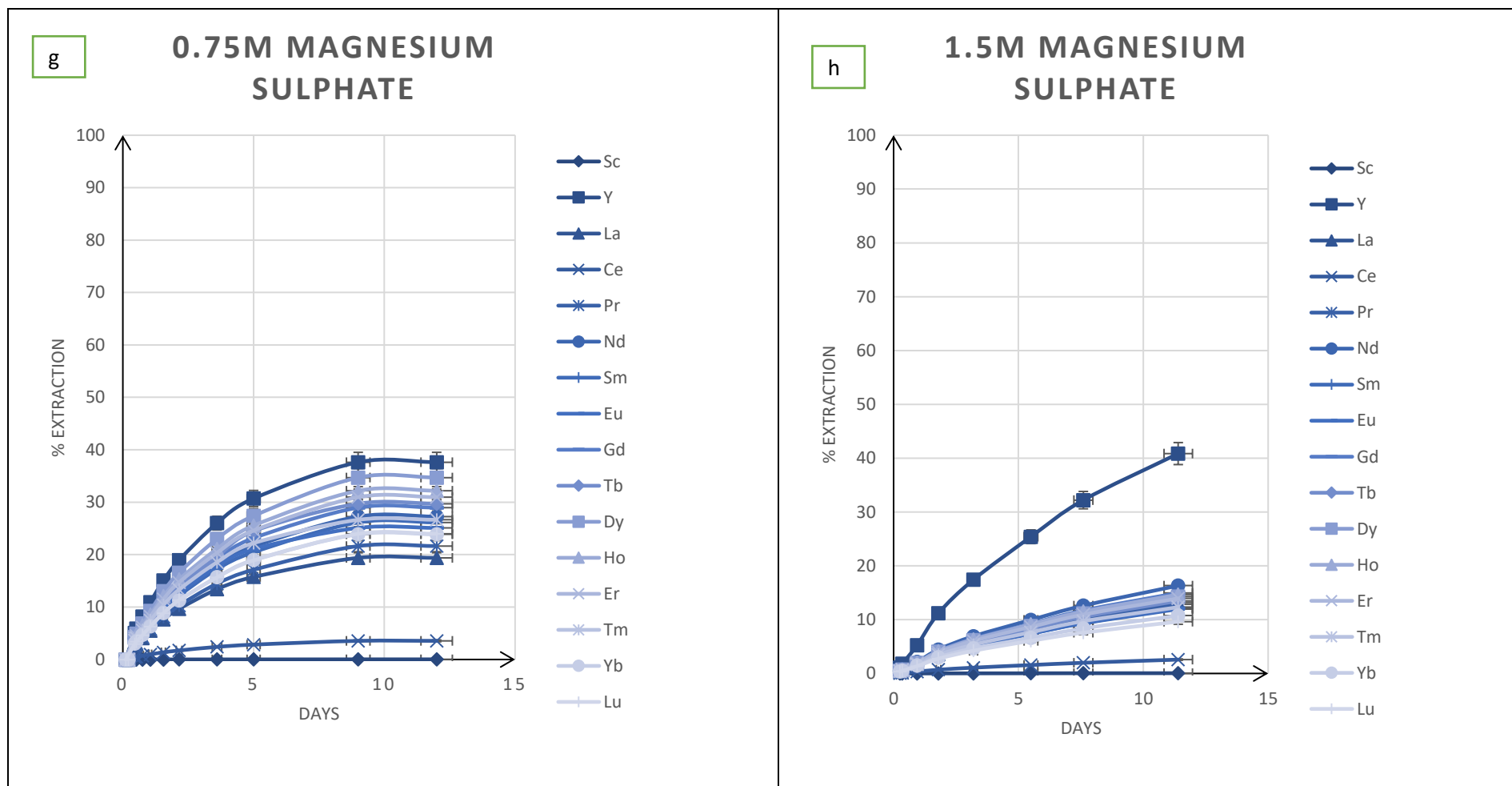


Figure 31: REE extraction efficiency of columns (g) 0.75M magnesium sulfate and (h) 1.5M magnesium sulfate

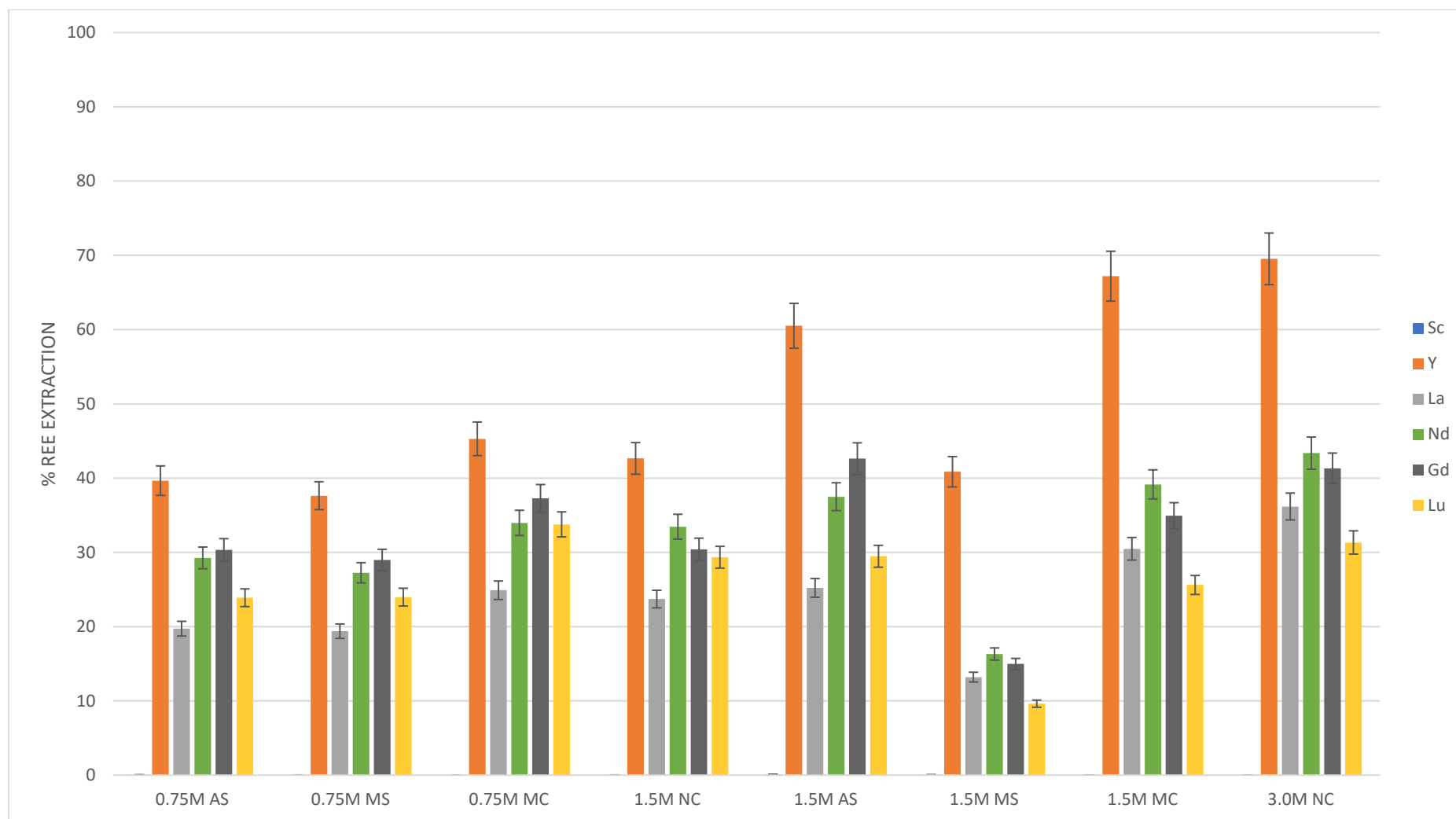


Figure 32: Maximum REE extraction of 0.75M and 1.5M ammonium sulfate (AS), 0.75M and 1.5M magnesium sulfate (MS), 0.75M and 1.5M magnesium chloride (MC), 1.5M and 3.0M sodium chloride (NC) in column reactors

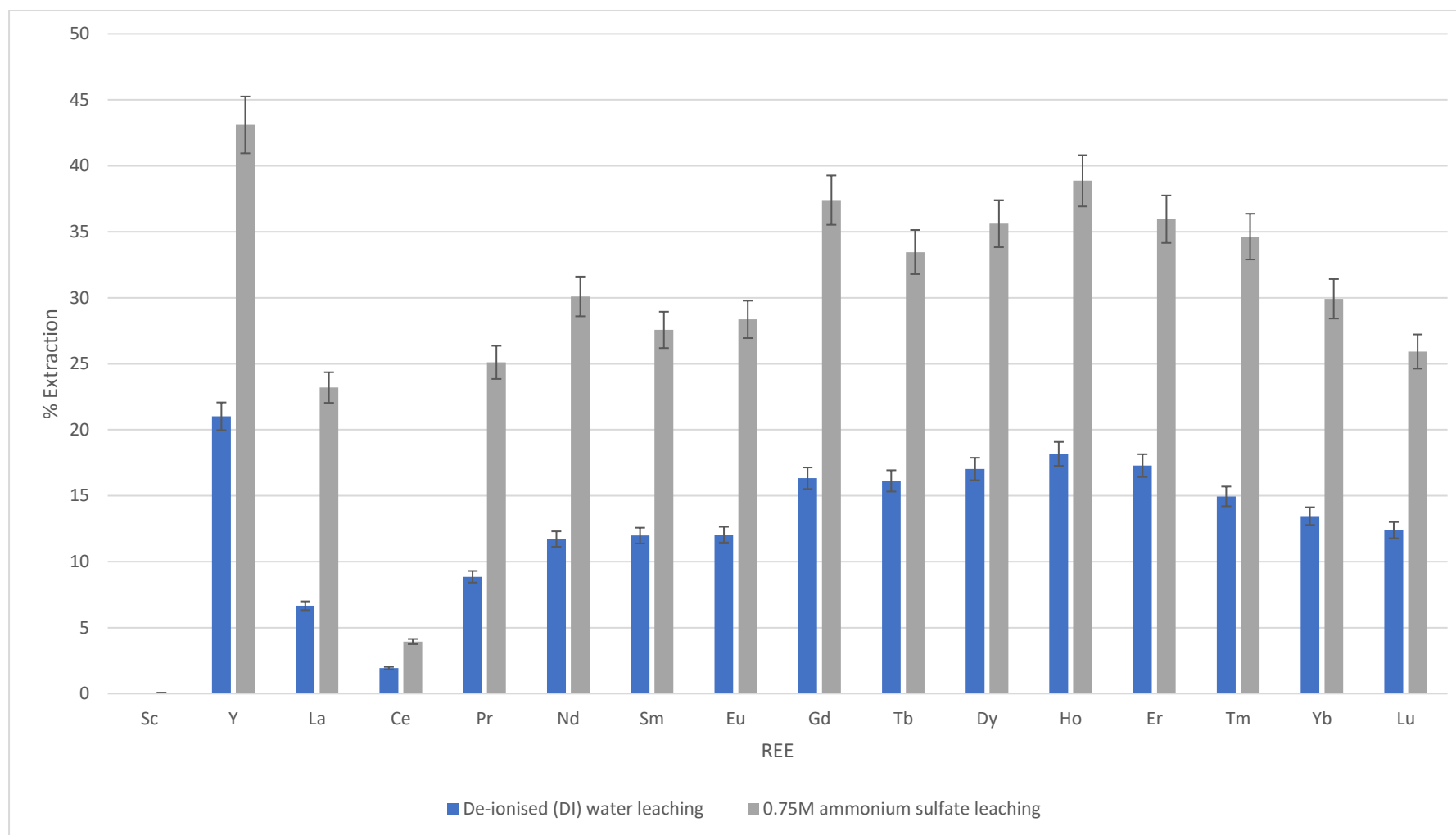


Figure 33: REE percentage extraction of 0.75M ammonium sulfate compared to de-ionised (DI) water leaching when agglomerated with ammonium sulfate at the same concentration of 0.75M and same PLS volume of 500mL

During the column leaching tests, there was a new development to agglomerate with salt solution then leach with DI water as compared to agglomerate with water and leach with salt solution (see Figure 33), and this was only done for 0.75M ammonium sulfate because there was lixiviant overflow for this setup after 500mL (in about 12 hours at 0.5L/day flow-rate) was collected off from the column and the experiment was stopped.

Leaching with 0.75M ammonium sulfate showed higher percentage extractions of REE compared to DI water leaching. The highest extracted REE for 0.75M ammonium sulfate were above 35% where as the highest extracted REE for DI water leaching were below 25% at the same PLS volume of 500mL taken before lixiviant overflow of the DI water leaching column setup. This was attributed to the salt already contained in the agglomerates after agglomeration limits the permeability of the agglomerate and diffusion of aqueous solution into the agglomerate because the voids are occupied by salt and the effect is more experienced when there is evaporation in the system. The overall effect may in fact cause the agglomerates in the bed to fuse, reducing also bed permeability resulting in eventual flooding.

Table 6: Comparison of the different leaching reagents in column leaching

Comparison variable	Highest Rare Earth Element % extraction at 1.0M or 50% higher than 1.0M	La, Nd, Gd, and Lu % extraction	Time is taken to reach a steady state extraction percentage	Extraction peak reached	Aluminium (Al) concentration is an impurity in the product
Ammonium sulfate	69% Y	29% La, 44% Nd, 48% Gd, 35% Lu	No steady state	Peak reached on day 12, extracted 69% Y	19.5 mg/L Al
Magnesium sulfate	40% Y	13% La, 16% Nd, 14% Gd, 9% Lu	Steady-state reached on day 9	No peak reached	11.1 mg/L Al
Sodium chloride	74% Y	36% La, 43% Nd, 41% Gd, 31% Lu	No steady state	No peak reached	19.1 mg/L Al
Magnesium chloride	72% Y	31% La, 39% Nd, 34% Gd, 25% Lu	Steady-state reached on day 11	Peak reached on day 8, extracted 72% Y	22.0 mg/L Al

4.2.3.3 Suspended agglomerate reactor extractions

The suspended ball (agglomerate) reactor setup was used to test for effect of reagent type and reagent concentration on agglomerate leaching. Eight different suspended ball reactors were setup at the same flow-rate of 0.5L/day, different reagents ((NH₄)₂SO₄, NaCl, MgCl₂, and MgSO₄) were varied in pairs of four suspended ball reactors to make the total of eight suspended ball reactors, and the reagent concentration was increased from 0.5 (half concentration strength) to 1.0 (full concentration strength) in all the eight reactors, this meant that the first four reactors were ran as a single batch at 0.5 (half concentration strength) and more four reactors were ran in the second batch at 1.0 (full concentration strength) to make a total of eight column reactors for this test.

This meant that (NH₄)₂SO₄ was used in two different suspended ball reactors at two different concentrations 0.75M and 1.5M, NaCl was also used in two different suspended ball reactors at two different concentrations 1.5M and 3.0M, MgCl₂ was as well used in two different suspended ball reactors at two different concentration 0.75M and 1.5M, MgSO₄ was also used in two different suspended ball reactors at two different concentrations 0.75M and 1.5M.

The operating conditions for suspended agglomerate leaching of Ugandan IAC when using different leaching reagents ((NH₄)₂SO₄, NaCl, MgCl₂, and MgSO₄) are: different reagent concentrations ((NH₄)₂SO₄ at two concentrations 0.75M and 1.5M, NaCl at two concentrations 1.5M and 3.0M, MgCl₂ at two concentrations 0.75M and 1.5M, and MgSO₄ at two concentrations 0.75M and 1.5M) to test for effect of reagent type and reagent concentration on agglomerate leaching in comparison of REE leaching in un-agitated systems and REE leaching in agitated systems, the eight suspended agglomerate (ball) reactors were maintained at pH 3-4, 0.5L/day flowrate, 3.0cm agglomerate size and temperature at 298K.

The nominal agglomerate size of 3.0cm was used because 3.0cm showed it would leach better as compared to the 2.5cm and 3.5cm agglomerate sizes.

The suspended agglomerate reactor extraction curves were later compared to stirred batch reactor extraction curves and column reactor extraction curves.

The leaching curves of (NH₄)₂SO₄, NaCl, MgCl₂ are somewhat similar however the MgSO₄ curves look quite different (see Figures 34-37). The different lixiviants achieve approximately

the same maximum percentage of extractions with 6 to 8 leaching days, the low concentration experiments were run for 10 days however at day 8 of agglomerate leaching, there was considerable evaporation of PLS hence the high concentration experiments were run for 6 days because evaporation losses became significant after 6 days of operation of the suspended agglomerate setup.

0.75M ammonium sulfate, 0.75M magnesium sulfate, 0.75M magnesium chloride, and 1.5M sodium chloride extracted 63%, 48%, 63%, and 45% Yttrium (Y) respectively, as the highest percentage extraction compared to the other Rare Earth Elements. Although all follow more or less the same trend over time. Scandium (Sc) was the least extracted with less than 0.1%. Similarly, at higher concentrations above 1.0M, the extraction curves of the different lixiviants were similar with 63% Y extracted for 1.5M ammonium sulfate, 56% Y extracted for 1.5M magnesium chloride, 56% Y extracted for 3.0M sodium chloride, and 57% Y extracted for 1.5M magnesium.

The RE leaching extent (see Figure 38) does not increase with the increase of lixiviant concentration. When the lixiviant concentration is doubled for $(\text{NH}_4)_2\text{SO}_4$, NaCl, MgCl_2 , and MgSO_4 , the REE extraction remains more or less constant within the same leaching time. The extent of leaching is in order of $0.75\text{M MgCl}_2 > 0.75\text{M } (\text{NH}_4)_2\text{SO}_4 > 0.75\text{M MgSO}_4 > 1.5\text{M NaCl}$ and this order changes at the higher concentrations, $1.5\text{M } (\text{NH}_4)_2\text{SO}_4 > 1.5\text{M MgCl}_2 > 3.0\text{M NaCl} > 1.5\text{M MgSO}_4$.

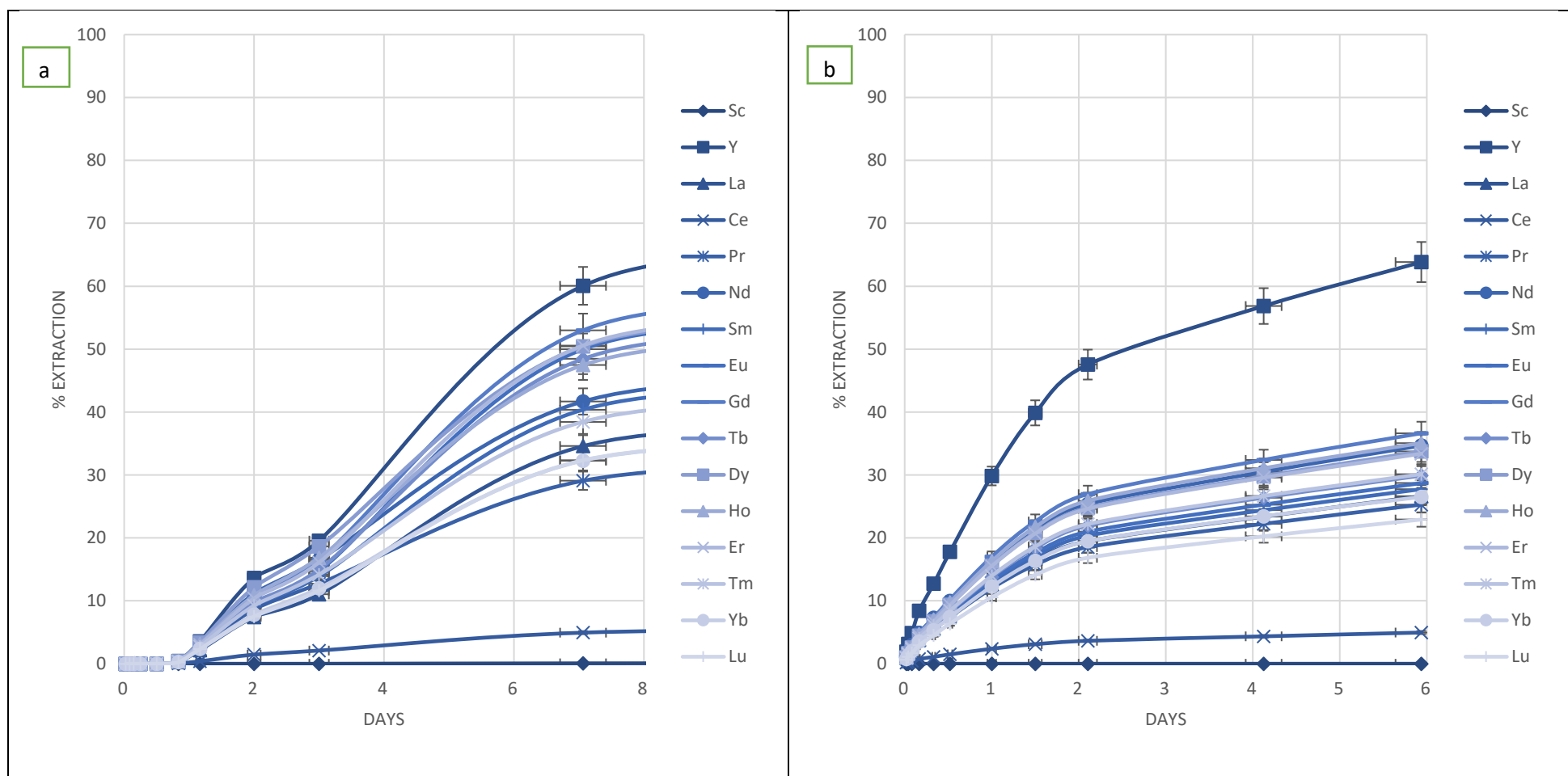


Figure 34: REE extraction of (a) 0.75M ammonium sulfate and (b) 1.5M ammonium sulfate from 2.5cm agglomerates suspended in two different suspended ball reactors

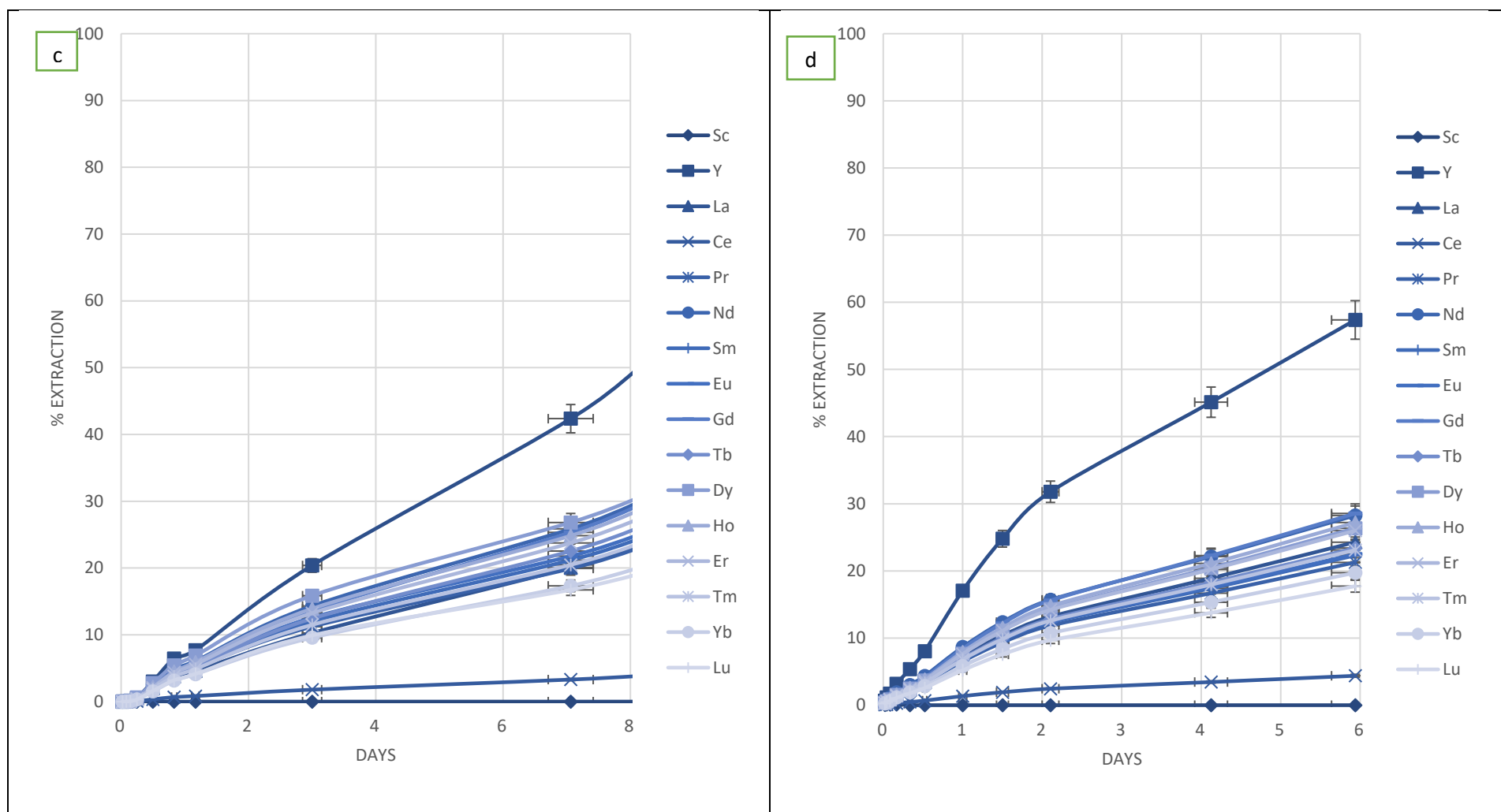


Figure 35: REE extraction of (c) 0.75M magnesium sulfate and (d) 1.5M magnesium sulfate from 2.5cm agglomerates suspended in two different suspended ball reactors

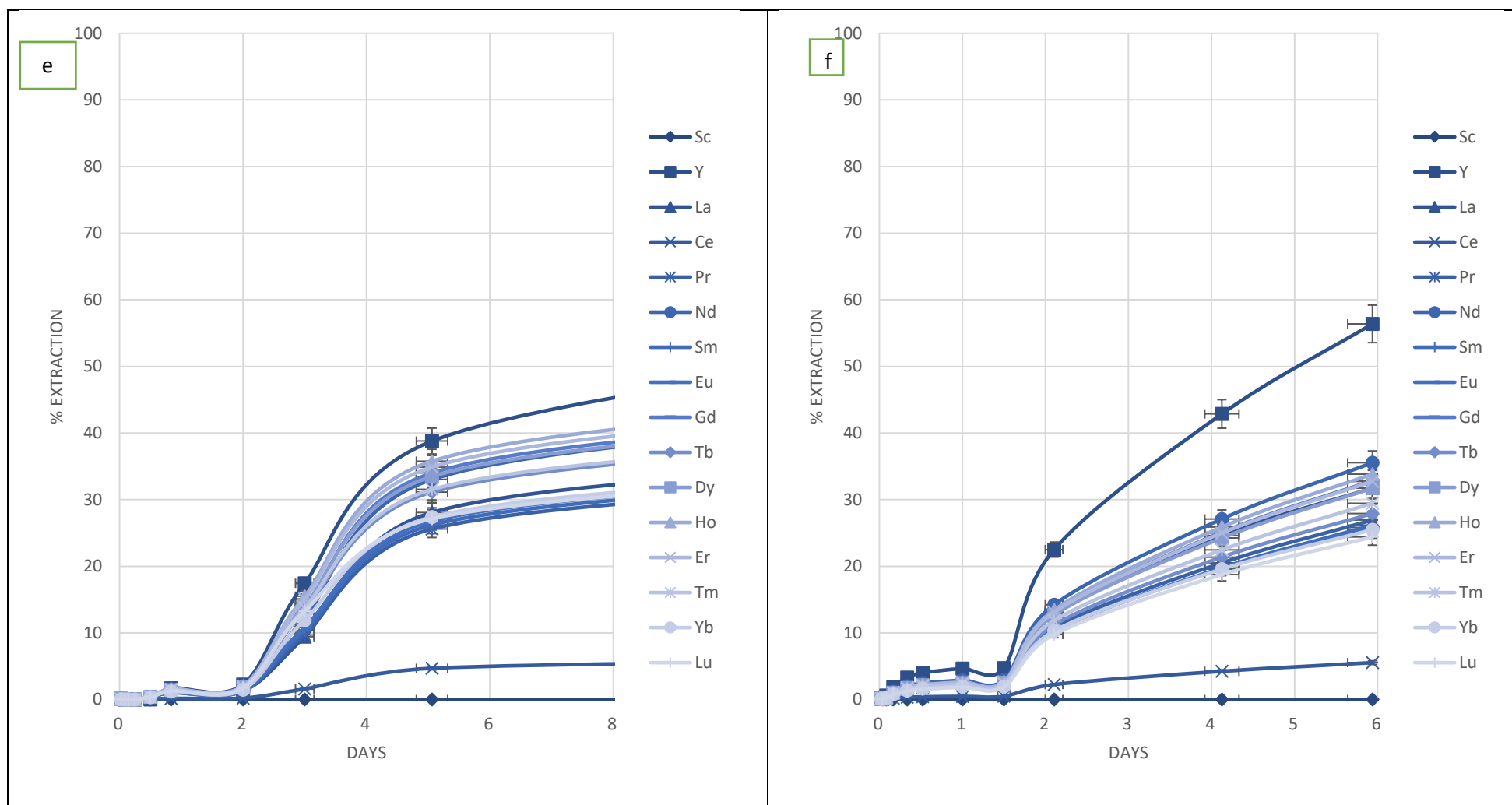


Figure 36: REE extraction of (e) 1.5M sodium chloride and (f) 3.0M sodium chloride from 2.5cm agglomerates suspended in two different suspended ball reactors

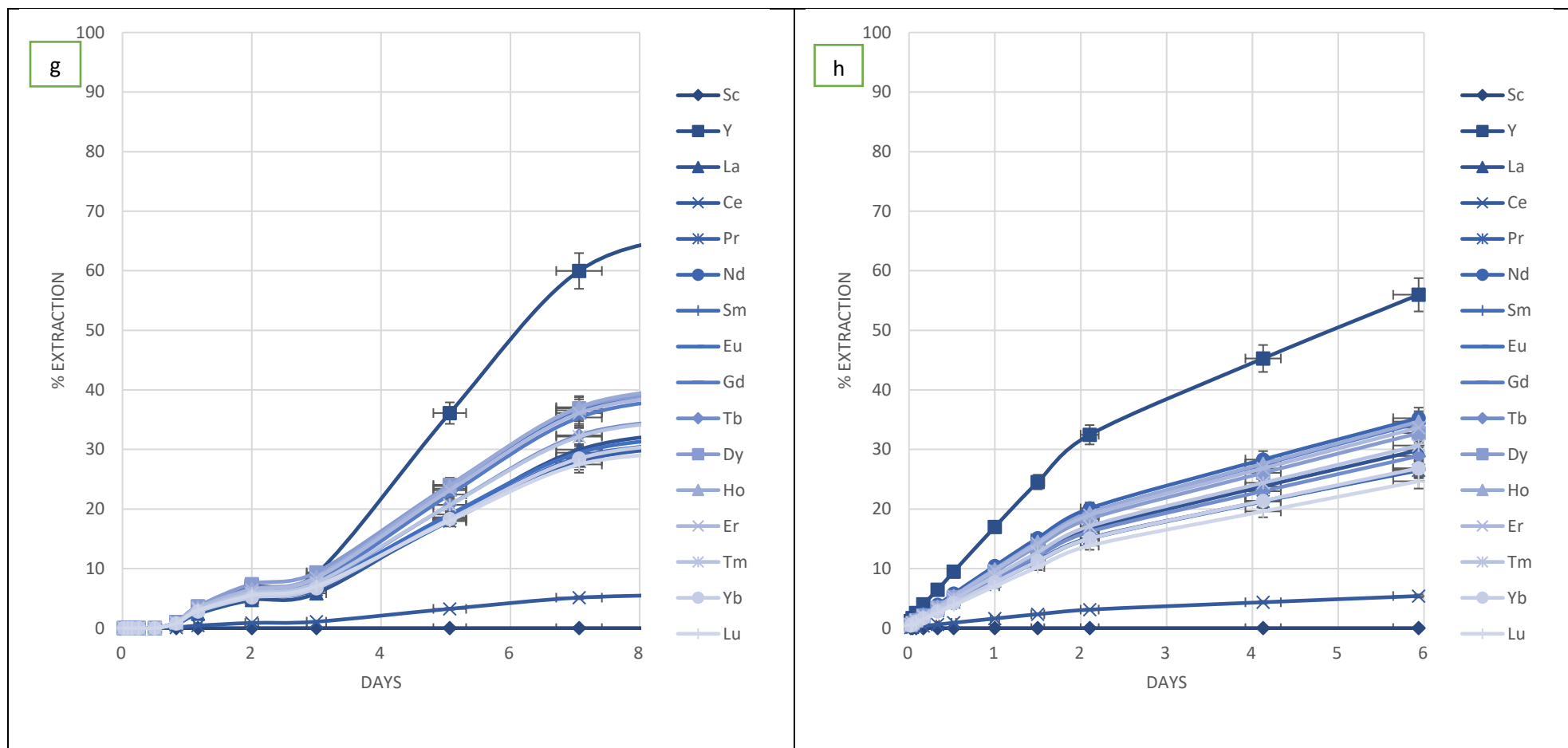


Figure 37: REE extraction of (g) 0.75M magnesium chloride and (h) 1.5M magnesium chloride from 2.5cm agglomerates suspended in two different suspended ball reactors

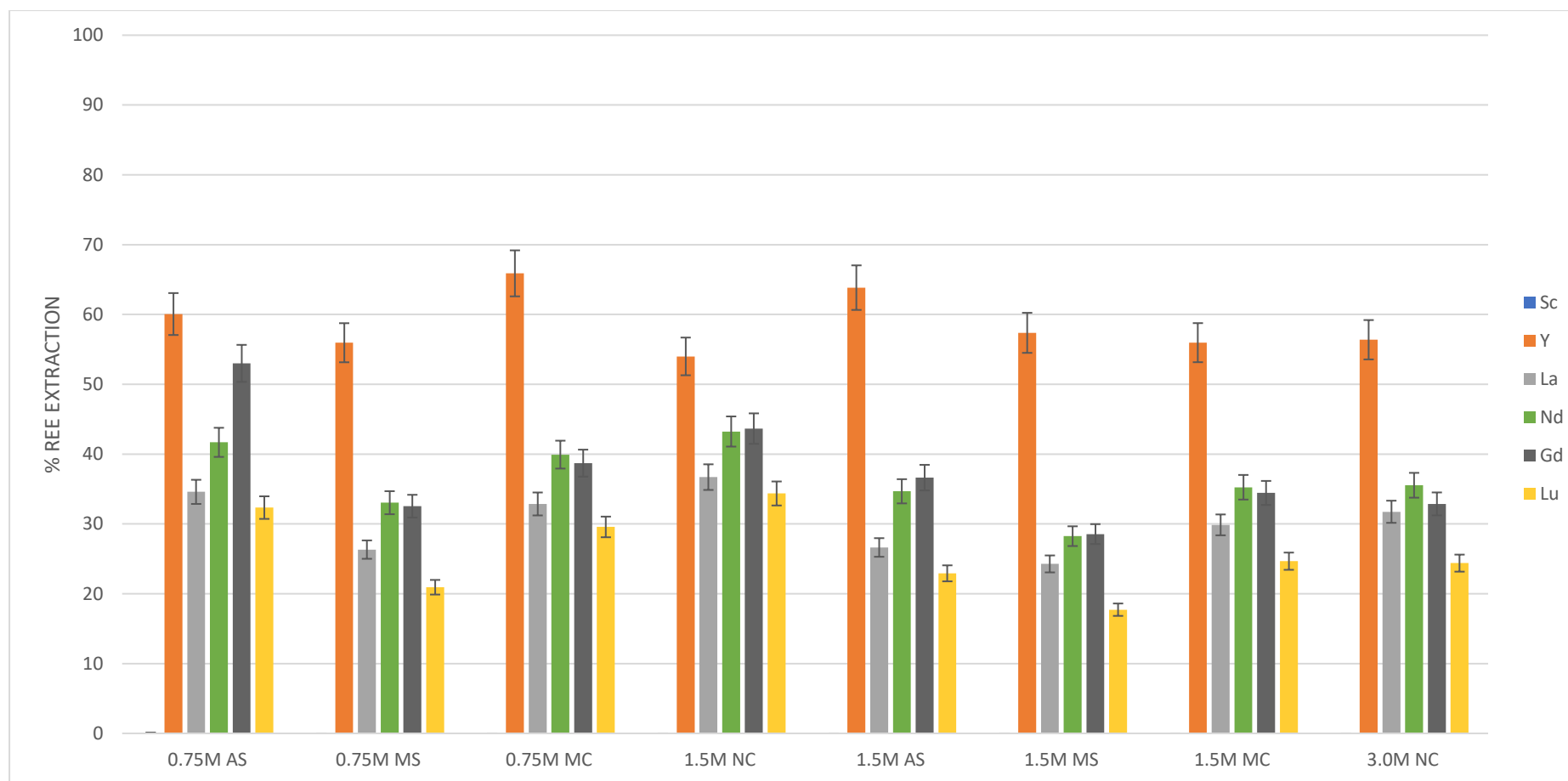


Figure 38: Maximum REE extraction of 0.75M and 1.5M ammonium sulfate (AS), 0.75M and 1.5M magnesium sulfate (MS), 0.75M and 1.5M magnesium chloride (MC), 1.5M and 3.0M sodium chloride (NC) in suspended ball reactors

4.2.4 Reactor comparison

Given the intention of the study was to assess the characterization of lixivants in the context of their intended use in agglomerated heap leaching, there is a need to compare the results from the leaching columns to the stirred reactor results and also compare with the suspended agglomerate reactor where just a single agglomerate is studied. The column reactor and the suspended agglomerate reactor were run with 0.75M ammonium sulfate as a leaching reagent, with the average agglomerate size of 3.0cm packed in the column reactor and nominal agglomerate size of 3.0cm was used in the suspended agglomerate reactor, and a flow rate of 0.5L/day was used.

The leaching went on for 10 days and at day 5 of leaching only 34% Yttrium was extracted for the column reactor while 54% Yttrium was extracted for the suspended agglomerate reactor after 5 days of leaching and when column setup leaching continued for 10 days approximately 43% Yttrium extraction is achieved. Continued leaching in the suspended agglomerate reactor resulted in excessive evaporation of solution, even when properly covered, and was therefore discontinued.

The stirred reactor was set at 1100rpm the highest speed for stable stirring without risking damage to the glassware of the reactor setup. 0.75M ammonium sulfate was used and 55% Yttrium was extracted for the stirred reactor after one hour of leaching and a steady state was reached at 30 minutes of leaching time. This value is very similar to the extraction achieved for the agglomerate leaching.

However (see Figure 39), the stirred reactor setup, Dysprosium (Dy) was the highest leached REE at 57% Dy extraction after one hour of leaching and it reached only 43% Dy after 5 days of leaching for the suspended agglomerate leaching and 40% Dy after 10 days of leaching for the column leaching experiment. This showed the difference between the stirred reactor and column reactor, and therefore stirred reactor cannot be used to mimic leaching in un-agitated systems as would be expected in heap leaching. This was the rationale why the suspended agglomerate reactor was developed, which appears to yield similar extractions as the stirred tank reactor, but over more realistic time-frames. Nonetheless there is clearly a need to scale further in terms of the extraction rate from the suspended agglomerate to the column reactors and further to actual heap scenarios. The relative fastness of the agglomerate in comparison to

previous diffusion experiments suggests that the leaching mechanism must be a combination of diffusion and permeation through the agglomerate.

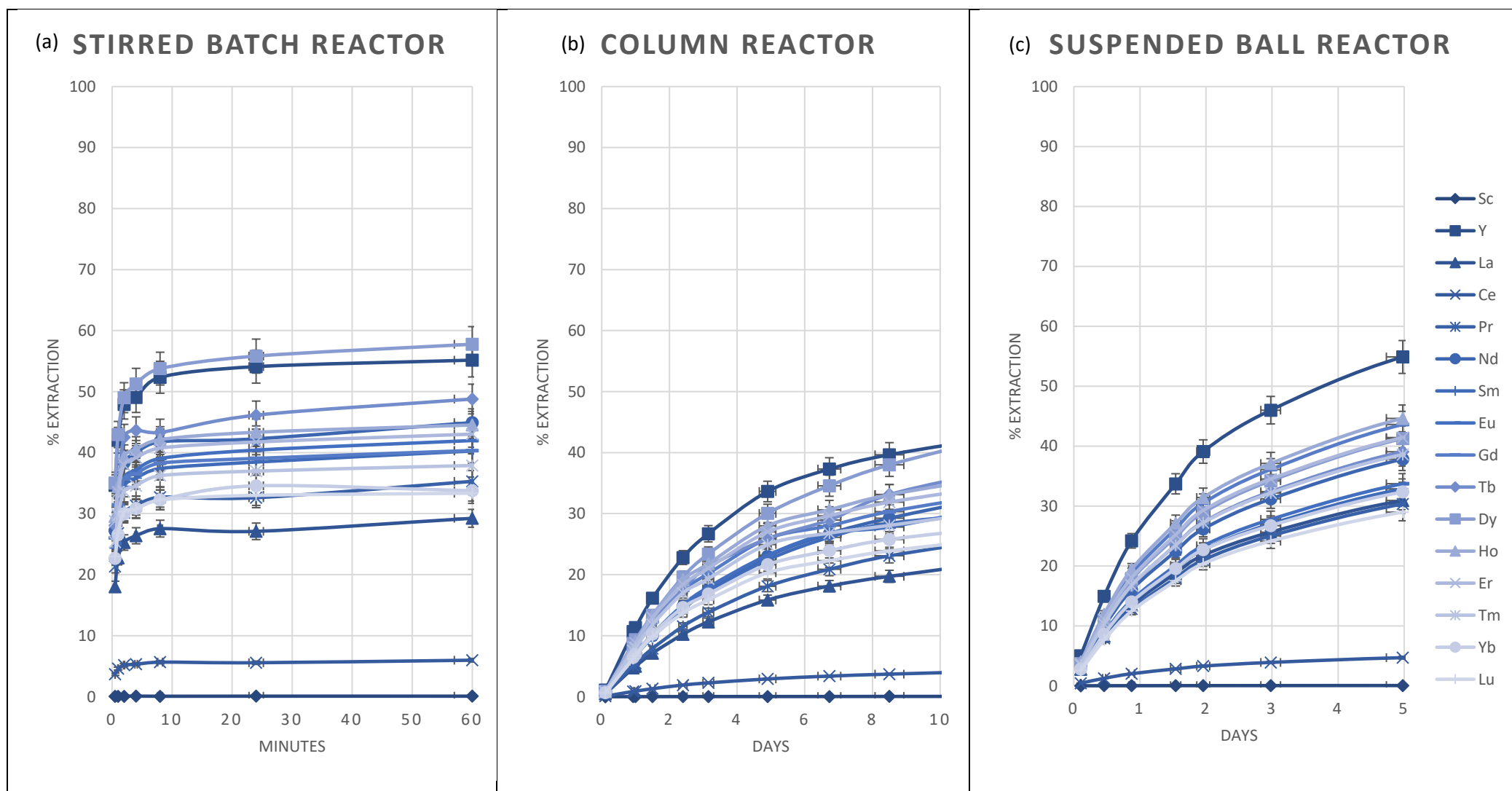


Figure 39: Comparison of REE extraction efficiency of 0.75M ammonium sulfate in different reactors (a) stirred batch reactor, (b) column reactor, and (c) suspended ball reactor

5 CONCLUSIONS AND RECOMMENDATIONS

Agglomeration of ion adsorption clay ore prevents leaching reagent overflow when macro clay agglomerates are packed in a laboratory column, this improves permeability of the ion adsorption clay ore because of the independent solution flow channels uniformly created when clay agglomerates are used and the column reactor does not overflow with leaching reagent. Flow rates of 3L/day and 5L/day yielded very similar results, however, the very slow flow rate of 0.5L/day yielded a lower percentage extraction of REE even after 10 days of leaching and yet at increased flow rates of 5L/day and 3L/day, 40% extraction of Yttrium (as the highest extracted REE) was reached in less than one day of leaching. 0.5L/day only reached 10% extraction of Yttrium in 1 day and 34% extraction of Yttrium in 5 days. A steady state was reached within 24 hours when using a 3L/day flow rate whereas a 5L/day flow rate showed higher extraction of 43% Yttrium compared to a 40% Yttrium extraction that levelled off in 24 hours at a 3L/day flow rate. The higher flow rates of 5L/day and 3L/day extracted more REE compared to 0.5L/day. The problem is at higher flow rates there is the risk of overflowing the column with the leaching reagent this is because the stability of ore agglomerates packed in the column reduces faster with the increasing flow rate of the leaching reagent.

The lixiviant of preference in terms of REE extraction from ion adsorption clays is in the order $(\text{NH}_4)_2\text{SO}_4 > \text{MgCl}_2 \cdot 6\text{H}_2\text{O} > \text{NaCl} > \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in un-agitated systems because (see Table 6) more test work on the Ugandan ion adsorption clay ore investigated the extraction efficiency of ammonium sulfate, sodium chloride, magnesium sulfate, and magnesium chloride. 0.75M Magnesium sulfate reached steady state extraction much faster at 9 days 37% Y was extracted, followed by 0.75M magnesium chloride at 11 days 46% Y was extracted. 0.75M ammonium sulfate and 1.5M sodium chloride showed they were still extracting even at 12 days. Ammonium sulfate at 1.5M reached an extraction peak at 69% Y on day 12 and fewer percentage extractions were realized after day 12. The same extraction peak was got for magnesium chloride at 1.5M extracted at 72% Y on day 8 and fewer percentage extractions were realized after day 8 however 3.0M sodium chloride showed it was still extracting even at 14 days reaching 74% Y this was attributed to the higher concentration used for sodium chloride so higher concentrations of lixiviants perform better reaching above 70% for the highest extracted Rare Earth Element (REE), the only problem is using more salt for the high concentrations and holding the heap for long to reach higher extractions.

There was the need to compare the aluminum (Al) concentration in the product from the different lixiviants as an impurity in the product. The quality of product in terms of less Al as impurity in PLS for leaching reagents is in order of $\text{MgSO}_4 > \text{NaCl} > (\text{NH}_4)_2\text{SO}_4 > \text{MgCl}_2$ for un-agitated systems. The aluminum (impurity in PLS) was 22.0 mg/L Al for magnesium chloride, 19.5 mg/L Al for ammonium sulfate, 19.1 mg/L Al for sodium chloride, and 11.1 mg/L Al for magnesium sulfate. This showed that ammonium sulfate extracts less aluminum content than magnesium chloride. Even when magnesium sulfate (hydrate) extracts less aluminum (impurity in PLS) content than the other lixiviants used in the study, there was an unexpected result when magnesium sulfate extracts less REE compared to the other lixiviants in the same leaching time, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ was used because magnesium sulfate without the hydrate was much more expensive compared to the prices of the other leaching reagents.

For 0.5M ammonium sulfate, about 70% of the highest REE including Y, La, Nd, and Gd was obtained from the Madagascan ore. The kinetics of REE desorption were fast, less than 10 days for column leaching using 0.5M ammonium sulfate at 5L/day flow rate.

The agglomerates were agglomerated manually by hand and this was highly dependent on the average size obtained after the agglomeration process and the size was in the range (2.5cm to 3.5cm). The agglomerate size was investigated with the use of the suspended agglomerate semi-continuous reactor and this showed that the larger agglomerates at 3.5cm, and 3.0cm, more or less REE were extracted, and substantially more than at 2.5cm size of agglomerate and this is essentially counter-intuitive. The relative fastness of the agglomerate in comparison to previous diffusion experiments suggests that the leaching mechanism must be a combination of diffusion and permeation through the agglomerate.

There is a significant difference between the stirred reactor and column reactor, and therefore stirred reactor cannot be used to mimic leaching in un-agitated systems as would be expected in heap leaching. The suspended ball reactor was developed to test for the effect of diffusion and permeation through the agglomerate as it would have been in a heap leach scenario.

Recommendations

Conducting the experimental study highlighted a few areas that merit further investigation/improvement.

- The agglomeration of clay ore to macro-size agglomerates can further be improved by mechanizing the process to make more uniform-size agglomerates that improve the clay heap permeability.
- Leaching of REE in unagitated systems for example column leaching is dependent on permeation of the lixivants through the clay ore, and there is need to further investigate dependence of REE leaching on the permeation, and the difference in physical properties of the lixivants for example density, viscosity of various lixivants.
- The irrigation flowrate of the ion-adsorption clay systems should further be investigated because high irrigation flowrate extracts more REE from ion-adsorption clay agglomerates in a relatively less leaching time; however high irrigation flowrates tend to erode the clay agglomerates decreasing the stability of the agglomerates within the heap which may cause heap clogging or collapse.
- There is need to develop innovative techniques to characterize and analyse the clay residue and agglomerates after leaching to inform the mass balance, this was not done because at the end of the test the clay would shatter on cutting yet an immediate analysis could show what parts of the clay agglomerate were not leached, this limited how much of analysis could be carried out on the clay residue.
- The re-characterization of residue ore after leaching for the different lixiviant types gives insight into the reason for different extraction efficiencies, especially with depth into the particle. However this part of the project was not completed because it required innovation in cutting and preparation of the residue agglomerates for analysis and characterization.

6 REFERENCES

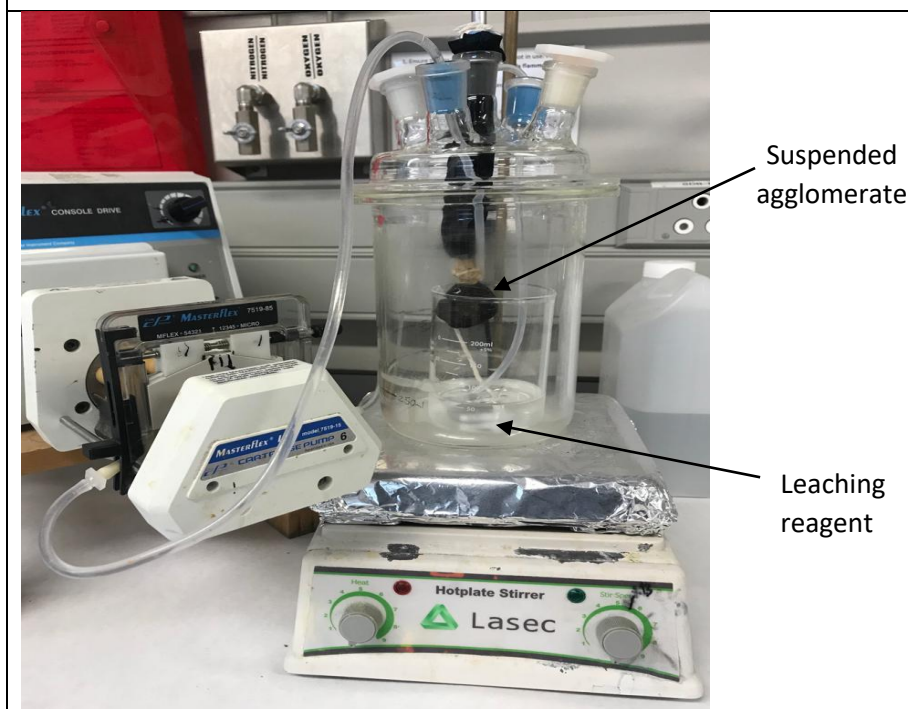
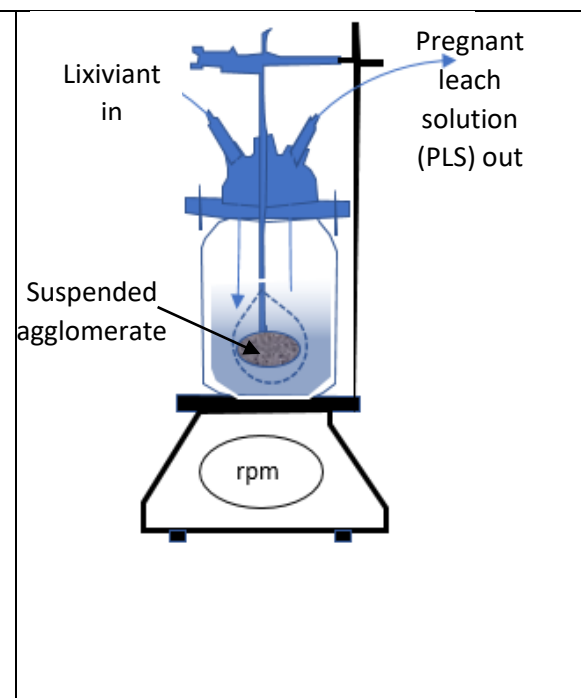
- Arshi, P. S., Vahidi, E., & Zhao, F. (2018). Behind the Scenes of Clean Energy: The Environmental Footprint of Rare Earth Products. *ACS Sustainable Chemistry and Engineering*, 6(3). <https://doi.org/10.1021/acssuschemeng.7b03484>
- Balaram, V. (2019). Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact. *Geoscience Frontiers*, 10(4), 1285–1303. <https://doi.org/10.1016/j.gsf.2018.12.005>
- Banerjee, R., Mohanty, A., Chakravarty, S., Chakladar, S., & Biswas, P. (2021). A single-step process to leach out rare earth elements from coal ash using organic carboxylic acids. *Hydrometallurgy*, 201. <https://doi.org/10.1016/j.hydromet.2021.105575>
- Chakhmouradian, A. R., & Wall, F. (2012). Rare earth elements: Minerals, mines, magnets (and more). *Elements*, 8(5). <https://doi.org/10.2113/gselements.8.5.333>
- Chen, Z., Li, Z., Chen, J., Kallem, P., Banat, F., & Qiu, H. (2022). Recent advances in selective separation technologies of rare earth elements: a review. In *Journal of Environmental Chemical Engineering* (Vol. 10, Issue 1). <https://doi.org/10.1016/j.jece.2021.107104>
- Dushyantha, N., Batapola, N., Ilankoon, I. M. S. K., Rohitha, S., Premasiri, R., Abeysinghe, B., Ratnayake, N., & Dissanayake, K. (2020). The story of rare earth elements (REEs): Occurrences, global distribution, genesis, geology, mineralogy and global production. In *Ore Geology Reviews* (Vol. 122). <https://doi.org/10.1016/j.oregeorev.2020.103521>
- Ghorbani, Y., Franzidis, J. P., & Petersen, J. (2016). Heap leaching technology - Current State, innovations, and future directions: A review. *Mineral Processing and Extractive Metallurgy Review*, 37(2), 73–119. <https://doi.org/10.1080/08827508.2015.1115990>
- Goodenough, K. M., Wall, F., & Merriman, D. (2018). The Rare Earth Elements: Demand, Global Resources, and Challenges for Resourcing Future Generations. *Natural Resources Research*, 27(2). <https://doi.org/10.1007/s11053-017-9336-5>
- Jordens, A., Cheng, Y. P., & Waters, K. E. (2013). A review of the beneficiation of rare earth

- element bearing minerals. In *Minerals Engineering* (Vol. 41).
<https://doi.org/10.1016/j.mineng.2012.10.017>
- Kanazawa, Y., & Kamitani, M. (2006). Rare earth minerals and resources in the world. *Journal of Alloys and Compounds*, 408–412, 1339–1343. <https://doi.org/10.1016/j.jallcom.2005.04.033>
- Malhotra, N., Hsu, H. S., Liang, S. T., Roldan, M. J. M., Lee, J. S., Ger, T. R., & Hsiao, C. Der. (2020). An updated review of toxicity effect of the rare earth elements (REEs) on aquatic organisms. In *Animals* (Vol. 10, Issue 9). <https://doi.org/10.3390/ani10091663>
- Mkhize, S. S. (2020). *Diffusion-reaction study of rare earth elements from ion- adsorption clays. February.*
- Moldoveanu, G. A., & Papangelakis, V. G. (2012). Recovery of rare earth elements adsorbed on clay minerals: I. Desorption mechanism. *Hydrometallurgy*, 117–118, 71–78. <https://doi.org/10.1016/j.hydromet.2012.02.007>
- Moldoveanu, G. A., & Papangelakis, V. G. (2013). Recovery of rare earth elements adsorbed on clay minerals: II. Leaching with ammonium sulfate. *Hydrometallurgy*, 131–132, 158–166. <https://doi.org/10.1016/j.hydromet.2012.10.011>
- Petersen, J. (2016). Heap leaching as a key technology for recovery of values from low-grade ores – A brief overview. *Hydrometallurgy*, 165, 206–212. <https://doi.org/10.1016/j.hydromet.2015.09.001>
- Ram, R., Becker, M., Brugger, J., Etschmann, B., Burcher-Jones, C., Howard, D., Kooyman, P. J., & Petersen, J. (2019). Characterisation of a rare earth element- and zirconium-bearing ion-adsorption clay deposit in Madagascar. *Chemical Geology*, 522(January), 93–107. <https://doi.org/10.1016/j.chemgeo.2019.05.011>
- Silva, G. A., Petter, C. O., & Albuquerque, N. R. (2018). Factors and competitiveness analysis in rare earth mining, new methodology: case study from Brazil. *Heliyon*, 4(3), e00570. <https://doi.org/10.1016/j.heliyon.2018.e00570>
- Su, X., Wang, Y., Su, J., Lai, W., Gao, Y., & Sun, X. (2019). Enrichment of rare earths in magnesium sulfate leach solutions of ion-absorbed ores by extraction-precipitation. *Hydrometallurgy*, 189(258), 105119. <https://doi.org/10.1016/j.hydromet.2019.105119>

- Vahidi, E., Navarro, J., & Zhao, F. (2016). An initial life cycle assessment of rare earth oxides production from ion-adsorption clays. *Resources, Conservation and Recycling*, 113, 1–11. <https://doi.org/10.1016/j.resconrec.2016.05.006>
- Wassink, B., Edouard, A., & The University of British Columbia. (2013). Copper Hydrometallurgy Principles and Practice. In *Analisis pendapatan dan tingkat kesejahteraan rumah tangga petani* (Vol. 53, Issue 9).
- Xiao, Y., Huang, L., Long, Z., Feng, Z., & Wang, L. (2016). Adsorption ability of rare earth elements on clay minerals and its practical performance. *Journal of Rare Earths*, 34(5), 543–548. [https://doi.org/10.1016/S1002-0721\(16\)60060-1](https://doi.org/10.1016/S1002-0721(16)60060-1)
- Xu, Q., Sun, Y., Yang, L., Li, C., Zhou, X., Chen, W., & Li, Y. (2019). Leaching mechanism of ion-adsorption rare earth by mono valence cation electrolytes and the corresponding environmental impact. *Journal of Cleaner Production*, 211, 566–573. <https://doi.org/10.1016/j.jclepro.2018.11.112>
- Yan, H., Liang, T., Liu, Q., Qiu, T., & Ai, G. (2018). Compound leaching behavior and regularity of ionic rare earth ore. *Powder Technology*, 333, 106–114. <https://doi.org/10.1016/j.powtec.2018.04.010>
- Yanfei, X., Zongyu, F., Xiaowei, H., Li, H., Yingying, C., Liangshi, W., & Zhiqi, L. (2015). Recovery of rare earths from weathered crust elution-deposited rare earth ore without ammonia-nitrogen pollution: I. leaching with magnesium sulfate. *Hydrometallurgy*, 153, 58–65. <https://doi.org/10.1016/j.hydromet.2015.02.011>
- Yang, X. J., Lin, A., Li, X. L., Wu, Y., Zhou, W., & Chen, Z. (2013). China's ion-adsorption rare earth resources, mining consequences and preservation. *Environmental Development*, 8(1), 131–136. <https://doi.org/10.1016/j.envdev.2013.03.006>
- Chi, R. and Tian, J (2012) The basic research on the weathered crust elution-deposited rare earth ores. *Nonferrous Metals Science and Engineering*, 4, pp 1-13, 123-130

7 APPENDICES

Appendix A: Suspended ball model



Description:

The leaching reagent is initially placed in a small beaker at the bottom of the reactor, a small beaker is used to maintain 2:1 liquid to solid ratio.

The agglomerate is wrapped in a permeable cloth-membrane to allow the leaching reagent pass through it and reactants diffuse into the agglomerate and products diffuse out of the agglomerate and collected off as PLS (pregnant leach solution), the flow-rate was reduced down from 3L/day to 0.5L/day.

The whole volume of PLS was collected off each time of sampling and an exact volume of leaching reagent was replaced.

Appendix B: Leaching tests raw data sets

The following steps can be followed to access data files

1. Go to Zivahub.uct.ac.za on any internet browser application
2. On the website, search for the data files either by author or description. Authors are Eddy Miiro and Jochen Petersen
3. On the search results, click on the file description name: raw data – Eddy Miiro “Hydrometallurgical Processing of Rare Earth Elements from Ion Adsorption Clays”
4. All data can be opened on the website or downloaded

Appendix C: Turnitin originality report

I herewith confirm that I have seen the Turnitin report for Eddy's thesis and have no concerns about potential plagiarism of his work. The large similarity refers to the students own research proposal on this work, submitted in Jun 2021).

Signed by candidate

11 Feb 2023

Turnitin Originality Report

Processed on: 30-Jan-2023 05:16 SAST

ID: 2002068889

Word Count: 13835

Submitted: 1

mrxedd001:Thesis_-
_Eddy_Miir.pdf By Eddy Miir

Similarity Index	Similarity by source
37%	Internet Sources: 26 %
	Publications: 20 %
	Student Papers: 21 %

11% match (student papers from 03-Jun-2021)

[SubmittedtoUniversityofCapeTownon2021-06-03](#)

6% match (Internet from 29-Aug-2018)

http://tmrcorp.com/_resources/pdf/China_Ionic_Clay_Pollution.pdf

1% match (student papers from 26-May-2021)

[SubmittedtoUniversityofCapeTownon2021-05-26](#)

1% match (student papers from 10-Nov-2020)

[SubmittedtoUniversityofCapeTownon2020-11-10](#)

1% match (Internet from 14-Jan-2022)

https://www.researchgate.net/publication/257131119_Recovery_of_rare_earth_elements_adsorbed_on

1% match (Internet from 28-Jan-2023)

https://www.researchgate.net/publication/325827708_The_current_state_and_future_directions_of_per

1% match (Internet from 29-Sep-2022)

https://uknowledge.uky.edu/cgi/viewcontent.cgi?article=1066&context=mng_etds

1% match (Internet from 24-Jul-2022)

<https://coek.info/pdf-characterisation-of-a-rare-earth-element-and-zirconium-bearing-ion-adsorption-cl.html>

1% match (Internet from 26-Sep-2022)

https://open.uct.ac.za/bitstream/handle/11427/20488/thesis_ebe_2016_shaik_kathija%20%281%29.p

[sequence=1](#)

1% match (Internet from 23-Sep-2022)

https://vtechworks.lib.vt.edu/bitstream/handle/10919/96555/Liu_S_T_2020.pdf?isAllowed=y&sequence=1

1% match (Xu Qihua, Sun Yuanyuan, Yang Lifeng, Li Cuicui, Zhou Xuezhen, Chen Weifan, Li Yongxiu. "Leaching mechanism of ion-adsorption rare earth by mono valence cation electrolytes and the corresponding environmental impact", Journal of Cleaner Production, 2018)

[XuQihua,SunYuanyuan,YangLifeng,LiCuicui,ZhouXuezhen,ChenWeifan,LiYongxiu. "Leaching mechanism of ion-adsorption rare earth by mono valence cation electrolytes and the corresponding environmental impact", Journal of Cleaner Production, 2018](#)

1% match (Internet from 18-Jan-2023)

<https://worldwidescience.org/topicpages/e/earth%2Belements%2Bce.html>

1% match (Internet from 27-Feb-2019)

<http://spilpunt.blogspot.com/2010/>

< 1% match (student papers from 28-May-2021)

[Submitted to University of Cape Town on 2021-05-28](#)

< 1% match (student papers from 02-Nov-2021)

[Submitted to University of Cape Town on 2021-11-02](#)

< 1% match (Internet from 27-Jan-2023)

Appendix D: Approval of Ethics in Research Projects

Application for Approval of Ethics in Research (EiR) Projects
Faculty of Engineering and the Built Environment, University of Cape Town

ETHICS APPLICATION FORM

Please Note:

Any person planning to undertake research in the Faculty of Engineering and the Built Environment (EBE) at the University of Cape Town is required to complete this form **before** collecting or analysing data. The objective of submitting this application *prior* to embarking on research is to ensure that the highest ethical standards in research, conducted under the auspices of the EBE Faculty, are met. Please ensure that you have read, and understood the **EBE Ethics in Research Handbook** (available from the UCT EBE, Research Ethics website) prior to completing this application form: <http://www.ebe.uct.ac.za/ebe/research/ethics1>

APPLICANT'S DETAILS		
Name of principal researcher, student or external applicant		EDDY MIIRO
Department		CHEMICAL ENGINEERING
Preferred email address of applicant:		MRXEDD001@myuct.ac.za
If Student	Your Degree: e.g., MSc, PhD, etc.	MSc
	Credit Value of Research: e.g., 60/120/180/360 etc.	180
	Name of Supervisor (if supervised):	Prof. Jochen Petersen
If this is a research contract, indicate the source of funding/sponsorship		Government of Uganda
Project Title		Hydrometallurgical processing of Rare Earth Elements

I hereby undertake to carry out my research in such a way that:

- there is no apparent legal objection to the nature or the method of research; and
- the research will not compromise staff or students or the other responsibilities of the University;
- the stated objective will be achieved, and the findings will have a high degree of validity;
- limitations and alternative interpretations will be considered;
- the findings could be subject to peer review and publicly available; and
- I will comply with the conventions of copyright and avoid any practice that would constitute plagiarism.

APPLICATION BY	Full name	Signature	Date
Principal Researcher/ Student/External applicant	EDDY MIIRO	Signed by candidate	18/06/2021
SUPPORTED BY	Full name	Signature	Date
Supervisor (where applicable)	Jochen Petersen	Signed by candidate	11/08/2021
APPROVED BY	Full name	Signature	Date
HOD (or delegated nominee) Final authority for all applicants who have answered NO to all questions in Section 1; and for all Undergraduate research (Including Honours).	Elaine Opitz	Signed by candidate	19.09.2021
Chair: Faculty EIR Committee For applicants other than undergraduate students who have answered YES to any of the questions in Section 1.	81		