



Leaching behaviour of light rare earth elements from lignite-derived ash

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PREFACE

Declaration of authorship

I, Hanko Skaar Beyers, hereby declare that the dissertation entitled: ***Leaching behaviour of light rare earth elements from lignite-derived ash***, which I herewith submit to the North-West University is in compliance with the requirements set for the degree: Master's in Chemical Engineering, is my own work, has been text-edited in accordance with the requirements and has not already been submitted to any other university.

Signature:

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ABSTRACT

The growing demand for rare earth elements (REEs) has driven research into secondary sources such as coal ash. However, recovery from these materials remains challenging, particularly due to the high thermal treatment temperatures typically applied to parent coals. This study explores the potential of lignite, used in fluidized bed combustion (FBC) boilers, as a secondary source of REEs under lower thermal treatment conditions.

Lignite coal and its derived ash, obtained at various laboratory-controlled temperatures below 1000 °C, were systematically characterised. The results revealed 8 times enrichment of REEs content from the raw coal to the derived ash, although the total rare earth element (TREE) concentration remained below 1000 ppm. Thermal treatment reduced particle size and induced mineralogical transformations consistent with the conversion of kaolinite to amorphous metakaolinite. To better replicate FBC conditions, the duration of thermal treatment was subsequently reduced based on observed combustion behaviour.

Sequential leaching experiments demonstrated that, in raw lignite, that most light rare earth elements (LREEs) were associated with monosulfides and carbonates. In contrast, the derived ash exhibited primarily acid-soluble LREEs, with a fraction complex-bound and a substantial portion rendered insoluble following thermal treatment.

The derived ash was subjected to leaching tests using a mineral acid (HCl) and an organic acid (tartaric acid). Screening results indicated that HCl achieved a 50% recovery of light rare earth elements (LREEs) compared to 36% for tartaric acid. The influence of key operational parameters, including liquid-to-solid ratio, lixiviant concentration, leaching duration, and temperature, was systematically evaluated. Among these, the liquid-to-solid ratio was identified as the most influential factor, although the range tested was narrower than in comparable studies. Kinetic experiments involving leaching duration and temperature revealed that the overall process is diffusion controlled. Model fitting suggested multiple rate-controlling mechanisms: product-layer diffusion dominated during the initial 5 minutes, followed by film-layer diffusion control over the remaining leaching period.

The experimental results suggest that the use of lignite coal as a secondary source of REEs may be limited under the conditions investigated. Although the material exhibited a promising distribution of elements, the total rare earth element (TREE) content remained low even after enrichment. Leaching experiments at low thermal treatment temperatures achieved a maximum LREE recovery of 77%, but this required relatively high HCl concentrations (3 M) and a high liquid-to-solid ratio (100:1), which may constrain the process's practical applicability.

Finally, a preliminary design of a 35 t/h coal-fired power plant was presented on the basis of the experimental results. A mass balance over the leaching section of the design resulted in a PLS TREE mass flow rate of 28 t/yr. To achieve this amount, high amounts of HCl would be required. Therefore, further separation steps would be required to recycle large amounts of the lixiviant back to the leaching section.

Keywords: *Leaching; Rare earth elements; Low rank coal; Low temperature thermal treatment; Kinetic modelling; Fluidized bed combustion*

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LIST OF ABBREVIATIONS

Abbreviation	Description
BA	Bottom ash
CA	Cyclone ash
CFA	Coal fly ash
CFPP	Coal-fired power plants
CI	Confidence interval
CREE	Critical rare earth element
CRM	Coal-related material
DAFR	Dry air flow rate
EXREE	Excessive rare earth elements
FBC	Fluidized bed combustion
HREE	Heavy rare earth element
ICP-MS	Inductively coupled plasma mass spectroscopy
ICP-OES	Inductively coupled plasma optical emission spectroscopy
IEA	International Energy Agency
LDA	Laboratory derived ash
LLDA	Lignite laboratory derived ash
LREE	Light rare earth element
MSA	Methanesulphonic acid
PC	Pulverized coal
PCC	Pulverized coal combustion
PCM	Progressive core model
PLS	Pregnant leach solution
PSD	Particle size distribution
REE	Rare earth element
REF	Relative enrichment factor
REO	Rare earth oxide

Abbreviation	Description
REY	Rare earth elements + Y (excluding Sc)
RLC	Raw lignite coal
SCM	Shrinking core model
SEM	Scanning Electron Microscopy
SLP	Sequential leaching procedure
SPM	Shrinking particle model
TA	Tartaric acid
TGA	Thermogravimetric analyser
TREE	Total rare earth element
UCC	Upper continental crust
UCREE	Uncritical rare earth elements
XRD	X-ray diffraction
XRF	X-ray fluorescence

CHAPTER 1 INTRODUCTION

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1.1 Background and motivation

Rare earth elements (REEs) consist of 17 elements, including the lanthanide group, scandium (^{21}Sc), and yttrium (^{39}Y). The demand for these metals has seen a significant increase in recent years, which has put pressure on countries to strengthen their supply of rare earth oxides (REOs). Currently, the supply of these metals is not evenly distributed, with China being the leading producer of rare earth oxides (REOs). In 2023, the approximate amount of REOs produced by China was 240 000 metric tons (MT), representing 69% of global REO production. In comparison, the remaining countries such as the United States, Australia, Brazil, Myanmar, India, Madagascar, Malaysia, Russia, Thailand, and Vietnam produced 113 322 MT combined [1]. The concentration of REO supply within a limited number of producers introduces economic vulnerability, as fluctuations in political or trade relations can significantly impact global availability and pricing [2]. China made export restrictions since 2009, causing the price of REEs to increase dramatically [3]. This has resulted in global competition to increase REE resources, resulting in an increase in the production of REEs from primary and secondary sources.

Currently, most of the REOs that are produced are from primary sources such as monazite, bastnaesite and xenotime ore deposits [4]. The traditional mining methods used for these ores have become less attractive compared to secondary source usage. This is due to the complicated multi-step nature of the process that requires more capital investments, more energy, generates large quantities of undesired tailings, and negatively impacts the environment [5]. The effect of these disadvantages can be seen from the cease of operation of the Mountain Pass mine in the US, in 1998. From 1965, the mine was a leading producer of REEs [6], and stopped its operation due to competition from China and environmental concerns [7, 8]. These types of complications have led many of the new research to be conducted on secondary sources.

More recently, research has been conducted on secondary sources such as electronic waste [9], mining tailings [10], red mud [11], phosphogypsum [12], and coal. Coal has received considerable attention because of its abundance and remaining usage as fuel for electricity generation. From 2022 the demand for electricity is set to increase by 80% to 150% by 2050 [13]. Even though a global incentive has been made to use cleaner alternatives, coal will still remain as the primary energy source for a few years in developing countries. Currently, China remains the largest producer and consumer of coal to accommodate the increase in electricity demand [13]. Ongoing dependency on coal has led to more coal being mined, resulting in the production of more waste products, i.e., coal fly ash (CFA) and bottom ash (BA).

The presence of REEs in coals of different ranks and origins has further motivated the use of coal-related material (CRM) as a secondary source of REEs [14-17]. The concentration of REEs in coal differs depending on the origin of formation. Some of the highest concentrations of REEs found in coal are above 1000 ppm [18]. Because the REEs in coal are non-volatile, the combustion of coal results in the enrichment of REEs. In a paper published by Seredin and Dai (2012), extreme cases of enrichment have been found [17]. Studies focusing on the analysis of REEs in coal have been conducted for several years. Only in recent years has research focused on the extraction of these elements from coal and coal ash [19]. As a result, the usage of coal ash rather than the parent coal material was found to be more advantageous due to REE enrichment [20-23]. Furthermore, it has been found that the thermal treatment conditions can have a significant effect on the leaching recovery of the REEs.

Temperatures of thermal treatment (combustion/calcination) can have a significant impact on the formation of silicates, inhibiting the extraction of REEs. Calcination and combustion experiments have been conducted at temperatures that mimic fluidized bed combustion (FBC) boilers (750-900 °C) [24] or pulverized coal combustion (PCC) boilers (1300-1700 °C) [25]. These studies have shown that higher temperature thermal treatment produces ash containing higher amounts of aluminosilicate-bound REEs, resulting in lower REE extraction. There are several uncertainties about the effect of thermal treatment on different ranks of coal. Specifically, the impact on the leaching efficiency of the respective coal or derived ash. Since REEs have been found in coals of different ranks and origins, it can be motivated to investigate the usage of low rank coal for the extraction of REEs. Furthermore, lower ranks of coal are used more frequently in FBC boilers than in other conventional combustion boilers [26].

1.2 Problem statement

A significant proportion of the world's electricity is generated from coal, resulting in large quantities of ash that are often discarded or repurposed in other industries. Both coal and its combustion ash have been identified as potential secondary sources of rare earth elements (REEs) due to their abundance and widespread availability. Harnessing these materials for REE recovery could offer notable economic and sustainability benefits by transforming an existing waste stream into a valuable resource.

1.3 Aim and Objectives

This study investigates the leaching behaviour of low-rank coal ash generated under low temperature thermal treatment conditions representative of fluidized bed combustion boilers, with the goal of assessing its potential as a secondary source of rare earth elements.

The following objectives apply to the research:

1. To characterize the lignite coal and the derived ash generated under low temperature thermal treatment conditions.
2. To determine the modes of occurrence, solubility forms, and thermal transformation behaviours REEs in both the lignite coal and the resulting ash.
3. To evaluate the influence of different lixiviants and leaching parameters on REE recovery and leachate composition.
4. To investigate the effect of thermal treatment temperature on ash properties and subsequent REE extraction efficiency.
5. To determine the leaching kinetics and develop a preliminary process design based on the experimental results

1.4 Scope

The experiments in this study will be conducted using a low-rank lignite coal sourced from the Middle East. No beneficiation of the feed material or the resulting ash will be performed. The coal will be pulverized to a specified mesh size, homogenized, and subjected to thermal treatment, without further sieving after treatment. Sequential leaching procedures will be employed to gain insight into the potential associations and speciation of REEs, but they will not be used to fully characterize the mechanisms driving changes in REE minerals from raw coal to derived ash, as this is beyond the scope of the study. For thermal treatment, only the temperature and dry air flow rate will be varied. Leaching experiments will examine the influence of lixiviant concentration, liquid-to-solid ratio, temperature, and duration on REE recovery and leachate concentration. Fractional recovery will be estimated based on characterization data. An orthogonal array assessment will focus solely on lixiviant concentration and liquid-to-solid ratio to determine the minimum stoichiometric amount of acid required for the resulting recovery and leachate concentration. Kinetic analysis will consider multiple models according to their respective assumptions, including three based on the shrinking core model, two based on the shrinking particle model, and three based on the pseudo-homogeneous reaction model.

1.4.1 Limitations of this study

The limitations that are present in the current study are as follows:

- The study was limited to an available lignite coal with a low TREE concentration since there are no lignite coal mines or FBC units in South Africa
- The study is limited to a low rank coal of a specific region and could therefore be influenced by geological factors. A lignite from a different region could produce different results

- The thermal treatment of the lignite coal is limited to the tube furnace and does not represent the large-scale operation of a FBC boiler
- The leaching process is limited to a batch process and can differ if the process was experimentally tested for a continuous leaching process

1.5 Chapter division

The chapter division for the study on using low rank coal as a secondary source of REEs is as follows:

1.5.1 Chapter 1 – Introduction

In the first chapter the introduction for the study is given. The introduction of the study includes an overview of the study, the problem statement, and its significance. The chapter includes the relevant information such as the aim, objectives, dissertation structure, and the scope of the study.

1.5.2 Chapter 2 – Literature review

In the second chapter there is an extensive literature review regarding the relevant topics associated with the research. The following topics are discussed in the literature review:

- A brief introduction to REEs, their mineral associations and the current primary and secondary sources of the elements.
- A brief introduction to the formation of coal, coal rank, its current usage and the associated waste products.
- Current literature of REEs in coal with regards to concentrations, association and occurrence as well as the current initial viability testing methods.
- Current literature of REE extraction from coal, specifically the usage of pretreatment methods (thermal or alkaline) and the effect of leaching parameters.
- An overview of kinetics, specifically the models applying to the extraction of REEs from coal material as well as other fundamental concepts.

1.5.3 Chapter 3 – Research methodology

In this chapter the research methodology is explained in detail. It is supported by experimental procedures and accompanied by a list of equipment and materials used to achieve the aim of the study. The following topics are discussed in chapter 3:

- Brief overview of the experimental approach (experimental plan)
- Details of the feed material, chemicals used, sample preparation and characterization
- Description of the thermal treatment procedure
- Description of the leaching procedures
- Experimental conditions used throughout the study
- Analytical methods used throughout the study

1.5.4 Chapter 4 – Results and discussion

In this chapter the results obtained from the research methods is analysed and discussed. The results include the characterization of the coal and derived coal ashes. Furthermore, the leaching propensity of the REEs from the coal ash is thoroughly discussed. The following is presented in chapter 4:

- Proximate analysis of the feed coal
- Elemental and phase analysis of the feed coal and coal derived ash
- Particle size distribution of the feed coal and the coal derived ash
- Mineralogical changes after thermal treatment of the feed coal
- Sequential leaching results of the feed coal and the derived ash
- Preliminary screening tests results of the coal derived ash
- Primary leaching test results of the coal derived ash
- Leaching kinetics results of the coal derived ash

1.5.5 Chapter 5 – Conclusion, evaluations and recommendations

In the final chapter of the dissertation, the following aspects are addressed:

- Conclusions based on the results of the study
- Critical evaluation of the impact of the findings of the study
- Recommendations based on the results of the study

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2.1 Introduction

REEs were first discovered at the end of the 18th century in Sweden [1, 2], with the first application reported in the 1890s in Vienna [3]. Since then, technology has advanced with more applications that depend on these elements. The most prominent advancement being the production of “green technologies,” which are based specifically on REEs for fabrication. The title ‘The Vitamins of Modern Industry’ has been given to these metals due to their ability to increase the efficiency of modern technologies [4]. Some of these modern technologies include, but are not limited to, circuit boards, solar panels, magnets, catalysts, batteries, automotive and medical technologies [1, 5-7].

The demand for REEs began its initial climb with the introduction of colourized televisions in the 1960s. The estimated demand for REOs in 1953 was around 1000 tons of REOs, in 1997 the demand grew to an estimated 66,000 tons which increased further to 125,000 tons in 2008 [8]. The current effort to develop and produce “green technologies” is expected to further increase the demand for REE. This is evident from the fact that in 2019, 60% of the REO demand was solely for new technological applications [9]. The demand for these elements is set to increase in upcoming years with some predictions being 7-8% annually [10].

Higher costs and availability issues associated with primary sources of REEs have fuelled research on the use of secondary sources. Furthermore, the usage of secondary sources enhances the sustainability of REE production and supports the development of a circular economy. Coal as a secondary source of REEs is an example of such research efforts. Although many attempts have been made to extract REEs from coal and coal ash [11-14], studies still fail to produce a conceptual design or implementation of such a process. Furthermore, the utilization of low thermal treated coal, specifically low rank coal such as lignite, has not been thoroughly investigated.

To develop and implement a large-scale REE extraction process, several topics need to be well understood. This Chapter aims to address the current state of literature regarding these topics and include: (i) a basic understanding of coal and REEs, (ii) the occurrence and association of REEs in coal and ash, (iii) the effect of thermal treatment temperature on extraction efficiency, (iv) the effect of leaching parameters on extraction efficiency, (v) the most recent results on optimum conditions for REE recovery from coal and coal ash, and (vi) leaching kinetics and kinetic modelling.

2.2 Rare earth elements

REEs are 17 elements that include the lanthanide group (^{57}La – ^{71}Lu), ^{21}Sc , and ^{39}Y . Since Sc and Y have geochemical behaviour similar to that of the lanthanide group, they are considered REEs [1]. REEs can be categorized into two sub-groups, namely, light rare earth elements (LREEs) and heavy rare earth elements (HREEs). LREEs include ^{57}La up to ^{63}Eu , whereas HREEs include ^{64}Gd to ^{71}Lu , as well as ^{39}Y . These two sub-groups of REEs occur together in REE bearing deposits, except for Sc. Furthermore, REEs can be classified as critical rare earth elements (CREEs) and uncritical rare earth elements (UCREEs), based on global demand and supply of these elements [15]. CREEs consist of Nd, Eu, Tb, Dy, Y and Er, whilst UCREEs consist of La, Pr, Sm and Gd [15, 16]. Some REEs have also been categorized as excessive (EXREEs) due to their abundance and non-critical demand and include Ce, Ho, Tm, Yb and Lu [17, 18].

REEs are not necessarily rare as the name suggests, since the reported total concentration in the upper continental crust (UCC) (220 ppm), is higher than that of carbon (200 ppm) [19]. The name is, however, associated with exploration shortcomings, especially the discovery of deposits with concentrations that are economically viable for exploitation [19, 20]. Additionally, the difficulty in separating these elements from each other has emphasized their “rare” status as pure oxides. This is due to their similarity in ionic radii, which means that REEs are interchangeable and very difficult to separate [21]. The rarity of these elements is therefore more associated with the difficulty of separation as well as with the locating of deposits containing exploitable concentrations.

2.2.1 Minerals

REEs are not found as native metals such as gold, silver, and copper. Instead, REEs are found together in several ores/accessory minerals in small or large concentrations. Although REEs are found together, they are bound to certain geological environments and do not fit into all mineral structures. More than 250 REE-bearing minerals have been found, but not all are being mined in large quantities. Some of the most important minerals bearing REE are listed in Table 2-1.

In general, deposits containing bastnaesite, xenotime, monazite, synchysite, loparite, eudialyte, and parasite have been exploited economically [22]. Commercially mined REE-bearing deposits are currently dominated by deposits containing monazite, bastnaesite and xenotime [4]. This is due to the fact that most REE resources are associated with these REE-containing minerals [23, 24]. Of these three minerals, bastnaesite and monazite are sources for the extraction of LREEs, while HREEs are extracted from clays of xenotime and ion-adsorption clays [25].

Table 2-1: Important REE-bearing minerals associated with REE deposits [22]

Mineral	Formula
Allanite	$(Y, La, Ca)_2(Al, Fe^{3+})_3(SiO_4)_3(OH)$
Apatite	$(Ca, La)_5(PO_4)_3(F, Cl, OH)$
Bastnaesite*	$(La, Y)(CO_3)F$
Eudialyte	$Na_4(Ca, La)_2(Fe^{2+}, Mn^{2+}, Y)ZrSi_8O_{22}(OH, Cl)_2$
Fergusonite	$(La, Y)NbO_4$
Gittinsite	$CaZrSi_2O_7$
Limoriite	$Y_2(SiO_4)(CO_3)$
Kainosite	$Ca_2(Y, La)_2Si_4O_{12}(CO_3) \cdot H_2O$
Loparite	$(La, Na, Ca)(Ti, Nb)O_3$
Monazite*	$(REE, Th)PO_4$
Mosandrite	$(Na, Ca)_3Ca_3La (Ti, Nb, Zr)(Si_2O_7)_2(O, OH, F)_4$
Parasite	$Ca(La)_2(CO_3)_3F_2$
Pyrochlore	$(Ca, Na, La)_2Nb_2O_6(OH, F)$
Rinkite	$(Ca, La)_4Na(Na, Ca)_2Ti(Si_2O_7)_2(O, F)_2$
Steenstrupine	$Na_{14}La_6Mn_2Fe_2(Zr, Th)(Si_6O_{18})_2(PO_4)_7 \cdot 3H_2O$
Synchysite	$Ca(La)(CO_3)_2F$
Xenotime*	YPO_4
Zircon	$(Zr, La)SiO_4$

*(Commercially mined)

Bastnaesite and monazite are considered the most common REE-bearing mineral found in REE deposits. It has been approximated that monazite and bastnaesite minerals can contain up to 70 wt% REOs [1, 26]. Most of this large portion of REOs consist of La, Ce, Pr and Nd [26]. Most bastnaesite-bearing deposits are distributed in China and the USA and are considered to be the main source of LREEs. Monazite-bearing deposits have been found in Australia, Brazil, China, India, Malaysia, South Africa, Sri Lanka, Thailand, and the USA. The mineral is known to be a widespread REE mineral, commonly found in beach sands [27]. Mining deposits containing monazite have health and environmental concerns since Th and U are present in this REE mineral [21, 28]. The amount of Th and U differ in the type of deposit, with more being found in placer deposits than in carbonatite deposits [7]. Xenotime is a much rarer REE-bearing mineral, containing much less amounts of La, Ce, Pr and Nd. It is described as a yttrium phosphate mineral, with some xenotime deposits containing 61% Y of the total REOs content [26].

2.2.2 REE sources

2.2.2.1 Primary sources

Primary REE deposits can be grouped as primary and secondary deposits, depending on the formation of the deposits. The primary group of deposits are formed from magmatic, hydrothermal, and/or metamorphic processes. The secondary group of deposits are the result of erosion and weathering and can include placers, laterites, and bauxites. These two groups can be further divided into sub-groups, depending on their genetic associations, mineralogy, and the form of occurrences [4]. In terms of the association of these deposits, primary deposits are commonly associated with carbonatites and alkaline-peralkaline igneous rocks. However, secondary deposits are associated with the weathering and erosion of the primary deposits [29, 30].

The majority of all REEs that are mined are from four deposits, namely Bayan Obo, Mountain Pass, Mount Weld, and Ion adsorption clay deposits. The Bayan Obo deposit is located in inner Mongolia, China, and is considered the largest REE deposit [31]. The genesis of REE ores has been found to be associated with carbonatite. This is due to the wide distribution of carbonatite dikes in the Bayan Obo deposit [7]. The deposit reveals an uneven distribution of REE concentrations in several types of carbonatite dikes. An example of this is the higher concentration of REEs in calcite type carbonatite dikes [32]. The Mountain Pass deposit is located in California, USA and is considered the second largest REE deposit. Among all REE-bearing minerals, bastnaesite is the predominant phase in the Mountain Pass deposit. However, minerals such as monazite and parisite are present as minor REE minerals [33]. The mine has faced some difficulties due to competition and environmental concerns associated with monazite mining. The Mount Weld deposit is located in Western Australia, and the deposits are found in a 70-130 m thick lateritic profile over an alkaline carbonatite complex [34]. The lateritic regolith is considered to be the main host of REE resources. The deposit contains phosphates as secondary mineralogy, mostly monazite, which is contained in iron oxide minerals [35]. Finally, ion-adsorption clay deposits are a unique deposit containing REEs and can be found in Southern China. It is found as deposits of weathered crack elution with enriched concentration of REEs [1, 36]. The formation of these clays can be attributed to the weathering of granite, granite porphyry, and gneiss by groundwater. The REEs are weakly adsorbed onto the surface clay-rich thick soil layer that is developed above the granite bedrock [37, 38]. Ion-adsorption clay deposits have been found to have no radioactive material and even though there are lower REE concentrations compared to the other deposits, the extractability has made these deposits economically viable.

When considering the primary deposits of REEs, it has already been established that 34 countries have viable deposits of REEs from 2011 [39]. Not all of these deposits have been exploited due to production and processing challenges. These issues include the production and processing of metals that are energy-intensive and highly dependent on toxic chemicals and the production of radioactive by-products such as thorium [40]. According to Delaney, some of the more unique challenges that have to be faced by REE producers are: (i) limited technical expertise outside of China, (ii) a high degree of capital outlay associated with new REE plants, (iii) the difficult nature of obtaining a predictable and readily available market price for REEs, (iv) a short start-up time for the mine with to ensure a sufficient demand for the product [41]. These downsides/difficulties in mining primary deposits have not stopped the development of REE mines, but certainly slowed the progress to achieve a well-diversified supply market of REOs.

2.2.2.2 Secondary sources

Secondary sources refer to sources of REEs that are currently considered non-conventional due to a lack of material specific experimental data or other restricting factors. Many secondary sources of REEs are considered waste products from upstream processes. The use of secondary sources has increased because of a slow growing supply of REEs and an increase in demand for REEs for future technologies. Using secondary sources also has the benefit of contributing to the sustainable development of REE recycling, further improving the supply chain of these precious metals.

The use of secondary sources has shown promising benefits compared to the use of primary sources. Some of the benefits include less energy consumption, little to no radioactive material, and abundant already available sources [42]. Although there are known advantages to using secondary sources, extraction of REEs from secondary sources is still under development. In 2019, the recycling of REEs from secondary sources accounted for less than 5% of the global REE supply, emphasizing this point [43]. Furthermore, the already introduced technologies for the extraction of REEs from secondary sources have their own set of challenges. These challenges include extraction efficiency and selectivity as well as economic considerations, compounding to the fact that it has remained in its infancy phase [44].

For any secondary source to be considered, the concentration in the material should be higher than that found in the upper continental crust (UCC). An even more promising source would be a secondary source that resembles the concentrations found in the conventional primary sources being mined. Several secondary sources that meet the first criteria as a bare minimum requirement have been identified. These secondary sources include E-waste, mine-tailings, phosphogypsum, bauxite residue, and coal [4, 7].

2.2.3 Preliminary viability assessment

The preliminary viability assessment of a potential REE source is critical in eradicating unnecessary investigative efforts. Two such assessment factors include the outlook coefficient and the percentage of CREEs in the total REE concentration (TREE). The equations used to equate these values are given as [45]:

$$C_{outl} = \frac{(Nd + Eu + Tb + Dy + Er + Y)}{TREE} \bigg/ \frac{(Ce + Ho + Tm + Yb + Lu)}{TREE} \quad \text{E- 1}$$

$$CREE\% = (Nd + Eu + Tb + Dy + Er + Y) / TREE \quad \text{E- 2}$$

The criteria are based on conventional ores for the extraction of REEs. Together, these two factors are used to determine whether an ore source is unpromising, promising, or highly promising. The criteria for such estimation can be given as follows: (i) Unpromising, with $C_{outl} \leq 0.7$ and $CREE\% \leq 26\%$, (ii) promising, with $0.9 \leq C_{outl} \leq 3.1$ and $33\% \leq CREE\% \leq 50\%$, and (iii) highly promising, with $2.8 \leq C_{outl}$ and $62\% \leq CREE\%$ [45]. The parameters has been proposed by Seredin in 2010 and it should be noted that it is based on the market demand at the time [45]. If a secondary source of REEs should be investigated, estimations based on the aforementioned parameters can be used together with other assessment criteria that applies to that source.

2.3 Coal

Coal is considered to be one of the most complex and challenging materials to analyse and understand. Most rocks consists predominantly of crystalline mineral grains, whereas coal is largely a collection of amorphous, degraded plant remains metamorphosed to various degrees [46]. Coal also contains a generous sprinkling of tiny syngenetic, diagenetic, epigenetic, and detrital mineral grains. Since different coals underwent different geological processes, it has always been a major challenge to obtain a coherent picture of the geochemistry of the coals, as well as the processes that influence the chemical composition of coal [46].

The importance of coal in the modern world demands a thorough understanding of its chemistry and geology. Such importance is mainly attributed to its use for the production of electricity and some less widely known uses; a source of coke for steel production, chemicals, pharmaceuticals and perfumes [47]. New, developing uses, such as an alternative source for REEs, further require a thorough understanding of this complex material.

2.3.1 Coal formation

The formation of coal is complex, and the resulting compositions of different coals differ on the basis of their unique geological location of formation. The formation of coal deposits results from the chemical and physical transformation of plant biopolymers. These transformations are mainly due to the biodegradation that occurs in the early stages of peat formation and the effects of pressure and temperature that act on buried peat over a long period of time [48]. Coal is therefore a product of biological and geological processes acting on plant remains over time [46].

The formation of coal begins with the formation of peat (peatification), accompanied by early diagenesis [49]. The formation of peat occurs under specific conditions that allow the accumulation of organic matter to exceed the microbial degradation of organic matter. Natural environments that allow this anaerobic microbial process to dominate include swamps, fens, and marshes [46]. The formation of peat also depends on the type of plants that undergo the microbial degradation process. For example, woody plants persist better in peat as a result of a much lower rate of microbial degradation compared to non-woody plants [50]. The formation of peat therefore depends on factors that influence the microbial degradation process, as well as the type of plant material subject to the process.

The peat that has now been formed is further subject to different conditions that allow the formation of low rank coal. Early stage coalification occurs under different conditions and includes thermal gradients, lithostatic pressures, and fluid pressures [51]. During the early stages of coalification, the loss of oxygen continues as well as the loss of hydrogen, but to a lesser extent [46]. In addition, nitrogen-containing compounds such as amides continue to be lost from the peatification stage to the early coalification stage [52]. The formation of lignite or brown coal occurs during early-stage coalification and is characterized by changes such as: a loss in residual cellulose, a loss of methoxyl functional groups on lignin, and the formation of catechol-like structures from lignin [53]. Early-stage coalification therefore results in the formation of low rank coal (lignite or brown coal) as a result of chemical changes of the organic structures found in peat (specifically lignin).

The late-stage coalification process occurs when the low rank coal has undergone a deeper burial and further exposure to more extreme pressures and temperatures. Higher temperatures and pressures result in chemical changes of the organic molecules as well as physical changes in the appearance of coal [53, 54]. Physical changes result in a change in appearance from a dull, brown substance (lignite or brown coal), to a lustrous, shiny, black organic rock (bituminous and anthracite coal) [46].

2.3.2 Coal rank

The rank of coal refers to the extent of alteration that the original organic material has undergone to form the coal. The higher the rank of the coal, the greater the extent of alteration [46]. The classification of a coal towards a certain rank can be understood using Table 2-2.

Table 2-2: Classification used for different coal ranks based on chemical and physical characteristics [46, 55, 56]

Rank	Subcategory	Refl.Rm _{oil}	Atomic H/C	Atomic O/C	Org.C (%) Dry-ash free	Volatile matter %
Peat		0.2	0.80-1.4	0.4-0.7	50-60	> 37
Lignite		0.3	0.80-1.20	0.2-0.5	60-70	
Sub-Bituminous	C	0.4				10-37
	B	0.4-0.5	0.75-1.00	0.15	70-80	
	A	0.5				
High Volatile bituminous	C	0.6				
	B	0.7	0.60-0.75	0.1	80-90	
	A	0.8-1.1				
Medium Volatile bituminous		1.1-1.5	0.50-0.75	0.05-0.10	80-90	
Low Volatile bituminous		1.5-1.9	0.50-0.75	0.05-0.10	85-90	
Semi-anthracite		2.0	0.50	0.05	90	
Anthracite		3.0	0.25-0.50	<0.05	>90	
Meta-Anthracite		>4.0	0.25	<0.05	>90	

It is well known that the fixed carbon content increases with the rank of the coal. For the highest coal rank, anthracite, the fixed carbon content is typically above 75%. The lowest coal rank, lignite, typically has a fixed carbon content between 25% and 30% [56]. In terms of the volatile matter of coal, the volatility of coal decreases with an increase in rank. For anthracite, the volatile matter is typically below 10%, for bituminous coal the volatile matter can be between 10-37%, and for lignite the volatile matter is typically above 37% [55, 56]. Of these classification parameters, the most accurate way to determine the rank of a coal is by conducting a vitrinite reflectance analysis. This method makes use of a petrographic microscope and its accessories to measure the amount of light reflected from the surface of well-polished collotelinite [57].

Additionally, the rank of a coal can be determined using the ASTM D338 method. Using this method requires proximate-, ultimate analysis and gross calorific value analysis calculated to the mineral-matter-free basis [58]. Higher rank coals are classified based on the fixed carbon content on the dry basis, whilst lower-rank coals are classified based on the gross calorific value on a moisture free basis [58]. The Parr formula can be used to estimate the original mineral matter in a coal and is given as follows [58]:

$$Mm = 1.08A + 0.55S \quad \text{E- 3}$$

Where Mm is the estimated original mineral matter content (%), A is the ash content (%) of the coal and S is the total sulphur content (%) of the coal. The following two formulas can then be used to determine the dry, mineral matter (Mm)-free fixed carbon (FC) and volatile matter (VM) value and the moist mineral matter free gross calorific value [58]:

$$\text{Dry, Mm-free FC} = \frac{100(FC - 0.15S)}{(100 - (M + 1.08A + 0.55S))} \quad \text{E- 4}$$

$$\text{Dry, Mm-free VM} = 100 - \text{Dry, Mm-free FC} \quad \text{E- 5}$$

$$\text{Moist, Mm-free Btu} = \frac{100(Btu - 50S)}{(100 - (1.08A + 0.55S))} \quad \text{E- 6}$$

Where FC is the fixed carbon content (%) of the coal and Btu is the gross calorific value in Btu/lb. Initially the fixed carbon, moisture, ash and sulphur content of the coal is determined and with Equations E- 4, E- 5 and E- 6 the rank of the coal is determined with the ASTM D388 method [58].

2.3.3 Usage

Coal is primarily used for thermal and metallurgical purposes, with the bulk consumed for electricity generation in coal-fired power plants. In 2023, global coal consumption totalled 8,536 million tons (Mt), comprising 7,435 Mt of thermal and lignite coal and 1,101 Mt of metallurgical coal [59]. China and India together accounted for about 70% of this consumption, while Europe, North America, Eurasia, and Africa contributed roughly 18%, reflecting policy-driven reductions in coal-based electricity generation [59].

2.3.3.1 Coal-fired power plants

The process of generating electricity using coal has been applied for centuries, creating a major turning point for the human civilization in the Industrial Revolution [60]. Today, electricity generation using coal is conducted in CFPPs, which entail a series of complex steps ranging from mining, transportation, combustion, and energy conversion [60]. Coal is combusted in the CFPP boiler, which then generates heat that is used to produce steam. Due to the development of supercritical and ultra-supercritical steam cycles, CFPPs have maintained their status as a competitive method of electricity production [61-63]. An oversimplified flow diagram of a conventional CFPP is given in Figure 2-1 [64].

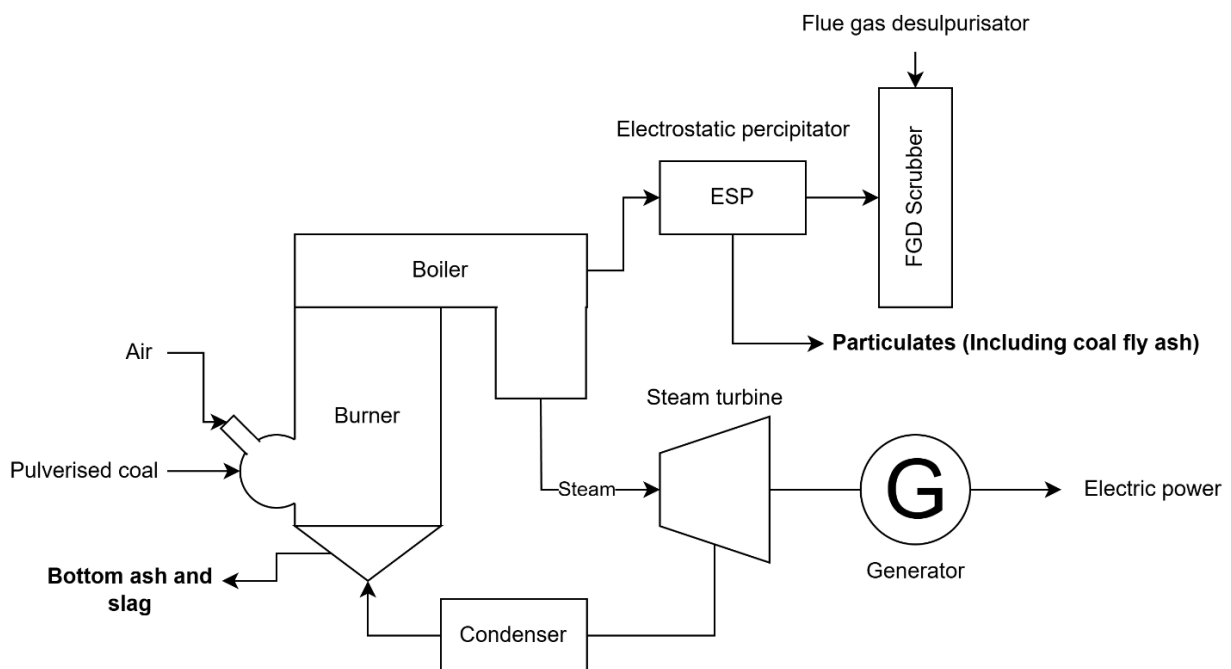


Figure 2-1: Oversimplified flow diagram of conventional CFPP, adapted from [64]

The main challenges associated with CFPPs are released pollutants, such as carbon dioxide, sulfur dioxide, nitrogen oxides, and particulate matter [65]. To reduce these environmental concerns, technologies such as electrostatic precipitators and flue gas desulfurization systems have been developed [60]. Additional waste products result from the combustion of coal that have to be discarded. As a result, different coal combustion methods, combined with burners and boilers, have become common. Two combustion methods addressing both environmental concerns and operational efficiency are pulverized fuel combustion and fluidized bed combustion [66, 67].

2.3.3.1.1 CFPP combustion

All CFPPs make use of a burner and a boiler, which introduces coal and air for combustion to produce steam. The conventional type of boiler used to produce electricity is called a pulverized coal combustion (PCC) boiler [11]. The coal used for these boilers is initially milled, pulverized, and then injected into the boiler with a mixture of air to allow combustion [68]. Another type of boiler commonly used is a fluidized bed combustion (FBC) boiler. FBC boilers have better fuel usage and heat transference for power generation [68]. These boilers consist of a bed of inert material, either sand or limestone, which is then suspended with air that is injected from below.

A major difference between a PCC- and an FCB boiler is the temperature of combustion. The combustion temperature of PCC boilers is typically greater than 1400 °C [69], while for an FBC boiler, the bed temperature is kept at lower temperatures (800-900 °C). This is done to reduce pollutant formation, particle agglomeration, ash deposition, and corrosion [70]. Other differences between PCC- and FBC boilers include the combustion time of the char and the devolatilization time. The combination of a longer residence time (char combustion and devolatilization time) and lower temperatures of FBC boilers reduces NO_x production and reduces SO₂ emission if limestone is added to the coal or fluidized bed [71]. A summary of the differences between the PPC and FBC boilers is given in Table 2-3.

Table 2-3: Summary of important parameters associated with the combustion of fuel for PCC- and FBC boilers

Parameter	PCC	REF	FBC	REF
Combustion temperature	≥ 1400 °C	[69, 70]	800-900°C	
Particle size	20-100 µm		1-10 mm	
Char combustion time	1-2 s		100-500 s	[70]
Devolatilization time	<0.2 s	[70]	10-50 s	
Fuel type	Bituminous or lignite		Wood chips, SRF ¹ and coal	

¹ SRF: Solid recovered fuels

2.3.3.1.2 Waste products

Whether the coal undergoes combustion while using a PCC or FBC, waste/by products will be formed. One of the main waste products includes coal ash that results from the combustion process. It can be categorized into three main fractions, (i) coal fly ash (CFA), (ii) bottom ash (BA), and (iii) slag [72, 73]. Slag and BA accumulate in the furnace/burner section of the CFPP, which is normally flushed with water or air [74]. The CFA generated from the combustion process must be removed with alternative technologies, as the particles escape with the flue gas. These technologies include fabric filters, mechanical collectors, wet scrubbers, and electrostatic precipitators [72]. When comparing CFA and BA, CFA generally constitutes the dominant waste fraction, with a typical CFPP generating roughly 80% CFA and 20% BA [75].

The generation of CFA remains problematic if not properly disposed of, leading to serious environmental pollution [76]. In terms of quantity, 600-800 million tons of CFA is estimated to be produced annually [77], with China and India as forerunners in this regard [78, 79]. Most CFA is stored in landfills, monofills and ponds or is disposed of by a simple stack [80]. However, these methods have been shown to negatively affect the environment as stored CFA can be highly leachable, radioactive, and toxic, contaminating soil and water sources [75]. The use of CFA/BA waste would be highly beneficial if the eminent danger of environmental pollution is to be avoided.

2.4 REEs in coal related material

The promising concentrations of REEs in several coal and coal ashes around the world have prompted research efforts towards its use as a secondary source. Since coal has been an essential fuel source, there have been several studies investigating the major and trace elements present. The TREE content reported in coal-related materials (CRMs) varies widely, ranging from as low as 193 ppm [81] to as high as 8246 ppm [16], indicating the broad variability in REE concentrations within CRMs. Based on TREE concentrations and additional factors, the initial viability of a CRM can be established. However, using TREE concentration and viability parameters only indicates the elemental composition of the CRM. For further consideration, the association or speciation of REEs (for an ash) in the CRM can be assessed.

2.4.1 Abundance

Investigative studies have revealed CRM samples containing REE concentrations well above UCC concentrations, with some samples having concentrations similar to those of conventional ores. Additionally, the derived ash, whether CFA or BA, has shown enrichment in the concentrations of REEs. In Table 2-4, some of the concentrations found for different CRMs from different countries such as India (IND1), Russia (R 1&2), South Africa (SA 1-3), the United States (US 1-3), China (Ch 1&2), and the Philippines (Ph 1) are given.

Table 2-4: Total rare earth concentration, outlook coefficient and critical rare earth element fraction of different CRMs

INDEX	Rank of parent coal	Type of sample	TREE (ppm)	Ref
IND1	Lignite	CFA	2100	[82]
R1	Lignite	Seam	4551	[16]
R2	Lignite	Seam	8426	
SA1	Bituminous	CFA	526	[83]
SA2	Bituminous	ROM ¹	225	[84]
SA3	Bituminous	DC ²	245	
US1	Sub-Bituminous	BA	211	[85]
US2	Sub-Bituminous	BA	279	
US3	Sub-Bituminous	CFA	314	
Ch1	Anthracite	Seam	1968	[16]
Ch2	Anthracite	Seam	1880	
Ph1	UNKOWN	CFA	193	[81]
UCC	N/A	N/A	179	[86]

¹ROM: Run of mine; ²DC: Discard coal

The average concentration for rare earth elements and yttrium (REY), excluding Sc, in world coals and ashes is estimated to be 69 ppm and 404 ppm respectively [87]. As shown in Table 2-4, there are CRM sources, whether coal or coal ash, found to have much greater concentrations. Furthermore, a correlation between concentrations and rank of coal has not been made since several geological factors influence the resulting concentrations.

2.4.2 Initial viability assessment

As explained in Section 2.2.3, the viability of an ore can be determined by using the outlook coefficient (C_{outl}) and CREE% using equations E- 1 and E- 2 respectively. In Table 2-5, the C_{out} and CREE% is given for some of the CRMs from Table 2-4.

Table 2-5: Outlook coefficient and critical rare earth percentage for some CRMs

INDEX	C_{out}	CREE%	Ref
IND1	1.5	44.2	[82]
R1	3.6	63.1	[16]
R2	3.8	63.2	
SA1	0.8	29.2	[83]
SA2	1.0	27.0	[84]
SA3	0.9	25.2	
Ch1	1.5	45.2	[16]
Ch2	1.1	38.4	
Ph1	1.0	33.3	[81]
UCC	1.2	29.6	[86]

Seredin and Dai (2012), have suggested parameters, specifically for a CRM, allowing categorization as a unpromising, promising or highly promising source [16]. Values for these categories are as follows: (i) unpromising, with $C_{outl} \leq 0.7$ and $CREE\% \leq 26\%$, (ii) promising, with $0.7 \leq C_{outl} \leq 1.9$ and $30 \leq CREE\% \leq 51$ and (iii) highly promising, with $C_{outl} \geq 2.4$ and $CREE\% \geq 60\%$. It should however, be noted that the authors paper was published in 2012, subjected to the supply and demand for REEs at the time of publication [16].

Additional assessment criteria can be utilized towards characterizing whether a CRM source is viable or not. One method is to normalize the concentration of the REEs in the target source with the average concentration found in the UCC. The concentrations of the REEs in the UCC used for this normalization is given in Table 2-6 [86]. Three different types of enrichment can be identified through the normalization of the REEs in the CRM to the UCC: L-type REE distribution ($La_N/Lu_N > 1$), M-type REE distribution ($La_N/Sm_N < 1$, $Gd_N/Lu_N > 1$), and H-type REE distribution ($La_N/Lu_N < 1$) [16].

Table 2-6: REE concentrations found in the UCC used for normalization [86]

Element	Concentration (ppm)	Element	Concentration (ppm)
La	30	Ho	0.80
Ce	64	Er	2.3
Pr	7.1	Tm	0.33
Nd	26	Yb	2.2
Sm	4.5	Lu	0.32
Eu	0.88	Sc	11
Gd	3.8	Y	22
Tb	0.64		
Dy	3.5		

The relative enrichment factor (REF) can also be of importance when considering the usage of ash as a secondary source. The parameter can be calculated using equation E- 7, where REE_{ash} is the REE concentration in the ash, A_{ad} is the ash yield of the feed coal/raw coal and REE_{fuel} is the REE concentration in the feed coal/raw coal [88].

$$REF = \frac{REE_{ash} \times A_{ad}}{REE_{fuel}} \quad \text{E- 7}$$

A preliminary assessment of a CRM is essential and therefore all possible factors should be considered. In the case of an ash this would include the C_{out} , CREE%, REF, and the type of distribution based on normalized data.

2.4.3 Occurrence in coal

Determining the modes of occurrence of REEs in a CRM is essential if it is to be considered as a secondary source. The distribution of REEs in organic and inorganic content will establish the best or most economical extraction method [13]. Generally higher rank coals, such as bituminous and anthracite, consist of more mineral matter (inorganic), whilst lower rank coal, such as lignite, consist of more organic matter. In the case of REEs, it is found primarily in mineral matter, especially in higher rank coals [89]. For lower rank coals the REEs may also be bound to carbon functional groups (-COOH and OH) or form organometallics [90]. However, there is a level of uncertainty for any rank of coal since the proportions of organically or inorganically associated REEs can differ between coal deposits and even single coal beds [91]. Figure 2-2 gives a summary of the modes of occurrence of REEs found in coal [91].

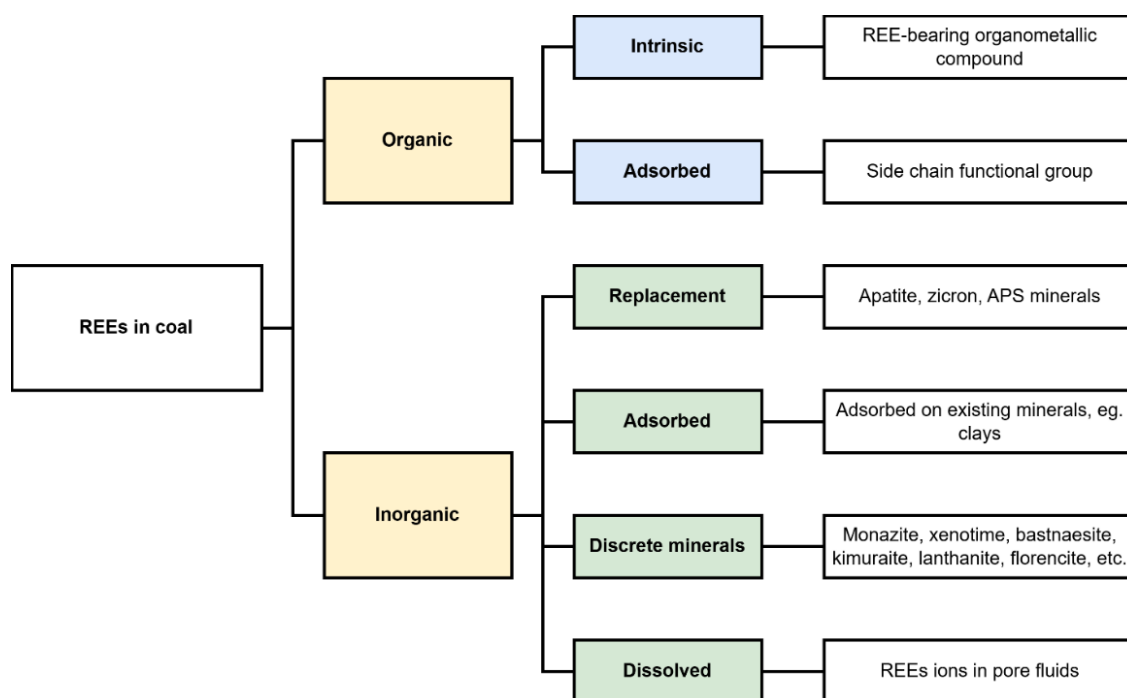


Figure 2-2: Summary of the modes of occurrence of REEs in coal [91]

As discussed briefly in Section 2.3, the formation of coal is dependent on the geological location. Therefore, obtaining concrete knowledge regarding the speciation of REEs in coal has remained a challenge. This is mainly due to (i) the association of REEs being a function of multiple modes of mineralization [92], and (ii) the concentration of an individual REE is commonly less than 100 ppm [91]. This is evident from different proportions of organically and inorganically bound REEs found in coal from different coal deposits or even the same coal bed [16, 93].

2.4.4 Speciation in coal ash

The speciation of REEs refers to the association of the REEs in the ash resulting after combustion has occurred. Significant alteration of REEs speciation from coal to ash occurs during the combustion process [94]. Some of the most noticeable alterations include REE-organic complexes, REE carbonates, and REE-bearing carbonates that convert to REE oxides after combustion [95]. Additional alteration can include fragmentation of phosphates into very small particles (micro or nano-sized), or transformation of phosphates into metal oxides if calcium oxides are present [91, 96]. Furthermore, the resulting ash material consists predominantly of glassy materials, crystalline minerals, and unburned carbon [91]. In which of these phases the REEs are bound and to what extent, depends highly on the coal used as feed material as well as the combustion temperature. A summary of the classification of the REEs association in coal ash is given in Figure 2-3.

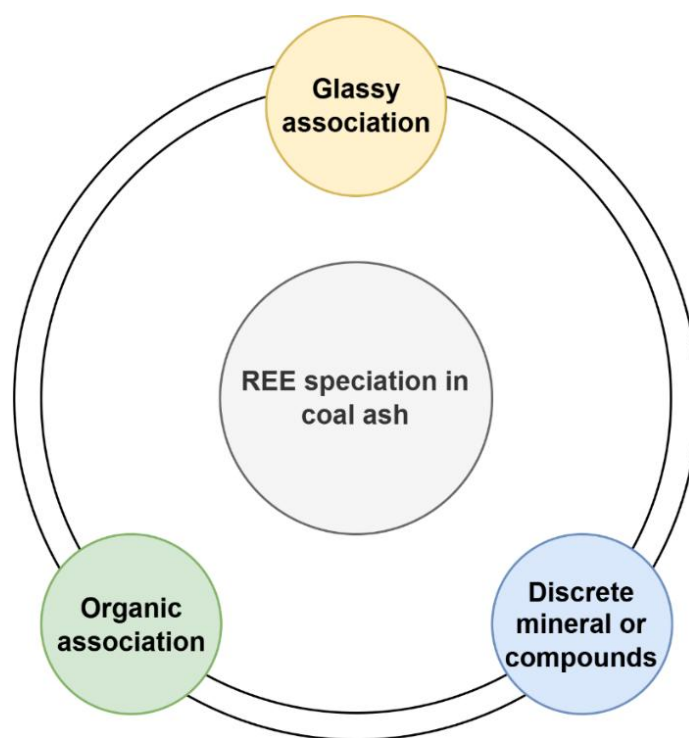


Figure 2-3: Classification of REEs speciation in coal ash [91]

Aluminosilicate glass phases are predominantly found in CFA, specifically in Class F fly ashes, with several studies suggesting it as the dominant form of the association of REEs in coal ash [97-99]. Using SLP methods, studies on CFA samples from Southwestern China [100], Eastern United States [101], and Northeast Spain [102] have indicated a majority (above 70%) of the REEs to be associated with the hard to leach aluminosilicate glass phase as well as the silicates. It should be noted that the type of boiler used can significantly alter whether the REEs will be associated with the aluminosilicate glass phase. This is because of the influence of the combustion conditions (mostly temperature) on the alteration pathways of the REE minerals in the coal [94]. Therefore, lower thermal treatment temperatures might not result in the encapsulation of the REEs in the aluminosilicate glass phases.

In addition to the aluminosilicate glass phase, REEs have been found to be associated with discrete minerals or compounds and unburned carbon (organic material). For discrete minerals, REE bearing minerals have shown a degree of independence from the glassy phases [98, 103]. Discrete REE minerals typically include REE phosphates, REE carbonates, REE oxides, REE silicates, REE sulphates, REE bearing iron oxides and several others, all of which have been found in coal ash [91]. Furthermore, REEs have been observed to be associated with nanosized carbons [104]. Although this has been observed for coal ash, the association of REEs with unburned carbons requires more research to resolve the issues of the formation mechanism and the current level of uncertainty [91].

2.5 Extraction of REEs from CRM

The extraction of REEs from CRM can be performed using physical beneficiation as well as hydrometallurgical extraction. Physical beneficiation can produce a preconcentrate, since REEs are more associated with fine-particle size, medium density, and non-magnetic fractions [105, 106]. The resulting preconcentrate would then have to undergo hydrometallurgical extraction, separation and purification to obtain a high-grade REE product [91]. Considering the hydrometallurgical extraction methods, leaching of the REEs from the CRM is a crucial step. Specifically, since the complexity and economic viability of separating the REEs from the contaminating elements is influenced by the recovery and selectivity during the leaching process. Therefore, for the purposes of this study, the leaching stage was only considered and will therefore be reported in the subsequent sections.

2.5.1 Leaching

Leaching refers to the removal of a soluble fraction from an insoluble phase from which it is associated [107]. The target elements to be leached from the chosen material can be the soluble fraction in solution or the insoluble fraction remaining. The leaching step of the target elements from the feed material forms part of a larger hydrometallurgical process to obtain the final desired product. Overall the hydrometallurgical extraction of REEs from CRM involves (i) leaching, (ii) liquid-liquid extraction and (iii) precipitation [108]. These hydrometallurgical processes have been identified as suitable applications for the recovery of valuable metals and handling of toxic heavy metals, specifically in the mining industry [109]. Some of the advantages of using hydrometallurgical techniques include high leaching efficiencies, good operating environments, and a continuous and automated process [110].

CRM as a source material to leach REEs has received a considerable amount of attention in the past few years. Investigative effort mainly fuelled by several advantages when compared to using commercial/conventional rare earth ores containing monazite, bastnaesite and xenotime minerals. These advantages include (i) higher concentrations of HREEs and CREEs compared to LREEs [16, 111], (ii) negligible mining costs since REEs can be extracted from coal utilization and coal production by-products [108], (iii) lower concentrations of radioactive material such as U and Th [112], and (iv) improvement towards mitigation or elimination of legacy environmental issues [113]. Considering the non-volatile nature of REEs [114], the enrichment of REE concentration from raw feed coal toward the resulting ash serves as an additional advantage. Thus, more studies have been conducted on the usage of coal ash compared to raw coal.

2.5.1.1 Methods and findings

The methods used to leach REEs from coal ash involve the usage of a lixiviant, which normally involves mineral acids. The most promising of which is HCl, with several studies indicating promising leaching efficiencies [11, 115]. Other mineral acids have also been tested including HNO₃ [116], and H₂SO₄ [117]. Additional types of solutions have also been investigated as a possible lixiviant, including salt [118], organic acids [119], ionic liquid [120], and bioleaching agents [121]. There is no definitive consensus on the optimal lixiviant, with current recommendations serving primarily as guidance for further research into REE recovery from specific coal ashes. Lixiviants must be evaluated for each new ash type, as the morphological and mineralogical characteristics of coal ash are influenced by both the coal source and the combustion conditions.

Considering the most promising lixiviant, HCl showcases a major challenge of directly leaching REEs from CFA. Specifically, CFA that has been obtained from elevated temperature combustion, typical for PCC boilers as discussed in Section 2.3.3.1.1. The encapsulation of REEs in the aluminosilicate glass phase results in harsh reaction conditions, low extraction efficiencies, or both [14, 104, 122]. To overcome this issue, chemical/thermal pretreatment methods have been used to liberate the REEs. These methods are performed on the ash prior to the leaching step, using chemical roasting [123] or hydrothermal treatment [124]. After pretreatment of the CFA, the leachability of REEs are enhanced by destroying the amorphous glassy structure, liberating the REE-bearing particles [125]. For example, the average leaching efficiency of REEs increasing from 24.48% to 84.95% after pretreatment of the CFA using NaOH [100]. Coal ash derived from lower combustion temperatures, however, indicates relatively high leaching efficiencies without pretreatment.

Direct acid leaching from lower combustion temperature derived ash has shown relatively high leaching efficiencies. This can be attributed to the lack of aluminosilicate melts formed, which would undergo rapid cooling, forming the dense glassy material that encapsulates the REEs [70]. Lower combustion temperatures are common in FBC boilers as discussed in Section 2.3.3.1.1. The leaching characteristics of FBC boiler derived ash, is similar to low-temperature calcined ash (600-700 °C) [11, 126]. Using feed coal and ash obtained from a circulating FBC (CFBC), Fu et al. (2024) was able to extract 21.3% and 71.1% of REEs respectively using 1 M HCl [94]. From another study that produced coal ash at 750 °C, 72.4% of REEs were leached using 1 M HNO₃ [116]. Thus, the extraction of REEs from CFA or BA or laboratory ash will include the choice of whether pretreatment will be required based on the combustion conditions (mainly temperature). For the scope of this study, the ash generated will be well below PCC boiler temperatures, therefore only direct acid leaching is considered. Furthermore, direct acid leaching using organic acids might also prove useful since the ash derived in this study is from a lignite coal.

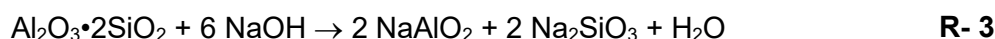
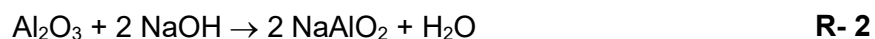
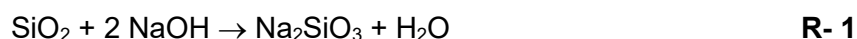
Organic acids have also shown their potential as leaching agents for the extraction of REEs from coal ash. The usage of different carboxylic acids (mono, di, and tricarboxylic), such as tartaric, lactic, malonic, succinic, and citric acids, has indicated high leaching efficiencies without pretreatment of an ash. More specifically, 62% of the REE content was extracted using a 5% tartaric acid solution at 90 °C for a duration of 60 min [127]. Organosulphonic acids such as methanesulphonic- (MSA) and *p*-Toluenesulphonic (PTSA) acid have also been investigated. Using these acids have proved to be suitable lixiviants with 1 M MSA leaching 70% of the REE content at 90 °C for 60 min. For 0.5 M PTSA, 60% of the REE content was leached at similar conditions [128]. Both the mentioned studies utilized ash not directly obtained from CFPPs, but rather from combusting the coal in a muffle furnace at 850 °C for 1 h [127, 128].

Choosing between HCl and tartaric acid would require a comparison of the advantages and disadvantages. A major disadvantage of using mineral acids is the further utilization of the ash material and the selectivity. Leaching with mineral acids causes the degradation of the chemical structure of the ash material [127]. The degradation of the chemical structure leads to the inability to use the ash for the production of cement or bricks. In terms of selectivity, the leach liquor will require more separation steps since other major elements are also co-extracted [127]. An advantage of mineral acids would be their extensive use for REE extraction, for both primary sources and secondary, resulting in a better understanding of the leaching process [11, 81, 83, 115, 118, 122]. To the authors' knowledge, only a few studies have explored the use of organic acids on coal ash [127, 129-131].

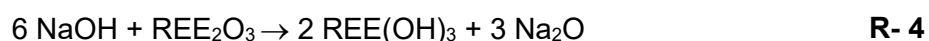
2.5.1.2 Important reactions

The reactions associated with the extraction of REEs from the host minerals can either be the result of pyrometallurgical- or hydrometallurgical process/methods. For the purpose of extracting the REEs from CRMs, roasting is normally implemented as a pretreatment method, followed by direct leaching [132]. In the case of this study, the reactions occurring during the pretreatment and direct leaching processes are given.

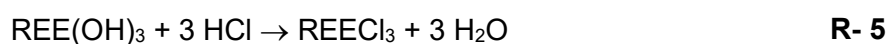
The major challenge that is faced with extracting REEs is the encapsulation of the precious metals in the aluminosilicate glass. For the lixiviant to effectively react with the target minerals, the glassy phase needs to be dissolved. Dissolving the glassy phase can be done using alkali-pretreatment, utilizing roasting additives such as Na_2O_2 , NaOH , CaO , Na_2CO_3 , CaSO_4 , and $(\text{NH}_4)_2\text{SO}_4$ at elevated temperatures [123]. Alternatively, the CA can be contacted with NaOH as a liquid, at elevated temperature [100, 133, 134]. Either way the NaOH reacts with the aluminosilicate phase resulting in the following reactions [100, 135]:



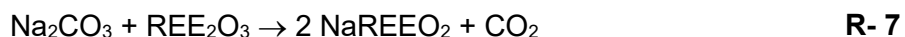
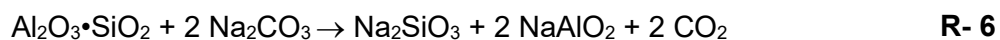
Furthermore, the NaOH reacts with the REE oxides to produce the insoluble REE hydroxides [100, 135]:



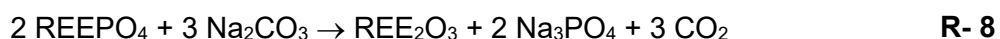
Once the REEs are in hydroxide form, HCl can be used to obtain a soluble REE chlorides [100, 135]:



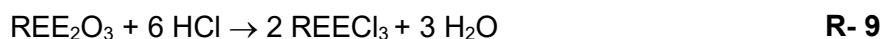
There is however a major assumption that is made regarding the REEs in the CRM. As shown in reaction R- 4, the REEs are assumed to be in an oxide form. Recalling from the different minerals forms of REEs in Table 2-1, this would have to be justified. Using Na_2CO_3 as a roasting additive results in the following reactions [125]:



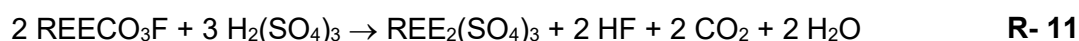
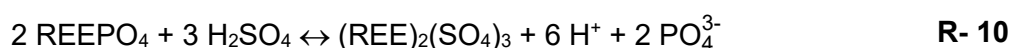
Again, the assumption is made that the REEs in the CRM is found as an REE oxide. An alternative reaction of REE phosphate, which could be monazite or xenotime, with Na_2CO_3 has been presented [125]:



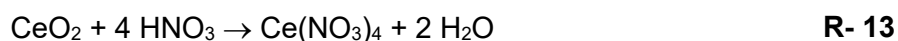
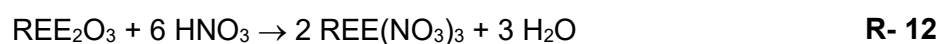
As discussed in the previous section, mineral acids such HCl , H_2SO_4 and HNO_3 have been used as lixiviants to extract REEs from CRMs. Of these three, HCl has been tested vigorously, assumed to follow reaction R- 5 with REE hydroxides. The reaction of HCl with REE oxides has been documented as [100, 135]:



This again highlights a major shortcoming with regards to the understanding of the reactions that could take place between HCl and the other minerals forms of REEs. Using H_2SO_4 on CRM with the presence of REE phosphate and carbonate minerals have been documented to follow the reactions [136]:



Using HNO_3 as a lixiviant for the extraction of REEs from CRMs has also been investigated using pretreatment [123] or no pretreatment [116, 137, 138]. Reaction R- 12 and R- 13 has been used to describe the reaction between HNO_3 and REE oxides [139]:



2.5.1.3 Important parameters

Leaching is affected by several parameters which are normally optimized for the highest leaching efficiency. The parameters usually investigated include temperature (°C), contact time (min), liquid-to-solid ratio (pulp density/solid-to-liquid ratio; g/ml or ml/g), lixiviant concentration (M), particle size (μm), and stirring intensity (rpm). Several studies have been conducted to optimize the leaching efficiency using mineral acids such as HCl [115, 118, 140]. For organic acids, there are much less thorough investigations of its utilization and optimization on different coals or coal ashes [127, 128]. For both lixiviant types, the leaching parameters having the most prevalent effect on the leaching efficiency are of most importance.

A study conducted on the direct leaching of La, Ce and Nd from CFA indicated significant influence of HCl concentration, liquid-to-solid ratio, contact time and temperature [115]. Stirring intensity was also investigated, indicating a small effect compared to the other parameters. Similar trends were observed when investigating the leaching of REEs from an Indian coal bottom ash [118]. For both these studies an increase in temperature and liquid-to-solid ratio resulted in an increase in leaching efficiency of the REEs. Increasing the lixiviant concentration led to an increase in leaching efficiency up to a certain point, after which a plateau was observed [115, 118]. Another study compared the effect of stirring intensity, HCl concentration and liquid-to-solid ratio with an orthogonal array assessment. The study has shown HCl concentration to have the greatest effect on the leaching efficiency of the REEs as well as the final solution concentration. The stirring intensity and the liquid-to-solid ratio indicated a lesser effect for the final solution concentration and leaching efficiency, respectively [141]. Table 2-7 summarizes the effect of the different leaching parameters on leaching recovery when using HCl.

Table 2-7: Summary of leaching parameters effect on leaching efficiency from CFA using HCl and their optimum conditions as found in literature

Parameter	Effect of increase	Key observations	Optimum value		
			[115]	[118]	[141]
Lixiviant concentration (HCl)	Increase in LE ¹ and LSC ²	Plateau after 4 M	3 M	4 M	3 M
Liquid-to-solid ratio	Increase in LE and decrease in LSC	No plateau observed past max values	10:1	20:1	10:1
Contact time	Increase in LE	Plateau observed past 120 mins	120 min	120 min	120 min
Temperature	Increase in LE	Significant impact	60 °C	90 °C	60 °C
Stirring intensity	Slight increase in LE	N/A	200 rpm	N/A	400 rpm

¹ Leaching efficiency, ² Leach solution concentration

Direct leaching using organic acids has been conducted to evaluate the influence of leaching parameters on REE recovery efficiency. Among the various organic acids studied, only those demonstrating optimal leaching performance were considered. In that case, TA and MSA have shown similar changes in leaching efficiency by varying temperature, contact time, liquid-to-solid ratio, and lixiviant concentration [127, 128]. Increasing the leaching temperature results in higher leaching efficiencies. For both MSA and TA the leaching efficiency increases with an increase in lixiviant concentration as well as the liquid-to-solid ratio. However, the liquid-to-solid ratio did indicate a plateau occurring after a ratio of 200:1. The duration of leaching with MSA and TA was found to be optimal at 60 min since REE extraction plateaued after this point [127, 128].

2.5.2 Kinetics

Kinetics involves the investigation of reaction- and/or diffusion mechanisms, specifically the speed at which these changes occur. Differently stated, the kinetics of a process involves the investigation of the rate of chemical reactions, and gaining an understanding of the way in which the processes are affected [142]. Leaching REEs from coal ash requires a thorough investigation of the kinetics since it is used for industrial design [143]. Some design considerations include the size, volume and material of reactors as well as the control, optimization and scale-up of the leaching process [144]. Thus, the understanding of kinetics and the models that are generally used is of utmost importance.

2.5.2.1 Heterogeneous models

Different kinetic models have been used to describe the leaching of a target element from a solid particle, i.e., heterogeneous reactions (solid/liquid). The three main models include the progressive conversion model (PCM), the shrinking particle model (SPM), and the shrinking core model (SCM) [143, 145]. These models have their own set of assumptions, applying to the characteristics of the particle as well as the interaction of the particle with the leaching agent(s) [145]. Therefore, attempting to describe the leaching process with these models requires validation of the assumptions that were made. The description, resulting equations and assumptions of these models are given in this section.

The PCM has been used to describe the leaching of a target element from a particle that does not reduce in size. The model assumes that the particle is highly porous leading to a uniform concentration profile throughout the particle. Thus, the diffusion rate of the leaching agent(s) through the pores are much higher compared to the chemical reaction rate. In terms of rate determining step, PCM assumes that the chemical reaction rate is always rate limiting [146, 147]. The PCM is illustrated in Figure 2-4.

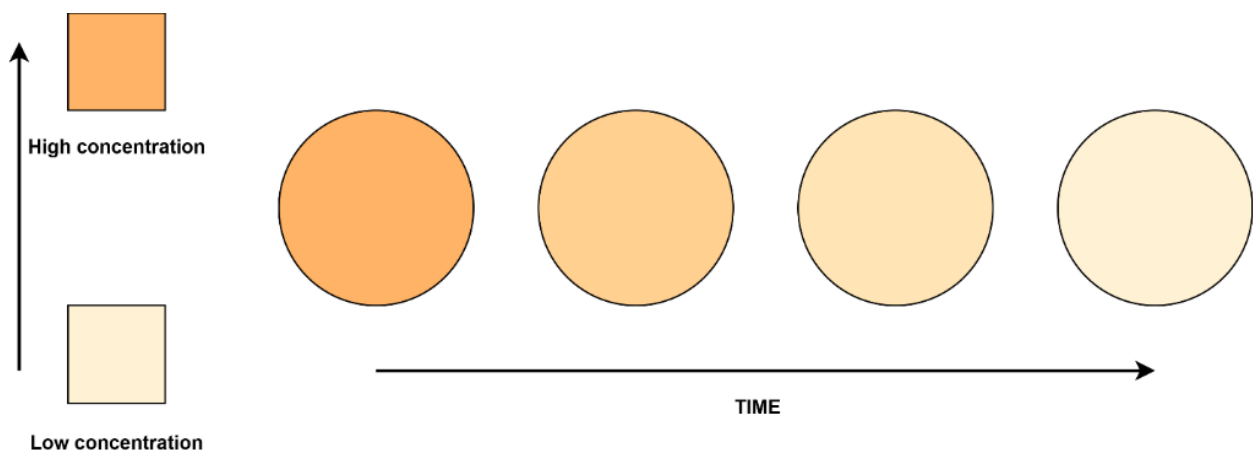


Figure 2-4: Concentration of target element(s) as described by the PCM, adapted from [145]

On the opposite end, the SPM assumes that the particle reduces in size but does not create a product layer on the outer surface. Thus, the resulting product(s) is either a liquid, diffusing through the thin liquid film to the bulk, or a solid that does not stick to the outer surface of the particle [148, 149]. The SPM is illustrated in Figure 2-5.

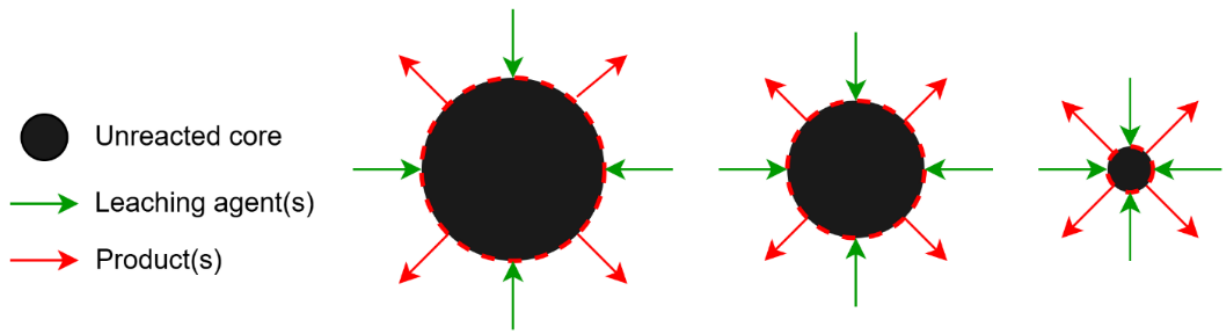


Figure 2-5: Interaction of leaching agent(s) with unreacted core as described by the SPM, adapted from [145]

The SCM, or a modified version of it, has been found to describe the leaching kinetics of REEs [143]. Two main SCMs are usually used, either the constant particle size SCM or the shrinking particle size SCM. The SCM differs from SPM and PCM in that a product layer is formed which can result in further diffusion limitations. The SCM is illustrated in Figure 2-6.

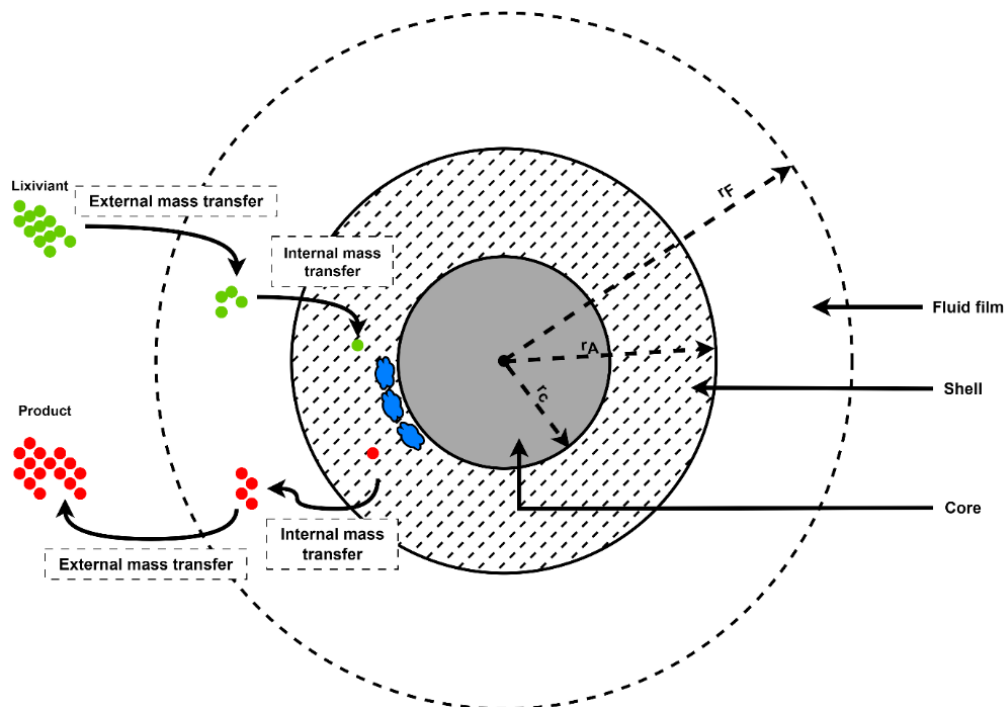


Figure 2-6: Schematic of the shrinking core model (SCM), adapted from [150]

The SCM is used to describe the following steps that occur in series: (i) diffusion of the leaching agent(s) from the bulk through the thin liquid film, (ii) diffusion of the leaching agent(s) through the product layer, (iii) reaction(s) on the surface of the unreacted core. A soluble product would then have to be evacuated by (i) diffusing through the product layer, (ii) through the thin liquid film into the bulk [151, 152]. In short, the SCM describes the kinetics to be either internally-, externally diffusion, or chemical reaction controlled. Equations E- 8, E- 9 and E- 10 are used when the rate controlling step is the chemical reaction, external diffusion- (through thin liquid film) and internal diffusion (through product layer) respectively.

$$k_1 t = 1 - (1 - X)^{\frac{1}{3}} \quad \text{E- 8}$$

$$k_2 t = X \quad \text{E- 9}$$

$$k_3 t = 1 - 3(1 - X)^{\frac{2}{3}} + 2(1 - X) \quad \text{E- 10}$$

Where k_i are the apparent rate constants, X is the leaching efficiency of the chosen element (%), and t is the chemical reaction leaching time (min). The equations describing the diffusion of the leaching agent through the thin liquid film (E- 9) and the product layer (E- 10) apply to a constant particle size SCM. The shrinking particle size SCM will not be considered in this study due to the difficulty of measuring and estimating the thickness of the covering product layer [145]. The SPM also has its own set of mathematical expressions that differ in terms of the diffusion of the leaching agent through the thin film. Equations E- 11 and E- 12 is used for the SPM when the particle is assumed to be small and large respectively [145].

$$k_4 t = 1 - (1 - X)^{\frac{2}{3}} \quad \text{E- 11}$$

$$k_5 t = 1 - (1 - X)^{\frac{1}{2}} \quad \text{E- 12}$$

When using these models, the right-hand side terms are plotted against time, indicating whether it is a “good fit.” The model with the best correlation coefficient (R^2) is regarded as the rate controlling step [151, 153]. It should be noted that more than one model may have a correlation coefficient close to one. This may indicate a combination of rate controlling mechanisms or a change in the rate controlling mechanism over time [154, 155].

2.5.2.2 Pseudo-homogeneous models

The models presented in the previous section consider heterogeneous reactions that occur between the lixiviant and the solid particle. Alternatively, the reaction between the lixiviant and the solid particle can be considered pseudo-homogeneous (PH). This assumes that the particles are uniformly dispersed in the leach solution so that it can be considered liquid [145]. In doing so, the rate equation resembles the equation derived for a batch homogeneous reaction process. Different orders of reaction can be tested, of which the first, second, and three halves orders are of interest. Equations E- 13, E- 14 and E- 15, first-, second- and three halves' order reaction kinetics, respectively, have been used in several studies [156, 157].

$$k_6 t = -\ln(1 - X) \quad \text{E- 13}$$

$$k_7 t = \frac{1}{1 - X} \quad \text{E- 14}$$

$$k_8 t = (1 - X)^{-\frac{1}{2}} - 1 \quad \text{E- 15}$$

2.5.2.3 Activation energy

The expressions used above to describe the kinetics can then be used to determine the activation energies. The Arrhenius equation, Equation E- 16, is used to determine the dependence of the rate constant k on the change in reaction temperature. This equation can then be used to determine the activation energy, E_a (J.mol⁻¹).

$$k(T) = Ae^{\left(\frac{-E_a}{RT}\right)} \quad \text{E- 16}$$

Parameter A is defined as the pre-exponential factor and R as the gas constant (J.mol⁻¹.K⁻¹). Equation E- 16 is linearized to give Equation E- 17, which is used to plot $\ln(k)$ vs $1/T$, giving rise to a linear line if an adequate kinetic model is used.

$$\ln(k(T)) = \frac{-E_a}{R} \cdot \frac{1}{T} + \ln(A) \quad \text{E- 17}$$

The activation energy is determined once the Arrhenius plot has shown a satisfactory fit ($R^2 > 0.95$). The slope of the straight line, $-E_a.R^{-1}$, is then used to determine the apparent activation energy.

2.5.2.4 Confirmation and change of rate limiting step(s)

The models fitted with the experimental data require further interpretation to establish whether these rate limiting steps are accurate. Interpreting the apparent activation energy for each model, the effect of particle size and agitation on the leaching efficiency, are ways to achieve this [158, 159]. Additionally, the models fit over the entire period may also indicate a change in the rate limiting step [150, 160, 161]. The fit of the model, apparent activation energies, and effect of particle size and agitation can be investigated together to attain the best overall combination representing the experimental data.

Considering the apparent activation energy, it is known that the chemical reaction limiting step is sensitive to a temperature change [162-164]. Thus, a high apparent activation for the chemical reaction limiting step would be expected. For diffusion-controlled steps, internal or external, an increase in temperature will have less of an effect on leaching efficiency [162-164]. In general, the apparent activation energy for the chemical reaction-controlled mechanism is more than 40 kJ/mol while it is less than 20 kJ/mol for the diffusion-controlled mechanism [165-167]. If the apparent activation energy is between these values, then both the chemical reaction and diffusion rates are involved [168].

Other factors such as particle size and agitation speed can be changed to obtain a better understanding of the leaching kinetics. For particle size, the diffusion rates will increase significantly with a decrease in particle size since the total contact area has increased. Furthermore, the boundary layer becomes thinner, increasing the leaching rate [158, 164]. The agitation speed mainly influences the external diffusion rate because the thickness of the liquid film layer is affected. This in turn affects the contact of the reactive species with the unreacted core [142, 169]. Increased agitation speed has been found to not increase leaching efficiency beyond a certain point. It has also been found that going beyond this point might decrease the leaching efficiency due to mass transfer limitations [169].

Fitting the models given in Section 2.5.2.1 to the experimental data can indicate a change in the rate controlling step at a certain time. The expected plot of leaching efficiency versus time would normally have a sharp increase initially, plateauing after a set amount of contact time. Any deviation from this could indicate a change in the rate control mechanism [164, 170]. If the models presented in Section 2.5.2.1 are fitted to the second stage, the models must be modified to account for the conversion obtained from the first stage [154]. Taking this into account, the equations are modified for the SCM and SPM models that are presented in Section 2.5.2.1. For the chemical reaction-controlled mechanism, the equation becomes:

$$k_1(t - t_1) = (1 - X_1)^{\frac{1}{3}} - (1 - X)^{\frac{1}{3}} \quad \text{E- 18}$$

For the external diffusion-controlled mechanism the equation becomes:

$$k_2(t - t_1) = X - X_1 \quad \text{E- 19}$$

For the internal diffusion-controlled mechanism the equation becomes:

$$k_3(t - t_1) = 3(1 - X_1)^{\frac{2}{3}} + 2(1 - X_1) - 3(1 - X)^{\frac{2}{3}} + 2(1 - X)$$

$$k_3(t - t_1) = 3 \left[(1 - X_1)^{\frac{2}{3}} - (1 - X)^{\frac{2}{3}} \right] - 2(X - X_1) \quad \text{E- 20}$$

For the SPM model, small and large particle cases, the equations become:

$$k_4(t - t_1) = (1 - X_1)^{\frac{2}{3}} - (1 - X)^{\frac{2}{3}} \quad \text{E- 21}$$

$$k_5(t - t_1) = (1 - X_1)^{\frac{1}{2}} - (1 - X)^{\frac{1}{2}} \quad \text{E- 22}$$

For these models t_1 corresponds to the time when the rate controlling step has changed and X_1 is the recovery/leaching efficiency at this time [154]. The same principle can also be applied to the PH models, Equation E- 13, E- 14 and E- 15, resulting in the following equations:

$$k_6(t - t_1) = \ln\left(\frac{1 - X_1}{1 - X}\right) \quad \text{E- 23}$$

$$k_7(t - t_1) = \frac{1}{1 - X} - \frac{1}{1 - X_1} \quad \text{E- 24}$$

$$k_8(t - t_1) = (1 - X)^{\frac{1}{2}} - (1 - X_1)^{\frac{1}{2}} \quad \text{E- 25}$$

2.5.2.5 Current findings

With the basic concepts behind the kinetic models discussed, it would be highly beneficial to investigate the most current findings for the leaching kinetics of REEs from CRMs. With regard to the leaching kinetics of REEs from coal and coal ash, only a limited number of studies were found. Studies that adequately investigate the kinetics based on several kinetic models (from Section 2.5.2) or other models, as well as reporting the resulting activation energies was found to be lacking.

As discussed in Section 2.5.1.1, mineral acids have been used in a multitude of studies to extract REEs from coal ash. However, these studies have only reported on the effect of the leaching temperature and duration of leaching. A study by Zhang and Honaker (2020) on a high volatile bituminous coal reported rapid leaching kinetics [171]. Using the ash obtained after the thermal treatment of the coal, the study found that for both LREEs and HREEs, extraction occurred within the first 5 min of the leaching process followed by minimal recovery changes afterwards [171]. A similar result has been reported by Honaker et al. (2019) on ash obtained directly from a FBC as well as ash obtained from the thermal treatment of different coals [11]. It was evident as with the previous study that a high leaching recovery of the REEs occurs within a short time (5 min) [11, 171]. In a recent study by Gupta et al. (2023), it was again confirmed that the thermal treatment of coal can significantly increase the leaching rate of the REEs [12]. Although these aforementioned studies on REE recovery report fast kinetics, none investigate different leaching models or report apparent activation energies [11, 12, 171].

Mineral acids have been used in several attempts to extract REEs from CRMs as well as organic acids as discussed in Section 2.5.1.1. As with mineral acids, the usage of organic acids on CRMs for the extractions of REEs have been done but only a few studies report on the reaction kinetics. A study conducted by Karagulanova et al. (2025) has indicated relatively rapid kinetics with the extraction of the REEs reaching its optimum point at 120 min [172]. The study utilized TA combined with magnesium sulphate, reporting an activation energy of 20-22 kJ/mol [172]. A study done by Banerjee et al. (2022), reported relatively fast kinetics using MSA [128]. Ultimately the kinetics was reported to be diffusion controlled with the activation energies reported between 11.5-18.5 kJ/mol [128]. Banerjee et al. (2023) investigated several reaction-controlled models for the usage of organocarboxylic acids (lactic acid, TA and citric acid) [143]. The study reported the leaching process to be a mixed model mechanism based off several kinetic models [143].

2.6 Summary

In the literature review, there is constant emphasis on the rapid growth of the demand for rare earth elements. Firstly, as a result of their critical role in the development of advanced, low-carbon technologies. Although the abundance of REEs in the Earth's crust has been found to be higher than that of other metals such as gold and silver, their economic extraction has been constrained by complex mineralogy, environmental risks, and geopolitical challenges. Hence, motivating research toward the utilisation of secondary sources such as CRMs, which has showcased a wide range of REE concentration.

The REEs in coal have been reported numerous times as being associated with either the organic or inorganic phase, depending on whether it is LREEs or HREEs. For coal derived ash the organic phase reacts with oxygen, which results in a distribution of REEs now only associated with mineral matter. The speciation of REEs in the resulting coal ash is highly dependent on the thermal treatment conditions. It is these thermal treatment conditions that are different for different CFPPs, and from previous studies a higher thermal treatment temperature leads to REE encapsulation. The encapsulation of the REEs is caused by the transformation of different minerals present in the coal. The main mineral found to be responsible for the encapsulation, and thereby inhibition of REE extraction, is the aluminosilicate glass phase.

Acid leaching has been used as the main method for extracting REEs from CRMs. For a coal ash, the extraction of REEs can be done either by direct acid leaching or by pretreatment of the coal ash, followed by acid leaching. In general, HCl has been used numerous times to optimise the recovery of REEs from coal ash. However, there have recently been attempts to recover REEs from coal ash using organic acids such as TA and MSA. Although leaching parameters are usually investigated, only several attempts at fitting different kinetics models were found. However, the kinetics for leaching REEs from coal ash was found to be significantly enhanced when exposed to low thermal treatment temperatures.

It is generally accepted that the direct leaching method would be less costly, but it requires a coal ash derived from a low temperature. On a large scale, FBC type boiler CFPPs produce ash at a much lower temperature compared to other alternatives. The progress towards utilising coal ash as a secondary source has seen substantial progress, but a gap remains: a lack of integrated, process-level understanding that links coal rank, combustion conditions, REE speciation changes, and kinetic behaviour to produce validated, scalable extraction strategies – especially for low rank coals such as lignite and for ash produced below typical PCC boiler combustion temperatures.

2.7 References

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3.1 Introduction and experimental approach

This section of the dissertation outlines the experimental approach and procedures used in this study, covering sample preparation through to enhanced leaching aimed at maximising recovery and leachate concentration. The primary material used in this study was a low-rank coal (lignite) obtained from a confidential location in the Middle East. To achieve the objectives defined in Section 1.3, the experimental plan in Figure 3-1 was followed.

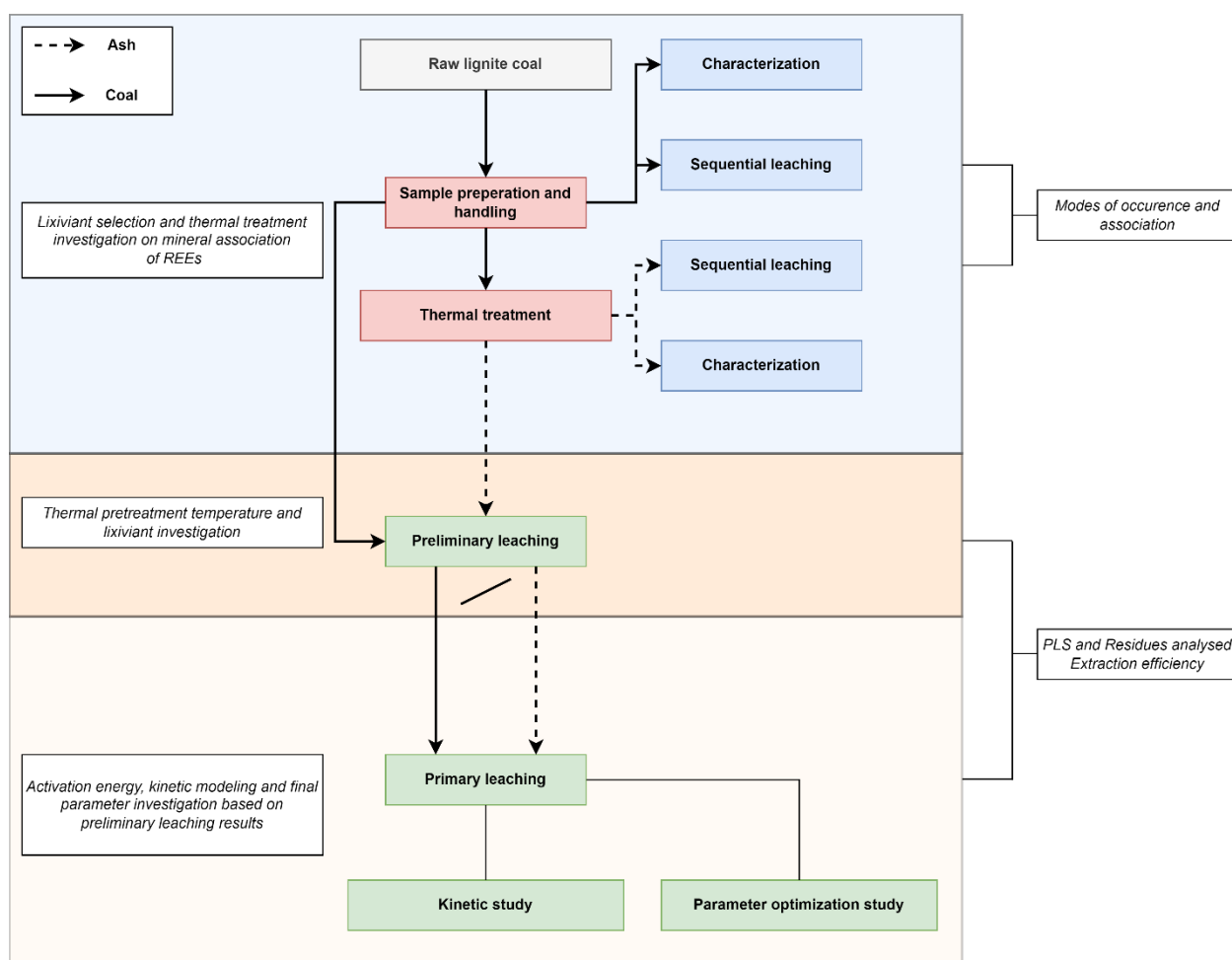


Figure 3-1: Overall experimental plan used for this study

The experimental procedures are divided into three sections. The first section involves the characterization of the coal and ash, including an overview of the modes of occurrence and associations of the REEs. The second section comprises a preliminary leaching phase to identify a suitable lixiviant and combustion temperature for subsequent experiments. The final set of experiments focuses on optimizing the leaching parameters and developing an appropriate kinetic model.

3.2 Material

3.2.1 Material preparation and handling

Sample handling and preparation involved crushing, milling, sieving, coning and quartering, splitting, pulverizing, and drying. The lignite coal was received in two separate bags: one containing coarser particles and the other already crushed to below 3 mm. The contents of both bags were combined, reflecting their original mixed state, and milled using a roll mill. The entire sample was homogenized to a particle size below 500 μm , with a 500 μm sieve and mechanical shaker used throughout the preparation process. Coning and quartering were performed after milling, followed by rotary splitting to obtain representative subsamples. Samples designated for proximate analysis were dried, whereas those intended for leaching experiments were used without drying. (ISO 18283 standard preparation method [1])

3.2.2 Chemical reagents

The chemicals, their respective suppliers and purities used throughout this study, are listed in Table 3-1. The chemicals listed in Table 3-1 were used for microwave digestion, calcination- and leaching experiments. The chemical grade of all the chemicals used in this study was of analytical grade (AR). Deionized water was used throughout all experiments, purified with a Millipore Milli-Q® Q-pack CPMQ004R1.

Table 3-1: Chemicals used throughout this study

Chemical	Chemical formula	Supplier	Purity
Ammonium acetate	$\text{C}_2\text{H}_7\text{NO}_2$	LabChem	$\geq 98\%$
Ammonium sulphate	$(\text{NH}_4)_2\text{SO}_4$	Fluka Analytical	$\geq 99\%$
Boric acid	BH_3O_3	ACE Chemicals	97%
Hydrochloric acid	HCl	ACE Chemicals	32% & 37%
Hydrofluoric acid	HF	Merck	48%
Nitric acid	HNO_3	ACE Chemicals	55%
Perchloric acid	HClO_4	LabChem	70%
Sulfuric acid	H_2SO_4	ACE Chemicals	95%
Tartaric acid	$\text{C}_4\text{H}_6\text{O}_6$	Promark Chemicals	$\geq 95\%$
Toluene	$\text{C}_6\text{H}_5\text{CH}_3$	MINEMA Chemicals	$\geq 99.5\%$

3.3 Methods

3.3.1 Coal classification

Proximate analysis of the coal was conducted using standard methods. These methods included ISO 11722: 2013 [2], ISO 562: 2010 [3] and ISO 1171: 2010 [4], used to determine the moisture content, volatile matter and ash content respectively. The fixed carbon content was then determined by difference after the ash content was determined. The ultimate- and gross caloric value analysis of the coal material has been performed prior to this study [5], using ISO 17247: 2020 [6] for the carbon-, hydrogen- and nitrogen content, ISO 19579: 2006 [7] for the total sulphur content, and ISO 1928: 2020 [8] for the gross calorific value analysis. The results of these analyses were then used to determine the rank of the coal as discussed in Section 2.3.2.

3.3.2 Sequential leaching – Raw coal

The association and occurrence of the REEs in coal have been studied using different methods. One such method, that was used in this study, was taken from a study reported by Finkelman et al. (2018) on the modes and occurrence of REEs in coals of Northern China [9]. The overall methodology of the procedure followed is given in Figure 3-2.

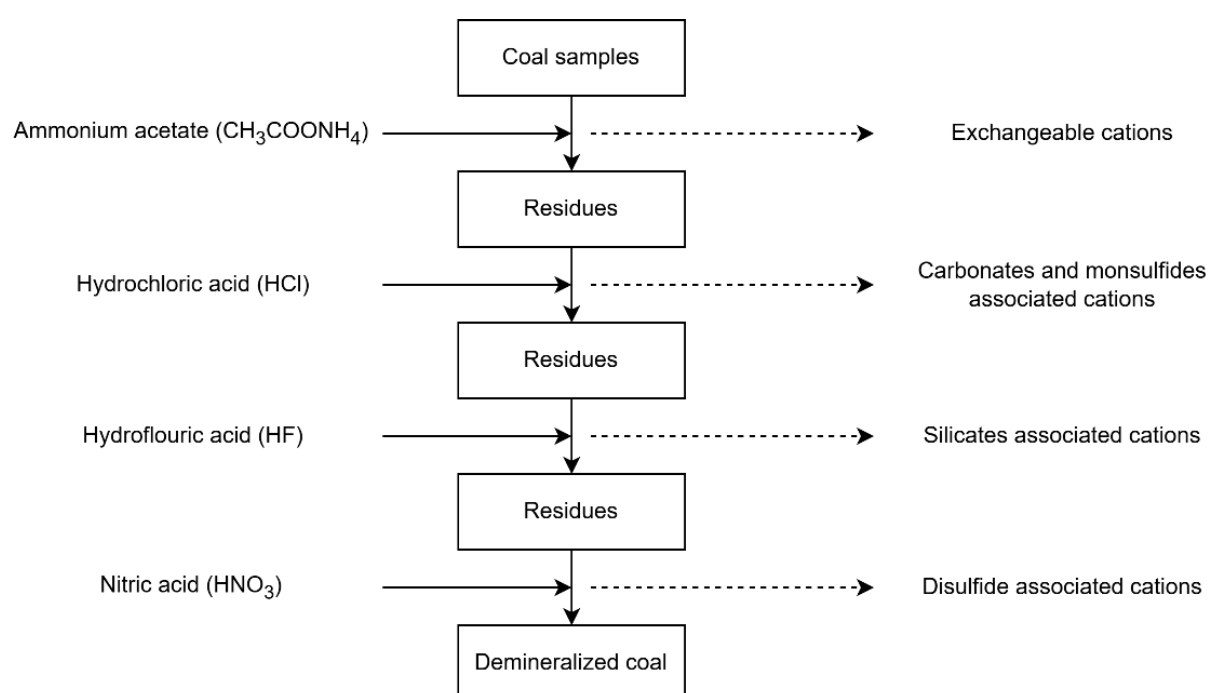


Figure 3-2: Sequential leaching procedure used for the raw lignite coal with no chemical or thermal pre-treatment [9]

Sample preparation for the sequential leaching procedure only involved the pulverization of the coal to pass 60 mesh (248 μm). In this study, the sample was comminuted to pass through a 212 μm sieve. For each run, 5 g of sample was sequentially leached using 1 M ammonium acetate, 3 M hydrochloric acid, 48% (w/w) hydrofluoric acid, and 2 M nitric acid. For each step of the sequential leaching procedure, the volume of the solution was kept at 35 ml. The leaching of the samples occurred inside polypropylene bottles that were shaken in an oven shaker for 18 h at room temperature. The mixture was filtered, and the resulting solid cake was then washed and dried overnight for use in the subsequent step, while the pregnant leach solution (PLS) was sent for analysis via ICP-OES (Section 3.6.1).

3.3.3 Thermal pretreatment

The thermal treatment of the feed coal samples was conducted using a tube furnace provided by Lenton Laboratory & Scientific Equipment. The tube furnace was fitted with a temperature controller provided by Elite Thermal Systems Ltd (Model number: THS12/75/610), operating at a temperature of 400 – 1000 $^{\circ}\text{C}$, operating at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ using dry air at a flow rate of 95 or 295 ml/min. A schematic of the setup used for the thermal treatment of the samples is given in Figure 3-3.

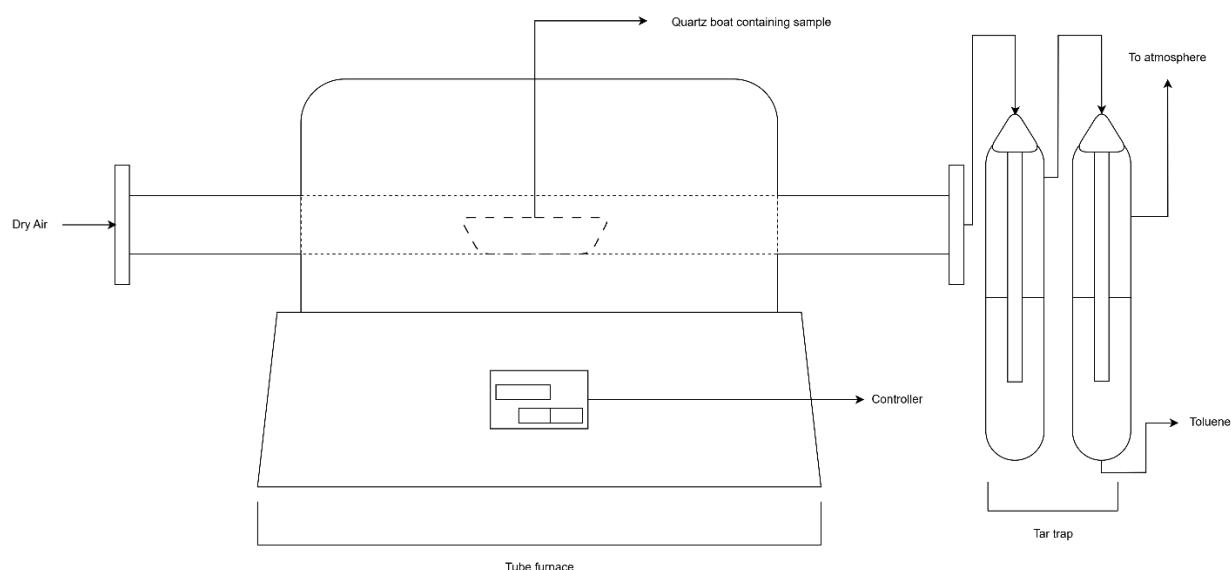


Figure 3-3: Setup used for the thermal treatment of the samples

The samples were treated at the designated temperature and were not subjected to the ramping stage of the tube furnace. For each run of the thermal treatment, the flow rate of the air was set to the desired amount. The temperature was set to the desired amount and set to a specified dwelling time. The amount of coal sample weighed was kept between 12-16 g to allow for enough ash sample after each run. During thermal pretreatment, the flue gases were then sent to a tar trap using toluene as illustrated in Figure 3-3. The quartz boat was then removed once the final time was reached and allowed to cool to room temperature.

3.3.4 Sequential leaching – Coal ash

The sequential leaching procedure used for the resulting ash differs due to mineralogical changes taking place during the combustion of the coal. A summary for the sequential leaching method used, taken from Banerjee et al., 2024 [10], is shown in Figure 3-4. The ashes that were obtained from the combustion of the coal (Section 3.3.3) were subjected to this sequential leaching procedure. For each run, 5 g of the sample was sequentially leached using milli-Q water, ammonium sulphate, tartaric acid, and hydrochloric acid, with the volume kept constant at 50 ml.

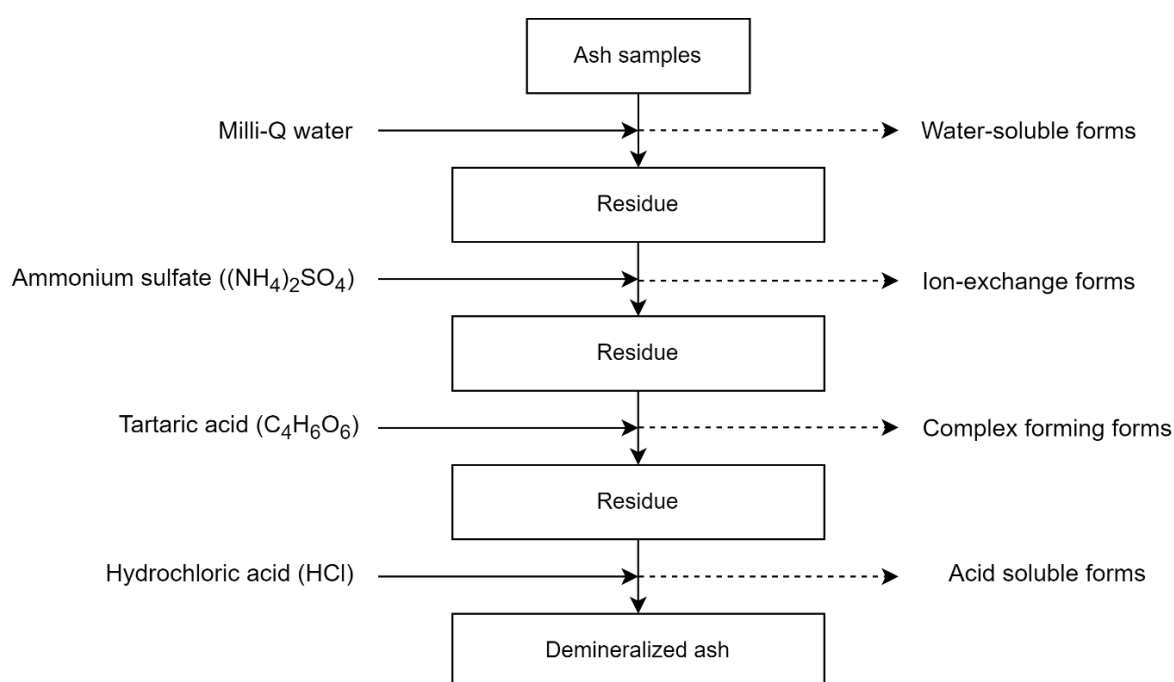


Figure 3-4: Sequential leaching procedure used for the resulting ashes from thermal treatment [10]

The conditions used for the sequential leaching procedure on the ash is presented in Table 3-2. The resulting residue, from the steps shown in Table 3-2, was then digested via microwave digestion which was sent for analysis via ICP-OES (Section 3.6.1).

Table 3-2: Sequential leaching conditions used for the resulting ashes [10]

Step	Chemical	Time	Concentration	Temperature
1	Milli-Q water	24 hours	N/A	RT*
2	Ammonium sulphate	24 hours	2 M [#]	RT*
3	Tartaric acid	24 hours	0.3 M	RT*
4	Hydrochloric acid	2 hours	1 M	90 °C

* RT = Room temperature; Concentration not specified in previous study

3.3.5 Coal and ash digestion

The raw coal and ash characterization involved the full dissolution of the samples using microwave digestion, followed by the analysis of the solution with ICP-OES and ICP-MS. The full digestion of the samples was performed using a Multiwave 5000 microwave digestion system, supplied by Antor Paar Southern Africa (Pty.) Ltd. The digestion of the samples differed depending on whether it was a raw coal sample or an ash.

The microwave system contained pre-loaded methods which were used to digest the samples. For the analysis of the raw coal, 200-400 mg was weighed and then 4-6 ml of HNO₃ (55%), 0-2 ml of H₂O₂ (35%), 0-1 ml of HF (48%) and 0-2 ml of HClO₄ (70%) were added for digestion. For the digestion of the ashes, 100-300 mg was weighed and then 3 ml HNO₃ (55%), 3 ml HCl (37%), 2 ml HF (48%) and 0-2 ml HClO₄ (70%) was added. For both these methods it was ensured that there was no visible residue remaining after digestion. For complexation of the HF, 6 ml (approximately 1 M) H₃BO₃ was added for every 1 ml HF, resulting in the final solution that was analysed via ICP-OES (Section 3.6.1) and ICP-MS (Section 3.6.2).

3.3.6 Main leaching setup

The main leaching setup that was used throughout the study is given in Figure 3-5. The setup included hotplates with magnetic stirrers and temperature control, purchased from Eins Sci. A reflux apparatus was used to ensure a constant liquid-to-solid ratio for all experiments. The sample was added to the lixiviant once the target temperature was reached. The three-necked flask was removed from the reflux apparatus and was then emptied into a vacuum filtration setup resulting in a residue cake and PLS. The PLS was then sent for analysis via ICP-OES (Section 3.6.1). The resulting residue was thoroughly washed with Milli-Q water when further analysis of the residue was required.

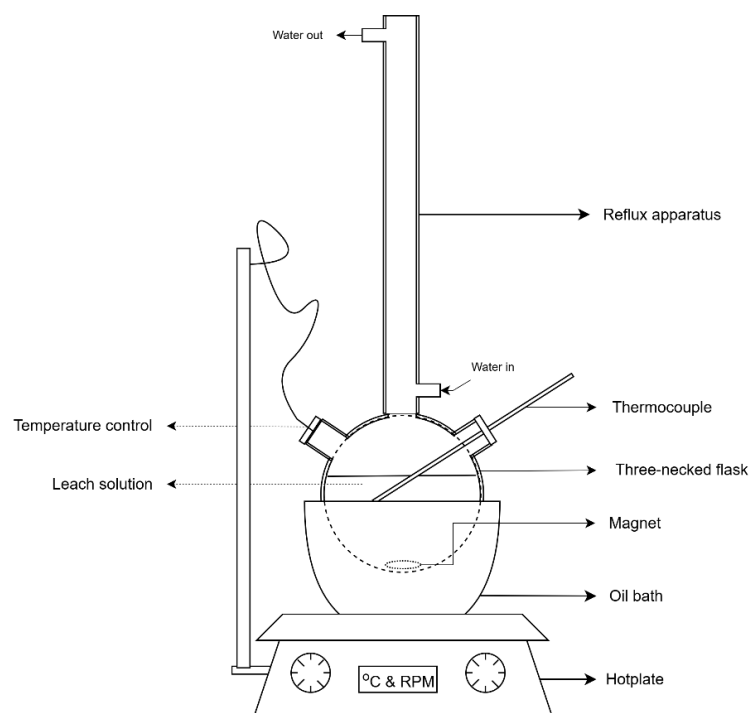


Figure 3-5: Schematic of leaching setup utilized throughout the study

3.4 Experimental procedures

3.4.1 Preliminary Leaching

The preliminary leaching step involved the investigation of two types of lixivants and the thermal treatment temperatures. The two lixivants tested for this study included a mineral acid (HCl) and an organic acid (Tartaric acid). These acids were tested on ash obtained from thermal treatment at 800 °C, resembling the temperature found in FBC boilers, with a thermal treatment dwelling time of 2 hours. The conditions that were used for lixiviant determination is given in Table 3-3.

Table 3-3: Leaching conditions tested during the preliminary stage of experimentations

Lixiviant			
Hydrochloric acid (HCl) [11]		Tartaric acid (C ₄ H ₆ O ₆) [12]	
Parameter	Value	Parameter	Value
Liquid-to-solid ratio	10:1	Liquid-to-solid ratio	150:1
Temperature	90 °C	Temperature	90 °C
Contact time	120 min	Contact time	60 min
Concentration	3 M	Concentration	0.3 M
Stirring intensity	300 rpm	Stirring intensity	300 rpm

The best lixiviant was identified and then used in the investigation of lower and higher thermal treatment temperatures. The temperatures that were chosen ranged from 400 °C up to 1000 °C using the same thermal treatment dwelling time. The experimental procedures that follow were therefore conducted under a fixed temperature of thermal treatment as well as the type of lixiviant.

3.4.2 Primary parameters investigation

3.4.2.1 Liquid-to-solid ratio and lixiviant concentration

The optimization of the leaching parameters was conducted based on the results obtained from the preliminary leaching stage. As stated before, the optimization stage was conducted under a fixed thermal treatment temperature, a fixed thermal treatment dwelling time, and the type of lixiviant. At this stage of the experiments, the leaching temperature, stirring intensity, and leaching duration were kept constant. The values of these parameters were chosen from the best conditions reported in the previous Section (Section 3.4.1).

For the parameter investigation stage, the liquid-to-solid ratio and the lixiviant concentration were varied. To do this, a full factorial experimental design was implemented. The design of experiment (DOE) consisted of three levels and two factors, which can be seen in Table 3-4.

Table 3-4: Description of the 3 levels associated with factors A and B that were used for the orthogonal array

Level	Factor A: Liquid-to-solid ratio	Factor B: Lixiviant concentration
1	5:1	1
2	10:1	3
3	100:1	5

Using this method leads to 9 unique runs, establishing the optimum combination for the liquid-to-solid ratio and the concentration of the lixiviant. The final run was then repeated 3 more times which resulted in 4 repetitions ($n = 4$) for a unique run which was then used for repeatability.

3.4.2.2 Temperature and contact time

The effect of the leaching duration and leaching temperature was investigated simultaneously during the kinetic study. To do this, the sample was introduced to the chosen lixiviant, at a selected temperature and then filtered after a predetermined contact time. Three temperatures were selected from 30 °C up to 90 °C and 13 different time intervals, resulting in a total of 39 unique runs which is shown in Table 3-5.

Table 3-5: Leaching parameters used during the kinetic experiments investigating the effect of temperature on leaching efficiency

Parameter	Values
Temperature (°C)	30, 60 & 90
Contact time (min)	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 20, 40, 120
Stirring intensity (rpm)	Constant
Lixiviant concentration (M)	Constant
Liquid-to-solid ratio (L:S)	Constant

The type of lixiviant, lixiviant concentration, liquid-to-solid ratio, and thermal treatment temperature were fixed based on the previous experimental procedures (Section 3.4.1 & Section 3.4.2.1). After completing the kinetic study, the optimum contact time and leaching temperature were established. Furthermore, the kinetic models discussed in Section 2.5.2.1 were fitted to the resulting data. The apparent rate constants that were obtained from fitting these models to the resulting data were then used to determine the apparent activation energies, as discussed in Section 2.5.2.3.

3.5 Data interpretation

3.5.1 Leaching recovery

For all the leaching experiments the PLS was analysed for the concentration of the REEs. Determination of the leaching efficiency or fraction leached was then calculated using Equation E- 26.

$$X_i = \frac{C_{PLS,i} \cdot V_{PLS}}{C_{s,i} \cdot m} \quad \text{E- 26}$$

Where X_i is the leaching efficiency/fraction leached of species i (%), $C_{PLS,i}$ is the concentration of species i in the PLS (ug/ml or mg/L), V_{PLS} is the volume of the PLS (ml), $C_{s,i}$ is the concentration of species i in the solid sample (ug/g or mg/kg) and m is the total mass that was weighed for leaching (g).

3.5.2 Repeatability

The repeatability of the experiments was determined using a 90 and 95% confidence interval. The number of repetitions was kept to a minimum of 3 ($n = 3$) where repeatability was tested. Using the t-table for a two-tailed test, with a significant level (α) of 0.1 and 0.05, the confidence of the leaching efficiencies was determined. Equation E- 27 was used to determine the values for the repeated runs reported in Chapter 4.

$$CI = \bar{x} \pm z \frac{s}{\sqrt{n}} \quad \text{E- 27}$$

Where CI is the reported confidence interval, $\bar{x}$ is the sample mean, z is the confidence interval value (dependent on the number of repeated runs), s is the sample standard deviation and n is the sample size.

3.5.3 Root mean square error

The root mean square error (RMSE) values were used to compare the data points of the kinetic models with the actual experimental data. Specifically, the LREE leaching recovery obtained and the values predicted by the different kinetic models. The RMSE values were determined using Equation E- 28.

$$RMSE (\%) = \sqrt{\frac{\sum_{i=1}^n (X_{experimental,i} - X_{model,i})^2}{n}} \quad \text{E- 28}$$

Where $X_{experimental,i}$ and $X_{model,i}$ are the values for the experimental data and that which was predicted by the models for the point i , respectively. The summation of the errors squared over the specific time interval is then divided by the number of data points which are represented by n .

3.5.4 Model fit

As discussed in Section 2.5.2.4, the fit of the kinetic models can be assessed graphically by the resulting R^2 values. For the single fit of the kinetic models the R^2 were found to be well below 0.95 for all the tested models. Therefore, the implementations of several time sections were done as discussed in Section 2.5.2.4 for the different models. A systematic approach was utilized to determine which of the models have the most accurate prediction. This approach included the testing of all the kinetic models at each time section. Once a model was chosen based on the best fit (R^2 value) and the lowest RMSE, then the next fit was built from the first using the same fitting criteria.

3.6 Analytical methods

3.6.1 ICP–OES

Inductively coupled plasma - optical emission spectroscopy (Agilent , 5110 ICP-OES) was used to analyse all resulting solutions. Certified reference materials obtained from De Bruyn Spectroscopic Solutions were used for calibrating the instrument. Before accurate analysis, the samples were subjected to IntelliQuant for a preliminary scan of major elements. The appropriate calibration solutions were then made, which included 16 REEs (Pm does not occur naturally) and the major elements (Al, Fe, Si, etc.). Quality control (QC) was implemented by analysing the minimum and maximum concentrations of the calibration solutions after every 10 samples analysed. QC was implemented to ensure the highest measurement accuracy and to validate the concentration of the prepared calibration standards.

3.6.2 ICP–MS

Inductively coupled plasma mass spectroscopy (ICP-MS) was used for the characterization of the feed material. The analysis was outsourced to the University of Johannesburg (UJ), making use of a Perkin Elmer Nexlon 300D. The concentrations of all REEs were determined for the lignite coal and the laboratory derived ash. To ensure quality control of the analysis, CRM (NIST 1643 CRM) were used throughout the analysis. The acceptable recoveries for the CRMs were in the range of 80-120%.

3.6.3 XRD

The x-ray diffraction (XRD) analysis of the samples was outsourced to XRD Analytical and Consulting. The samples were prepared for XRD analysis using a back-loading preparation method. Diffractograms were obtained using a Malvern Pananalytical Aeris diffractometer with a PIXcel detector and fixed slits, utilizing Fe-filtered Co-K α radiation. The phases were identified using X'Pert Highscore Plus software and the relative phase amounts (weight %) were estimated using the Rietveld method. The values reported by the instrument with a wt% below 0.5 % was below the detection limit (DL) and was considered an unreliable result.

3.6.4 XRF

The x-ray fluorescence spectroscopy (XRF) of the samples was outsourced to Bureau Veritas Testing and Inspections South Africa. Sample preparation prior to analysis was performed by Bureau Veritas, as was the analysis. The analysis was conducted using Thermo Fisher AdvantX and Thermo Fisher PerformX XRF analysers manufactured by Thermo Fisher Scientific Inc. The procedure followed for the analysis was the ASTM D4326 XRF – By fusion bead (Subcontracted Test) procedure. The XRF instruments were calibrated for different sample types to ensure a comprehensive concentration range was achieved.

3.6.5 TGA

Thermogravimetric analysis (TGA) was performed on the samples using a Q600 SDT provided by TA Instruments. Roughly 15 mg of sample was weighed into the designated crucible, following the set procedure of the instrument. For the TGA analysis of the sample, the change in temperature was set to 5 °C/min up to a maximum of 1000 °C. Once the temperature was reached, the instrument was set to dwell for 120 minutes. The instrument recorded data such as the loss of mass and temperature changes over time. During the TGA analysis, dry air was also used as with the tube furnace with a flow rate of 95 ml/min.

3.6.6 PSD

The particle size distribution (PSD) of the chosen samples was measured using a Mastersizer 3000, manufactured by Malvern Panalytical. The reflective index was chosen based on a built-in value termed “CFA” and “coal.” The PSD was then determined using wet and dry dispersion methods to compare the results.

3.6.7 SEM

Scanning Electron Microscopy (SEM) was conducted on the ash/residue samples using a FEI Quanta FEG 250 SEM with xT microscope Server and xT microscope Control software. The analysing voltage used for the SEM analysis was set to 20 kV. The samples were coated with carbon using a Q150 Es Plus (Quorum Technologies) and then inspected using the SEM.

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CHAPTER 4 RESULT AND DISCUSSION

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4.1 Sample characterization

4.1.1 Coal rank determination

For the determination of the coal rank, the results of the proximate-, ultimate and gross calorific value analysis is required. A standard proximate procedure was performed on the raw coal as discussed in Section 3.3.1 and the results are presented in Table 4-1. For the ultimate- and gross calorific value analysis of the coal, the results from a prior study on the same coal material is presented in Table 4-2.

Table 4-1: Proximate analysis results obtained (wt%) for the coal samples with 95% confidence interval (n = 3)

Properties	Method	Adb ¹	Db ²	Dafb ³
Inherent moisture content	ISO 11722: 2013 [1]	12.0 ± 0.5	-	-
Volatile matter	ISO 562: 2010 [2]	44.8 ± 0.6	50.9 ± 0.4	62.40 ± 0.6
Ash content	ISO 1171: 2010 [3]	16.2 ± 0.1	18.5 ± 0.1	-
Fixed carbon	By difference	27.0 ± 0.4	30.7 ± 0.5	37.60 ± 0.6

¹Air dry basis, ²Dry basis, ³Dry ash free basis

From Table 4-1, it is evident that the moisture content of the coal sample is relatively high, i.e. 12.0 wt%. The coal sample was then found to have a volatile matter-, ash- and fixed carbon content of 50.9, 18.5 and 30.7 wt% on a dry basis respectively. The values that were obtained from Table 4-1, would however have to be converted to a mineral matter free basis. The mineral matter content of the coal sample can be estimated using Equation E- 3 from Section 2.3.2 and results in a value of 18.7 wt%.

Table 4-2: Ultimate- (wt%) and gross caloric value analysis as reported from previous report [4]

Properties	Method	Adb	Dafb
Carbon content	ISO 17247: 2020 [5]	49.90	68.92
Hydrogen content	ISO 17247: 2020 [5]	4.52	6.24
Nitrogen content	ISO 17247: 2020 [5]	0.56	0.77
Total sulphur content	ISO 19579: 2006 [6]	2.18	3.01
Oxygen content	By difference	15.24	21.05
Gross calorific value (MJ/kg)	ISO 1928: 2020 [7]	20.70	-

To accurately determine the rank of the coal, the dry, Mm-free FC and VM content was determined. Using Equation E- 4 and E- 5 and the results of Table 4-1 and Table 4-2 resulted in a value for the dry, Mm-free FC and VM of 38.5 wt% and 61.5 wt% respectively. Since the value for the dry, Mm-free FC content was below 69 wt% and the dry, Mm-free VM content was above 31 wt%, the coal rank was determined using the gross calorific value on a moist, Mm-free Btu basis [8]. From Table 4-2 the gross calorific value was previously determined as 20.7 KJ/mol which is roughly 8900 Btu/lb. Using Equation E- 6, the value for the gross calorific value on a moist, Mm-free basis was calculated as 10 812 Btu/lb. Based on the ASTM D388 the coal is classified as a high volatile C bituminous coal since the gross calorific value on a moist, Mm-free basis is greater than 10 500 Btu/lb and less than 11 500 Btu/lb [8]. The appearance of the material indicated a lower rank which led to the analysis of the vitrinite reflectance analysis of the material.

As discussed in Section 2.3.2, the rank of the coal can also be determined with the vitrinite reflectance analysis which was previously conducted on the coal sample resulting in a mean vitrinite random reflectance (Rr) value of 0.28% [4]. The coal material was classified according to ISO-11760 [9] and it was determined to be a low rank lignite coal. As discussed in Section 2.3.2, the analysis of a coal material using this method produces the most accurate result to determine the rank of the coal [10]. Therefore, the naming of the raw coal sample and the laboratory derived ash will be termed raw lignite coal (RLC) and lignite laboratory derived ash (LLDA) further on based on the petrographic analysis of the material. It should also be kept in mind that the result from the ASTM D338 method indicates a lignite coal with a volatility that is comparable to a high volatile C bituminous coal.

4.1.2 Elemental composition

4.1.2.1 Major

XRF analysis was conducted to obtain the major elements that are present in the LLDA and the RLC as part of the characterization of the feed material. The procedure used is discussed in Section 3.6.4 and the result for the LLDA is shown in Figure 4-1. It should be noted that the result of Figure 4-1 represents the composition of the LLDA; for the RLC sample a loss of ignition (LOI) of 83.8% should be considered.

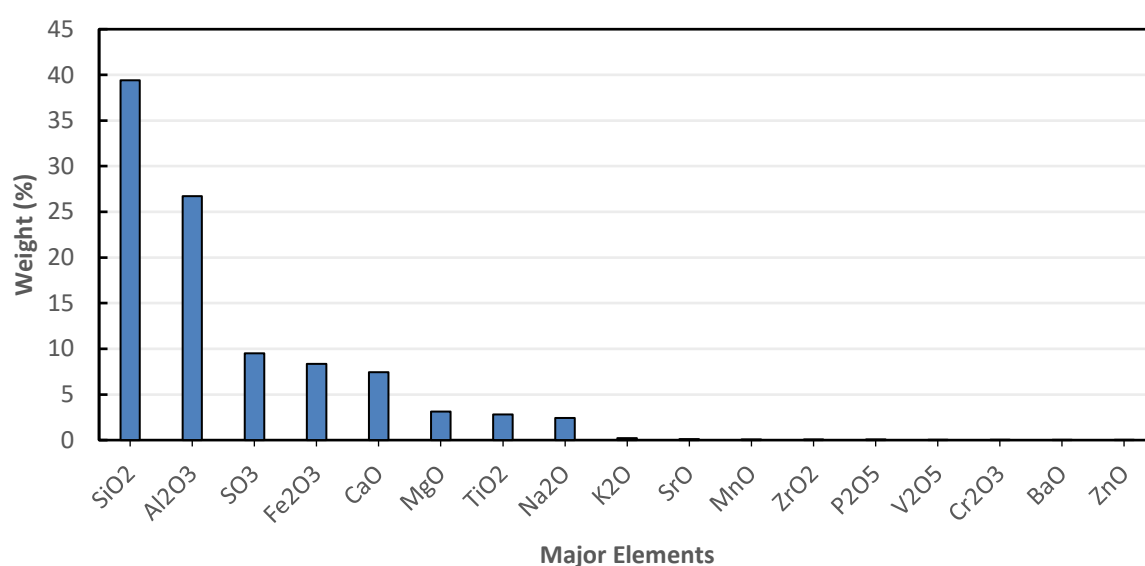


Figure 4-1: Major Elements present in the LLDA (T = 800 °C, t = 18 h, DAFR = 95 ml/min) as determined by XRF

From Figure 4-1 above, the dominant elements expressed as oxides in the LLDA are SiO₂ and Al₂O₃, which together account for 66.1 wt%. Other oxides such as SO₃, Fe₂O₃, CaO, MgO, TiO₂ and Na₂O account for 33.7 wt%. The sample contains a relatively high amount of sulfur trioxide (9.5 wt%), as reported, calculated to 3.8 wt% sulfur content, compared to other studies. Dahan et al. (2022), Cao et al. (2018), and Tang et al. (2018), have reported sulfur content close to and lower than 1 wt% for CFAs [11-13]. Furthermore, the amount of iron- and calcium oxide present may already indicate the possibility of high leaching efficiencies without pretreatment. This could be attributed to the Fe,Ca-rich aluminosilicate glass phase having higher REE content than the pure Al-Si glass phase [14]. Additionally, the presence of calcium is advantageous since its dissolution can form calcium silicates, reducing the amount of silicate gel forming that result in lower leaching efficiencies [15].

4.1.2.2 Trace

To determine the initial viability of the RLC and LLDA, the concentration of REEs in the material had to be measured. The concentration measurements were performed by first dissolving the material via microwave digestion, as discussed in Section 3.3.5. The resulting solution was then analysed via ICP-MS as discussed in Section 3.6.2. For LLDA, the coal was combusted at 800 °C in the tube furnace, as discussed in Section 3.3.3, for 18 hours with a dry air flow rate (DAFR) of 95 ml/min. The results of the REE concentrations, obtained from ICP-MS for the RLC and LLDA, are given in Table 4-3.

Table 4-3: Rare earth element concentration in the RLC and LLDA (T = 800 °C, t = 18 h, DAFR = 95 ml/min) as determined by ICP-MS (mg/kg)

Element	Sample		Element	Sample	
	RLC	LLDA		RLC	LLDA
Sc	5.2	42.8	Gd	0.6	7.9
Y	5.4	41.8	Tb	0.2	1.3
La	6.9	57.4	Dy	0.6	7.6
Ce	15	112.9	Ho	0.2	1.5
Pr	1.4	12.5	Er	0.1	4.3
Nd	7.4	51.4	Tm	0.2	0.5
Sm	0.9	8.5	Yb	0.3	4.1
Eu	0.2	2.0	Lu	0.2	0.5
LREE	31.3	244.8	TREE	44.3	357.1
HREE	7.8	71.6	CREE	13.9	104.2

Comparing the TREE in the RLC to the average TREE concentration in world coals (69 ppm) [16] and the UCC (179 ppm) [17], indicates an uneconomic source. Comparison of the RLC with the LLDA shows the enrichment of all the REEs. The TREE concentration increases by a factor of 8 without considering the ash content. However, if the relative enrichment factor (REF) is considered (Equation E- 7), taking into account the ash content as shown in Table 4-1, the TREE REF is 1.5 on a dry basis. The enrichment was expected since the REEs are non-volatile at the respective combustion temperature, therefore partitioning into the resulting ash [18, 19]. The enrichment of the TREE concentration occurs but remains below the world average for coal ashes (404 ppm) [16]. Furthermore, the TREE content are in trace quantities compared to primary sources such as bastnaesite and monazite having TREE content in weight % values [20].

The cut-off grade of ≥ 1000 ppm, suggested by a study conducted in 2004, further emphasizes the unviability of the RLC [21]. Despite this, the suggested cut-off grade may not apply to the increase in REE demand and market price to date. Taking this into account, it will be sensible to assume a decreasing cut-off grade with an increase in demand. Therefore, using the LLDA could be beneficial, with a TREE concentration above the UCC concentration and closer to the world average for coal ashes. Thus, optimization and kinetic investigation will focus only on the extraction of the La, Ce, and Nd from the LLDA since it accounts for roughly 62% of the TREES and 91% of the LREEs.

4.1.2.2.1 Viability assessment

To further investigate the viability of the LLDA, the C_{out} and $CREE\%$ parameters can be evaluated. Other CRM sources are considered for comparison, with their respective values given in Table 2-5. Additionally, bastnaesite, monazite and xenotime bearing deposits viability is also given to compare the distribution to primary sources of REEs [22]. The values of C_{out} and $CREE\%$ is plotted in Figure 4-2 using the viability of an ore source as discussed Section 2.2.3.

The results indicate a source of REEs that has an almost promising distribution, i.e. between unpromising and promising. However, if the viability assessment changes to a CRM source, the viability areas change, indicating a source that is close to the promising area. In Figure 4-3, the viability of the LLDA is shown based on the assessment criteria given in Section 2.4.1.

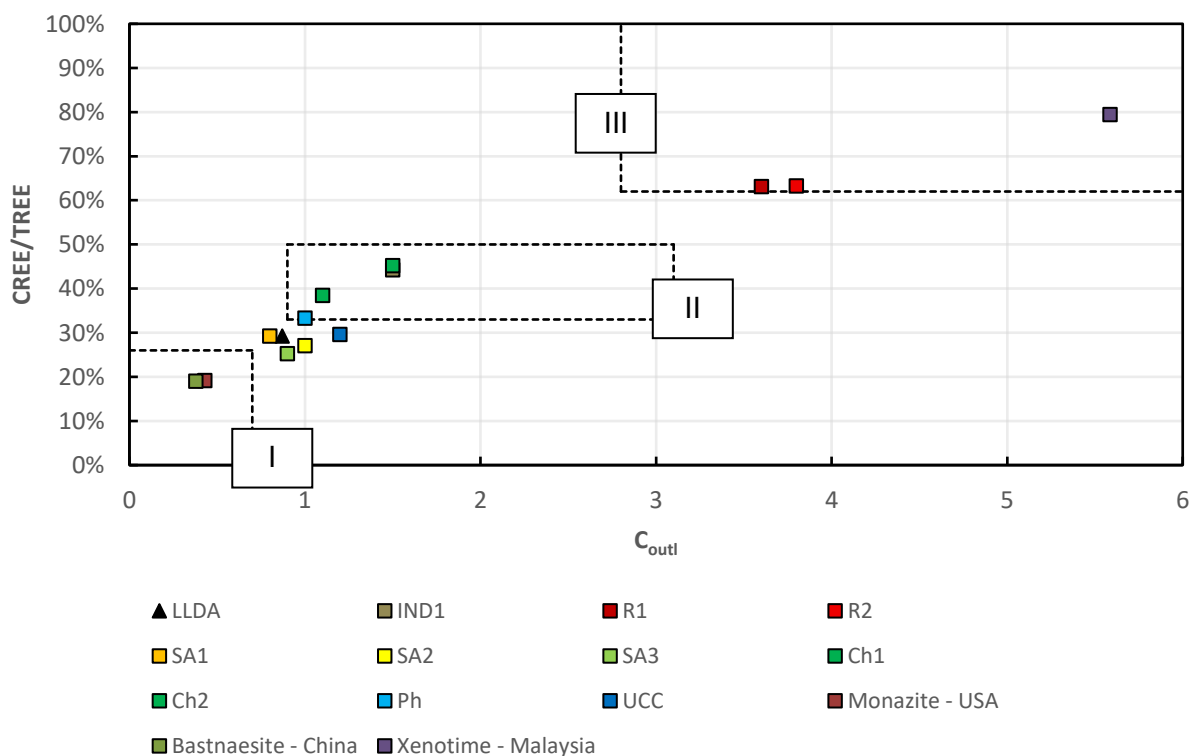


Figure 4-2: Outlook coefficient and CREE content compared to criteria set out by Seredin for promising ore sources, (I) unpromising, (II) promising & (III) highly promising [23]

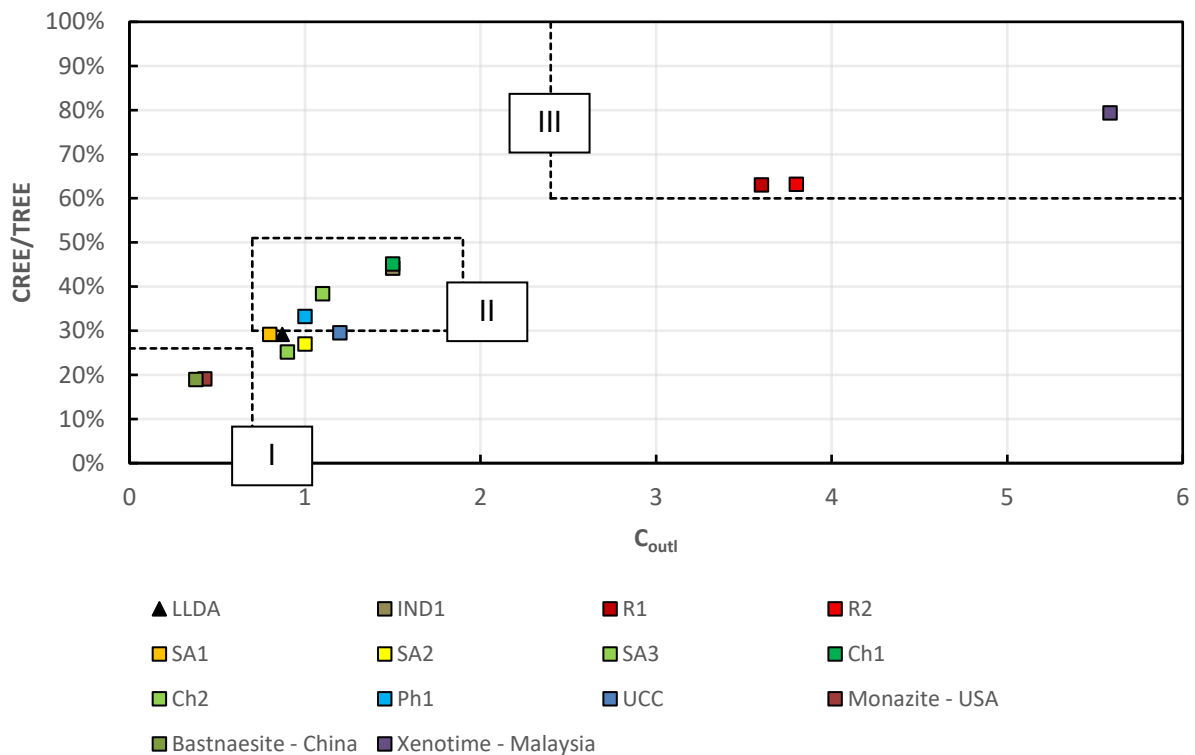


Figure 4-3: Outlook coefficient and CREE content compared to criteria set out by Seredin and Dai for promising coal sources of REEs, (I) unpromising, (II) promising & (III) highly promising [24]

In Figure 4-2 and Figure 4-3, the LLDA has a nearly promising ratio of CREEs to EXREEs and a fraction of CREEs to TREES. It is not clear whether the viability parameters change based on the source considered, purely based on the demand for these elements, or both. In either case, the method indicates that this lignite coal has a promising distribution of REEs. Comparison of the LLDA, bastnaesite, monazite, and the other CRMs with the UCC further motivates the utilization of CRMs as secondary sources. All CRMs considered, including the LLDA, have distributions that are close to or higher than those of the UCC. Two of the primary sources, bastnaesite and monazite, have REE distribution values below those of the UCC, falling into the unpromising area.

Using the normalized data for the content of REEs in the LLDA can shed light on the type of distribution of the REEs. The distribution criteria discussed in Section 2.4.2 were used to determine whether the LLDA had distribution patterns of type L, type M, or type H. The values of these types of distributions were determined using the concentrations found in the UCC as shown in Table 2-6 [25]. The normalization of the individual REEs to the concentration in the UCC of the LLDA is given in Figure 4-4 together with other secondary sources such as phosphogypsum (PG1&2), coals from Russia (R1&2), and CFA from South Africa (SA1).

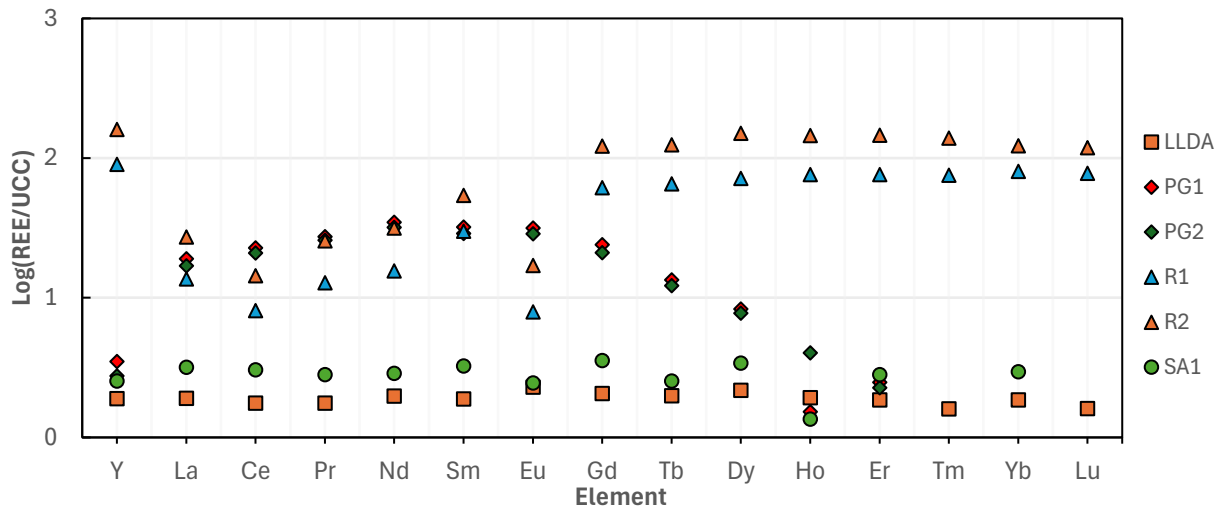


Figure 4-4: Normalization of REEs in LLDA (T = 800 °C, t = 18 h, DAFR = 95 ml/min) using concentration found in the UCC [25]

The values of the distribution parameters for the LLDA were calculated as $La_N/Lu_N = 1.18$, $La_N/Sm_N = 1.01$ and $Gd_N/Lu_N = 1.28$. This correlates with a weak L-type distribution, with the criteria of M-type and H-type distributions almost satisfied. This indicates that the LLDA under investigation closely resembles the distribution of REEs in the UCC except for Sc. Considering the CREEs (Nd, Eu, Tb, Dy, Y, and Er), a strong H-type and/or M-type distribution would be more advantageous. Primarily since the scarcity of REEs increases with the increase in atomic number or stated otherwise, the concentration of HREEs is much lower than that of LREEs in the UCC [25]. Traditional sources such as bastnaesite, monazite, and xenotime also have their own type of distribution. The distribution of REEs in these primary sources is strongly towards an individual type of distribution. For example, bastnaesite and monazite both have strong L-type distributions, whilst xenotime has a strong H-type distribution [26].

4.1.3 Particle size distribution

As discussed in Section 3.2.1, the RLC was homogenized by milling and crushing the sample to pass a 500 µm sieve. The reduced particle size RLC was then used for thermal treatment, which can affect the PSD of the resulting LLDA. The PSD of the RLC and LLDA was determined using the method given in Section 3.6.6 and the result is given in Table 4-4.

Table 4-4: Size distribution summary of the RLC and the LLDA (T = 800 °C, t = 18 h, DAFR = 95 ml/min)

Sample	Uniformity	Span	D [3,2]	D [4,3]	Dv (10)	Dv (50)	Dv (90)
RLC	1.3	4.1	13.2 µm	135 µm	5.63 µm	83.7 µm	342 µm
LLDA	1.2	3.5	17.3 µm	80.7 µm	8.61 µm	49.1 µm	182 µm

From the table above, it can be observed that the RLC and the LLDA have average particle sizes of 13.2 μm and 17.3 μm , respectively. The span for both the RLC and the LLDA indicates that the average particle size is not representative of all the particles. A span value close to 0 would designate a sample with a more uniform particle size (narrower size distribution) [27]. Although this is the case, there are clear differences in the PSD of the RLC and the resulting LLDA. Firstly, the span decreases from 4.1 to 3.5 and the particle sizes of D_{50} and D_{90} decrease, which is due to the removal of organic matter [28]. A slight increase in the sizes of D_{10} particles might demonstrate the initiation of particle agglomeration/fusion [28].

4.1.4 Mineralogy

The RLC is subjected to elevated temperatures which result in mineralogical changes. Minerals occurring at different temperatures can help interpret the association of REEs with a certain mineral. The minerals that were detected after the pretreatment of the RLC, as discussed in Section 3.6.3, are given in Table 4-5.

Table 4-5: Minerals detected with XRD in the RLC (ash basis) and the LLDA ($T = 800\text{ }^{\circ}\text{C}$, $t = 18\text{ h}$, DAFR = 95 ml/min)

Mineral	RLC	800 $^{\circ}\text{C}$
Amorphous	0.0	54.8
Anhydrite	0.0	22.8
Quartz	7.8	11.2
Hematite	0.0	6.0
Perkovaite	0.0	4.3
Kaolinite	77.3	0.0
Gypsum	14.9	0.0

From Table 4-5, it can be seen that the RLC sample (ash basis) consisted mainly of kaolinite (77.3 wt%), gypsum (14.9 wt%) and quartz (7.8 wt%). After thermal treatment of the RLC, most of the mineralogical composition has been identified as amorphous minerals (54.8 wt%). The rest of the mineral composition of the LLDA is anhydrite (22.8 wt%), quartz (11.2 wt%), hematite (6.0 wt%) and perkovaite (4.3 wt%). For the RLC and the LLDA, the XRD has detected none of the primary REE-bearing minerals presented in Table 2-1. Due to the detection limit of XRD, minerals present at less than 0.5 wt% are considered unreliable. Therefore, the presence of the REE-bearing minerals, being overshadowed by other major mineral fractions, was not detected. This is supported by the low concentrations of REEs detected by ICP-MS, showcasing a TREE value below 400 ppm.

During the thermal pretreatment of the RLC, mineralogical changes have occurred. Taking first into account the loss of kaolinite, it has been shown that during kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) dehydroxylation, the alumina-silica structure undergoes recombination to the meta-kaolinite structure at 600 °C [29]. Since meta-kaolinite is a complex amorphous structure [30], the presence of amorphous minerals in the LLDA can be explained. Secondly, the gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) present in the RLC undergoes complete dehydration to form anhydrite (CaSO_4). This occurs because the thermal treatment temperature of 800 °C is far above the reversible change from anhydrite back to gypsum [31].

4.1.5 Combustion behaviour

The combustion behaviour of the RLC was investigated using a thermogravimetric analyser (TGA) to determine the time required for complete combustion. Additionally, differential thermogravimetric (DTG) values corresponding to the slope at a point for the TGA were also recorded. The procedure used is discussed in Section 3.6.5 and the results are given in Figure 4-5 and Figure 4-6.

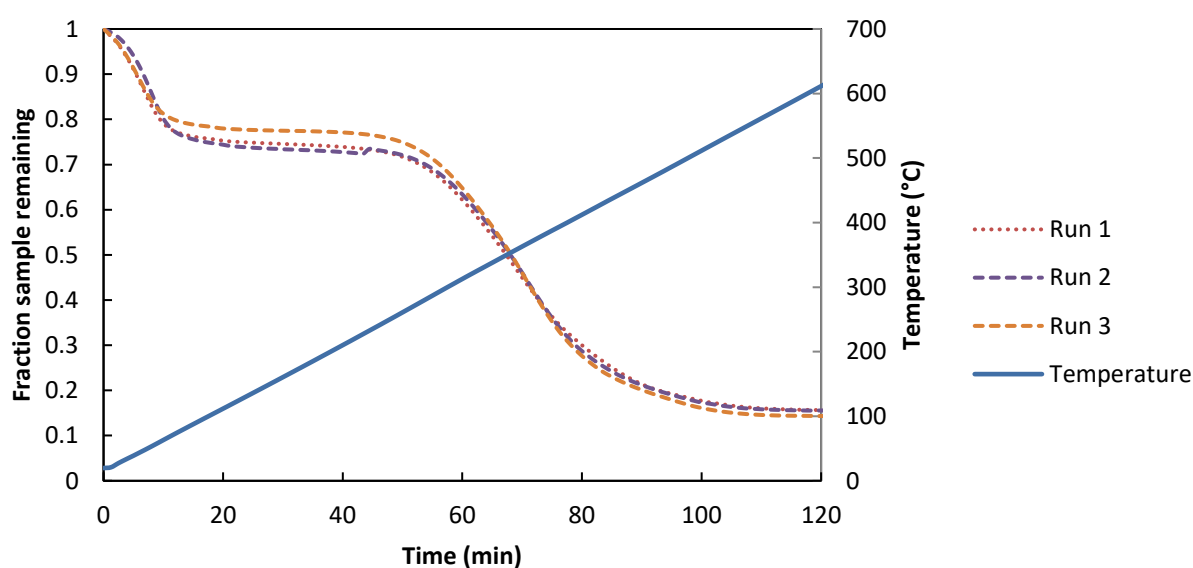


Figure 4-5: TGA result for the RLC sample indicating the fraction of sample remaining and the temperature with respect to time (DAFR = 95 ml/min)

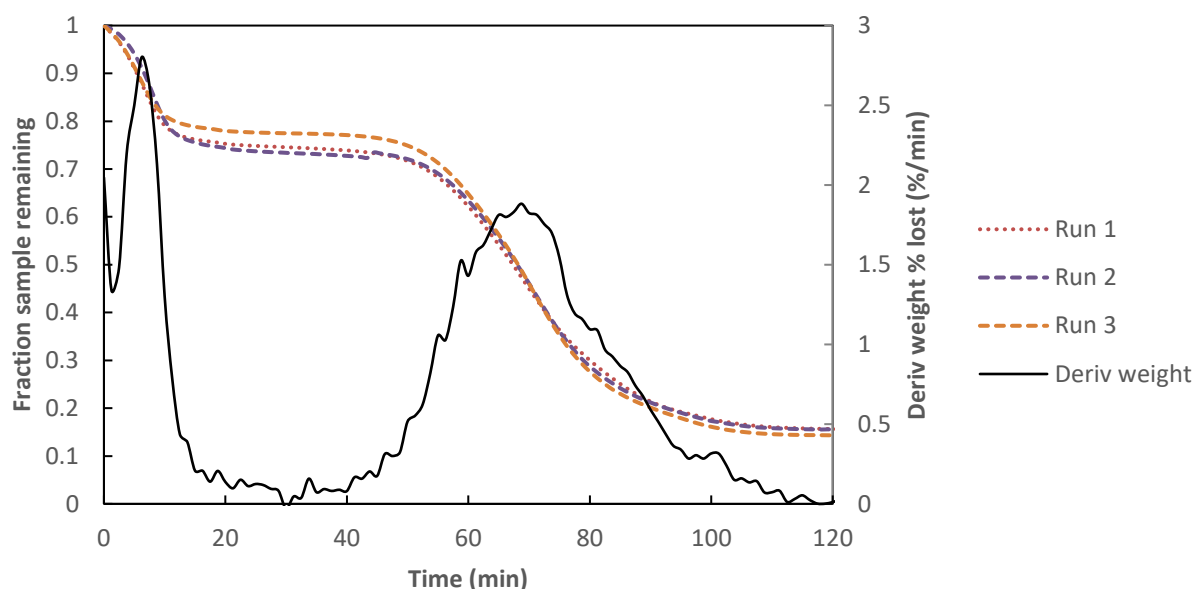


Figure 4-6: TGA and DTG result for RLC sample indicating the fraction of sample remaining and derivate weight loss with respect to time (DAFR = 95 ml/min)

From Figure 4-5 and Figure 4-6, most of the dehydration of the RLC occurs between 20-80 °C. The RLC then undergoes combustion, starting at a temperature of 220 °C, rapidly losing weight, the highest change in weight percent occurring at 357 °C. From the TGA results presented in Figure 4-5, the RLC has stopped losing weight after reaching a temperature of 600 °C. At this temperature, the RLC has been subjected to an increase in temperature for approximately 110 min. This is much higher than the char combustion and devolatilization times reported for FBC boilers [32]. For the purposes of this study, the duration was kept at 18 h for the sequential leaching of the resulting LLDA. Whilst the experiments afterwards are done on LLDA derived at a thermal treatment duration of 2 h.

In summary the coal was determined to be a lignite with 12 wt% moisture content and 16 wt% ash content on an air-dry basis. Furthermore, using the classification of coal rank, discussed in Section 2.3.2, the coal was determined to be a low rank lignite. The REE content in the RLC is significantly lower compared to the 357-ppm found in the LLDA. Evaluating the distribution of the REEs in the LLDA indicated a C_{out} of 0.87, a CREE% of 29% and a weak L-type distribution. After analysing the PSD of the RLC and the LLDA it was clear that a reduction in particle size has occurred. The mineral content in the RLC underwent changes during the thermal treatment, which mainly included the transformation of kaolinite to meta-kaolinite and gypsum to anhydrite. Unfortunately, no discrete REE-minerals were detected due to the low REE content in the RLC and LLDA. Finally, it was determined that 2 h would be a sufficient duration for thermal treatment of the RLC.

4.2 Association and speciation

4.2.1 Lignite coal

Sequential leaching of the RLC was conducted to investigate the association of REEs in the raw material. The procedure used on the RLC is given in Section 3.3.2 and the results are given in Figure 4-7 with the repeatability data given in Annexure A.2.1 (Section 6.1.2.1).

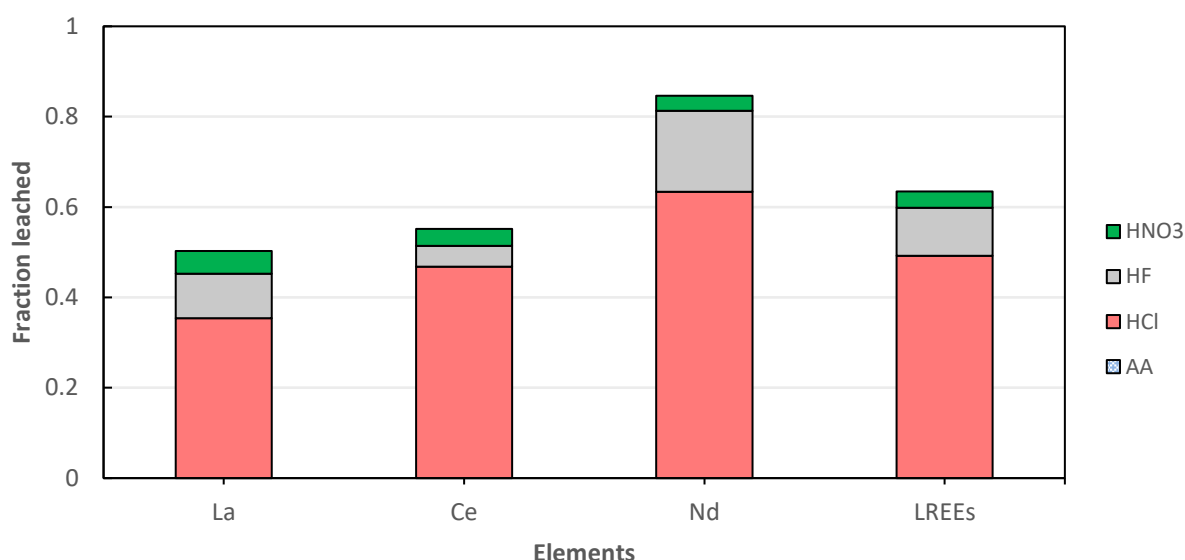


Figure 4-7: Sequential leaching of selected REEs from the RLC

The proposed solvents used for the sequential leaching of the RLC have been adopted by Finkelman et al. (2018) [33]. First exchangeable REE cations are removed, using ammonium acetate ($\text{CH}_3\text{COONH}_4$, AA), then REE cations associated with the carbonates and monosulfides, using hydrochloric acid (HCl), then REE cations associated with the silicates with hydrofluoric acid (HF). The REEs associated with the disulfides would then be removed with nitric acid (HNO_3). The final residue should then contain the insoluble fraction of REEs [33].

In Figure 4-7, there is no ion-exchangeable fraction of LREEs in the RLC. The lack of exchangeable cations was also observed for REEs such as Y, Ce, La, Lu, Nd, Sm and Yb for low- and higher rank coals of North America [33]. An additional study conducted on North Dakota lignites observed the same lack of exchangeable cations for all REEs [34]. This might imply a lack of exchangeable cations for lignite coal, but this cannot be assumed for all CRMs. A study conducted on low temperature ash (LTA), cyclone ash (CA), CFA, and BA from a FBC boiler found that CA and CFA can have relatively high fractions of REEs bound as exchangeable cations [35]. For the investigated RLC, the lack of ion-exchangeable sites for LREEs can be explained by their stability in the environment, lacking migration and transformation [36].

The LREEs are mainly associated with carbonates and monosulfides with approximately 49% being leached using HCl. As discussed in Section 2.2.1, bastnaesite is a carbonate mineral and monazite and xenotime are phosphate minerals [37]. This might imply the presence of bastnaesite in the RLC. High REE extraction percentages using HCl has also inferred REEs bound to other acid soluble minerals, non-mineral inorganic forms [34], or strong ion-exchangeable forms [33]. Compared to a lignite from North Dakota, obtained from the Fort Union bed, majority (60%) of the LREEs (La, Ce, Nd, Sm) were extracted using HCl [33]. The study used Ce as a proxy for the LREEs and differences between the LREEs, evident in Figure 4-7, were not illustrated. Another study was conducted on several lignite samples also obtained from the Fort Union formation. The HCl leachable fraction of the REEs was between 80-95 wt% [34]. These differences emphasizes the influence of geological factors on the organic- and inorganic association of REEs within the same coal deposit or coal bed [38].

The fraction of LREEs leached with HF is bound to silicates and aluminosilicates [33, 39], whereas the fraction leached with HNO₃ is bound to disulfides and phosphates [33, 36]. Because the RLC has not undergone any combustion or thermal pretreatment, the silicate and aluminosilicate content is limited to the fraction of mineral matter. For the LREEs, as shown in Figure 4-7, 11% is bound to the silicates and the aluminosilicates. The LREEs association with disulfides and phosphates was determined to be roughly 4%. Compared to the North Dakota lignite, the association of the LREEs is roughly similar. The only major difference identified is the fraction of LREEs extracted using HNO₃ was slightly higher [33]. The LREEs fraction remaining in the residual category has been identified to be associated with organic matter, acid-insoluble minerals, or fine-grained minerals enclosed by the organic matter [33, 40]. Thus, 37% of the LREEs in the RLC can be said to be insoluble. This is considerably higher than the results obtained for the North Dakota lignite with a residual fraction of 10% for the LREEs [33].

4.2.2 Lignite ash

Sequential leaching of the LLDA was conducted to investigate the speciation of the REEs in the resulting ash. The procedure used is given in Section 3.3.4 and the results are given in Figure 4-8 with the repeatability data given in Annexure A.2.2 (Section 6.1.2.2).

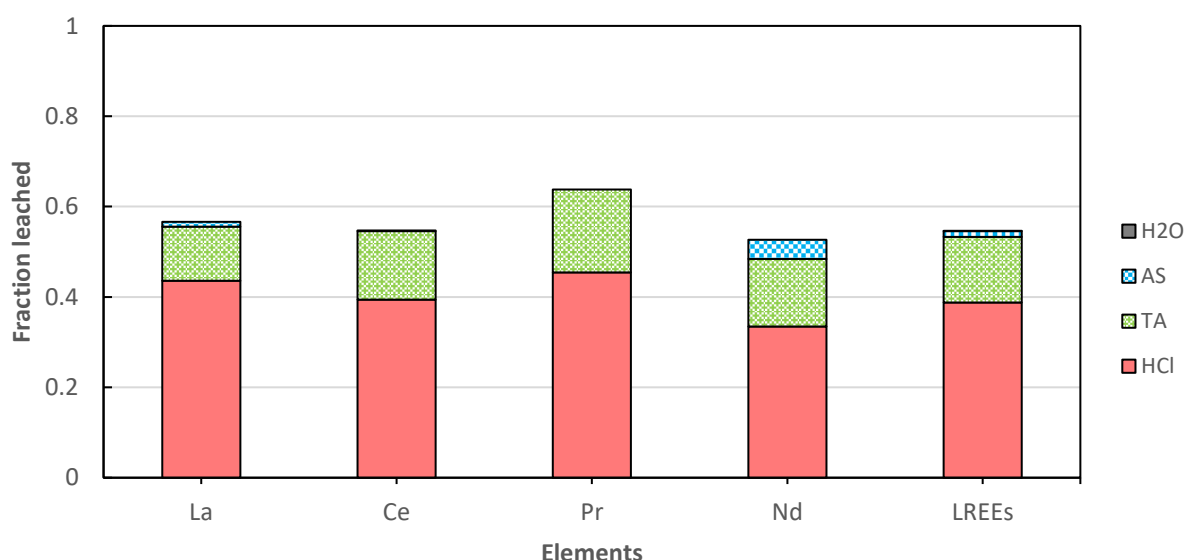


Figure 4-8: Sequential leaching of selected REEs from the LLDA (T = 800 °C, t = 18 h, DAFR = 95 ml/min)

The proposed solvent used for the sequential leaching of the LLDA has been adopted by Banerjee et al. [41]. First, the water-soluble fraction is removed, then the ion exchangeable cations using ammonium sulphate ((NH₄)₂SO₄), then the complex bound using tartaric acid (C₄H₆O₆). HCl is then used to remove the acid soluble fraction, leaving a residual that is considered insoluble [41].

In Figure 4-8, none of the selected LREEs were in the water-soluble form. The lack of water soluble LREEs was also observed when investigating the occurrence of REEs in bituminous coal and its respective CA, FA, and LTA [35]. Using ammonium sulphate extracted 4.3% of Nd and 1% of the LREEs. Studies conducted on higher rank coals have shown the LREE ion-exchangeable fraction to undergo insignificant change after thermal treatment [35, 42]. There was however an exception for the ion-exchangeable fraction of the CFA obtained directly from a FBC [35]. As shown in Figure 4-7 and Figure 4-8, the change in ion-exchangeable fraction of the LREEs is also insignificant.

Considering the major fractions leached, the total extractable fraction of the LREEs was determined to be roughly 55%. The soluble fraction consisted of the acid soluble LREEs (39%) and the complex bound LREEs (15%). The total extractable fraction LREEs (water-soluble, ion-exchangeable, complex bound and acid soluble) of the study proposing the methodology used, showcase similar results for a laboratory derived ash [41]. There were, however, no distinctions given for the different associations in the coal ash. It is also worth noting that the study utilized different ashes for sequential leaching. The laboratory ash was obtained by combustion at 815 °C (1 h) whilst the BA and CFA were obtained from Indian coal based thermal power plants [41]. The difference in LREE association in the laboratory derived ash and the thermal power plant ash was quite notable. The BA and CFA that was used were obtained from high temperature combustion (1200 °C) resulting in low extractable fractions (10-15%) [41].

As discussed in Section 2.4.4, REEs speciation in CFA has been found to be primarily in the aluminosilicate glass phase. This is more prevalent for ashes that are obtained from high temperature combustion/calcination conditions [41, 42]. For the LLDA, the RLC was treated at a lower temperature (800 °C). After treatment, the aluminosilicate glass phase was detected in the LLDA, as shown by XRF and XRD analysis in Figure 4-1 and Table 4-5 respectively. Together with the residual fraction (45%) obtained in Figure 4-8; the results might imply the association of LREEs to the aluminosilicate glass phase. However, this might only be applicable to some (major/minor fractions) of the insoluble material since discrete REE phosphates, REE carbonates, REE oxides, REE silicates, REE sulphates, REE iron oxides, etc. have been observed in CFA [38]. For the purposes of this study, the confirmation of discrete REE minerals were deemed unnecessary.

In summary the sequential leaching from the RLC has shown that the majority of the LREEs to be in carbonate, monosulfides and insoluble form. The sequential leaching of the LLDA has shown the potential of TA and HCl as leaching lixiviants to extract the LREEs. As discussed in Section 2.5.1.1, TA and especially HCl have been used to directly leach REEs from coal ash. Therefore, the screening of different acids was constrained to one mineral acid (HCl) and one organic acid (TA). These two acids are further tested with the thermal treatment conditions changed based on the results presented in Section 4.1.5.

4.3 Preliminary Leaching

4.3.1 Lixiviant screening

As mentioned in Section 2.5, several types of lixivants have been evaluated to extract REEs from CRMs. To determine the most suitable lixiviant, two lixivants were evaluated based on their optimum conditions using the methodology given in Section 3.4.1. The results for leaching the selected REEs from the LLDA, using two different types of lixivants, is given in Figure 4-9.

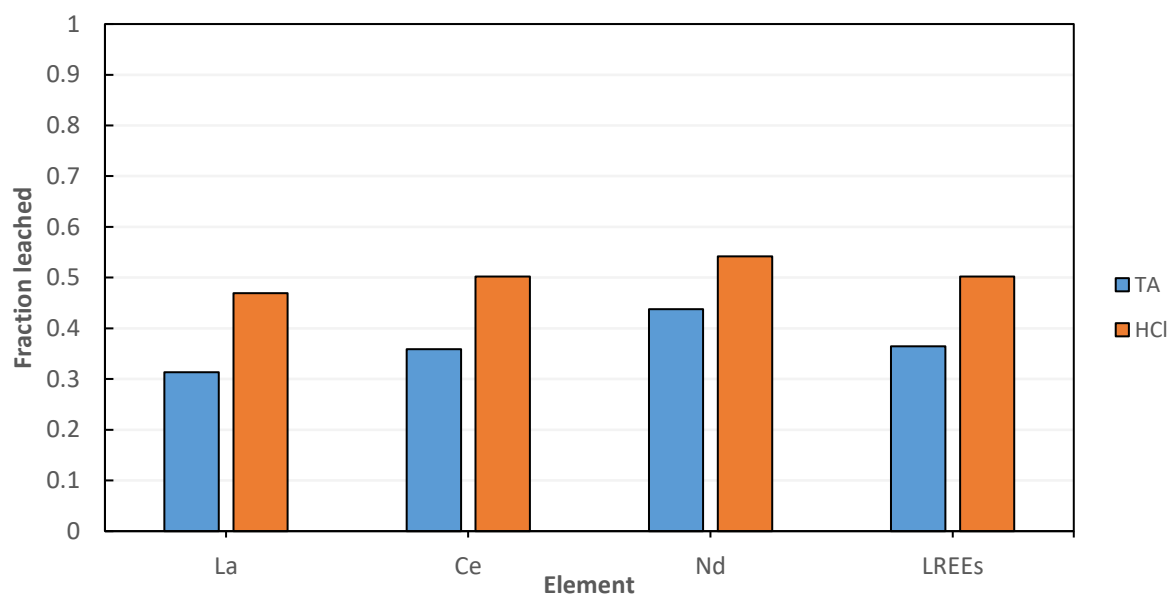


Figure 4-9: Leaching recovery of LREEs using an organic- (TA) and mineral acid (HCl) on the LLDA (T = 800 °C, t = 2 h, DAFR > 295 ml/min) at their respective optimum conditions

Under optimum conditions, HCl performed the best with 50% of the LREEs leached with HCl and 36% with TA. Considering one of the studies from which the optimum conditions were taken, the TA has underperformed. Banerjee et al. (2021) utilized a laboratory derived ash, combusted at a temperature of 850 °C for 1 h. The study was able to leach 65% of the LREEs using TA [43]. The study did not specify the type of coal utilized making it difficult to compare based on coal rank. For HCl, the REEs leached was less compared to an ash obtained under a similar thermal treatment temperature. Wen et al. (2020) utilized a CFA that resulted from the combustion of bituminous coal in a FBC boiler (850-1000 °C) [44]. The study was able to extract 86.5% La, 80.0% Ce and 71.1% Nd [44] which is much higher compared to the results in Figure 4-9. Reasons for the differences can be the thermal treatment conditions (temperature, duration, particle dispersion, and oxygen availability) and the rank of the feed coal. For the purpose of this study, a comprehensive analysis of all the thermal treatment parameters was not undertaken. However, the differences can be discussed based on the results of Figure 4-8 and Figure 4-9.

TA and HCl were used for the sequential leaching procedure of the LLDA and the screening tests; therefore the results of Figure 4-9 can be compared with those of Figure 4-8. The only thermal treatment parameters that change between these experiments is the duration of thermal treatment and the DAFR. Reducing the thermal treatment duration from 18 h to 2 h results in the extraction of more LREEs when using either TA or HCl. Thus, a reduction in the thermal treatment duration could increase the leaching recovery of the REEs. It is also worth noting that the leaching conditions used with TA have changed from the sequential leaching procedure to the screening tests. The result that is presented in Figure 4-8 was obtained by using TA at a contact time of 24 h and at room temperature. The result of Figure 4-9 was obtained by leaching with TA at 90 °C with a contact time of 1 h and a significant increase in the liquid-to-solid ratio (150:1).

There are implications for the difference in the leachability of the REEs from the LLDA at different thermal treatment conditions. The first would be that the characterization method indicated a significant increase in the entrapment of the REEs in the insoluble phase. The direct leaching methods was conducted on the ash obtained from a shorter thermal treatment duration, resulting in less of the REEs entrapped in the aluminosilicate glass phase. There could be numerous reasons for this but the most likely explanation would be due to inadequate thermal treatment of all the material in the quartz boat.

The results can further be compared to studies that have implemented thermal treatment of coal to produce ash. Coal of Indian origin has been subjected to thermal treatment, after which organic acids were used as an alternative to common mineral acids. The duration of thermal treatment for these studies has all been kept at 1 h. The recovery of LREEs from the ash was in relatively high amounts using different organic acids [43, 45, 46]. Unfortunately, there was no direct comparison given between the performance of these organic acids against mineral acids under the same thermal treatment conditions. Furthermore, a study conducted on coal ash derived from US coal indicated that using dilute HCl could recover roughly 65% of the REEs. Interestingly, using an organic acid (Maleic acid) resulted in a REE recovery of almost 60% from the same ash material [47]. Some key differences between the US coal and Indian coal studies are the thermal treatment temperature (600 °C vs 850 °C), duration (2 h vs 1 h) and coal rank [43, 45-47].

4.3.2 Effect of thermal treatment

4.3.2.1 Leaching

As discussed in Section 2.4.4, the temperature of combustion has a significant impact on the speciation of the REEs in the resulting ash. As a result, the leachability of REEs from the ash is affected by the temperature of combustion (thermal treatment temperature). The effect of different thermal treatment temperatures on the leaching of the selected REEs is given in Figure 4-10.

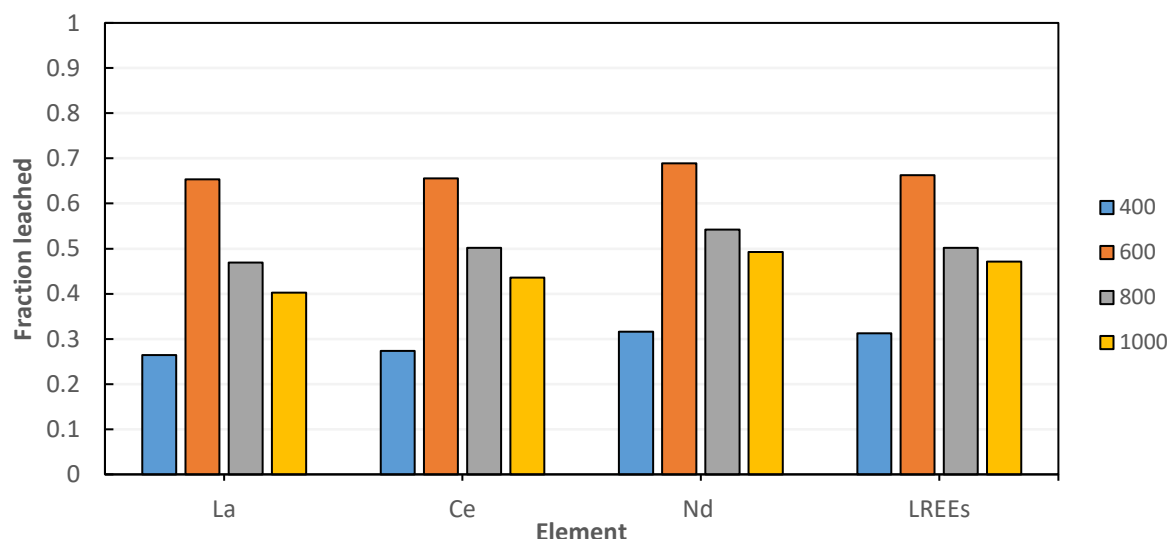


Figure 4-10: Leaching recovery of selected REEs from the LLDA derived at different temperatures (T = varied, t = 2 h, DAFR > 295 ml/min) using optimum conditions for HCl ([L] = 3 M, L:S = 10:1, CT = 120 min, T = 90 °C & SI = 300 rpm)

With the optimum leaching conditions, the effect of different thermal treatment temperatures on the extraction of LREEs from the resulting LLDA is evident in Figure 4-10. The leaching efficiency is at its lowest after thermal treatment at 400 °C. It increases to its highest at 600 °C and decreases when the temperature is increased to 1000 °C. To determine the choice of thermal treatment temperature based on these results would require comparing the results to similar studies.

The effect of thermal treatment temperature has been investigated for a high volatile bituminous coal from western Kentucky USA. Increasing the temperature of thermal treatment from 400 °C to 600 °C, resulted in a significant increase in REE recovery [42]. The same can be said with the results presented in Figure 4-10 with the leaching efficiency of the LREEs increasing from 31% to 66% at these respective temperatures. Using a coal ash obtained directly from an FBC boiler, operating at temperatures ranging from 707 °C to 976 °C, resulted in leaching efficiencies above 50% using dilute HCl [35]. A different attempt at recovering CREEs from a FBC boiler ash, from the Philippines, resulted in the extraction of 70% of Nd using 3 M HCl [11]. These findings, together with the result of this study, can further be compared to the usage of ash obtained from higher thermal treatment temperatures.

As discussed in Section 2.5.1.1, several studies have been conducted on CFA obtained from high thermal treatment temperatures, typical for PCC boilers. The findings presented in Figure 4-10 support the notion that high thermal treatment temperatures lead to low REE extraction using direct acid leaching. Although the highest temperature used (1000 °C) is lower than typical PCC boiler temperatures (> 1400 °C) [48], a clear decrease in LREE leaching recovery is shown from 600 °C to 1000 °C (66% to 47%). Low leaching recovery at high thermal treatment temperatures using direct acid leaching methods, has previously been explained by REE encapsulation in the aluminosilicate glass phase [13, 49, 50]. This has been well illustrated by the fact that REE leaching recoveries were never greater than 25% [13, 49, 50]. The difference in LREE recovery for the 1000 °C LLDA and PCC boiler ash might also be explained by an increase in aluminosilicate melts being formed due to higher thermal treatment temperatures [32, 51].

For further experiments, the thermal treatment temperature was kept constant based on the results of Figure 4-10. Although 600 °C LLDA showcased the highest leaching recovery, 800 °C or 1000 °C more accurately resembles the thermal treatment temperatures in FBC boilers. Choosing between 800 and 1000 °C was based on the highest leaching recovery and the average temperatures found in CFBC boilers. The 800 °C LLDA was therefore the most suitable with a higher recovery of LREE and a closer resemblance to the average temperature found in the lower dense zone (767 °C) and the upper dilute zone (771 °C) of an CFBC [35]. Based on the fixation of the thermal treatment temperature, the morphological changes occurring were also of interest.

4.3.2.2 Morphology

The effect of the thermal treatment on the morphology of the 800 °C LLDA is also of importance since the leaching can be directly affected by the shape of the resulting particles. Since the temperature has been established, the 800 °C LLDA was analysed via SEM as discussed in Section 3.6.7 and the results for the SEM analysis is given in Figure 4-11 and Figure 4-12.

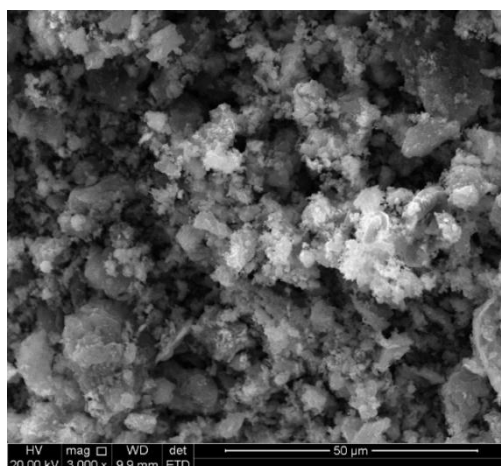


Figure 4-11: SEM image of the LLDA (T = 800 °C, t = 2 h, DAFR > 295 ml/min) before leaching with HCl at 3000 x magnification

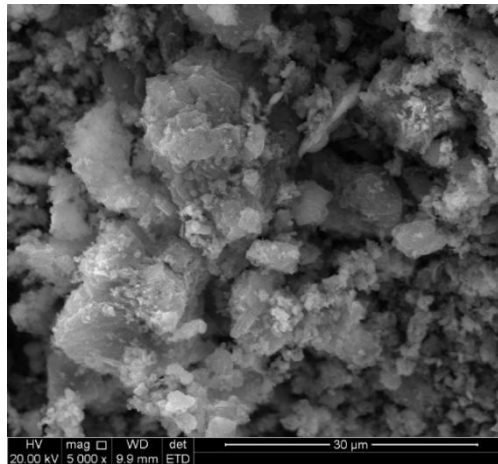


Figure 4-12: SEM image of the LLDA ($T = 800\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$, $\text{DAFR} > 295\text{ ml/min}$) before leaching with HCl at 5000 x magnification

High temperatures of thermal treatment have been shown to result in the formation of spherical, cenospherical, and plerosherical ash particles [52]. The thermal treatment of coal material under lower temperature conditions ($< 1000\text{ }^{\circ}\text{C}$) has shown a lack of these types of ash particles [28, 41]. The SEM images of the $800\text{ }^{\circ}\text{C}$ LLDA in Figure 4-11 and Figure 4-12 indicates similarities with regards to the lack of spherical particles (whether spherical, cenospherical or plerosherical) and the presence of irregularly shaped particles. It should be noted that these studies being referred to have utilized different durations of thermal treatment. Banerjee et al. (2024) obtained the ash from 1 h of thermal treatment at $850\text{ }^{\circ}\text{C}$ [41] whilst Lin et al. (2022) obtained the ash from 18 h of thermal treatment (max $950\text{ }^{\circ}\text{C}$) [28]. Thus, the thermal treatment duration does not seem to significantly affect the formation of spherical particles at low thermal treatment temperatures.

In summary, the screening of HCl and TA has shown that HCl has a higher leaching recovery of LREEs. HCl was therefore chosen as the lixiviant to be used for further experiments. Investigating the effect of thermal treatment has shown that the highest LREE recovery occurs at a thermal treatment temperature of $600\text{ }^{\circ}\text{C}$. Increasing the thermal treatment temperature further has resulted in a reduction in LREE recovery. Despite this, a thermal treatment temperature of $800\text{ }^{\circ}\text{C}$ was selected for further experimentation. Mainly because of a more accurate resemblance of the temperature found in FBC boilers. Finally, the LLDA resulting from this temperature was found to have no spherical particles whether cenospherical or plerosherical. Establishing the effect of thermal treatment temperature and lixiviant type leads to further investigation of the leaching process itself.

4.4 Primary leaching

4.4.1 Liquid-to-solid ratio and lixiviant concentration

As discussed in Section 0, the liquid-to-solid ratio and lixiviant concentration have a significant effect on both the recovery and the concentration of REEs in the leachate from coal ash. The effect of these parameters on the selected REEs was investigated based on the methodology outlined in Section 3.4.2.1 and the results are presented in Figure 4-13 and Figure 4-14.

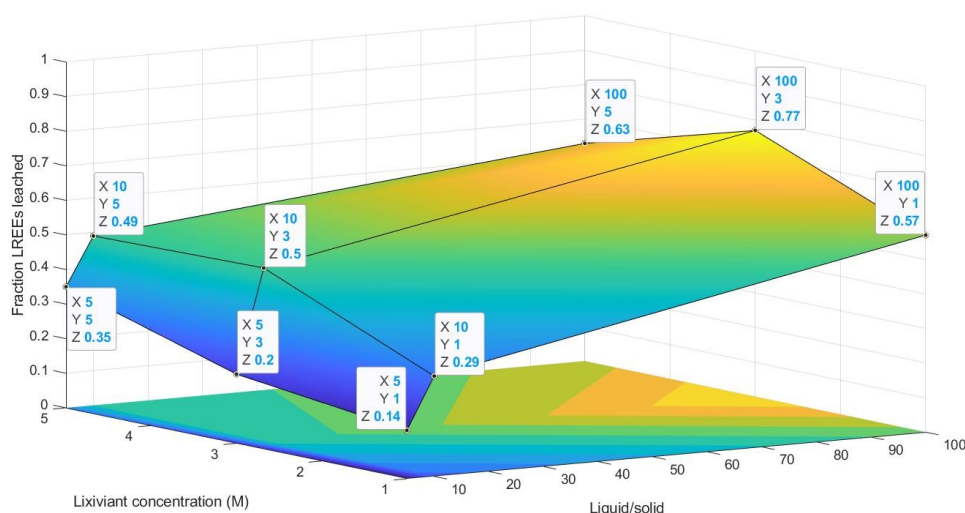


Figure 4-13: Effect of liquid-to-solid ratio and lixiviant concentration on the leaching recovery of LREEs (CT = 120 min, T = 90 °C & SI = 300 rpm) from the LLDA (T = 800 °C, t = 2 h, DAFR > 295 ml/min)

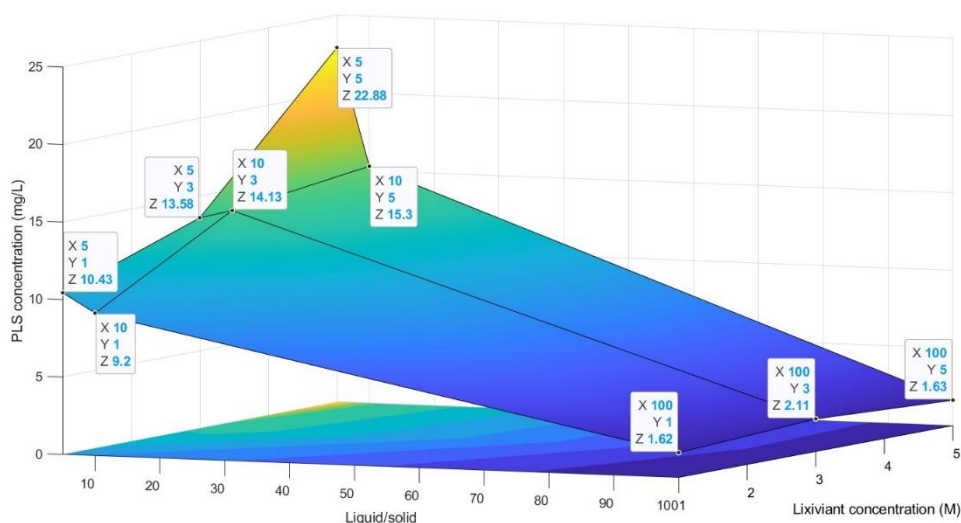


Figure 4-14: Effect of liquid-to-solid ratio and lixiviant concentration on the final LREE concentration of the PLS when leaching (CT = 120 min, T = 90 °C & SI = 300 rpm) from the LLDA (T = 800 °C, t = 2 h, DAFR > 295 ml/min)

The results showcased an increase in the recovery of LREEs when both the lixiviant concentration and the liquid-to-solid ratio were increased. An exception occurred at the highest liquid-to-solid ratio since the leaching recovery reduced from 77% to 63% at 3 M and 5 M, respectively. Such decreases at higher lixiviant concentrations has been observed for CFA that has been pretreated using alkali-fusion [13]. Flocculation formation was observed, hindering the contact between the H^+ ions and the solid particles [13]. The highest leaching efficiency occurred with a liquid-to-solid ratio of 100:1 and HCl concentration of 3 M. For the concentration of the LREEs in the PLS, the concentration decreased with an increase in the liquid-to-solid ratio. The highest LREE concentration in the PLS was obtained when the liquid-to-solid ratio was at 5:1 and the lixiviant concentration at 5 M. At lower liquid-to-solid ratio's, there is insufficient amount of H^+ ions to react with the REE oxides. Additionally, the entrapment of the REEs within the aluminosilicate glass phase required more lixiviant for the silica to be dissolved and reach the REEs.

The trends in LREE leaching recovery with changes in the liquid-to-solid ratio and lixiviant concentration can be compared with similar studies. BA obtained from the thermal treatment of coal from India indicated that the optimum conditions were 4 M HCl and 20:1 liquid-to-solid ratio. Increasing HCl's concentration beyond 4 M at a liquid-to-solid ratio of 10:1 resulted in an insignificant increase in REE recovery. Regarding the liquid-to-solid ratio, the highest value tested (20:1) did not show a maximum plateau in REE recovery [53]. A CFA collected from Panbei Power Plant in Guizhou Province of China indicated a maximum leaching recovery of REEs using 3 M HCl. Increasing the concentration of the lixiviant further resulted in a negligible increase in the recovery of REEs. For the liquid-to-solid ratio, the leaching efficiency of REEs remained similar beyond a liquid-to-solid ratio of 10:1 [12]. Leaching of CREEs from a CFA, obtained from a CFBC boiler, indicated that the optimum leaching conditions occur at 3 M HCl. Throughout the study, the liquid-to-solid ratio was kept constant at a ratio of 10:1 [11]. The major difference between these studies and the results shown in Figure 4-13 is the effect of increasing the liquid-to-solid ratio to 100:1. Kumari et al. [53], Cao et al. [12], and Dahan et al. [11] did not utilize or investigate such high liquid-to-solid ratios.

The liquid-to-solid ratio and lixiviant concentration that were chosen to be used for the kinetic study was based on the results shown in Figure 4-13 and Figure 4-14. The highest leaching recovery was obtained at a high liquid-to-solid ratio (100:1) and a moderate lixiviant concentration (3 M). Using such a high liquid-to-solid ratio will result in a PLS with low LREE concentrations. Additionally, the analysis of the PLS at this stage was limited to ICP-OES. Thus, a relatively high leaching recovery with a higher concentration of LREE in the PLS would be analysed more accurately. The precision may be motivated by the limitations associated with using ICP-OES to analyse for lanthanides, since the limit of detection (LOD) is between 0.1-100 µg/L [38]. Furthermore, the use of a lower lixiviant concentration (3 M instead of 5 M) and lower liquid-to-solid ratio would reduce the cost associated with the amount of acid used during leaching.

In addition to the figures presented above, the magnitude of effect of the liquid-to-solid ratio (factor A) and lixiviant concentration (factor B) can be determined by a range value analysis. The results for the range value analysis on the LREE concentration in the PLS and the recovery of the LREEs is given in Table 4-6 and Table 4-7 respectively.

Table 4-6: Range value assessment of the LREEs concentration (µg/g) in the PLS by changing liquid-to-solid ratio (A) and lixiviant concentration (B). (CT = 120 min, T = 90 °C & SI = 300 rpm)

	La		Ce		Nd		LREE	
	A	B	A	B	A	B	A	B
K ₁	10.36	4.80	21.53	10.03	10.02	4.88	46.88	21.25
K ₂	8.48	6.60	17.72	13.84	8.69	6.51	38.79	29.98
K ₃	1.21	8.65	2.40	17.78	1.18	8.50	5.36	39.81
R	9.15	3.85	19.13	7.75	8.84	3.62	41.52	18.56

Table 4-7: Range value assessment of the LREEs recovery fractions by changing liquid-to-solid ratio (A) and lixiviant concentration (B). (CT = 120 min, T = 90 °C & SI = 300 rpm)

	La		Ce		Nd		LREE	
	A	B	A	B	A	B	A	B
K ₁	0.65	0.98	0.69	1.04	0.70	1.07	0.69	1.00
K ₂	1.21	1.39	1.28	1.42	1.38	1.58	1.28	1.47
K ₃	1.92	1.40	1.93	1.44	2.08	1.52	1.97	1.47
R	1.26	0.43	1.24	0.39	1.38	0.51	1.28	0.46

From the range value analyses, the liquid-to-solid ratio has shown the greatest residual (R) values for both the LREE concentration in the PLS and the leaching recovery. This suggests that the liquid-to-solid ratio had a greater effect, over the chosen parameter range, on both the LREE concentration in the PLS and the leaching recovery. Tang et al. (2018) and Pan et al. (2020) investigated the effect of stirring intensity, lixiviant concentration and liquid-to-solid ratio on the leaching recovery and leachate concentration [13, 54]. The results indicated that the lixiviant concentration has a greater impact on the leaching recovery and the leachate concentration. Even though this was true for these studies, the highest liquid-to-solid ratios tested were much lower compared to this study. Furthermore, other differences might play a role in the effect of these parameters on the leaching recovery and the leachate concentration. Firstly, both used CFA obtained directly from a CFPP, which would dictate the thermal treatment conditions, and secondly the study conducted by Tang et al. (2018) utilized alkali fusion as a pretreatment method whilst Pan et al. (2020) utilized direct acid leaching [13, 54].

4.4.2 Temperature and contact time

As part of investigating the kinetics of recovering the LREEs from the LLDA, the effect of leaching temperature and contact time was done simultaneously. The experimental procedure is given in Section 3.4.2.2 and the result for the LREEs recovery at different temperatures, for a maximum duration of 120 min, is given in Figure 4-15.

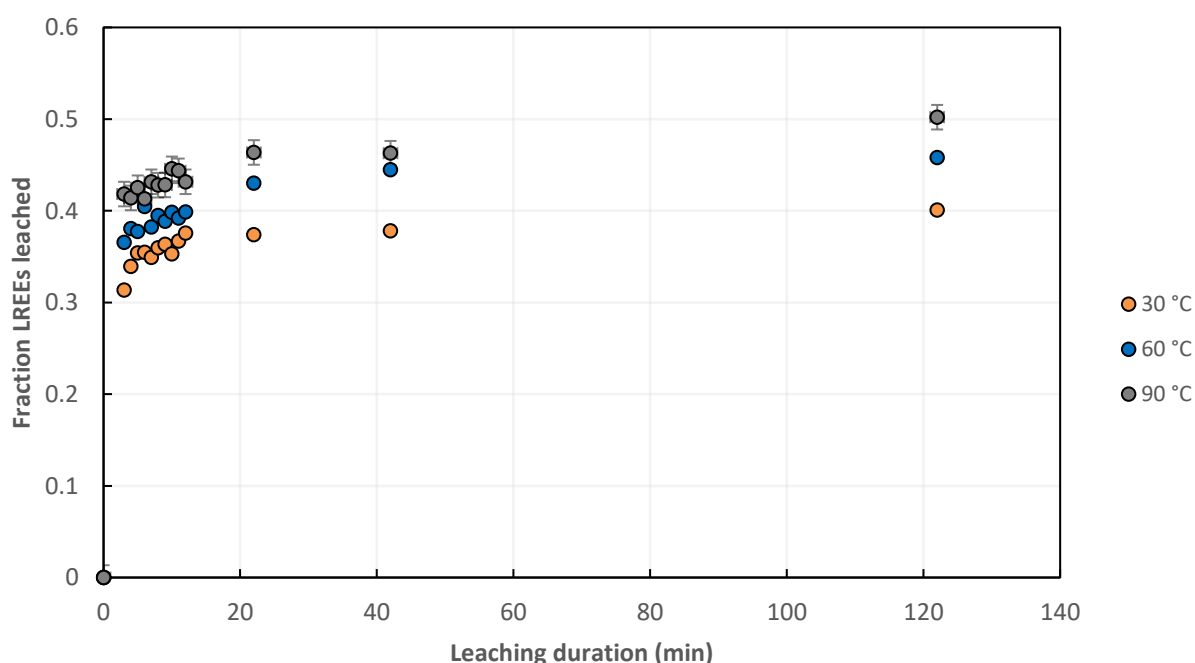


Figure 4-15: Leaching recovery of LREEs from the LLDA ($T = 800\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$, $\text{DAFR} > 295\text{ ml/min}$) with respect to the leaching duration at different temperatures using HCl ($[\text{L}] = 3\text{ M}$, $\text{L:S} = 10:1$ & $\text{SI} = 300\text{ rpm}$)

From Figure 4-15 it is evident that the recovery rate of the LREEs from the LLDA is rapid at all three temperatures of leaching. This is clearly shown by a LREE leaching recovery of 31, 37 and 42% at a time of 3 min for 30, 60 and 90 °C respectively. The minor effect of temperature on LREE recovery could already indicate that the chemical reaction is not the rate limiting step. As discussed in Section 2.5.2.4, this is because the chemical reaction limiting step is more sensitive to temperature changes [55-57]. This would have to be confirmed after the data is fitted with the proposed models and the activation energy is inspected. For the leaching duration, a time close to 20 min would suffice for the optimum extraction of the LREEs. This is shown in Figure 4-15 by the LREE recovery not significantly increasing beyond this time for all three temperatures.

The thermal treatment of coal has been shown to drastically increase the leaching rate compared to direct leaching. Although leaching kinetics of the RLC were not conducted in this study, rapid kinetics after thermal treatment were observed. Three studies have found similar results from leaching REEs from ash resulting from the thermal treatment of bituminous coal [42, 47, 58]. Although higher rank coal samples were used, the influence of low thermal treatment temperature was evident, as in this study. The study conducted by Zhang et al., found that the optimum thermal treatment temperature of 750 °C led to an LREE recovery of 86% within the first 5 min of leaching [42]. Similarly, Honaker et al. found a REE recovery of roughly 70% in the first 5 min of leaching after thermal treatment at 600 °C [58]. Interestingly, Ji et al. tested dilute HCl as well as several organic acids and found the same rapid kinetics. Using 0.25 M HCl, the LREE recovery reached approximately 70% in 5 min and with 0.05 M Maleic acid, almost 40% TREE content was recovered in 5 min [47]. Together with the results presented in Figure 4-15, the enhancement of the leaching kinetics is realized.

As discussed in Section 0, the leaching temperature has significantly affected the recovery of REEs from CFA. This is evident from higher leaching recoveries at higher leaching temperatures with the same leaching duration [11, 12, 53]. The result of Figure 4-15 indicates that an increase in the leaching temperature results in a small increase in the recovery of LREEs. For example, LREE recovery at 120 min of leaching increases from 40 to 50 % at 30 and 90 °C respectively. In terms of cost effectiveness, it would have to be considered whether a leaching temperature of 90 °C is worth an increase in LREE recovery of only a few percent. If 20 min of leaching is to be used as the optimum leaching duration, then an increase in LREE recovery of 3 % from 60 to 90 °C would apply. The introduction of the LLDA to the lixiviant resulted in a sudden increase in temperature indicating an exothermic reaction, which is further supported by the limited increase in leaching efficiency with an increase in leaching temperature.

In summary, the highest LREE leaching recovery was obtained with a lixiviant concentration of 3 M and a liquid-to-solid ratio of 100:1. Two reasons have been identified for the further use of a lower liquid-to-solid ratio at the expense of a lower LREE recovery. Firstly, the analysis of the leachate/PLS would present a challenge because of the LOD of an ICP-OES. Secondly, a large-scale operation whilst using a liquid-to-solid ratio of 100:1 would be more expensive compared to that of a 10:1 liquid-to-solid ratio. The range value analysis of the liquid-to-solid ratio and lixiviant concentration has shown the significant impact of utilizing such a high liquid-to-solid ratio. Investigating the effect of temperature and leaching duration has shown fast leaching kinetics. Increasing the leaching temperature has shown little change in the LREE leaching recovery which could already indicate the absence of the chemical reaction control mechanism. Further analysis of the models will have to be done to determine the rate limiting steps.

4.5 Model fit

4.5.1 Single fit

As discussed in Section 2.5.2, the different kinetic models can be fitted to the experimental data to obtain the best fit based on the R^2 values. The different kinetic models were fitted to the graphical result presented in Figure 4-15. The R^2 values for the SCM, SPM, and PH models are given in Table 4-8, and the graphical fitting results are provided in Annexure B.1 (Section 6.2.1).

Table 4-8: R^2 values for the single fitting of the different kinetic models at different temperatures for the recovery of LREEs from the LLDA ($T = 800\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$, $\text{DAFR} > 295\text{ ml/min}$)

Controlling mechanism	Model	Temperature ($^{\circ}\text{C}$)		
		30	60	90
Chemical reaction	SCM	0.34	0.36	0.35
Film layer diffusion		0.33	0.34	0.34
Product layer diffusion		0.38	0.41	0.41
Film layer diffusion - small particles	SPM	0.34	0.35	0.35
Film layer diffusion - large particles		0.34	0.35	0.35
First order	PH	0.34	0.36	0.36
Second order		0.32	0.33	0.33
Three halves order		0.35	0.37	0.37

The R^2 values presented in Table 4-8 show a change in the rate control mechanism. As explained in Section 2.5.2.4, a change in the rate control mechanism is evident through a significant change in the fit of the model [59, 60]. In this study, it is clearly shown by the low R^2 values, as well as the graphical fit of these models, as presented in Annexure B.1 (Section 6.2.1). Outside of this study, the evaluation of kinetics based on the leaching temperature and duration has yet to receive thorough attention. Specifically, for the extraction of REEs from low rank coal derived ash with HCl. There are studies that have been conducted using HCl; however, they have not produced adequate evaluations regarding the fitting of different kinetic models [11, 12, 42, 47, 53, 58]. A possible outcome has been illustrated by Karagulanova et al. (2025), who investigated the recovery of LREEs from coal ash using TA and magnesium sulphate [61]. The study indicated that the chemical reaction was the rate limiting step with the best fit. There are, however, issues evident, such as the fitting of the models with non-zero intercepts [61].

The experimental data has shown a sharp increase in the recovery of the LREEs within the first few minutes of leaching. Fitting the models indicated major deviation and it was therefore decided to limit the first kinetic model fitting to 3 min of leaching. After doing so, the results indicated another possible deviation from fitting the different kinetic models. Thus, another section was chosen for the second fit, which was from 3 min of leaching to 20 min. Finally, the remaining points, between 20 min and 120 min, were utilized to determine the final rate limiting step. It should be noted that the experiment described in Section 3.4.2.2 had a limitation regarding the measurement of the duration of leaching. Specifically, the accuracy of the time for the leaching process being determined from the introduction of the LLDA to the lixiviant and to the solid-liquid separation. Therefore, 2 mins were added to each data point to accommodate the time not accounted for.

4.5.2 Multiple fit

The kinetic models were fitted based on the findings and discussion of the previous section. The final combination of the models was compared based on their R^2 values as well as the RMSE values after fitting the experimental data. The graphical result of the final fitting is given in Figure 4-16 and the R^2 , RMSE, and activation energies are given in Table 4-9. The graphical results for the Arrhenius plots for the final chosen models are given in Figure 4-17. The graphical results for the different models evaluated on the different time slots are given in Annexure B.2 (Section 6.2.2).

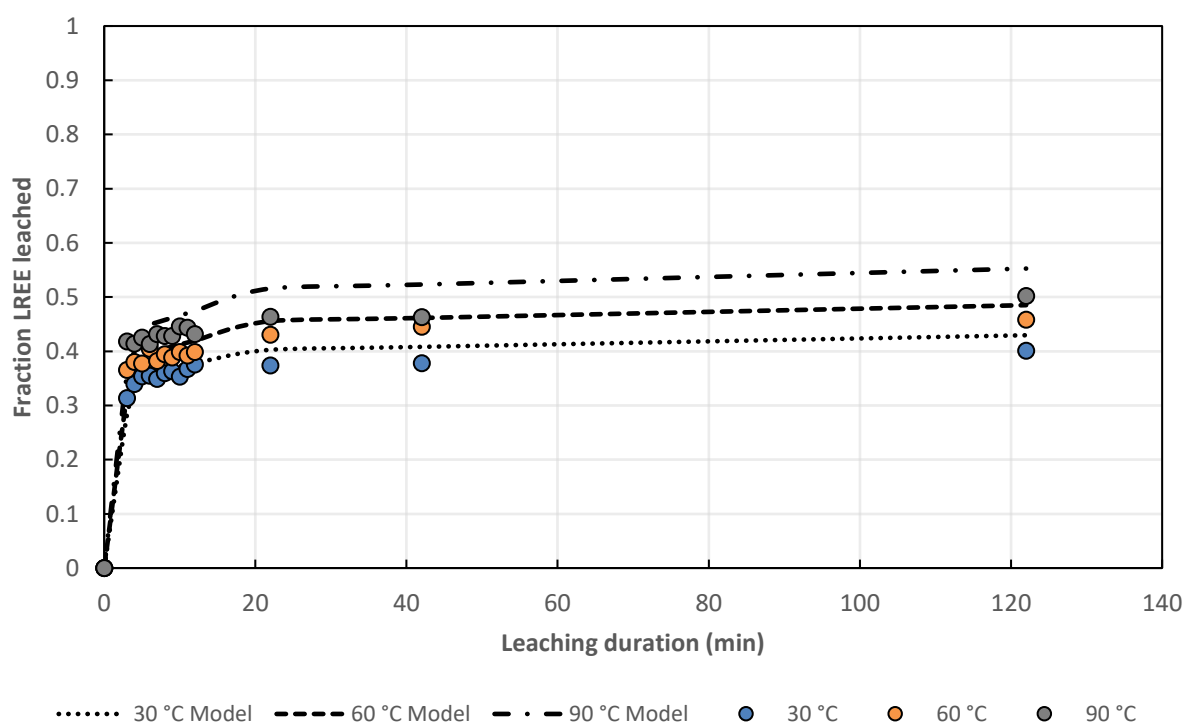


Figure 4-16: Final fitting of control mechanisms on the LREE recovery from the LLDA ($T = 800\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$, $\text{DAFR} > 295\text{ ml/min}$) using HCl ($[L] = 3\text{ M}$, $L:S = 10:1$ & $SI = 300\text{ rpm}$)

Table 4-9: Resulting R^2 , RMSE and activation energies obtained for the respective time slots from LREE leaching from the LLDA ($T = 800\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$, $\text{DAFR} > 295\text{ ml/min}$) using HCl ($[L] = 3\text{ M}$, $L:S = 10:1$ & $SI = 300\text{ rpm}$)

Time slot (min)	R^2			RMSE (%)			E_a (kJ/mol)	Controlling mechanism
	30 $^{\circ}\text{C}$	60 $^{\circ}\text{C}$	90 $^{\circ}\text{C}$	30 $^{\circ}\text{C}$	60 $^{\circ}\text{C}$	90 $^{\circ}\text{C}$		
0 – 5	0.99	0.97	0.97	1.99	3.18	3.84	7.34	Product layer (E- 10)
5 – 22	0.99	0.99	0.98	0.96	1.51	2.72	8.04	Small particle (E- 11)
22 – 122	0.99	0.92	0.95	2.93	2.24	5.56	4.79	Film layer (E- 9)
0 – 122	N/A	N/A	N/A	1.90	2.29	3.93	N/A	N/A

The combination of 3 controlling mechanisms at different times has resulted in the best fit, as shown in Figure 4-16. Fitting the models to different time sections has significantly increased the R^2 values as shown in Table 4-9. Most of the models have resulted in a better fit once the time sections were introduced, which can be seen in Annexure B.2 (Section 6.2.2). Therefore, all models were tested and the model that had the best prediction of the LREE leaching recovery (based on RMSE values) was utilized for that respective time section. The resulting Arrhenius plots that were done to determine the activation energies, as discussed in Section 2.5.2.3, showcase relatively good fits as shown in Figure 4-17.

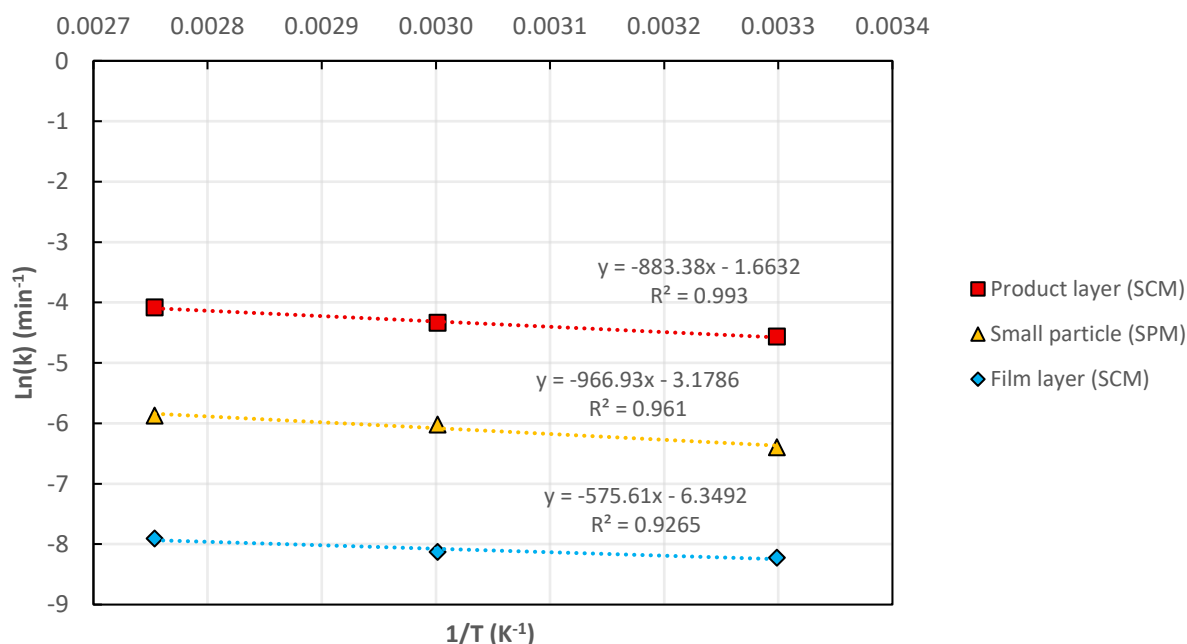


Figure 4-17: Arrhenius plots for the recovery of the LREEs from the LLDA ($T = 800\text{ }^{\circ}\text{C}$, $t = 2\text{ h}$, $\text{DAFR} > 295\text{ ml/min}$) using HCl ($[L] = 3\text{ M}$, $L:S = 10:1$ & $SI = 300\text{ rpm}$)

For all the time sections, the apparent activation energy (E_a) was below 20 kJ/mol. Consequently, the apparent activation energy corresponds well with the results, as an apparent activation energy higher than 40 kJ/mol would be the result of a chemical reaction-controlled mechanism. For diffusion-controlled mechanisms, the apparent activation energy is generally lower than 20 kJ/mol, and for mixed mechanisms it is between 20 and 40 kJ/mol [62-65]. Investigating the apparent activation energy for the recovery of REEs from CRMs has been lacking. However, several studies have indicated fast kinetic behaviour, but no values of the apparent activation energy are given [12, 42, 46]. The use of organocarboxylic acids on coal of Indian origin has been investigated with a focus on several different kinetic models and their apparent activation energies. The results indicated that multiple models have an appropriate fit, but the apparent activation energies were higher compared to this study [46].

The results shown in Table 4-9 indicate that the recovery of the LREEs is rate limited by the diffusion through the product layer and the film layer, specifically the diffusion process as described by the SCM and SPM as discussed in Section 2.5.2.1. It should however be noted that these models have the assumption that the particles are spherical [66]. From the results presented in Section 4.3.2.2, it was however clear that the thermal treatment of the RLC resulted in an ash with irregularly shaped particles.

There are, however, a few limitations regarding the method and interpretation of the results for the rate limiting steps. The times sections used to obtain the best fit was done based on the point of deviation. The deviations were not confirmed by changing parameters such as the stirring intensity and particle size and would be highly recommended for further studies. The repeatability of the smaller time periods (1-10 min) were not repeated but assumed based on the experimental error of the 2 h data point. Further investigation would also be required to explain the change in limiting step from the product layer to the film layer. In this regard, it could be possible that insoluble products were formed during the first few minutes of the reaction. After reacting these products might have had film layer diffusion limitations, inhibiting further reactions to occur to extract the REEs.

In summary, the single fitting procedure resulted in weak fits or low R^2 values, which indicates the possible change in the rate controlling mechanism. It was found that the rate controlling mechanism changes three times based on the non-linear fit that resulted after the investigated time. Based on the R^2 values, the activation energies and the RMSE values, suitable models were chosen that describe the leaching process. The leaching process consists of an initial stage, the product layer diffusion limiting step (SCM), a second stage, the small particle film layer diffusion limiting step (SPM), and then finally the film layer diffusion limiting step (SCM).

4.6 Proposed preliminary design

A preliminary conceptual design is given in this section of the dissertation. The main purpose of the design is to identify major shortcomings in LREE recovery from a low temperature derived ash. Primary parameters of concern include the concentration of the LREEs in the PLS, HCl usage and implications for downstream processing. For the purposes of this dissertation the preliminary conceptual design should, however, be considered, as the name suggests, preliminary with other factors not being considered.

4.6.1 Overview

The preliminary process flow diagram (PFD) is conducted to obtain a clear and more realistic expectation with regards to viability. Specifically, the incorporation of a LREE recovery plant with a FBC boiler CFPP that operates with lignite coal. The proposed PFD, which includes several processing sections with a particular focus on the leaching section, is presented in Figure 4-18.

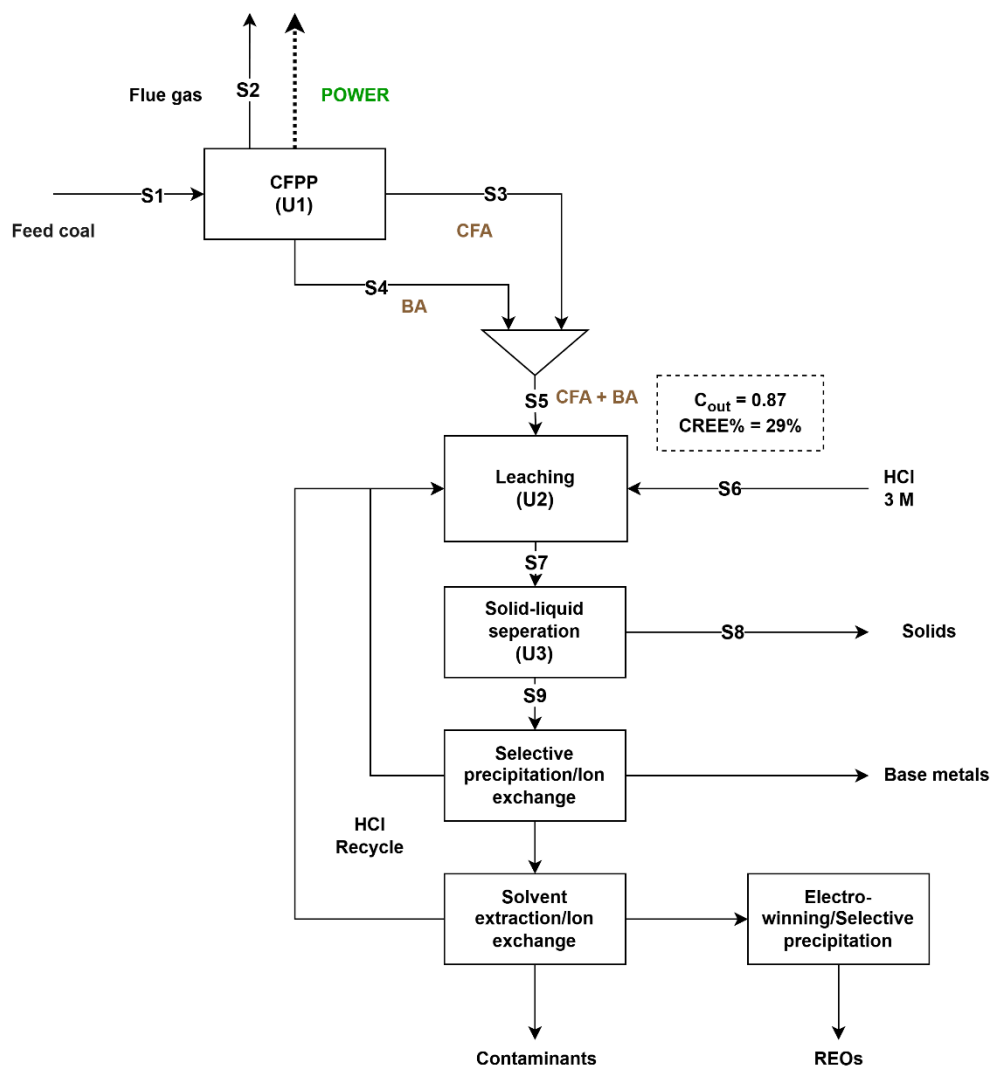


Figure 4-18: Proposed preliminary PFD

4.6.2 Leaching process

For the preliminary design the overall proposed process is given in Figure 4-18. From the results presented in the previous sections (Section 4.1 - 4.5), the design is limited to the section of interest shown in Figure 4-19.

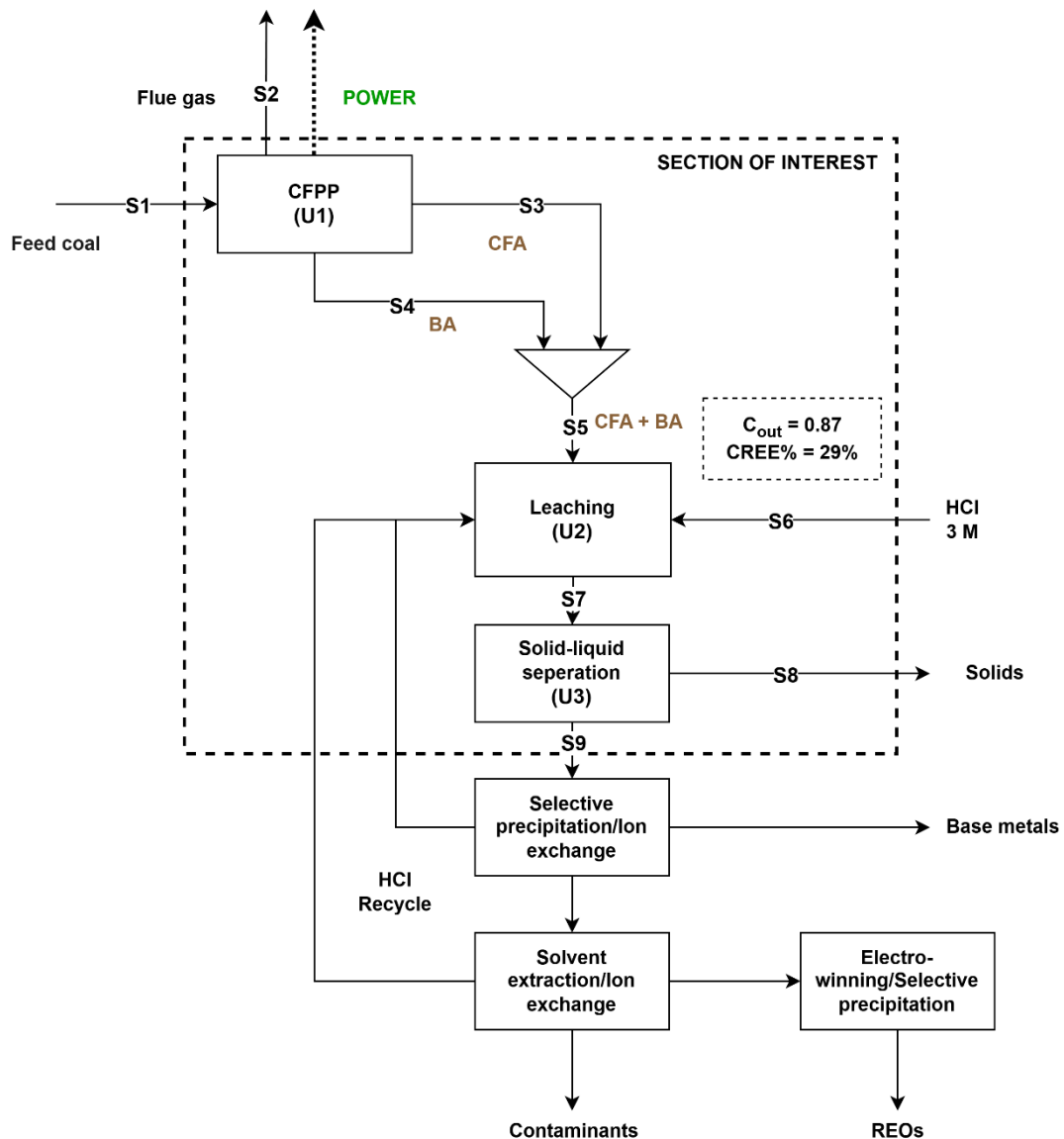


Figure 4-19: Proposed preliminary design with the leaching section of interest and relevant streams

The section of interest includes the FBC/CFBC CFPP, mixing of the CFA and BA to homogenize the material, the separation of the solid and liquid phase and then finally the leaching process. The process involves the feed coal (S1) being used to produce power by the CFPP, resulting in the production of CFA and BA (S3 & S4). The solid material is then treated by mixing to produce a homogenized feed material (S5) for the leaching process. The leaching occurs using HCl as the lixiviant (S6) to produce a leaching slurry (S7). The solid and liquid phase is then separated, resulting in the solid material (S8) and the PLS (S9).

4.6.2.1 Assumptions

For the above-mentioned process, the following assumptions have been made:

- The coal feed (S1) rate is 35 t/h [35], assuming the feed material has been dried (no moisture content)
- The FBC/CFBC CFPP (U1) operates at a temperature range of 707 – 976 °C [35] and therefore it is assumed that the ash does not require pretreatment (alkali fusion etc.)
- The ash content of the coal feed material (S1) is 18.5 wt% (Section 4.1.1)
- The fraction of the ash produced (S5) can be given as 20 wt% BA (S3) and 80 wt% CFA (S4) [67]
- The particles sizes are significantly reduced after combustion to a $D_v(90)$ of 342 μm (Section 4.1.3)
- The TREE concentration of the ash (S5) is 1000 ppm and has the same distribution pattern as the material used in this study (Section 4.1.2.2)
- The REF value for the REEs from the feed material (S1) to the feed material for the leaching process is 1.5 (Section 4.1.2.2.1)
- The viability assessment factor such as C_{out} and CREE% for the ash material is similar to the LLDA of this study i.e. 0.87 and 29% (Section 4.1.2.2.1)
- The conversion of all the REEs are similar to that of the LREEs from the solid material to the aqueous phase as 50% with a chosen contact time of 20 min and liquid-to-solid ratio of 10:1 (Section 4.4)
- It is assumed that 55% of the solid ash material is converted into solution under the aforementioned leaching conditions
- Under similar conditions, it is assumed that the recovery of the base metals can be based on the IntelliQuant results. Therefore, the recoveries are taken as 23%, 32%, 5% and 32% for Al, Fe, Cu and Mn respectively
- The leaching process is exothermic with the leaching process (U2) controlled at a temperature of 90 °C (Section 4.4.2)
- There is perfect separation (U3) of the solid and liquid phase to produce the PLS and the remaining solids
- For the purpose of the proposed preliminary design the recycle stream of the lixiviant from the separation steps are not accounted for
- It is assumed that lixiviant is not lost due to evaporation leading to the reduction in available lixiviant affecting the liquid-to-solid ratio

4.6.3 Mass balance

The mass balance over the system was done for further investigation of the viability of the recovery of the REEs from the resulting ash material. The result for the total mass flow rates for all of the streams presented in Figure 4-19, is given in Table 4-10.

Table 4-10: Total mass flow rates for the different streams of the leaching process

Stream	Total mass flow rate	
	t/h	t/yr
S1	35.0	306 600
S2	28.7	251 105
S3	1.27	11 099
S4	5.07	44 396
S5	6.34	55 495
S6	63.4	554 946
S7	69.7	610 441
S8	2.85	24 973
S9	66.8	585 468

From Table 4-10, the plant produces roughly 55 500 t/yr of ash which can be utilized for the recovery of REEs. It is also clear that the recycling of the lixiviant would be required. Therefore, for the development of the preliminary plant it would require 63.4 t/h of 3 M HCl in circulation, which will affect material costs associated with the process units. The leaching process produces roughly 580 000 t/yr of PLS that requires further purification and separation steps, recycling the HCl back to the leaching section. The leaching process also produces roughly 25 000 t/yr of solid material which can be further utilized for base metal recovery.

The streams of interest for the preliminary design only include S1, S5, S8 and S9 since they represent the raw feed material, the resulting ash (combination of CFA and BA), the resulting solid material and the PLS. The concentrations of the REEs and the base metals for the feed stream and resulting ash stream are known from the characterization of Section 4.1.2. A thorough mass balance of these streams is given in Table 4-11 with information given on the concentrations and mass flow rates in t/yr.

Table 4-11: Concentrations for REEs and base metals for the leaching process and flow rates of respective streams

Stream	REE content (ppm)		Base metal content (wt%)				
	TREE	LREE	Al	Fe	Cu	Mn	
S1	120	82	1.7	0.7	< 0.01	0.01	
S5	1 000	686	13.8	6.5	0.04	0.09	
S8	1 113	765	23.6	9.8	0.08	0.14	
Base metal content (ppm)							
S9 ¹	47	33	3 008	1 971	1.7	27	
Mass flow rate (t/yr)							
Stream	Total	TREE	LREE	Al	Fe	Cu	Mn
S1	306 600	36.8	25.1	5 243	2 085	9.2	31
S5	55 495	55.5	38.1	7 658	3 607	22	50
S6	554 946	-	-	-	-	-	-
S8	24 973	27.8	19.1	5 897	2 453	21	34
S9	585 468	27.8	19.1	1 761	1 154	1	16

¹Base metal recovery content given in ppm and not wt%

From Table 4-11, the leaching of the coal ash produces a PLS that could potentially yield approximately 28 t/yr of REEs. It should be noted that the PLS would require additional separation and purification steps, and the final recoverable amount of REEs will depend on the efficiency of these downstream processes. The solid residue after leaching (S8) shows a two-fold increase in TREE concentration than the original ash feed (S5), indicating its potential as a secondary source.

The preliminary design suggested would have to be developed further the make concrete conclusions on the entire process. There are also several design limitations that would have a significant impact on the economic viability of extracting REEs from CRMs. With regards to this dissertation, a preliminary design for the extraction of REEs from a low temperature derived ash was proposed. In the section that follows, the design limitations are given that should be attended to.

4.6.4 Design limitations

The design presented in Section 4.6 has several limitations that would have to be addressed for future work. The first would be that the material assumed as the feed would always have the same distribution/concentration of REEs. This would be highly unlikely and therefore a sensitivity analysis on alternating feed would be highly recommended. Secondly the amount of HCl used throughout the circuit as well as the concentration would have considerable impact on the cost of the building materials. The implication of such a design would have to be accounted for during a techno-economic evaluation. For the purpose of the leaching section of the design there remains one major design limitation that was not considered. This includes the recycle of the HCl from the separation steps back to the leaching section. This will have a significant impact on the make-up stream (S6) and ultimately the viability of extracting REE from LLDA on a large scale.

4.7 References

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CHAPTER 5 CONCLUSION, EVALUATION AND RECOMMENDATION

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In this section of the dissertation, the main conclusions, evaluations and recommendations are given based on the results of Chapter 4 and Chapter 5 with respect to the aim and objectives given in Chapter 1. The reader is reminded that the study aims to address the leaching behaviour of a low rank coal ash, derived from low thermal treatment temperature conditions, to be utilized as a secondary source of LREEs.

5.1 Conclusions

The following conclusions are drawn from the results presented in Chapter 4:

1. Characterisation of the lignite coal indicated TREE concentrations comparable to world averages. Assessment of the lignite coal ash based on REE content suggest it is a promising source, primarily considering the REE distribution.
2. The lower leaching recovery observed for the lignite-derived ash was influenced by several factors; however, the presence of the aluminosilicate glass phase did not result in extremely low recoveries.
3. Leaching with HCl and TA demonstrated that the mineral acid outperforms the organic acid under previously optimised conditions.
4. Thermal treatment temperature significantly affected LRE recovery. Increasing the temperature beyond the point of meta-kaolinite formation (600 °C) to typical FBC boiler temperatures (800 °C) decreased LREE recovery.
5. The absence of spherical ash particles at lower thermal treatment temperatures, coupled with higher leaching recoveries, confirms that REE entrapment in spherical particles due to ash fusion limits extraction.
6. An orthogonal array assessment of liquid-to-solid ratio and lixiviant concentration indicated that the liquid-to-solid ratio has the greatest influence on LREE recovery.
7. The effect of leaching duration and temperature on LREE recovery showed that a short contact time (≈ 20 min) is sufficient, while increasing temperature from 30 to 90 °C results in a slight improvement.
8. Kinetic analysis of the leaching process revealed extremely fast reactions, necessitating division into three-time segments for optimal model fitting, indicating changes in the rate-controlling mechanism.
9. During the initial 0-5 min, leaching was controlled by internal diffusion (product layer), followed by external diffusion control from 5-122 min.
10. Apparent activation energies for all segments did not exceed 20 kJ/mol, further confirming that the overall process is diffusion-limiting.

5.2 Evaluations

The following evaluations drawn from the results of this study, as presented in Chapter 4, and the original aim outlined in Chapter 1:

1. Characterisation of the lignite coal confirms that TREE content remains a critical parameter. Current supply and demand of REEs necessitate a critical evaluation of the minimum required TREE concentrations for practical exploitation.
2. The presence of the aluminosilicate glass phase in the ash was associated with higher REE recovery compared to ash from higher thermal treatment temperatures. This is advantageous, as the ash does not require additional pretreatment to break down the glass matrix and enhance leaching efficiency.
3. Sequential leaching studies suggest that LREEs may exist as discrete carbonate minerals (e.g., Bastnaesite). For the lignite ash studied, the majority of LREEs were acid-soluble, indicating possible transformation of REE carbonates into REE oxides during thermal treatment.
4. Thermal treatment conditions significantly influenced the leachability of REEs from the resulting ash. Despite the findings of this study and previous work, uncertainty remains regarding the optimal thermal treatment parameters for maximising REE recovery.
5. Reactor design considerations are guided by the rapid leaching kinetics and short optimum leaching duration. The reaction is highly exothermic, necessitating a reactor capable of accommodating temperature rises, which also reduces the heat supply requirements and associated costs.
6. Preliminary leaching operation indicates substantial production of other metals alongside REEs. Mass balance analysis shows significant quantities of Al and Fe relative to REEs, highlighting the need for effective separation of REEs from base metals and other contaminants in downstream processing.

5.3 Recommendations

Based on the results of this study, the recommendations for further investigation of a lignite coal ash as a secondary source are as follows:

1. For a more accurate representation of the thermal treatment conditions found in an FBC boiler, consider using the ash obtained therefrom
2. If the thermal treatment conditions are still to be tested with laboratory equipment, carefully consider the dispersion of the particles, particle sizes, duration, and dry air flow rate compared to an FBC boiler
3. Conduct experiments towards beneficiation of the derived ash, specifically gravimetric, magnetic and particle size separation methods
4. Conduct a thorough investigation with regard to the association and speciation of REEs in lignite coal and derived ash
5. Conduct experiments utilising alternative mineral acids such as HNO_3 , H_2SO_4 and other organic acids such as maleic acid and citric acid
6. Expand the orthogonal array assessment of the leaching process to include more parameters, achievable via a fractional factorial design
7. Conduct a thorough optimisation study including the thermal treatment process, the leaching of the REEs, and the recovery methods that follow
8. Evaluate the economic viability of a complete REE recovery plant incorporated with a FBC boiler type CFPP that also includes downstream separation processes

CHAPTER 6 ANNEXURE

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In this section of the dissertation, supplementary material for the different sections of the dissertation is given in Annexure A – C.

6.1 Annexure A: Repeatability

To ensure reliable analytical results, repeatability was performed for the characterization, sequential leaching and primary leaching procedures of the coal and coal ash material. Refer to Section 3.5.1 and 3.5.2 regarding the calculation of the leaching recovery and repeatability.

6.1.1 Annexure A.1: Characterization

Refer to Section 3.3.5 and 3.6.2 for the digestion and analysis procedures of the CRM.

Table A. 1: Repeatability data for ICP-MS analysis of RLC sample with averages as well as 90 and 95% confidence interval values (mg/kg or ppm)

Run	La	Ce	Pr	Nd	Sm	Eu	LREEs
1	8.8	19.0	1.7	7.9	1.0	0.0	38.4
2	6.1	12.6	1.0	5.2	0.5	0.2	25.7
3	6.5	14.3	1.1	6.2	0.9	0.2	29.2
4	6.1	12.5	1.6	10.4	1.0	0.2	31.8
Average	6.9	14.6	1.4	7.4	0.8	0.1	31.3
95% CI	±2	±5	±1	±4	±0	±0	±9

Table A. 2: Repeatability data for ICP-MS analysis of LLDA sample with averages as well as 90 and 95% confidence interval values (mg/kg or ppm)

Run	La	Ce	Pr	Nd	Sm	Eu	LREEs
1	59.8	114.6	12.7	51.5	8.9	2.1	249.7
2	54.9	111.1	12.3	51.4	8.5	1.9	240.1
Average	57.4	112.9	12.5	51.4	8.7	2.0	244.9
95% CI	±31	±22	±3	±1	±3	±1	±61

6.1.2 Annexure A.2: Sequential leaching procedure

Refer to Section 3.3.2, 3.3.3, 3.3.4 and 3.6.1 for the sequential leaching procedures, thermal treatment method and analysis of the leachate via ICP-OES.

6.1.2.1 Annexure A.2.1: Raw coal sample

Table A. 3: Recovery of selected REEs during the sequential leaching procedure on the RLC with averages as well as 90 and 95% confidence interval values

Step	La	Ce	Pr	Nd	Sm	LREEs
Ammonium acetate	0%	0%	0%	0%	0%	0%
	0%	0%	0%	0%	0%	0%
	0%	0%	0%	0%	0%	0%
	0%	0%	0%	0%	0%	0%
AVERAGE	0%	0%	0%	0%	0%	0%
<i>95% CI</i>	<i>±0%</i>	<i>±0%</i>	<i>±0%</i>	<i>±0%</i>	<i>±0%</i>	<i>±0%</i>
Hydrochloric acid	69%	86%	60%	72%	100%	76%
	73%	86%	60%	73%	100%	78%
	67%	82%	60%	73%	100%	75%
	73%	86%	54%	74%	100%	78%
AVERAGE	71%	85%	58%	73%	100%	77%
<i>95% CI</i>	<i>±4%</i>	<i>±3%</i>	<i>±4%</i>	<i>±1%</i>	<i>±0%</i>	<i>±2%</i>
Hydrofluoric acid	20%	9%	40%	25%	0%	18%
	21%	9%	40%	24%	0%	18%
	18%	7%	40%	22%	0%	16%
	21%	9%	46%	23%	0%	18%
AVERAGE	20%	8%	42%	23%	0%	18%
<i>95% CI</i>	<i>±2%</i>	<i>±1%</i>	<i>±4%</i>	<i>±2%</i>	<i>±0%</i>	<i>±2%</i>

Table A. 4: Recovery of selected REEs during the sequential leaching procedure on the RLC with averages as well as 90 and 95% confidence interval values (Continued)

Step	La	Ce	Pr	Nd	Sm	LREEs
Nitric acid	11%	5%	0%	3%	0%	5%
	6%	5%	0%	3%	0%	4%
	15%	11%	0%	6%	0%	9%
	6%	5%	0%	3%	0%	4%
AVERAGE	10%	7%	0%	4%	0%	6%
<i>95% CI</i>	$\pm 6\%$	$\pm 4\%$	$\pm 0\%$	$\pm 2\%$	$\pm 0\%$	$\pm 3\%$

6.1.2.2 Annexure A.2.2: Coal ash

Table A. 5: Recovery of selected REEs during the sequential leaching procedure on the LLDA (T = 600 °C, t = 18 h, DAFR = 95 ml/min) with averages as well as 90 and 95% confidence interval values

Step	La	Ce	Pr	Nd	Sm	LREEs
Milli-Q water	0%	0%	0%	0%	0%	0%
	0%	0%	0%	0%	0%	0%
	0%	0%	0%	0%	0%	0%
	0%	0%	0%	0%	0%	0%
	0%	0%	0%	0%	0%	0%
	0%	0%	0%	0%	0%	0%
	0%	0%	0%	0%	0%	0%
	0%	0%	0%	0%	0%	0%
AVERAGE	0%	0%	0%	0%	0%	0%
<i>95% CI</i>	$\pm 0\%$	$\pm 0\%$	$\pm 0\%$	$\pm 0\%$	$\pm 0\%$	$\pm 0\%$

Table A. 6: Recovery of selected REEs during the sequential leaching procedure on the LLDA (T = 600 °C, t = 18 h, DAFR = 95 ml/min) with averages as well as 90 and 95% confidence interval values
(Continued)

Step	La	Ce	Pr	Nd	Sm	LREEs
Ammonium sulphate	7%	3%	0%	5%	2%	4%
	7%	4%	0%	6%	2%	5%
	9%	4%	0%	7%	2%	6%
	10%	6%	0%	9%	5%	7%
	11%	6%	0%	8%	2%	7%
	10%	5%	0%	7%	2%	7%
	10%	5%	0%	7%	2%	6%
	11%	6%	0%	8%	2%	7%
AVERAGE	9%	5%	0%	7%	3%	6%
<i>95% CI</i>	<i>±1%</i>	<i>±1%</i>	<i>±0%</i>	<i>±1%</i>	<i>±1%</i>	<i>±1%</i>
Tartaric acid	13%	15%	20%	15%	18%	15%
	13%	16%	20%	15%	18%	15%
	13%	16%	20%	15%	19%	15%
	14%	17%	22%	16%	19%	16%
	12%	14%	18%	13%	16%	13%
	15%	19%	25%	17%	20%	18%
	16%	18%	26%	18%	20%	18%
	15%	18%	24%	17%	19%	17%
AVERAGE	14%	17%	22%	16%	18%	16%
<i>95% CI</i>	<i>±1%</i>	<i>±2%</i>	<i>±2%</i>	<i>±1%</i>	<i>±1%</i>	<i>±1%</i>

Table A. 7: Recovery of selected REEs during the sequential leaching procedure on the LLDA(T = 600 °C, t = 18 h, DAFR = 95 ml/min) with averages as well as 90 and 95% confidence interval values
(Continued)

Step	La	Ce	Pr	Nd	Sm	LREEs
Hydrochloric acid	42%	40%	45%	19%	15%	35%
	29%	29%	53%	20%	16%	28%
	29%	28%	53%	20%	16%	27%
	31%	30%	53%	19%	15%	29%
	28%	27%	52%	20%	13%	27%
	19%	28%	49%	17%	14%	24%
	19%	29%	49%	18%	15%	25%
	28%	27%	52%	18%	14%	26%
AVERAGE	28%	30%	51%	19%	15%	28%
<i>95% CI</i>	$\pm 6\%$	$\pm 3\%$	$\pm 2\%$	$\pm 1\%$	$\pm 1\%$	$\pm 3\%$

6.1.3 Annexure A.3: Primary leaching procedure

Refer to Section 3.3.3, 3.3.6 and 3.4.2 for the thermal treatment procedure, primary leaching setup and the experimental procedures used for the primary leaching tests.

Table A. 8: Leaching recovery of selected REEs from the LLDA (T = 800 °C, t = 2 h, DAFR > 295 ml/min) using HCl ([L] = 3 M, CT = 120 min, L:S = 10:1 & SI = 300 rpm)

Run	La	Ce	Pr	Nd	Sm	LREEs
1	47%	50%	51%	54%	51%	50%
2	47%	50%	50%	54%	53%	50%
3	49%	51%	48%	56%	41%	51%
4	45%	49%	51%	53%	51%	49%
AVERAGE	47%	50%	50%	54%	49%	50%
<i>95% CI</i>	$\pm 2\%$	$\pm 2\%$	$\pm 2\%$	$\pm 2\%$	$\pm 9\%$	$\pm 1\%$

6.2 Annexure B: Model fitting

Refer to Section 3.4.2.2 for the experimental procedure used and Section 2.5.2 for the relevant kinetic models.

6.2.1 Annexure B.1: Single mechanism fitting

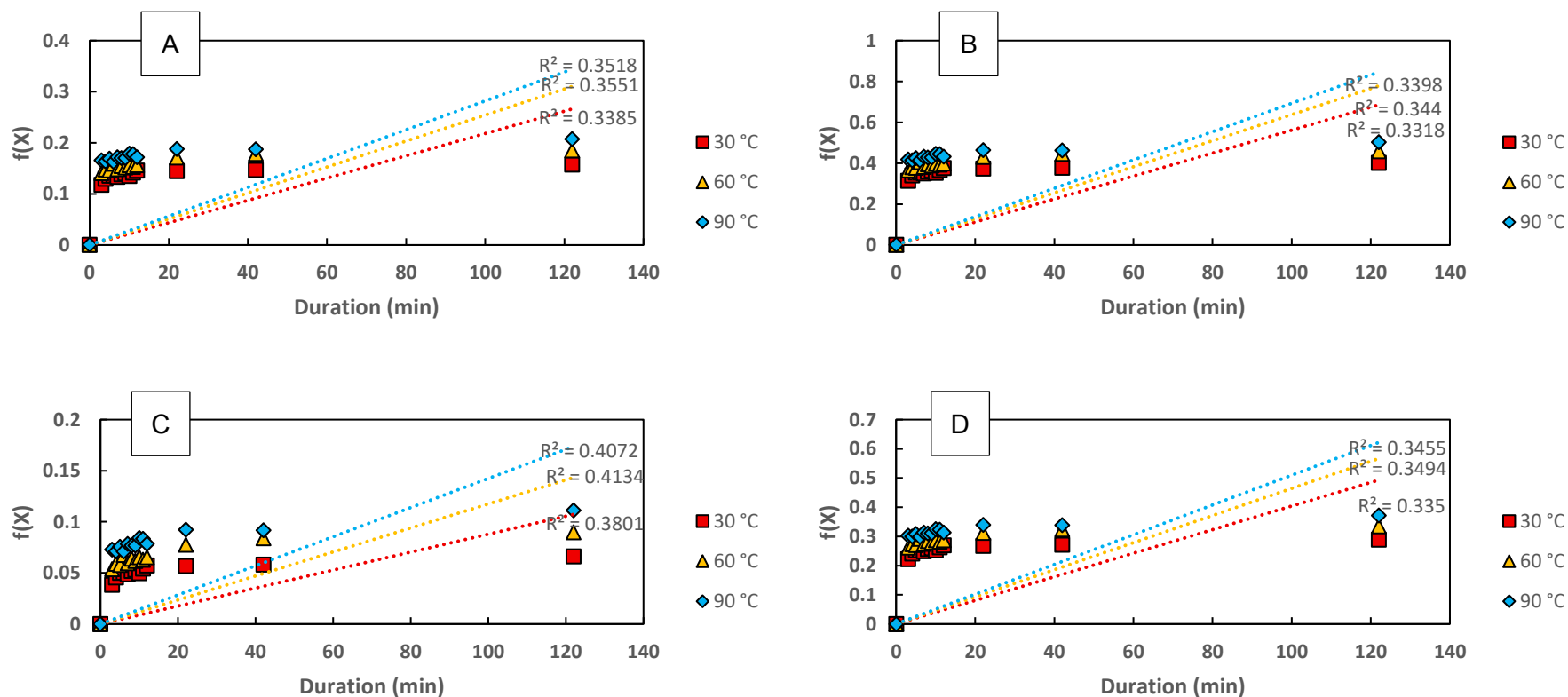


Figure B. 1: Graphical result for the single mechanism fitting for the recovery of the LREEs from the LLDA (**A:** Chemical reaction – SCM; **B:** External diffusion/film layer – SCM; **C:** Internal diffusion/product layer – SCM; **D:** Small particle – SPM)

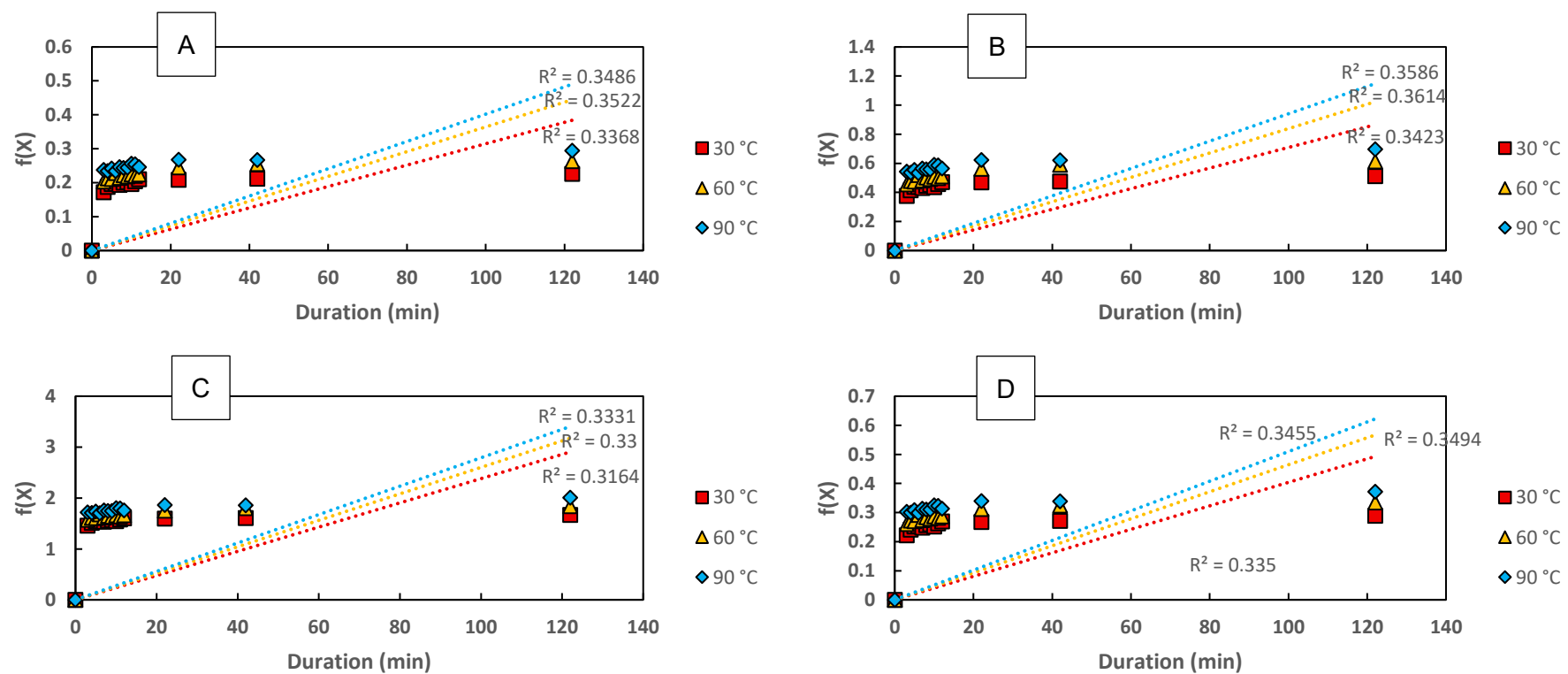


Figure B. 2: Graphical result for the single mechanism fitting for the recovery of the LREEs from the LLDA (**A:** Large particle – SPM; **B:** First order – PH; **C:** Second order – PH; **D:** Three halves order – PH)

6.2.2 Annexure B.2: Interval mechanism fitting

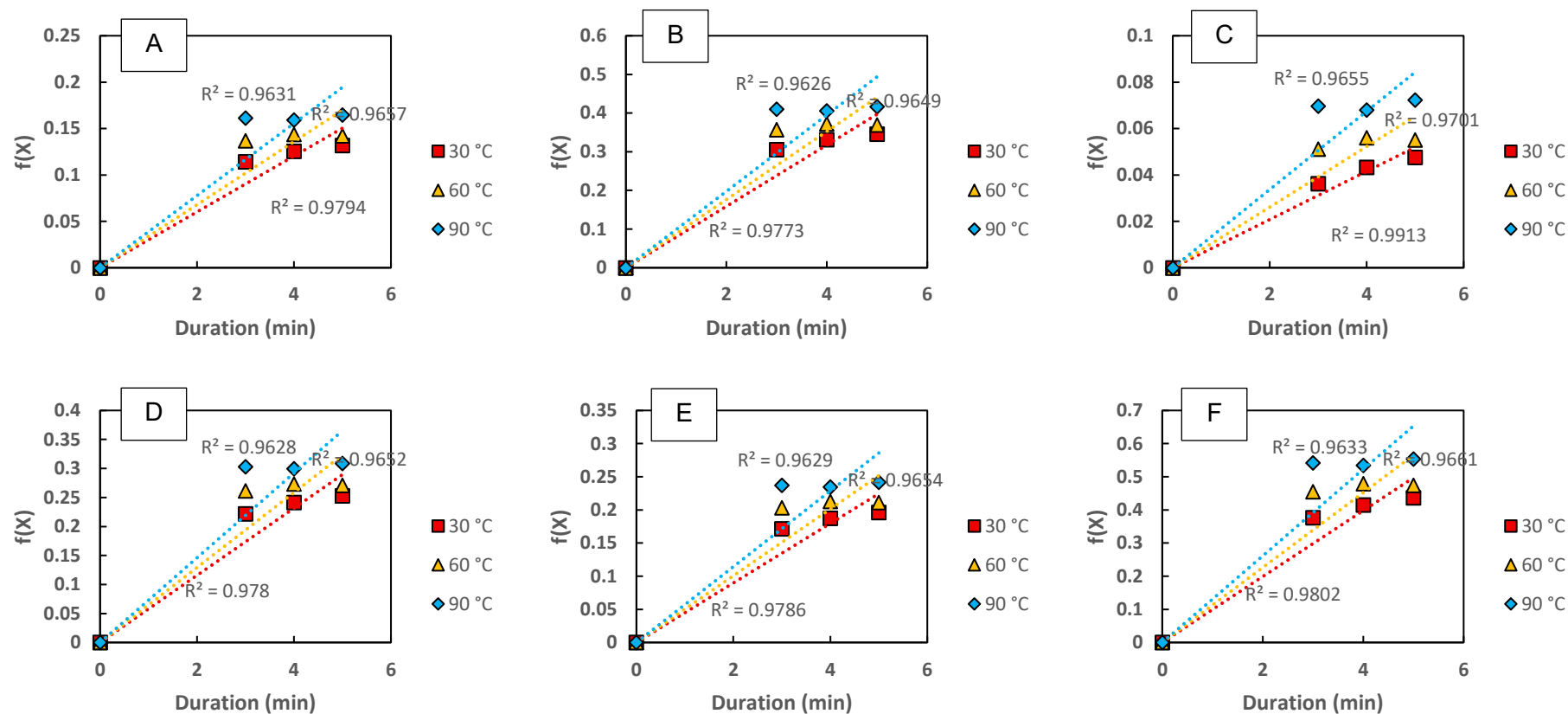


Figure B. 3: Graphical results for the fitting of different rate controlling mechanisms on respective time slots (**A:** Chemical reaction – SCM; **B:** External diffusion/film layer – SCM; **C:** Internal diffusion/product layer – SCM; **D:** Small particle – SPM; **E:** Large particle – SPM; **F:** First order – PH)

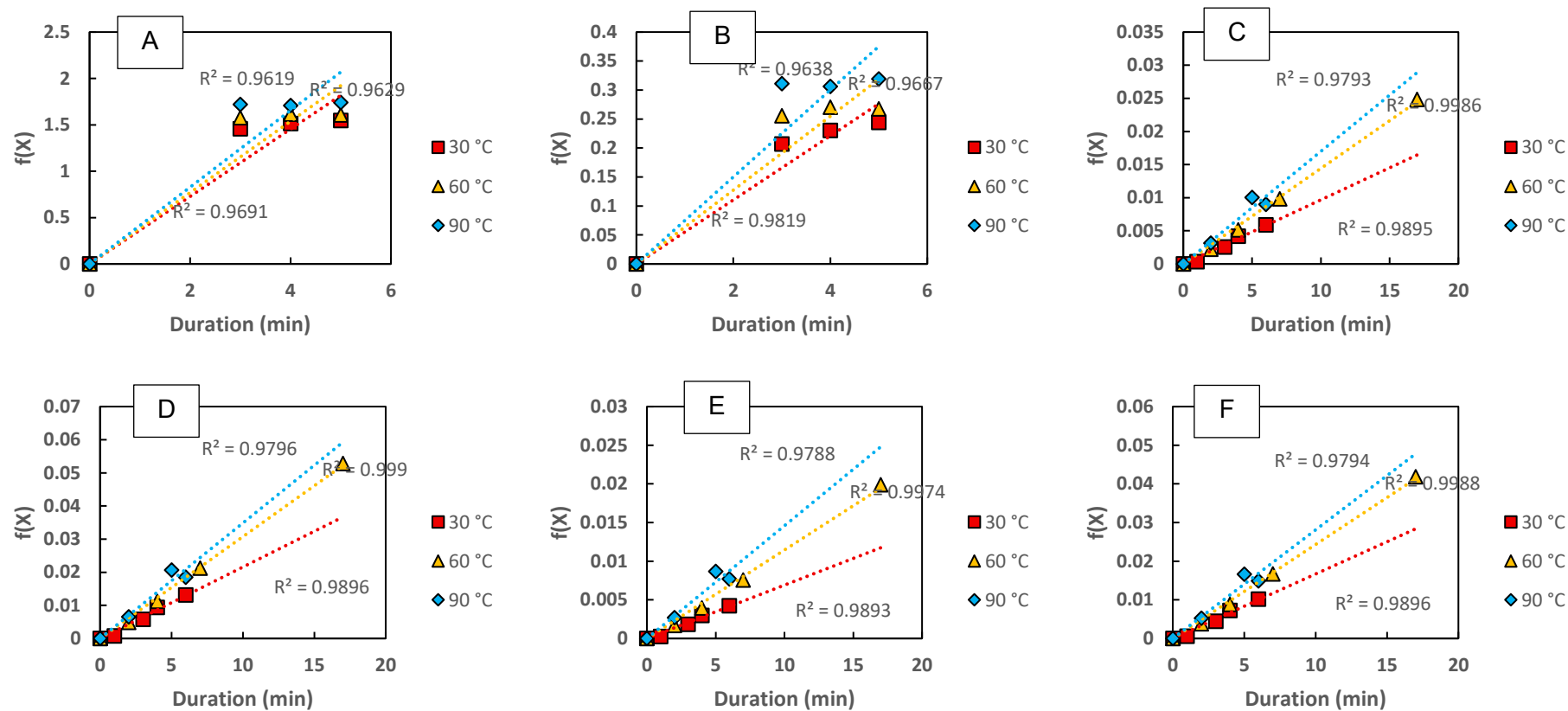


Figure B. 4: Graphical results for the fitting of different rate controlling mechanisms on respective time slots (**A:** Second order – PH; **B:** Three halves order – PH; **C:** Chemical reaction – SCM; **D:** External diffusion/film layer – SCM; **E:** Internal diffusion/product layer – SCM; **F:** Small particle – SPM)

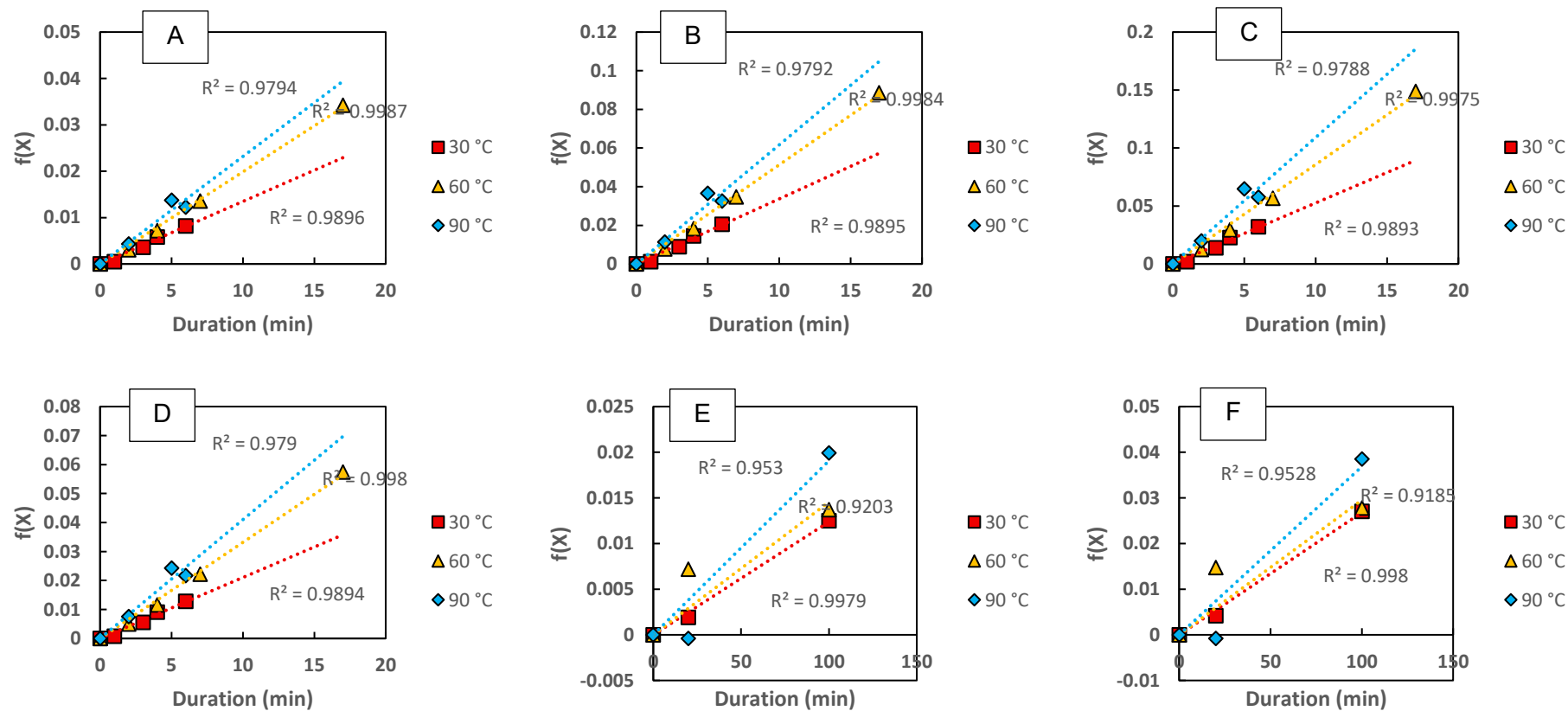


Figure B. 5: Graphical results for the fitting of different rate controlling mechanisms on respective time slots (**A:** Large particle – SPM; **B:** First order – PH; **C:** Second order – PH; **D:** Three halves order – PH; **E:** Chemical reaction – SCM; **F:** External diffusion/film layer – SCM)

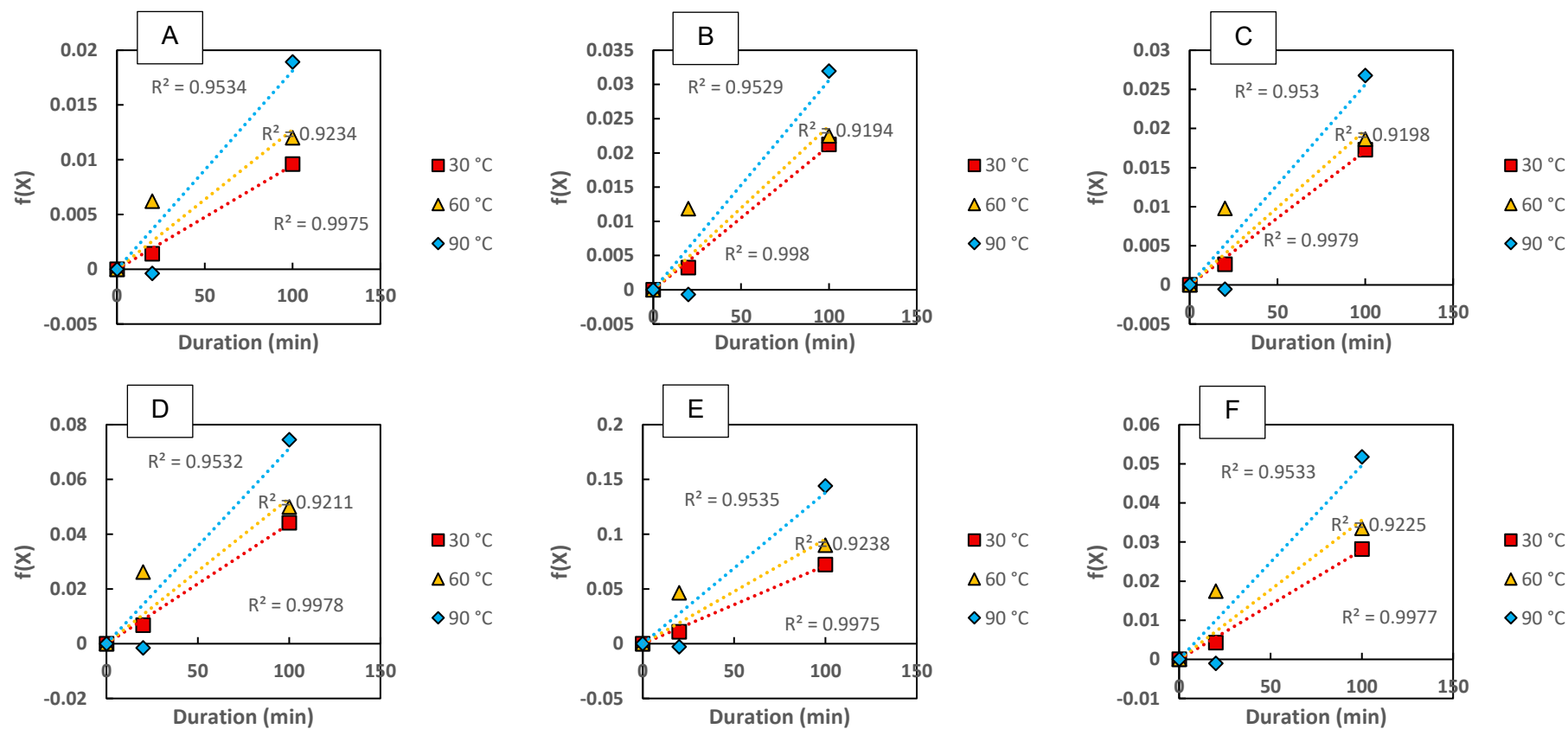


Figure B. 6: Graphical results for the fitting of different rate controlling mechanisms on respective time slots (**A:** Internal diffusion/product layer – SCM; **B:** Small particle – SPM; **C:** Large particle – SPM; **D:** First order – PH; **E:** Second order – PH; **F:** Three halves order – PH)

