SEQUENTIAL LEACHING OF MALAYSIAN'S ION ADSORPTION CLAY RARE EARTH ELEMENT

NURADRINA BINTI HARIS

UNIVERSITI SAINS MALAYSIA

2022

SCHOOL OF MATERIAL AND MINERAL RESOURCES ENGINEERING

UNIVERSITI SAINS MALAYSIA

SEQUENTIAL LEACHING OF MALAYSIAN'S ION ADSOPRTION CLAY RARE EARTH ELEMENT

By

NURADRINA BINTI HARIS
Supervisor DR NURUL 'AIN JABIT

Dissertation submitted in partial fulfillment of the requirements for the degree of

Bachelor of Engineering with Honours

(Mineral Resources Engineering)

Universiti Sains Malaysia

August 2022

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled ‘Sequential leaching of Malaysian’s Ion Adsorption Clay Rare Earth Element’. I also declare that it has not been previously submitted for the award of any degree and diploma or other similar title of this for any other examining body or University.

Name of Student: NURADRINA BINTI HARIS Signature:

Date: 18 AUGUST 2022

Witness by Supervisor: DR NURUL ‘AIN JABIT Signature:

Date: 18 AUGUST 2022

ACKNOWLEDGEMENT

First and foremost, all Praise to Allah SWT the Almighty for His blessing, potential knowledge, patience and success throughout this project. It is my pleasure to acknowledge all direct or indirect guidance, assistance and support from those who helped in finishing this research. I would like to thank the authority of School of Material and Mineral Resources Engineering, Universiti Sains Malaysia for providing a good environment and facilities to complete this project. Special acknowledgement to my project supervisor, Dr Nurul ‘Ain Jabit her encouragement, advice and guidance in completing my final year project. Her aids in whichever way possible and gives valuable feedback whenever I approach her. I am eternally in debt and thankful to my family especially my parents; for being the pillars who have supported me financially and emotionally throughout my life. I would also like to thank to all my fellow friends, for their encouragement, moral and financial support in completing this project. Lastly, finest regards and blessing for those who are directly and indirectly involved in my research in order for this final year report to be successfully done. Without their support and help, I could have never been able to accomplish my final year project (FYP).

TABLE OF CONTENTS

LIST OF TABLES

Page

LIST OF FIGURES

Page

LIST OF SYMBOLS

ζ	Zeta
mg	Milligram
2θ	2theta
ºC	Degree Celsius
kV	Kilovolt
M	Molarity
%	Percentage

LIST OF ABBREVIATIONS

5S	5 step
ASTM	American Standard Test Sieve Series
IAC	Ion adsorption clay
IAD	Ion adsorption deposit
ICP-MS	Inductively coupled mass spectrometry
K	Potassium
KBr	Potassium bromide
KEC	Ion adsorption clay sample
ppb	Parts per billion
ppm	Parts per million
Rb	Rubidium
REE	Rare earth element
rpm	Rotation per minute
SEM	Scanning Electron Microscope
SERC	Science and Engineering Research Centre
XRD	X-ray diffraction
XRF	X-ray fluorescence

SEQUENTIAL LEACHING OF MALAYSIAN’S ION ADSORPTION CLAY RARE EARTH ELEMENT

ABSTRAK

Unsur nadir bumi jenis endapan tanah telah mula dikenali untuk banyak aplikasi kepada industri. Malaysia mempunyai potensi batuan RE-bearing yang mencukupi untuk pembentukan tanah liat penjerapan ion. Walau bagaimanapun, tidak terdapat kajian menyeluruh yang mencukupi mengenai tanah liat penjerapan ion Malaysia. Oleh itu, tujuan penyelidikan ini adalah untuk menentukan ciri fizikal dan kimia tanah liat penjerapan ion Malaysia dan menentukan potensi pengekstrakan REE secara pengekstrakan berjujukan. Pengasingan mineral tanah liat disediakan untuk subjek sampel untuk XRD, dan SEM. Komposisi kimia dan unsur surih sampel dilakukan oleh XRF dan ICP-MS. Bijih terutamanya terdiri dengan kepekatan tinggi Cerium. Tanah liat penjerapan ion juga terdiri daripada silika, kuarza dan mineral tanah liat yang terdapat dalam sampel disertakan dengan yugawaralit, berlinit dan montmorilonit. Pengekstrakan berjujukan (SE) ammonium sulfat (1S) dan 5 langkah (5S) telah dijalankan ke atas sampel untuk menentukan potensi pengekstrakan dan kecekapan pengekstrakan. Keputusan melaporkan bahawa larut lesap ammonium sulfat boleh melarutkan hampir semua REE berbanding natrium asetat yang digunakan dalam 5S. ini menunjukkan bahawa larut lesap ammonium sulfat adalah reagen larut lesap yang sesuai untuk mengekstrak REE daripada bijih penjerapan ion. Bijih penjerapan ion juga berpotensi untuk ekstrak La, Nd dan Ce oleh ammonium sulfat. Potensi zeta zarah tanah liat dilakukan pada sisa daripada setiap langkah pengekstrakan. Tanah liat penjerapan ion yang dilarutkan dengan ammonium sulfat mempunyai nilai keelektronegatifan potensi zeta tertinggi, iaitu -23.5 mV. Ini

menunjukkan bahawa zarah tanah liat yang dilarutkan oleh ammonium sulfat mempunyai serakan yang tinggi yang tidak memberi manfaat kepada pembentukan tanah yang baik..

SEQUENTIAL LEACHING OF MALAYSIAN’S ION ADSORPTION CLAY RARE EARTH ELEMENT

ABSTRACT

Ion adsorption clay rare earth has been getting known for many applications to the industry. Malaysia has the enough potential of RE-bearing rocks for formation of ion adsorption clay. However, there are not enough extensive studies on Malaysian’s ion adsorption clay. Hence, the purposes of this research are to determine the physical and chemical characteristics of Malaysian’s ion adsorption clay and determine the potential extraction of REE by sequential extraction. Oriented clay sample was prepared from separation of clay minerals to subject the sample for XRD, and SEM. The chemical composition and trace elements of the sample done by XRF and ICP-MS. The ore is mainly composed with high concentration of Cerium. The ion adsorption clay was also composed with silica, quartz and the clay minerals present in the sample are included with yugawaralite, berlinite and montmorillonite. Ammonium sulfate leaching (1S) and 5-step (5S) sequential extraction (SE) were conducted on the samples to determine the potential extraction of and extraction efficiency. The results reported that ammonium sulfate leaching can leach almost all the REE compared to sodium acetate used in 5S. this indicates that ammonium sulfate leaching is suitable leaching reagent to extract REE from ion adsorption ore. The ion adsorption ore also has the potential to recover La, Nd and Ce by ammonium sulfate. Zeta potential of clay particle is done on residue from each extraction steps. Ion adsorption clay leached by ammonium sulfate had the highest electronegative value of zeta potential, which was -23.5 mV. This indicates that the clay particles leached by ammonium sulphate had high dispersion which does not beneficial of good soil formation.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Rare-earth elements (REE) are a collection of seventeen chemical elements in the periodic table, including the fifteen lanthanides as well as yttrium and scandium (Balaram, 2019). the latter two elements are categorised as REE because of their comparable physical and chemical characteristics to lanthanides, and they are typically associated with these elements in many ore deposits.

China possesses the world's greatest REE deposits (80%) and is a key producer of REEs for the global market (Charalampides *et al.*, 2015). Several REE compounds are found in smart batteries, which power all-electric and hybrid automobiles. Because of their distinct physical, chemical, magnetic, and luminous properties, these elements contribute to a variety of technological benefits such as lower energy consumption, increased efficiency, miniaturisation, speed, durability, and thermal stability. In recent years, there has been a surge in demand for energy-saving devices (green technology) that are quicker, lighter, smaller, and more efficient (Balaram, 2019).

Ion-adsorption rare earth deposits were formed as a result of chemical weathering, which led to the breakdown and dissolution of granite and granite porphyry, followed by adsorption and enrichment of rare earth minerals on clay minerals during the migration and penetration process of rare earth mineral solution (Yang *et al.*, 2013). Southeast Asia is one of the ion adsorptions deposits occurrences have been discovered outside China. The ion adsorption type prospects in Southeast Asia. In southeast Asia, Malaysia is included in one of the provinces that bearing RE in weathered granite crust (Tohar and Yunus, 2020).

1.2 Problem statement

The Kinta Valley in Malaysia has been a source of rare earth element minerals for several decades, and the nation is just now starting to revitalise its REE economy. The minerals were created from the by-products of alluvial tin mining in the valley. On the other hand, the fractionation of rare earth elements is controlled by the occurrences of rare earth element–bearing minerals. Each of these minerals has a distinct rare earth element distribution and a different amount of resistance to the effects of weathering. It is hard to provide a comprehensive description of the fractionation of rare earth elements due to these reasons. There have been a few research on Malaysian ion adsorption clay REE, but they are not particularly extensive.

The leachability of ion adsorption clay-hosted (IAC) REE can be tested with laboratory leaching and sequential extraction procedures. Sequential extraction is a method involving several extractions, which are sequentially applied to a solid sample aliquot. Lixiviants are applied in order so that the successive fractions obtained correspond to trace elements associated with different types of mode of presence. This is particularly useful in the assessment of the mobility and accessibility of ion exchangeable REEs.

1.3 Significance of study

This research will be beneficial in the development of REE industry in Malaysia which can give more exposure on characterization methods on ion-adsorption clay type of REE. Moreover, the sequential extraction recovery can be evaluated to study the potential of leachability of the REE. However, there is not enough research on mineralogy and geochemical of Malaysian ion adsorption clay REE. Hence, this project will be able to serve as a reference and guide in future studies.

1.4 Research Objectives

The objectives of this research are:

1. To study the physical and chemical characteristics Malaysia's ion-adsorption clay rare earth type of ore.

2. To investigate the potential to recover rare earth elements from ion adsorption clay ore by ammonium sulphate leaching and 5-step sequential extraction.

1.5 Scope of research

In this research, a single-step and 5-step of sequential extraction (SE) is conducted on ion adsorption clay. First, the raw sample was ground to -75µm for characterization of the sample. The physical and chemical characteristics of the sample was studied using X-ray fluorescence (XRF), X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and Fourier-transform Infrared Spectroscopy (FTIR). The total of REE content in the sample was determined by inductively coupled mass spectrometry (ICP-MS). Next, the study is continued with sequential extraction. The first step of extraction involved with leaching the raw sample with ammonium sulphate while the five (5)-step extraction used solutions such as sodium acetate, sodium pyrophosphate, hydroxylamine hydrochloride and aqua regia. The concentrations of REE from the extraction were analyzed through (ICP-MS). Solid residue from each step of sequential leaching was collected for zeta potential clay mineral.

1.6 Thesis outline

This thesis paper consists of five chapters. Chapter 1 was introduction chapter which cover the study background, problem statement, research objectives and scope of research. Next, in chapter 2 explanation on REE introduction, application, geological formation, mineralogy and formation of REE ion-adsorption clay. Besides, this chapter also discussed the comparison of sequential extraction method done by other researchers in different country. Chapter 3 discussed the details of procedures of the experiments that had been done in this project. The results from analysis and evaluation of the results obtained were presented in chapter 4. Lastly, chapter 5 is the conclusion of the study and proposed recommendations and suggestions in the future.

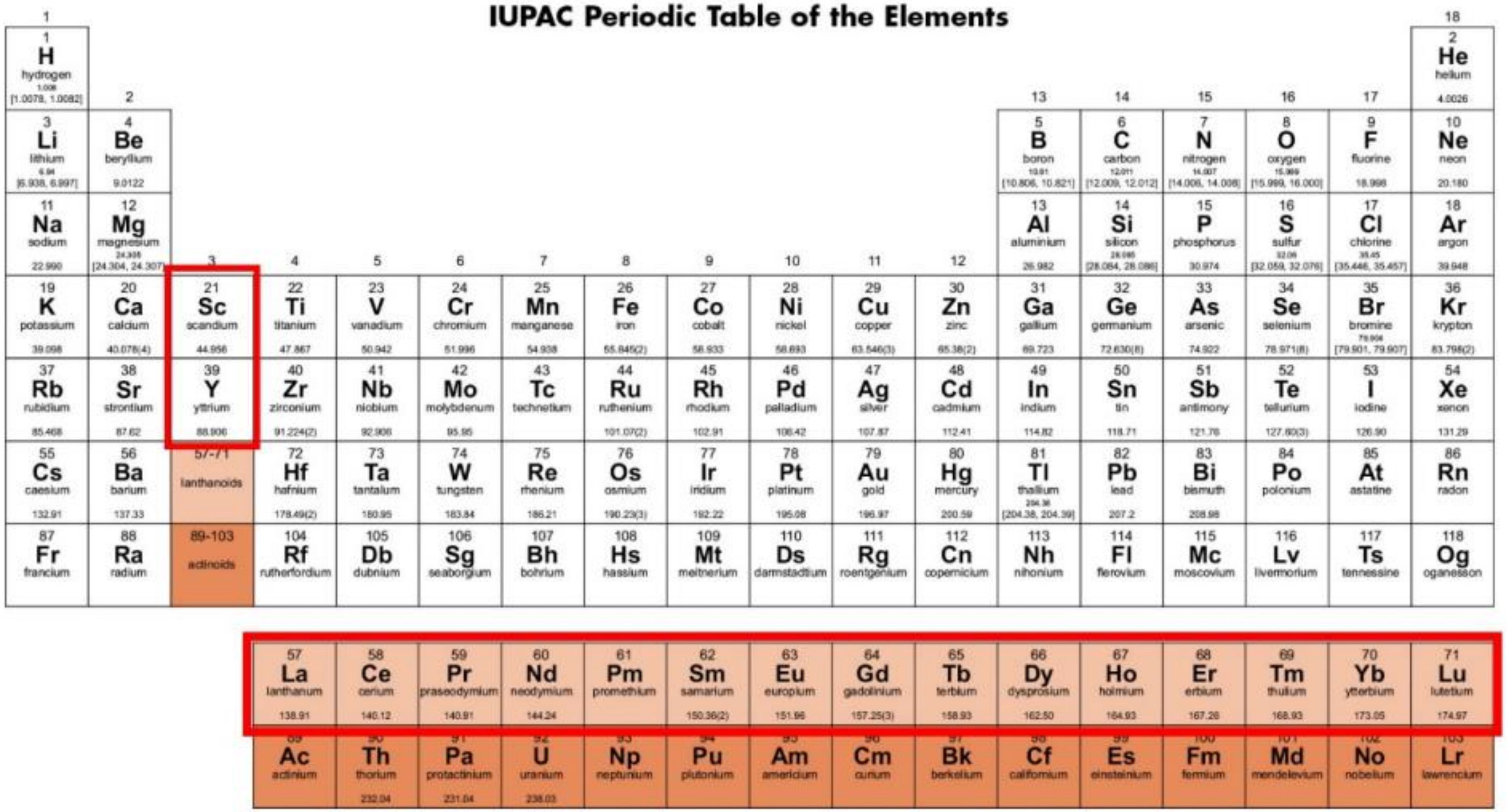
CHAPTER 2

LITERATURE REVIEW

2.1 Introduction of Rare Earth Element

The Rare Earth Elements are a group of seventeen chemically related metallic elements that together make up the fifteen lanthanide elements, according to the classification system used by the International Union of Pure and Applied Chemistry. Because of their similarity in both their physical and their chemical properties to those of the lanthanides, the latter two elements are categorised as Rare Earth Elements (REE), and they are typically associated to the lanthanides in many ore deposits (Mehmood, 2018).

REEs are typically grouped in two different categories: light rare earth elements (LREEs, atomic numbers 57–63), and heavy rare earth elements (HREEs, atomic numbers 64–71 plus yttrium 39). (Vahidi, Navarro and Zhao, 2016). The LREE listed are lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm) and europium (Eu) ; and heavy rare earth element (HREE) are gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb) and lutetium (Lu) (Mehmood, 2018).



For notes and updates to this table, see www.iupac.org. This version is dated 28 November 2016.
Copyright © 2016 IUPAC, the International Union of Pure and Applied Chemistry.

Figure 2.1 Classification of REE 15 lanthanides (La-Lu) with scandium (Sc) and yttrium (Y) marked with red box (Holden *et al.*, 2018)

2.2 REE crust abundance

Despite total rare earth resources content on Earth is plentiful, resources of individual REE have remained highly unequal ever since. REEs estimated concentration on the Earth's crust, ranges from 130 to 240 ppm or µg/g, whereas copper, iron as well as many other elements that are commonly exploited in an industrial scale barely reaches this figure and are usually much lower in concentration. REE depositions are more associated with igneous rocks, specifically alkaline rocks and carbonatites as opposed to the occurrence of other base and precious metals in mineable ore deposits.

The scarcity of an element is assessed generally by its crustal abundance, calculated by its average concentration on the earth's crust. Many estimates on REE crustal abundance have been made by various studies and values that show variation among one another have been presented. By looking at the abundance of REE, they are not uncommon as the total REE abundance of approximately 200 ppm is comparable to that of carbon (around 200 ppm).

Table 2.1 Average estimation of REE abundances on Earth's crust (Balaram, 2019)

Elements	(Balaram, 2019)			
La	30	29	30	39
Ce	60	70	60	66.5
Pr	8.2	9	6.7	9.2
Nd	28	37	27	41.5
Sm	6	8	5.3	7.05
Eu	1.2	1.3	1.3	2
Gd	5.4	8	4	6.2
Tb	0.9	2.5	0.65	1.2
Dy	3	5	3.8	5.2
Ho	1.2	1.7	0.8	1.3
Er	2.8	3.3	2.1	3.5
Tm	0.5	0.27	0.3	0.52
Yb	3.4	0.33	2	3.2
Lu	0.5	0.8	0.35	0.8
Y	33	29	24	33
Sc	22	-	16	22
Total	206.1	205.2	184.3	242.17

2.3 Uses of Rare Earth Element

China’s lead in total world mine production and reserves in 2010 stands at 97%; India with 2%; Brazil with 1%. In terms of total global mining reserves in REEs, China represents almost half of the total at 48%; the Commonwealth of Independent States 17%; the US 12%; India 3%; Australia 1%; and others 19% (Charalampides *et al.*, 2015). Figure 2.2 shows an overview of REE production by different countries and utilization for different applications in 2017. It is very interesting to note that the use of these materials in autocatalytic converters and industrial catalysts is by far the most common application of these materials.

REE are the elements that have become extremely important to our world of technology owing to their unique magnetic, phosphorescent, and catalytic properties. These elements are critical to technologies ranging from cell phones and televisions to LED light bulbs and wind turbines. During the last three decades, there has been an explosion in the applications of REE and their alloys in several technology devices (Balaram, 2019).

In recent years, there has been an increase in customer demand for energy efficient devices (green technology) that are also quicker, lighter, smaller, and more efficient. Specifically, this desire has been growing. Even the analytical equipment are benefiting from these technological advancements by becoming more compact and power-efficient. Table 2.1 shows the summarize of application of REE in the recent technological gadgets in different area.

Table 2.2 Applications of REE in various area (Balaram, 2019).

Area	Applications
Electronics	Television screen, computers, cell phones, silicon chips, monitor displays, long-life rechargeable batteries, camera lenses, light emitting diodes (LEDs), compact fluorescent lamps (CLFs), baggage scanner and marine propulsion systems
Manufacturing	High strength magnets, metal alloys, stress gauges, ceramic pigments, colorants in glassware, chemical oxidizing agent, polishing powders, plastic creation, additives for strengthening other metals, and automotive catalytic converters.
Medical sciences	Portable X-ray machines, X-ray tubes, magnetic resonance imagery (MRI) contrast agent, nuclear medicine imaging, cancer treatment applications and for genetic screening tests, medical and dental lasers.
Technology	Lasers, optical glass, fiber optics, masers, radar detection devices, nuclear fuel rods, mercury-vapor lamps, highly reflective glass, computer memory, nuclear batteries, high temperature superconductors.
Renewable energy	Hybrid automobiles, wind turbines, new. generation rechargeable batteries and biofuel catalysts
Others	Europium is used as method to identify legitimate bills for Euro bill supply and to dissuade counterfeiting. Holmium has the highest magnetic strength of any element and is used to create extremely powerful magnets. This application is useful to reduce the weight of many motors.

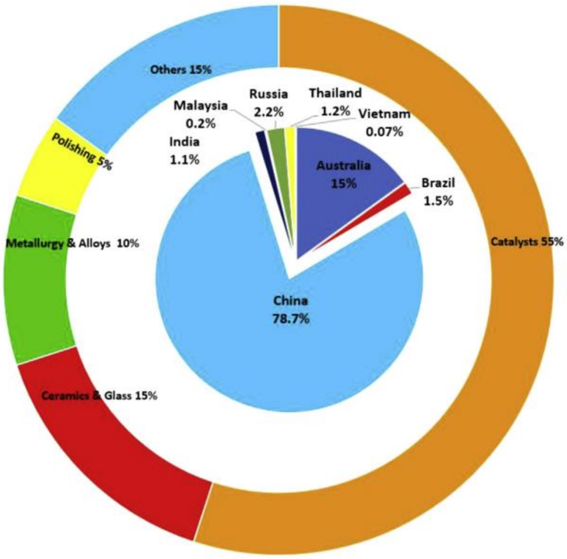


Figure 2.2 REE production by different countries for different applications in 2017 (Balaram, 2019)

2.4 Deposits of REE

REE potential resources are classified as primary and secondary deposits. The deposits that are considered to be primary are those that were created because of magmatic, hydrothermal, or metamorphic processes. Secondary deposits, which might include placers, laterites, and bauxites, are those formed by erosion and weathering. Because REE deposits can be found in a wide range of geological environments, categorizing them is difficult. REE deposits have been separated into the five types listed. Firstly, alkaline igneous rocks, such as pegmatites and carbonatites, residual deposits, heavy mineral placers, REE found in coal; and REE found in sediments found on the continental shelf and ocean bottom (Balaram, 2019).

Alkaline igneous rocks and carbonatites are typically associated with primary deposits. Deep mantle rocks partially melt and rise into the Earth's crust, where they cool to form alkaline igneous rocks. In general, alkaline magmas contain a greater abundance of Zr, Nb, Sr, and Li than they do REE. Magma goes through a series of chemical transformations as it rises because of the interaction of its rising temperature and pressure with the chemistry of the rocks that surround it. In addition to layered alkaline complexes, granitic stocks, and late-stage dikes, REE mineralization can also be found in granitic stocks. Less common are trachytic volcanic and volcaniclastic deposits (Balaram, 2019). The REE are highly incompatible in the vast majority of magmatic systems; as a result, they are concentrated in magmas that form as a result of low degree partial melting (or some other associated process such as the segregation of immiscible carbonatite melts) of the mantle, especially in metasomatically enriched regions of the mantle that contain higher concentrations of the REEs (Weng *et al.*, 2014). The summary of type of REE deposits is shown in Table 2.3.

Most hydrothermal processes are known to keep the REEs from moving, which suggests that to move (and effectively deposit and concentrate) these elements, unusual types of hydrothermal processes are needed. There are two types of hydrothermal systems that are linked to the formation of REE-enriched mineralization and REE mineral deposits. These are high temperature magmato-hydrothermal systems and F- and Cl-bearing hydrothermal systems. However, these two types of systems are not mutually exclusive (Weng *et al.*, 2014).

As previously mentioned, laterites are secondary deposits. Lateritic REE deposits, known as ion-adsorption clay type deposits, have been the world's largest source of heavy REE (HREE). Intensive lateritic weathering of bedrock under tropical or sub-tropical climatic conditions can form a variety of secondary, supergene-type deposits. These secondary deposits may range in composition from aluminous bauxites to iron and niobium, and include REE (Mclemore *et al.*, 2012).

Weathering is the process through which ion-adsorption clays, also known as weathered clays, become typical of specific locations across the world due to environmental factors. Ion-adsorption clays containing rare earth elements are most typically found in tropical areas with high rainfall. Rare earth elements are enriched in these places due to in situ lateritic weathering of igneous rocks. These rare earth elements (REEs) are removed from their host rocks as earth ions during the weathering process. They then go into the layer of lateritic soils that forms on top of the regolith, which is rich in clay minerals. The REEs will be taken up by the clay minerals that are already present in the soil once they have been mobilised. Rare earth elements are commonly clustered within certain horizons of the laterite profile due to their low mobility (Weng *et al.*, 2014).

Rare earth elements were found in a variety of mineral groups, including carbonates, silicates, halides, phosphates, and oxides. Several important rare earth minerals can be found in the deposits, including bastnaesite, monazite, xenotime, and ion-adsorption clays. The most important mineral was bastnaesite source of Low-Range Electron Energy Compounds, and it did not contain any radioactive elements like uranium (U) or thorium (Th) (Dushyantha *et al.*, 2020).

Xenotime was a mineral composed of yttrium phosphate, and the majority of its elements were HREEs. The mining of titanium, zirconium, and tin all result in the production of xenotime as a by-product (Papangelakis and Moldoveanu, 2014). Additionally, monazite is regarded as a primary source of LREEs as well as cerium (Ce). However, it was made up of uranium and thorium (Th) (U) (Dushyantha *et al.*, 2020). In several instances, monazite was discovered near other weather-resistant heavy minerals such ilmenite, zircon, rutile, and magnetite. They have a strength that enabled them to endure the river's current and concentrate in placer deposits (Wall, 2021).

Table 2.3 Classification of rare earth deposits modified after (Weng *et al.*, 2014)

Formation		Deposit type	Description	Major examples
Primary	Igneous	Peralkaline	Silica-unsaturated magmas concentrated in potassium, sodium and enrichment in high field strength elements (HFSE)	Lovozero, Russia; Thor Lake, Canada; Pajarito Mountains, USA; Norra Karr, Sweden; Strange Lake, Canada
		Carbonatite	Association with carbonate-rich igneous rocks containing high amount of carbonate minerals and low in silica content.	Oka, Canada; Bayan Obo, China; Bear Lodge, USA; Maoniuping, China; Mountain Pass, USA; Nolans Bore, Australia
	Hydrothermal	Skarn	Hydrothermal fluids break down REE hosting minerals, causing transportation and enrichment of REE in alteration haloes	Saima, China; Mary Kathleen, Australia
		Iron oxide-copper-gold	Mineralization occurring in oxides and carbonatites of iron deposits that host copper and gold	Olympic Dam, Australia; Milo, Australia
		Magmatic magnetic-hematite	REE bearing minerals recovered as a by-product from iron mining.	Pea Ridge, USA; Mineville, USA
Secondary	Weathered	Ion adsorption clay	Residual clay deposited from the weathering of granitic source rocks	Jiangxi, China; Guangxi, China; Dong Pao Mine, Vietnam
	Placer	Alluvial placer	Concentrations of resistant, heavy minerals in the river channels.	Guangxi, China; Idaho placers, USA; Perak, Malaysia; Carolina monazite belt, USA; Charley Creek, Australia
		Marine placer	Accumulations of high resistant heavy minerals, by coastal processes and found along or close to existing coastlines.	Alice Springs, Australia; Green Cove Springs, USA; Chavara, India; Cataby, Australia
		Paleoplacer	Consolidated, cemented rocks formed by weathering of Archean granite source rock	Elliot Lake, Canada; Bald Mountain, USA

2.4.1 Western Malaysia’s granite crust

Thailand, Malaysia, and western Indonesia are the countries that make up the Southeast Asian tin–granite belt. This belt is a large metallogenic province that has Sn deposits that are linked with ilmenite S- and/or I-type series of granitic rock (Yaraghi, Ariffin and Baharun, 2020).

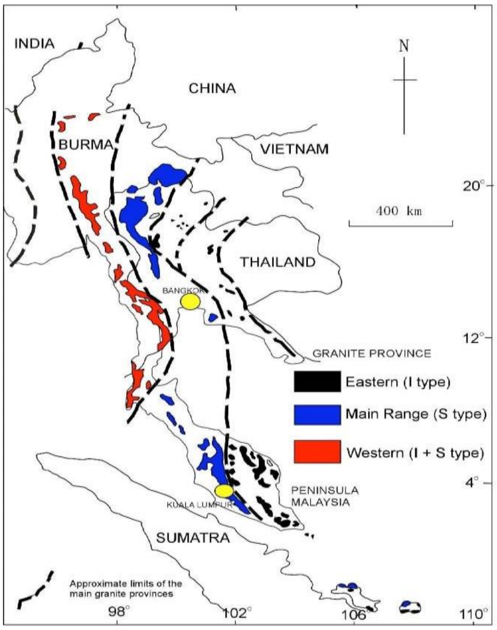


Figure 2.3 Granite belt of Southern Asia

Figure 2.3 displays a simplified version of the map that indicates the location of granitic rocks in the southeast Asian tin belt. The following three granitic bands were indicated in the area: the "Eastern belt," which had a high portion of I-type granites; the "Central belt," which contained a high amount of S-type granites; and the "Western belt," which contained a mixture of I-type granites and S-type granites.

There are several intensive geochemical assessments on Malaysian REE-rich weathered granitic crust by other researchers reported that Malaysia has high potential of REE associated with weathered granite (Yusoff, Ngwenya and Parsons, 2013; Tohar and Yunus, 2020; Yaraghi, Ariffin and Baharun, 2020). Malaysia with a wide range of granitic bedrocks has considerable potential considering ion-adsorption prospected areas. The potential area of REE associated with weathered granite are Taiping, Lumut, Bukit Tinggi, Bukit Tamping and Baling (Yaraghi, Ariffin and Baharun, 2020).

Table 2.4 Geochemistry and associated minerals of IAD at various location in Malaysia

No	Location	Parent rock speciation	Major minerals	REE-bearing accessory minerals	References
1.	Lumut and Teluk Murok, Perak	Peraluminous S-type granite, metamict texture	K-feldspar,mica & quartz	Zircon, monazite, xenotime, apatite & allanite	(Yaraghi, Ariffin and Baharun, 2020)
2.	Besar island, Tengah Island & Hujung island, Johor	Ultrafelsic A-type granite	K-feldspar, biotite, plagioclase & quartz	Zircon, monazite, titanic, bastnaesite-(Ce),allanite &apatite	(Tohar and Yunus, 2020)
3	Rawang & Cheras, Kuala Lumpur	I-type (Rawang) & S-type (Cheras)	K-feldspar, quartz, kaolin & muscovite	Zircon, apatite, anatase, epidote & monazite	(Yusoff, Ngwenya and Parsons, 2013)

2.5 Environmental effects of REE

Countries including China, the United States, India, Malaysia, and Brazil have seen major environmental and health impacts as a result of the intense mining and manufacture of rare earth elements (REE). Mining activities such as drilling, blasting, transportation, stockpiling, and physical processing can release dust into the air and surrounding water bodies that can impact local soil, wildlife, and vegetation in addition to human health. These dust releases can include rare earth elements (REE), other toxic metals and chemicals (Balaram, 2019).

Most of the negative impacts of REE exposure on people and their possible health impacts are based on studies of mine employees and those who work with REE or their products on a daily basis. This level of exposure is often substantially higher than that of the general population. According to the conclusions of certain research, the chemicals employed in the ore processing, extraction, and refining operations were responsible for the health concerns posed to employees as well as inhabitants of the surrounding region, as well as water supply contamination and agricultural degradation (Balaram, 2019).

The presence of the radioactive elements like thorium and uranium in deposits of rare earth elements is one of the most significant issues facing the environment. Particularly the HREE thorium tends to cluster in the same geological settings as other heavy REE. It is not uncommon for monazite that was generated in granitic rocks and the mineral sands that were derived from them to have a few percentage points of thorium by weight (Mehmood, 2018).

Under natural conditions, REE may only become available in small amounts via the groundwater and the atmosphere, however, their increased use has enhanced the amount of REE, and has created several new routes for bio-accumulation (in plants, animals, and human beings). Background level of REE content in waters, both surface and subsoil, varies significantly and also depends mostly on the local geology. Unfortunately, maximum acceptable limits for REE in drinking water are not available from any international health organization and also there is no sufficient data available about their toxicity to human health. Some of the REE minerals contain significant amounts of radioactive elements such as uranium and thorium, which can contaminate air, water, soil and groundwater (Balaram, 2019).

The recognized environmental disasters in agricultural areas and downstream waters of REE mining areas have been, and are likely to be, environmental emergencies in the regions affected by REE ore extraction and refining. The concomitant role of acidic pollutants should be highlighted, leading to the enhanced toxicity of inorganic chemical species, as is well-established for several cations and dissolved REEs (Rim, 2016). Environmental pollution is a serious problem to China since ammonium sulfate as leaching agent used by in-situ leaching ion adsorption clay rare earth. There are solutions done by researchers to reduce the environmental damaged by replacing ammonium sulfate with other leaching (Yanfei *et al.*, 2015; Yin *et al.*, 2018).

2.6 Ion adsorption clay

In 1970, ion-adsorption rare earth deposits were found in Ganzhou, China. It was first disregarded as a mineral phase because it behaved differently than any of the known phases of rare earth minerals. Ion-adsorption rare earth minerals exist at a simple trivalent cationic state, which is simply adsorbed onto clays (Yang *et al.*, 2013). RE^{3+} ions are mobilised during this stage of the process by being transported into an aqueous solution. This solution then percolates through the weathering body and becomes adsorbent on the clay mineral surfaces. Over time, tectosilicates undergo metamorphism, resulting in the progressive production of clay minerals (mainly feldspar) (Voenkaul *et al.*, 2015).

The adsorption of REE onto soils and clay minerals is strongly affected by the attribute of the adsorbent materials and ionic strength of the solution. Various weathered products such as organic matter, clay/non-clay minerals and amorphous materials are common adsorbents that are capable of being host for REEs. Even though REEs show good affinity towards different absorbent materials but their greatest affinity is always towards clay minerals. Clay minerals are made of many layers of octahedral and tetrahedral silicon sheets, falling under the phyllosilicate class, which allows water molecules and other charged ions to move freely between the layers (Moldoveanu and Papangelakis, 2016).

There are number studies done by researchers to study geochemical and mineralogical of ion adsorption clay that formed at certain country (Bao and Zhao, 2008; Sanematsu *et al.*, 2013; Yaraghi, Ariffin and Baharun, 2020). Different geochemical weather influenced the mineralogy of ion adsorption clay. The ion-adsorption deposit is different between other conventional REE deposit especially in their main bearing minerals (Sanematsu *et al.*, 2013).

In such deposits, the REEs are inferred to be weakly adsorbed onto clay minerals (dominantly kaolinite and halloysite), as well as oxides, at a range of structural sites, including broken edge sites, charged aluminol or siloxane groups at defects and isomorphic substitutions, the hydration shells of exchangeable cations or by direct substitution of exchangeable cations (Borst *et al.*, 2020).

A study done by Ram *et al.*, (2019) to perform an in-depth chemical and mineralogical characterisation of selected samples from two regolith profiles within the Ambohimirahavavy igneous complex in Madagascar. The sample was the ores are characterised by negative cerium anomalies, which are similar to those reported from the South China IAC ores, but contrast with positive anomalies reported in many regolith profiles developing on acid rocks, including in Madagascar. The Ambohimirahavavy ores are LREE-enriched but contain HREE concentrations that are like those of the South China ores, making them an economically viable REE source.

2.6.1 Weathering profile

Temperate and tropical regions have ion adsorption deposits. The important requirements are an underlying granite, although deposits can form on alkaline rocks, and soluble REE-bearing minerals in the granite, such as REE fluorcarbonates, eudialyte, and allanite. By altering feldspar in the weathering profile, clays are formed that can absorb REE. Extreme weathering can dissolve REE and break down clay. Because REE in parent granite is usually housed in insoluble minerals like monazite and xenotime, most weathered profiles do not contain REE ion adsorption clays. Although such insoluble minerals would not contribute to an ion-adsorption clay-hosted REE deposit, they may accumulate heavy mineral sands (Wall, 2021). The summary of typical weathering profile ion-adsorption clay is shown in Figure 2.4

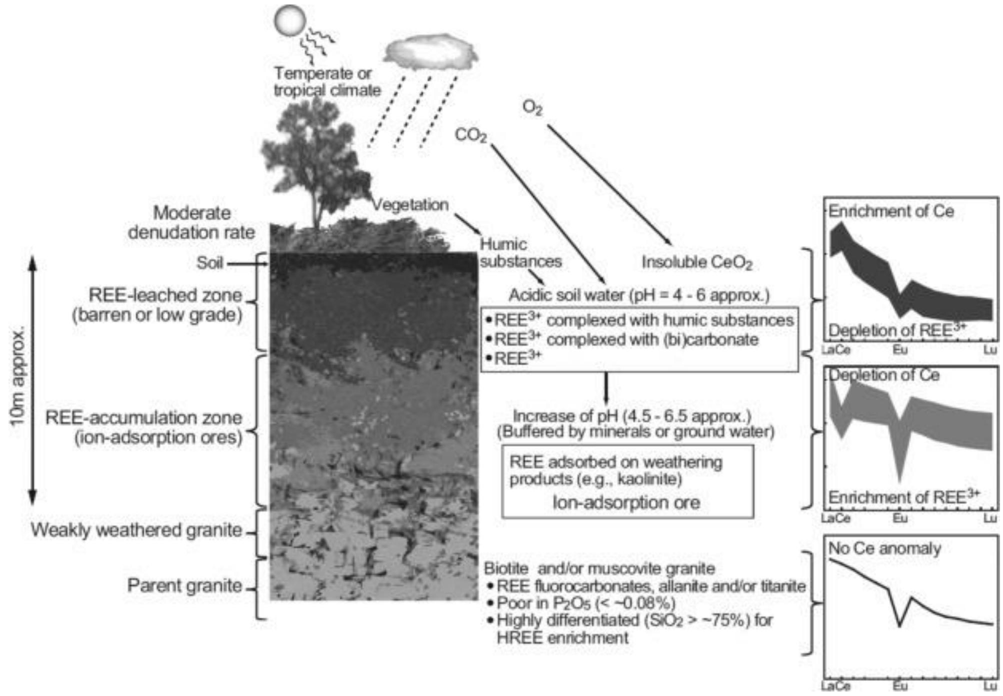


Figure 2.4 Simplified of typical weathering profile (Wall, 2021)

Sanematsu *et al.*, (2013) took several granite samples from weathering profile to determine the REE-bearing minerals of granite and parent granite. The redox boundary may be found at a depth of approximately 4.5 metres, and it serves as a divider between the top and lower regions of the weathering profile on the parent granite. The weathering crusts may reach a depth of up to 30 metres and are composed of the following four layers.

Figure 2.5 shows the weathering profile off granite crust. The first layer (A) is an upper humic layer composed of quartz, organic matter, and soil that is 0–2 metres thick and has a very low REE content. The second layer (B) is a strongly weathered layer that is enriched in REE and is 5–10 metres thick and contains kaolinite, halloysite, quartz, and mica. The next layered labelled as (C) a semi-weathered layer that is 3–5 metres thick and contains kaolinite and sericite; and the bottom layer (D) a weak heavily weathered layer. Layer (B) can host up to 80–90 percent of the adsorbed REE, whereas the semi-weathered layer only contains around 15 percent at layer (C) (Sanematsu *et al.*, 2013).

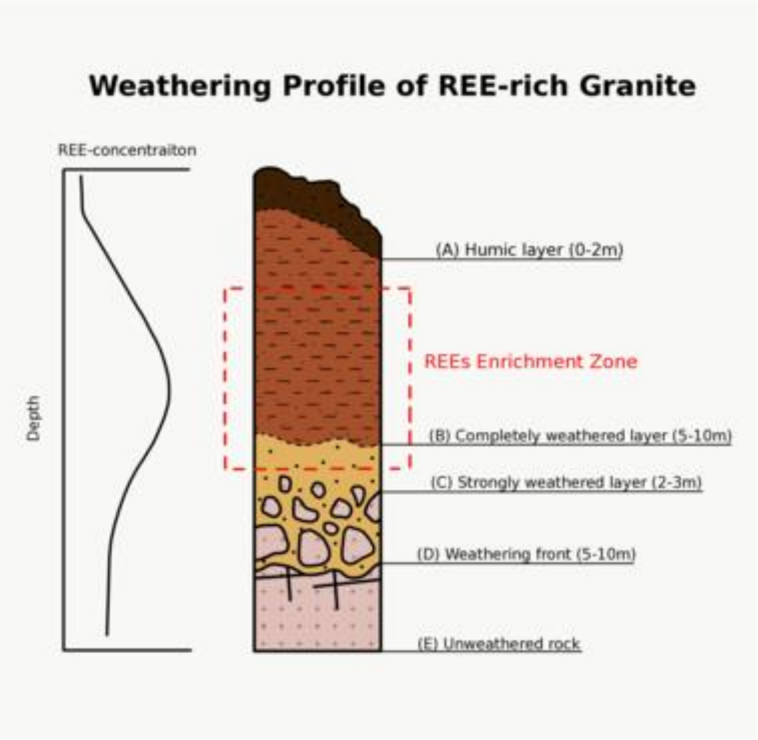


Figure 2.5 Weathering profile of crust granite

2.6.2 Ion exchange mechanism

The electrostatic adsorption of cations is achieved by the presence of clays inside the ion adsorption ores. These clays have a surface charge that is consistently negatively charged such as REE Due to varying weathering conditions, ion-adsorption clays contain three primary categories of REE: ion exchangeable phase, colloid phase, and mineral phase.. (Moldoveanu and Papangelakis, 2016). Leaching mechanism involving all three phases is shown in Figure 2.5

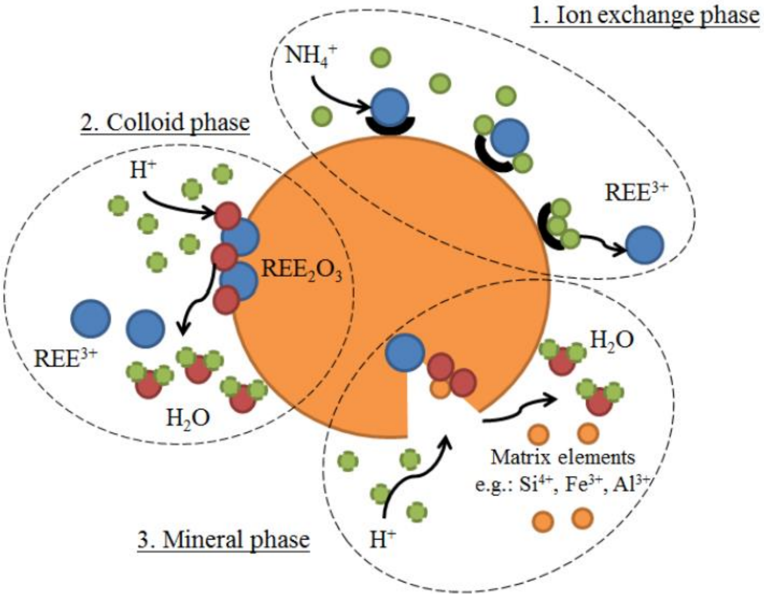


Figure 2.6 Illustration on leaching mechanism and their phases (Voenkaul *et al.*, 2015).

The following is a description of each stage in the process: The rare earth elements (REE) are deposited as insoluble oxides or hydroxides, or as colloidal polymeric organometallic complexes. This phase is referred to as the colloid phase. These species are not very frequent in ore deposits that are already naturally somewhat acidic, and the only way to extract them is by acid leaching.

Next, exchangeable phase where REE are present as soluble free cations/hydrated cations or as positively charged complexes in solution adsorbed on clays. These species make about 60–90% of the total rare earth content in ores and are recoverable via ion-exchange leaching with monovalent salts.

The third phase, mineral phase which REE comprise solid fine particles with the same mineral assemblage as the host rocks (REE part of the crystal lattice). This phase typically accounts for the remainder of the ion-exchangeable phase's contribution to the total rare-earth element (TREE) concentration and can be recovered only through alkaline baking or acid leaching of mineral phases (Voenkaul *et al.*, 2015).

2.7 Characterization of REE

The chemical analysis of REE in geological, industrial, and environmental materials is critical for geochemical exploration studies, mining, extraction, quality checks of both raw materials and final products in industry, and environmental monitoring. Because of their structural and chemical similarities, detecting REE is often a difficult and time-consuming task (Balaram, 2019).

ICP-MS and HR-ICP-MS are widely utilised for REE detection in a variety of materials because they can detect many elements, have a broad linear dynamic range, have less interferences, are easy to use, and are among the most accurate instrumental methods currently available. Furthermore, procedures such as X-ray fluorescence spectrometry (XRF), ICP-OES, GD-MS, LIBS, and the recently developed microwave plasma atomic emission spectrometry (MP-AES) have been shown to be particularly beneficial in such research (Balaram, 2019).

2.7.1 X-ray fluorescence spectrometry (XRF)

X-ray fluorescence spectrometry (XRF) is a viable technique for analysing trace elements at the mg/g level, while being rather insensitive to rare earth elements (REE). As a standard analytical methodology for REE analysis, XRF offers specific benefits over the other techniques in terms of its precision, speed, and cost. Low sensitivity is its only deficiency (Balaram, 2019).

2.7.2 Fourier-transform infrared spectroscopy (FTIR)

In FTIR analysis, which is used to identify organic, inorganic, and polymeric constituents, the samples are scanned using infrared light. Changes in the distinctive pattern of absorption bands indisputably indicate that the elemental composition of the material has changed (Titus, J ames Jebaseelan Samuel and Roopan, 2019).