Western Australia School of Mines

Leaching of Rare Earths from Eudialyte Minerals

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Author's Declaration

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

To the best of my knowledge and belief, this thesis contains no materials previously published by any other person except where due acknowledgment has been made.

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Date: June 2019

Abstract

Rare earths are critical materials which are valued for their use in advanced and green technology applications. There is currently a preferential demand for heavy rare earths, owing to their significant applications in technological devices. At present, there is a global thrust for supply diversification to reduce dependence on China, the dominant world supplier of these elements.

Eudialyte is a minor mineral of zirconium, but it is currently gaining significance as an alternative source of rare earths due to its high content of heavy rare earths. Eudialyte is a complex polymetallic silicate mineral which exists in many chemical and structural variants. These variants can also be texturally classified as large or fine-grained. Huge economic deposits of eudialyte can be found in Russia, Greenland, Canada and Australia. Large-grained eudialyte mineralisations are more common than its counterpart.

The conventional method of eudialyte leaching is to use sulfuric acid. In few instances, rare earths are recovered as by-products after the preferential extraction of zirconium . As such, the conditions for the optimal leaching of rare earths, particularly of heavy rare earths from large-grained eudialyte are not known. Also, previous studies on eudialyte leaching were focused only on large-grained eudialyte and thus, there are no known studies on the sulfuric acid leaching of rare earths from finely textured eudialyte.

Additionally, the sulfuric acid leaching of eudialyte bears a cost disadvantage owing to the large volume of chemicals needed for leaching and for neutralising effluent acidity on disposal. The use of citric acid, a cheap and benign chemical is worth investigating as an alternative alternative leaching agent. The above gaps in knowledge were the motivations for setting out the objectives of this research work.

Material characterisation tests were used to define the variability of two textural types of eudialyte. Leaching studies were then conducted using fractional factorial and Taguchi designs of experiment. An analysis of means was used to determine the conditions for the preferential leaching of rare earths, mainly of heavy rare earths, in (a) sulfuric acid and (b) citric acid leaching of large and fine-grained eudialyte minerals. An analysis of variance was used to determine the significant factors affecting the leaching of rare earths. The co-leaching of zirconium and co-dissolution of impurities were also investigated owing to the economic impact of their deportment in the leaching streams.

The main findings of this work highlighted the significant influence of the mineralogical differences of two eudialyte variants. Large-grained eudialyte responded well to the direct leaching method, both with sulfuric and citric acid, while fine-grained eudialyte required a more vigorous leaching method.

A single stage leaching of large grained eudialyte, using sulfuric acid yielded comparably high recoveries of 82 % in conditions of 10 wt. % acid and a high liquid:solid ratio of 100 mL:g. Such findings provide for alternative processing conditions for the preferential recovery of rare earths. In previous investigations, multiple leaching of eudialyte using 5-21 % acid at a dilution of 4:1 to 6:1 was needed for increased rare earth recoveries of 90 %. A single stage leaching using citric acid also yielded high rare earth recoveries of 70-80 %. These are comparable leaching recoveries compared to those derived from the use of sulfuric acid. The citric acid method is a novel approach and showed potential for use as an alternative method.

A two–stage method based on sulfation baking and water leaching was needed to yield high high rare earth recoveries of 91% with the sulfuric acid leaching of fine-grained eudialyte minerals. Thermal cracking of the complex fine-grained eudialyte mass was a significant procedure in the lixiviation of rare earths by sulfuric acid. The optimal conditions for

leaching heavy rare earths, devised as a result of this study were: baking at 320 °C for 3 h using 3.2 g/g acid-ore ratio followed by water leaching for 3 h at 20 °C on 20 mL:g and 300-420 µm grind size. This finding provided information on detailed processing conditions for rare earths from fine-grained eudialyte. This hydrometallurgical knowledge had not been available publicly.

A similar approach to two-stage leaching could not be applied to the citric acid leaching of fine-grained eudialyte minerals, owing to the low decomposition temperature and low corrosivity of citric acid. A single stage leaching yielded low recoveries of 8 % at 8 h leaching and 40 % at 400 h leaching.

The co-leaching of zirconium on sulfuric acid leaching of eudialyte was high at 70-80 % for both large and fine-grained eudialyte while it was lower at 39 % with citric acid leaching of large-grained eudialyte, due to the formation of hydrolysis products. Consistent with rare earth leaching results, the citric acid leaching of fine-grained eudialyte experienced slow kinetics which resulted in nil recoveries.

The co-dissolution of non-desirable components including silica was also dictated by mineralogy. Dissolution of these non-desirable components was higher in large-grained eudialyte as the rock-forming minerals were cyclosilicates which are known to decompose totally in acid. In contrast, the rock-forming minerals in fine-grained eudialyte were mainly tectosilicates which only partially decompose on acid attack.

The findings on the sulfuric acid leaching of rare earths will be useful in scenarios of highly attractive rare earth market prices, in that, the preferential leaching of rare earths from eudialyte can provide economic merit. The findings on the citric acid leaching of eudialyte provided basic information on a novel method, which will open up new approaches to eudialyte processing. It will also provide direction for further investigations into subsequent steps such as impurity removal from leach solutions, and rare earths extraction.

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It is with the thought of these wonderful people that I find the will to ***keep moving forward.***

List of Publications

The following publications have resulted from the research presented in this thesis:

Lim, H., D. Ibana and J. Eksteen (2016). "Leaching of rare earths from fine-grained zirconosilicate ore." Journal of Rare Earths **34**(9): 908-916.

Lim, H., D. Ibana and J. Eksteen (2017). The citric acid leaching of eudialyte. 28th Rare Earth Research Conference. Ames, Iowa, U.S.A.

Lim, H., D. Ibana and J. Eksteen (2017). Leaching of Rare Earths from Eudialyte. Society of Metallurgical Engineers of the Philippines (SMEP) Conference 2017. Ilocos Norte, Philippines.

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Chapter 1

Introduction

1.1 Overview and Uses of Rare Earth Elements

Rare earth elements (REEs) consist of a uniquely coherent group of metals, namely Sc, Y and the lanthanides[1] which have remarkably similar chemical properties. REEs normally occur in assemblage at various proportions in any ore. REEs are generally classified into two groups according to atomic weight: light rare earths (LREEs) which are the elements La to Sm, and heavy rare earths (HREEs) which are the elements Eu to Lu (Figure 1-1). Y is classified under HREEs for its chemical resemblance and its associated occurrence with HREE ore, while La and Ce are the most abundant of the LREEs.

REEs are used significantly in a wide range of modern technological applications in the areas of electronics, defence systems, medical instrumentation, and material science (Weng, Jowitt et al. 2015). They are highly valued for their extraordinary properties. For instance, the unique thermo-optical properties of Y are harnessed in laser technology which has resulted in the widespread use of lasers in non-invasive medical procedures (Berlien and Müller 2004). REEs are also preferred components for their effect on improving material efficiency and performance. This is exemplified in the use of La and Ce as catalysts for increasing fuel efficiency (Haxel, Hedrick et al. 2005) while Y is known for improving the electrochemical performance of lithium-ion batteries (Li, An et al. 2013).

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[1] elements with atomic numbers of 57 to 71 in the periodic table

Interestingly, REEs are considered as 'materials of the future' due to their increasing and expanding use in green technology applications (Baldi, Peri et al. 2014). Y is highly utilised in light-emitting diode lamps which consume 80 % less power compared to incandescent light bulbs (Milne and Reidy 2010). In petroleum refining, La is an essential element as it increases refinery yield while concurrently reduces power consumption (Walters, Lusty et al. 2011). Oxides of Ce are added in catalytic converters to lessen sulfur dioxide emissions (Hurst 2010). The above examples demonstrate the invaluable role of rare earths as key materials in clean energy technologies.

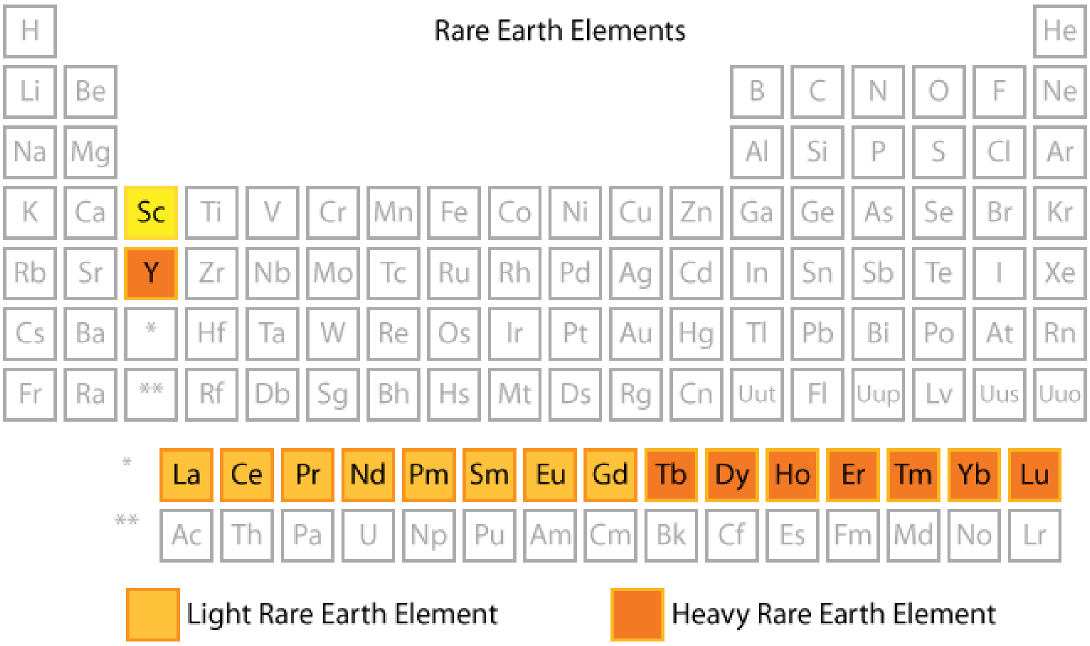


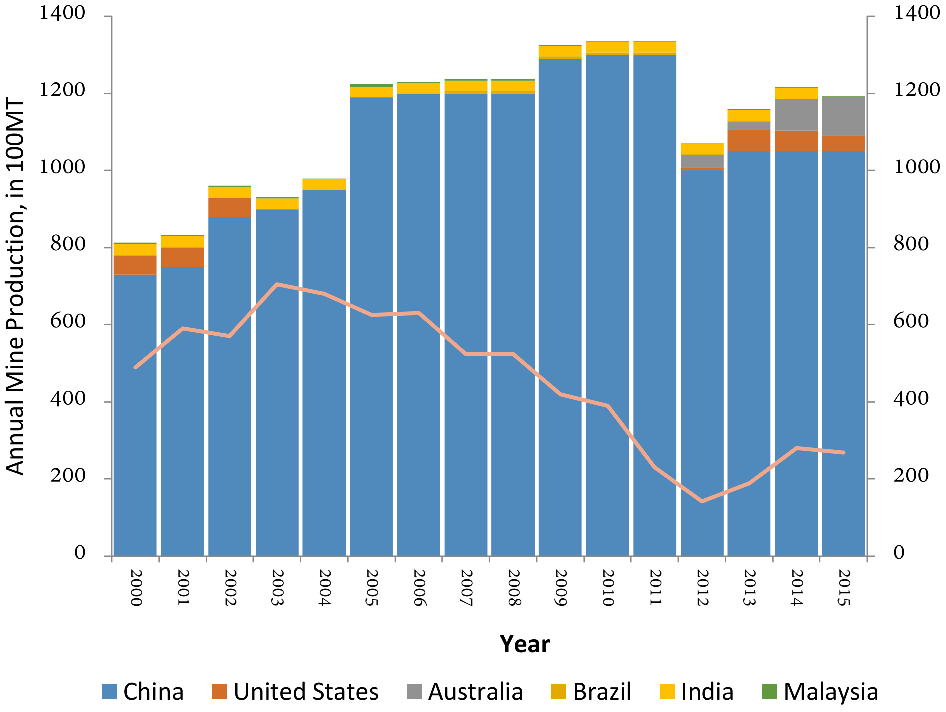
Figure 1-1: Periodic table of elements with rare earth elements highlighted (Walters, Lusty et al. 2011)

1.2 Rare Earth Elements on Critical Supply

Rare earths (except Pr) are naturally lithophile elements, in that they preferentially occur in rock-forming minerals. Thus, they are relatively plentiful in the earth's crust, but typically in mineral grades that are not conducive to economical extraction (Stosch 1998). Moreover, the host minerals for rare earths usually contain substantial amounts of radioactive Th and U which has discouraged commercial processing of some ores due to safety and environmental implications. Consequently, commercial production of rare earths is sourced from only four minerals, namely: bastnasite [$(Ce,La)(CO_3)F$], monazite [$(Ce,La,Nd,Y,Th)PO_4$], xenotime (YPO_4) and ion-adsorption clays (Yang, Lin et al. 2013, Lucas, Lucas et al. 2014).

China dominates the world supply of rare earths. In 2011, the country implemented an export quota on its REE products which resulted in serious global supply issues (Information Office of the State Council, The People's Republic of China 2012) and raised REEs as critical economic commodities. This situation opened up opportunities for the commercial extraction of otherwise unconventional rare earth minerals, and for new suppliers to enter the rare earths market (Haque, Hughes et al. 2014). As a result, China's reduced rare earth oxide (REO) production from 2012 was countered by an increased supply from non-Chinese producers (Figure 1-2). Though China's export restrictions were recently relaxed, weakened REE production in the country, and strong world market growth of REE end-products have propelled current demand for REE metals (Ge, Lei et al. 2016). It is forecasted that the continued rise of REE consumer products will propel future demand of these metals.

The critical status of a particular REE is defined by its level of importance to clean energy applications in relation to its current supply status (Graedel, Harper et al. 2015). The LREEs La and Ce are considered at near-critical level, while Y is at a critical level in United States of America (Figure 1-3) (Chu 2011). All REEs are considered critical materials in Australia, Japan, Korea and Europe (Skirrow, Huston et al. 2016, Chu 2011).



Line graph: China's REO export, x 100 MT

Figure 1-2: Bar graph of world annual REO production showing major production from China but with increased supply from non-Chinese suppliers after year 2012; line graph shows the declining trend of China's REE exports (Gambogi, 2016)

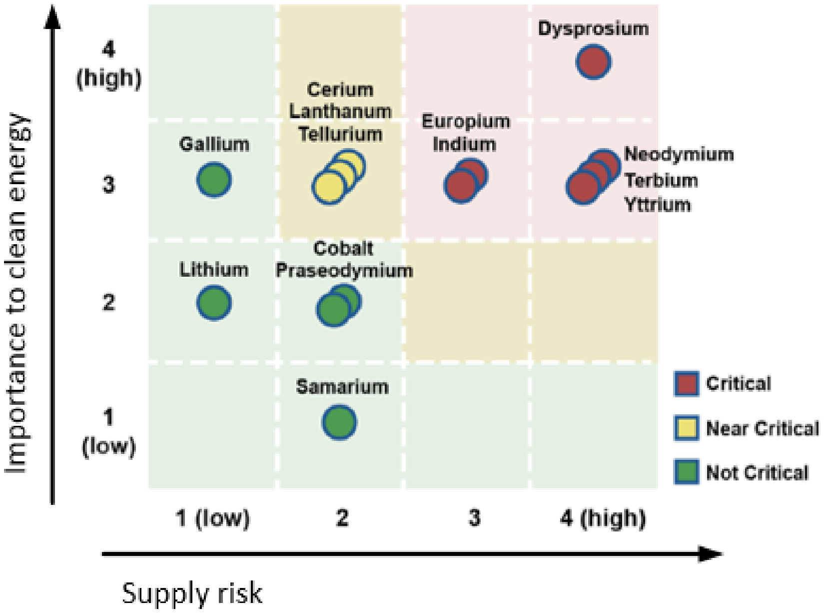


Figure 1-3: Materials criticality matrix (Chu 2011)

Market analysis predicts that in the long term, against increased REE production from non-Chinese REE producers, a shortage is still predicted for some HREEs namely Eu, Dy, Tb and Y (Kingsnorth 2012). This forecast has resulted in the classification of HREEs as a more economically significant group of materials compared to LREEs.

1.3 Eudialyte Minerals as Unconventional Source of Rare Earths

Eudialyte is a polymetallic mineral valued primarily as a minor mineral of Zr. Vast eudialyte deposits are located mainly in Russia's Khibina and Lovozero geological complexes and in South Greenland's Illimaussaq complex. To date, there is no commercial processing of eudialyte from these large deposits (Zaitsev and Kogarko 2012). Eudialyte contains 0.3-1% REO in ore which can increase to 3% in eudialyte concentrate, with a higher ratio of HREE:LREE than other REE conventional minerals (Tarkhanov, Kurko et al. 2012). As with any rare earth mineral, HREE content in eudialyte is largely composed of Y while LREE content is composed mainly of Ce and La.

The recent global shortage in REE has prompted investigations into alternative REE resources outside China (Hurst 2010). Growing attention has been placed on eudialyte minerals due to their high content of the much sought-after HREE and low content of associated radioactive elements Th and U (Dennis, Curtis et al. 2012, Buchanan, Reveley et al. 2014). These commercial interests resulted in the generation of a number of industrial projects of eudialyte processing for the production of valuable metals , which include Zr, REE and Nb (Buchanan, Reveley et al. 2014) (Appendix B).

1.3.1 Compositional and Mineralogical Variability of Eudialyte

Eudialyte is a complex Na-rich zirconosilicate[2] mineral which exists in many chemical and structural variants (Johnsen, Grice et al. 2003). Its chemical variability arises from its open

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[2] Zr silicate

crystal structure in that large cations (Ca, Fe, Al, K, REE, and Nb), anions (F and Cl), and water molecules can easily occupy the central spaces and interstices of its crystal structure, in varied concentration (Figure 1-4) (Johnsen and Gault 1997, Johnsen and Grice 1999). On the other hand, the structural variability of eudialyte is based on a number of repeating layers of three-membered and nine-membered rings of SiO_4 tetrahedra connected to a ZrO_2 octahedra, which can vary from 12 to 24 layers (Rastsvetaeva and Chukanov 2013). To date, there are 25 known eudialyte variants and this number is growing, with more variants under study (Appendix C).

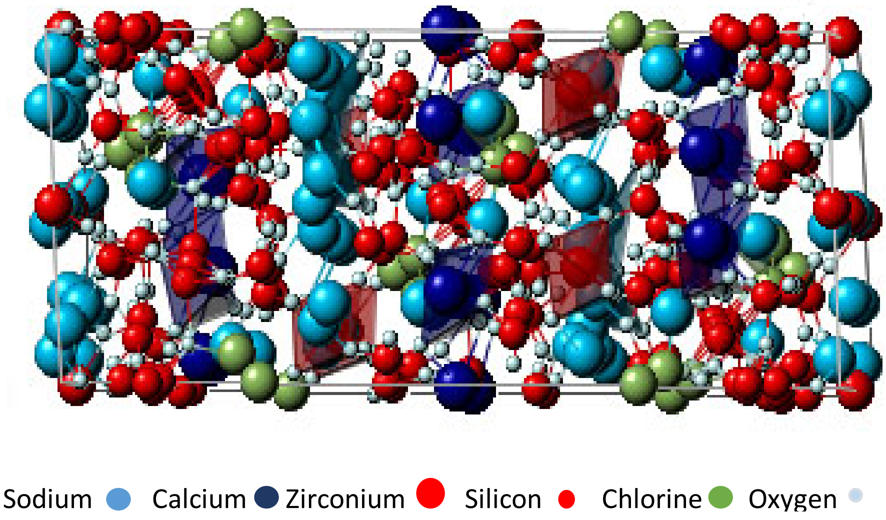

Figure 1-4: Eudialyte crystal structure, REE substitutes in sodium and calcium sites (Mirofoss Database)

Eudialyte is formed in peralkaline magma systems (Marks, Hettmann et al. 2011) where it can crystallise and grow into large crystals on slow magma cooling (Salvi and Williams-Jones 1996, Markl 2001, Sheard, Williams-Jones et al. 2012) or into fine crystals on rapid cooling (Spandler and Morris 2016). Texturally, large-grained eudialyte minerals are classified as the common type and they have been the subject of many geological and chemical investigations. In contrast, finely textured eudialyte minerals are rare and are characterised by the presence of ultrafine crystals (micron sizes) or finely-textured mineral masses with undefined grain boundaries (Spandler and Morris 2016). Little is known of their properties owing to the complexity of the mineralogy.

In summary, eudialyte is a complex Zr-bearing silicate that is formed in highly alkaline conditions. It exists in many mineralogical variants, differing in chemistry, structure and texture.

1.3.2 Sulfuric Acid Leaching of Eudialyte

Eudialyte subjects itself to easy dissolution with mineral acids, hence its name, which in Greek language means, '*easily decomposed*' (Giuseppetti, Mazzi et al. 1971). Previous investigations into the leaching of eudialyte reported preference on the use of sulfuric acid over nitric and hydrochloric acid due to the higher recovery of Zr values (Zakharov, cited in Lebedev 2003) and the recyclability of sulfuric acid (Lebedev 2003). The major challenges highlighted in these reports were the integrated recovery of all recoverable metals and the control of silica to prevent gel formation in solution.

Historically, studies on eudialyte processing had been approached in the interests of maximising Zr recovery over other metals, as Zr is the major element in the mineral (Lebedev 2003, Lebedev, Shchur et al. 2003, Zakharov, Maiorov et al. 2011, Zakharov, Skiba et al. 2011, Lebedev, Masloboev et al. 2012). The generic leaching method is to use heated sulfuric acid to leach metal values from the eudialyte concentrate. A variant to this method, as applied to eudialyte concentrate with a high content of rare metals (Nb,Ti), is the addition of a sulfation baking[3] step prior to leaching (Cox, Moreton et al. 2010, Buchanan, Reveley et al. 2014). In this method, valuable metals (Zr, Nb, REE) are converted into water soluble sulfates in the baking step and solubilised in the subsequent water leaching. With the former method, the reported leaching recovery rate of rare earths is low at 50-60 %, as leached rare earths

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[3] Sulfation baking is the term used in this thesis to denote low temperature heating of ore or mineral concentrate in the presence of sulfuric acid to effect sulfation reactions at the liquid-solid state as opposed to the gaseous-solid reactions in the roasting processes

precipitate and end-up in the leach residue on first leaching of eudialyte. Higher recoveries of 90 % were attained after multiple digestion of the leach residue (Lebedev 2003).

Against the increased economic importance of REEs, only a few of recent studies shifted focus on extraction of REEs from eudialyte (Davris, Stopic et al. 2016, Voßenkaul, Birich et al. 2016). For industry projects (Appendix B), Zr is still the main metal of interest and there is limited information on the processing conditions. For example, a recent industry project reports on the application of sulfation baking in the processing of fine-grained eudialyte ore (Chalmers 2016). However, the process details have been kept confidential, owing to the commercial nature of the undertaking. In these projects, rare earth extraction was regarded as secondary, and leaching conditions for maximising REE extraction are not fully known. Given the economic significance of rare earths, in particular of HREE over LREE, there is an incentive to study the conditions for optimal leaching of HREE in the sulfuric acid leaching of eudialyte.

Furthermore, the early studies of eudialyte processing focused mainly on eudialyte concentrate where large eudialyte crystals dominate the mineral mass. The sulfuric acid leaching of fine-grained eudialyte minerals has received poor attention. It is also of interest to investigate rare earths leaching, mainly of HREE, from finely-textured eudialyte minerals.

1.3.3 Citric Acid Leaching of Eudialyte

Against the recyclability of sulfuric acid, its use in the leaching of eudialyte bears a cost disadvantage. Estimated processing expenditures not only account for the large volume of sulfuric acid needed for leaching but also include the cost of neutralisation reagents needed for effluent disposal. In the proposed hydrometallurgical processing of Russia's Lovozero eudialyte deposit for instance, it was calculated that processing of at least one million tonnes of eudialyte is needed for the process to be profitable (Chistov, Okhrimenko et al. cited in Lebedev 2003). Thus, there is a need to look for alternative leaching agents for the recovery of REE from eudialyte minerals.

Citric acid, $C_6H_8O_7$, is an edible weak organic acid that was used briefly in the 1950s as an eluting solution for the extraction of rare earths via ion exchange technology (Spedding, Voigt et al. 1947a, Spedding, Fulmer et al. 1947b, Tompkins and Mayer 1947, Harris and Tompkins 1947, Spedding, Fulmer et al. 1951). The technique was soon replaced with the more cost-effective solvent extraction process (Kaczmarek 1981).

Numerous studies in solution chemistry report on the formation of stable hydrated complexes of rare earths in citric acid solution (Wood 1993, Shan, Lian et al. 2002, da Silva, Matos et al. 2008, Voskresenskaya and Skorik 2009, Williams and Cloete 2010). Moreover, citric acid is an environmentally benign chemical as it is found in most plants and is relatively cheap compared to other organic and inorganic acids alike. There are no known studies on the use of citric acid for the leaching of REE from eudialyte. Hence, there is both an economic and environmental merit in studying its use as an alternative lixiviant to sulfuric acid.

1.4 Motivation of the Study

Eudialyte is a minor mineral of Zr but it is becoming an emerging source of rare earths, particularly of the critical rare earths Y, La and Ce. This is due to the low content of associated radionuclides and the relatively high content of HREE in eudialyte minerals. The textural variability of eudialyte has previously been overlooked from a hydrometallurgical processing point of view. Previous studies focused only on the leaching of large-grained eudialyte minerals, while the leaching behaviour of fine-grained eudialyte has not been examined. Although fine-grained eudialyte deposits are currently uncommon, there is potential for increased geological exploration for this textural type of deposit as resources deplete in the future.

In the past, the leaching of eudialyte has always been approached at a preferred extraction of Zr which is the major metal component in the polymetallic mineral. It was only recently that REE extraction was given focus for eudialyte leaching. Consequently, there is limited information on the optimal conditions for REE leaching from eudialyte using sulfuric acid as a lixiviant. It is also not known how the leaching behaviour of HREEs differ from that of LREEs when leaching conditions are altered to favour the leaching of REE. Furthermore, in consideration of the cost and environmental implications associated with the large volume of corrosive chemicals used in the conventional leaching of eudialyte, there is a need to study alternative leaching agents to sulfuric acid in the hydrometallurgical processing of eudialyte. In this research work, citric acid was the chemical of choice as it is a cheap, environmentally benign chemical and is known to form stable complexes with REE.

The conduct of leaching studies aims to address the above identified gaps in knowledge. The leaching of REE from both large-grained and fine-grained eudialyte variants will extend current knowledge of hydrometallurgical processing of eudialyte. This new information will be significant in market scenarios of attractive REE metal prices. Studies on the use of citric acid as an alternative leaching agent to sulfuric acid should open up new and better methods of eudialyte processing.

1.5 Aims of this Research Work

This research aims to investigate the leaching of rare earths from two textural classes of eudialyte. Specifically, this study aims to:

- characterise and discuss the physical and chemical features of two textural types of eudialyte minerals;
- identify and investigate the statistically significant factors affecting the leaching of rare earths by sulfuric acid, from two differently textured types of eudialyte;
- identify and investigate the statistically significant factors affecting the leaching of rare earths by citric acid, from two textural classes of eudialyte;
- determine the optimal conditions for the leaching of HREE by (a) sulfuric and (b) citric acid from two textural classes of eudialyte;
- investigate the co-leaching of Zr in the leaching of REE by (a) sulfuric and (b) citric acid from two differently textured types of eudialyte; and

- investigate the co-leaching of silica and the deportment of impurities in the leaching of REE by (a) sulfuric and (b) citric acid from two differently textured types of eudialyte

1.6 Scope and Limitations of the Study

This research focuses on the determination of optimal conditions for the leaching of REE using (a) sulfuric and (b) citric acid from two textural classes of eudialyte. In the present work, the investigation of leaching responses is limited to three REEs namely Y, La and Ce. These three elements comprised more than 80 % of the total REE content in the ore specimens used in this research work. The leaching behaviour of Y was used as indicator of HREE leaching behaviour, while La and Ce were used as proxies to understand the leaching behaviour of LREE.

Eudialyte minerals exist in many variants, thus, the physical and chemical characterisation of the two ore samples used was a critical aspect of the research. The determination of the chemical composition of the eudialyte minerals in ore samples is important in defining the extent of variation of eudialyte, relative to other eudialyte variants, both from the same deposit and from other deposits. Furthermore, the difference in chemical composition before and after leaching can be used to determine the extent of leaching. The chemical characterisation conducted in this research work is limited by current equipment capabilities, particularly in terms of detection limit and spot size resolution. This is extremely relevant in the characterisation of fine-grained eudialyte minerals in DT ore, in which the low content of REE limited the analytical techniques which could be used for its characterisation. The complex morphology of these fine-grained eudialyte minerals also affected the spatial resolution on analysis, which made it difficult to determine the chemical composition of these micro-phases. In effect, a generalised chemical classification was used to characterise the fine-grained minerals in DT ore.

In the sulfuric acid leaching of REE from eudialyte, the determination of conditions for the favourable leaching of REE, as well as the conditions for the optimal leaching of HREE were the main focus. The recovery of REE from the sulfuric acid solution, including the preparatory steps of solution purification through impurity removal was not undertaken in this research work. This is because these procedures can follow established procedures of solvent extraction and impurity removal in the conventional processing of eudialyte. The determination of leaching kinetics was also not included. The literature on Zr solution chemistry has indicated that the metal easily undergoes hydrolysis (Lister & McDonald 1952, Baes 1976), generally in the presence of sulfate ions (Matijevic´ 1969) and in low acidic conditions (Ryabchikov, Marov et al. 1963). The precipitation of Zr hydrolysis products is likely to cause co-precipitation of REE which will significantly affect leaching kinetic measurements.

In order to assess the potential use of citric acid as an alternative lixiviant to sulfuric acid, it is imperative to study its application in the leachability of REE from eudialyte, as well as its recovery of REE from pregnant solutions. REE oxalate precipitation was investigated as the main method for REE recovery from citric acid. The scope of REE oxalate precipitation was restricted to preliminary investigations and not extended to the determination of optimal conditions for REE precipitation. The deportment of impurities was also investigated to provide direction for subsequent work in terms of solution purification. As in the sulfuric acid leaching of eudialyte, leaching kinetics were not determined in the citric acid leaching due to Zr hydrolysis reactions and the effect on REE concentration in solution.

1.7 Structure of the Thesis

This thesis has 8 chapters.

Chapter 2 provides a thorough review of studies on REE leaching of eudialyte. As these studies are limited, this chapter also provides a review on the solubility of REE in (a) sulfuric and (b) citric acid in order to better design an experimental plan for REE leaching.

Chapter 3 provides a review of studies on Zr leaching from eudialyte, in order to understand how the leaching conditions need to be changed when REE recovery is prioritised. This chapter also provides a short review on silica chemistry in both sulfuric and citric acid solutions, as well as current methods of silica and impurity management as practised in eudialyte processing.

Chapter 4 provides a material characterisation of the eudialyte ore samples used in this research work.

Chapter 5 discusses the sulfuric acid leaching of Y, La and Ce, comparatively, from two textural variants of eudialyte.

Chapter 6 discusses the citric acid leaching of Y, La and Ce, comparatively, from two differently textured eudialyte minerals.

Chapter 7 discusses the co-leaching of Zr, the deportment of major rock-forming elements and the deportment of radionuclides Th and U in the leaching of REEs by (a) sulfuric and (b) citric acid from two differently textured eudialyte minerals.

Chapter 8 concludes the study and describes further possible areas of research following developments made in the present study.

Chapter 2

Literature Review Part I

Review of Studies on (a) Sulfuric and (b) Citric acid Leaching of Rare Earths from Eudialyte

2.1. Introduction

Sulfuric acid has been used in conventional approaches in the leaching of valuable metals from eudialyte. Not only is sulfuric acid cheaper than other inorganic acids, it also has a higher corrosion activity resulting in a greater recovery of Zr from eudialyte leaching. There have only been a few studies conducted on sulfuric acid leaching of rare earths from eudialyte. This is due to the fact that earlier investigations were geared towards the recovery of Zr from the mineral with rare earths as by-products of the extraction process. No studies have been found on the citric acid leaching of rare earths from eudialyte. As very little is known on REE leaching from eudialyte, this literature review is approached on the basis of solution chemistry for rare earths in (a) sulfate and (b) citric acid systems. This chapter opens with a review on eudialyte crystal structure in order to gain an understanding of how rare earths, which are present as substitution elements, are positioned in the eudialyte crystal structure. The aim of the review is to pave the way for viewing REE leaching from a mineralogical basis. The discussion transitions into REE solution chemistry in (a) sulfate and (b) citric acid systems and how their solution chemistry is affected by relevant processing conditions. Where applicable, specific discussion is provided around Y, La and Ce. The chapter closes with a short review on existing studies on REE leaching from eudialyte. It is hoped that an understanding of REE solution chemistry in (a) sulfate and (b) citric acid systems will provide the theoretical concepts required to better design leaching conditions for the extraction of REEs from eudialyte.

2.2 Crystal Structure, Alteration and Rare Earths Inclusion in Eudialyte

Eudialyte is a Na-rich silicate mineral that is characterised by its zeolitic properties, that is, it has excellent cation exchange properties (Zubkova and Pushcharovsky 2008). The chemical composition of eudialyte is represented by the general formula $N(1)_3N(2)_3N(3)_3N(4)_3N(5)_3M(1)_6M(2)_{3\text{-}6}M(3)M(4)Z_3[Si_{24}O_{72}]O'_{4\text{-}6}X_2$ where N(1-5) = Na,H_3O^+,K,Sr,REE,Y,Ba,Mn and Ca; M(1) = Ca,Mn,REE,Na,Sr,Fe; M(2) =Fe,Mn,Na,Zr,Ta,Ti,K.Ba and H_3O; M(3) and M(4)=Si,S,Nb,Ti,W,Na;Z=Zr,Ti,Nb; O'= O,OH,H_2O; X(1) and X(2) =Cl,F,H_2O,OH,CO_3,SO_4,AlO_4,MnO_4 (Rastsvetaeva and Chukanov 2013).

The crystal structure of eudialyte is composed of complex layers of ternary and nonary rings of SiO_4 tetrahedra with Zr,Fe,Ca and Na present as framework elements. Extra Na, K, Cl and OH atoms exist as accessory elements occupying the large holes within the eudialyte structure (Giuseppetti, Mazzi et al. 1971, Golyshev, Simonov et al. 1971). A simplified polyhedral framework of eudialyte features a cage-like structure with alternating layers of SiO_4 and ZrO_2 polyhedron with the Na atoms occupying the central voids at N sites (Figure 2-1) (Johnsen, Grice et al. 2003). Given its open crystal structure, it is understandable why the mineral exists in many variants and how easy it is for it to undergo alteration into secondary mineral forms.

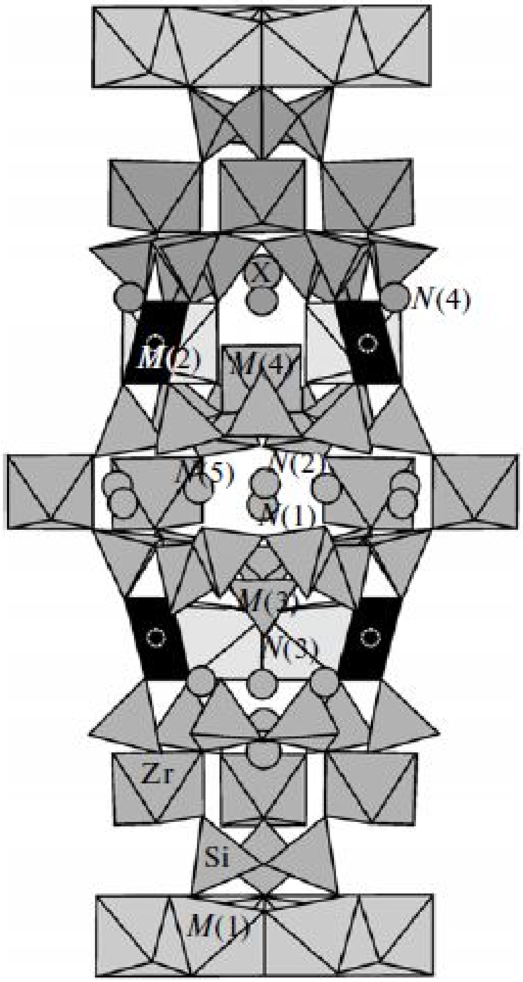


Figure 2-1: Polyhedral model of eudialyte structure showing layers of tetrahedral SiO_4 and octahedral ZrO_6 (Johnsen, Grice et al. 2003)

Alteration of eudialyte occurs via one of several geochemical processes, e.g. liquid immiscibility, magmatic crystal accumulation, hydrothermal alteration and metasomatic alteration (Salvi and Williams-Jones 1996, Markl 2001, Sheard, Williams-Jones et al. 2012). The altered minerals formed can either be a chemically simpler Zr mineral or a complex mineral of unknown composition. In a particular deposit, it is common for eudialyte to exist in both non-altered and altered form. For example, unaltered eudialyte minerals in Nora Karr, Sweden have been found to contain eudialyte minerals which underwent metasomatic alteration. The alteration produced three compositional varieties of eudialyte: (1) Fe-rich, REE-poor eudialyte, (2) Fe-Mn-bisected, HREE-rich eudialyte and (3) Mn-rich, LREE-rich eudialyte (Sjöqvist, Cornell et al. 2013). In the northern part of the Illimaussaq region of South Greenland, eudialyte minerals were found with their alteration minerals: catapleiite minerals and unknown REE-flourosilicate phases (Coulson 1997, Karup-Moller, Rose-Hansen et al. 2010). The presence of alteration minerals shows the inherent mineralogical variability of eudialyte.

REE inclusion in the eudialyte crystal structure depends largely on magma composition, geochemical conditions and favourable stereochemistry during the formation of unaltered and altered eudialyte minerals (Sjöqvist, Cornell et al. 2013). REE substitution occurs mainly in *M(1)* sites, mostly replacing Ca or Mn (Figure 2-1) (Johnsen and Grice 1999, Johnsen, Grice et al. 2003). Dictated by stereochemistry, REEs also substitute Na atoms generally on *N(4)* and a few at *N(3)* sites. Among the rare earths, and in accordance with the Oddo-Harkins rule of relative chemical abundance, Ce is found in greater abundance than La and Y, resulting in its higher inclusion in eudialyte crystal lattice (Moeller 1963).

Crystallography studies on unaltered eudialyte crystals confirmed REE substitution at the *M(1)* site and the presence of distorted lattices in the $M(1)O_6$ octahedron (Rastsvetaeva 2007, Rastsvetaeva and Chukanov 2013). The Na atoms are generally substituted with Ca, REE, Sr and K. In large-grained eudialyte minerals, substitution of REEs in Na and Ca in *N(4)* site was reported (Chakhmouradian and Mitchell 2000, Merlino, Pasero et al. 2004, Mesto, Kaneva et al. 2014). There are no reported substitutions in the silicate polyhedral, and calculation of the bond-valence sums over valence sums of Na at the $M(1)O_6$ site indicated weak bonding (Johnsen and Grice 1999, Johnsen, Grice et al. 2003). Weak bonds are found at the release points of metals during leaching (Crundwell 2013). Further, the easy dissolution of Na ions in mineral acids facilitates the release of any Na-substituting elements into the leach solution (Stillings and Brantley 1995). These mechanisms are believed to be the precursor for REE release on eudialyte leaching. There have been no reports found on REE substitution sites in finely textured eudialyte minerals. This is understandable as the application of crystallography techniques is hindered by the lack of defined crystal boundaries for these micro-mineral phases.

2.3 Solution Chemistry of Rare Earths in Sulfuric Acid

The leaching of rare earths with sulfuric acid is represented by the reaction in Equation (2-1) (Chelishchev, Motov et al. 1983):

$$(Na,REE)_{12}(Ca,REE)_6Fe_3Zr_3[Si_3O_9]_2[Si_9O_{24}(OH)_3]_2+18H_2SO_4 + 3H_2O \rightarrow 6Na_2SO_4 +6CaSO_4+3FeSO_4+3REESO_4 + 3ZrOSO_4+ 24SiO(OH)_2 \qquad (2\text{-}1)$$

Rare earths form sulfate complexes which are kinetically labile due to their fast formation and the strong ionic nature of their f-bonds (Nathan, Wallace et al. 1943, Vercouter, Amekraz et al. 2005). In effect, lanthanide sulfate chemistry is complex and not yet fully understood (Vercouter, Amekraz et al. 2005). Despite this, it can be seen that the most stable complex species of rare earths are formed by hydration and by strongly chelating ligands, mainly with highly electronegative donor atoms like oxygen and chlorine (Moeller, Martin et al. 1965). The hydrated complexes of rare earths and their properties in aqueous solution are reviewed and discussed in the following sections.

2.3.1 Hydrolysis of rare earth sulfates

The hydration of a lanthanide ion can be expressed in terms of the Eigen-Diebler multi-step complexation reaction in Equation (2-2) (Purdie and Vincent 1967):

$$REE^{3+}(aq)+SO_4^{2-}(aq) \rightleftarrows REE^{3+}(H_2O)_xSO_4^{2-} \rightleftarrows REE^{3+}(H_2O)_ySO_4^{2-} \rightleftarrows REESO_4^{+}(aq) \qquad (2\text{-}2)$$

where reaction rate studies reveal that the formation of the ligand ion is the limiting step.

Hydrolysis tends to increase with a decrease in the cation radius which means that Y hydrolyses more extensively than other rare earth sulfates (Moeller 1946). The reported sulfate complexes of Y include YSO_4^+, $Y_2(SO_4)_3$ and its hydrated form $Y_2SO_4{\cdot}8H_2O$ (da Silva, Ogasawara et al. 1996).

La can exist as an acid sulfate $La(HSO_4)_3$ and forms hydrated compounds with water in the forms $La(OH)(SO_4)$ or $La(HSO_4)^2$ (Simpson and Matijević 1987). The most stable is the hexagonal enneahydrate $La_2(SO_4)_3.9H_2O$ that can exist in temperatures from 0˚C to 100˚C. In natural waters where the concentration of sulfuric acid is between 0.1–0.31 M, the dominant species of La is $LaSO_4^+$, followed by $La(SO_4)_2^-$ and La^{3+} (Vercouter, Amekraz et al. 2005). The di-sulfate species $La(SO_4)_2^-$ is dominant in concentrated solutions (Simpson and Matijević 1987).

The dissolution of $Ce(SO_4)_2$ in water can result in the formation of the metastable forms $H_2Ce(SO_4)_3$ and $H_4Ce(SO_4)_4$ (Paulenova, Creager et al. 2002). In oxidising conditions, trivalent Ce Ce(IIII) can easily oxidise into tetravalent Ce Ce(IV). The conversion to the tetravalent state is unique to only three REEs namely Ce, Pr and Tb (Moeller 1963). The higher oxidation state of Ce is more soluble than that of the trivalent state (Paulenova, Creager et al. 2000). There is a progressive hydrolysis of Ce^{4+} with decreasing concentration of sulfuric acid resulting in the formation of $H_2Ce(OH)_2(SO_4)_2$ which then becomes a solid, $HCe(OH)_2(SO_4)_3$. A complex form cerous-ceric hydroxylsulfates $Ce^{3+}[Ce^{4+}(OH)(SO_4)_3]$ can also co-exist (Paulenova, Creager et al. 2002).

In summary, various hydrolysed species of rare earths co-exist in sulfate solutions. The hydrolysed complexes formed are dictated by solution chemistry and system conditions. It is essential to understand how common leaching factors such as temperature, pH and ionic strength affect the solubility of rare earths.

2.3.2 Effect of temperature and pH on solubility of rare earth sulfates

Unlike the sulfates of transition metals, rare earth sulfates have retrograde solubility in which solubility decreases with increasing temperature. The inverse relationship of solubility and temperature is clearly shown by the solubility graphs of Y, La and Ce sulfates where in the case of Ce for example, the solubility of its sulfate $Ce_2(SO_4)_3{\cdot}2H_2O$ dropped from 21.4 g at 0 °C to 3.87 at 60 °C (per 100 g of water) (Figure 2-2) (Spedding and Jaffe 1954, Sazonov and Shaw March 2006). This behaviour is due to the exothermic reaction associated with REE sulfates formation. The continued rise of the solution temperature brought about by the formation of REE sulfates is countered with a decrease in solubility which minimises the effect of thermal stress. This is consistent with the principles of Le Chatelier on equilibirum (Moeller 1963). The effect of temperature on REE solubility implies limitations on the ratio of L:S that can be used for the leaching of REEs.

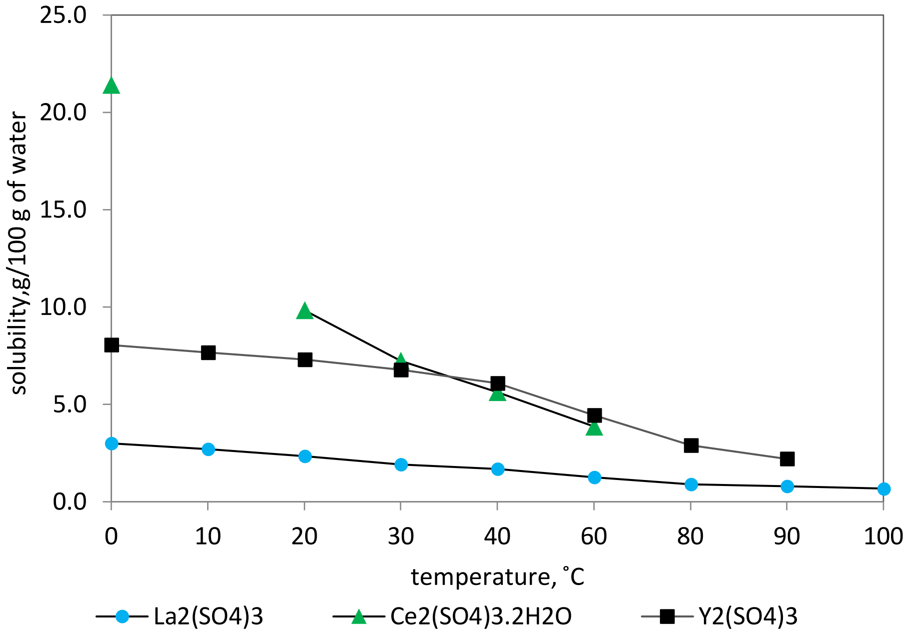
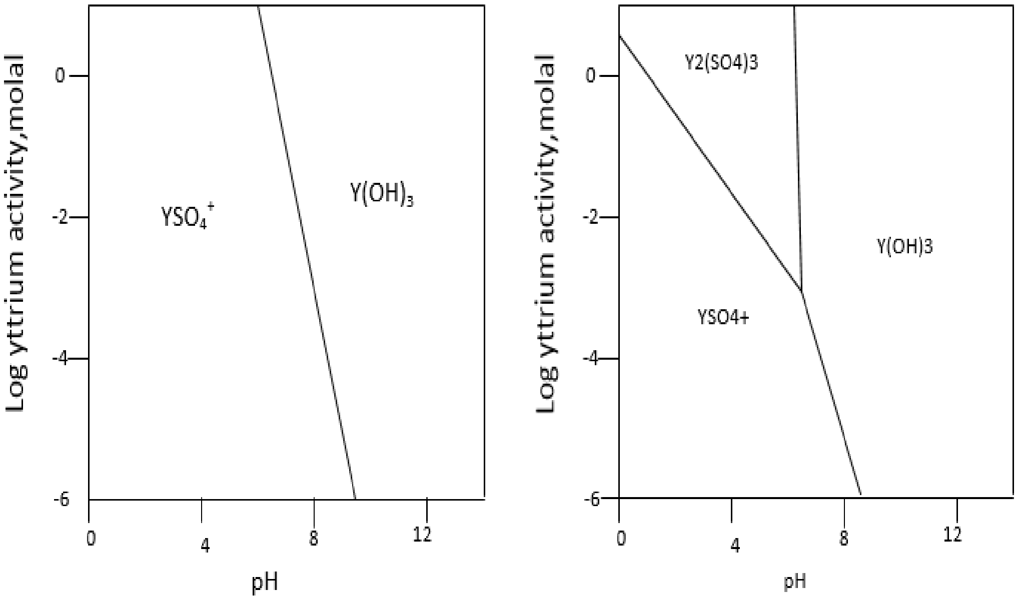


Figure 2-2: Solubility of La, Ce and Y sulfates per 100 g of water at different temperatures (Spedding and Jaffe 1954, Sazonov and Shaw March 2006)

The inverse relationship of temperature and solubility of REE sulfates is supported by the equilibrium plots of Y-S-H_2O (Figure 2-3) which show that the activity of the Y monosulfate ion (YSO_4^+) is favoured at low temperature, high dilution and low pH conditions (da Silva, Ogasawara et al. 1996). Figure 2-3a presents stability regions of YSO_4^+ and $Y_2(SO_4)_3$ at low pH and at low molal Y activity and highlights a reduced region for YSO_4^+ at increased temperature, resulting in the formation of Y sulfate Y_2SO_4 at 100 °C and 1.0 m (Figure 2-3b). The graph also highlights the effect of pH in dictating the dominant Y sulfate speciation relative to Y molal activity.



(a) (b)

Figure 2-3: Activity-pH diagram of Y-S-H_2O system at (a) 25 °C and at (b) 100 °C for sulfur activity at 1.0 molal (da Silva, Ogasawara et al. 1996)

Generally, while REE solubility decreases with temperature, the stability of the REE complexes increases with temperature. The formation constants K_1 (Equation 2-3) and K_2 (Equation 2-4) for mono-sulfate $La(SO4)^+$ and di-sulfate $La(SO4)^{2-}$ complexes reflect the increasing stability of these complexes at increased temperatures (Table 2-1) (Simpson and Matijević 1987).

Table 2-1: Stability constants of mono and di-sulfate La complexes at 1.0 M ionic strength (Simpson and Matijević 1987)

Temperature, °C	K_1, mol/dm^3	K_2,mol/dm^3
25	6.33	1.59
35	12.94	1.72
45	26.31	1.82
55	50.40	1.83

where $La^{3+} + SO_4^{2-} \rightleftharpoons La(SO_4)^+$ K_1 (2-3)

$La(SO_4)+ + SO_4^{2-} \rightleftharpoons La(SO_4)^{2-}$ K_2 (2-4)

2.3.3 Effect of sulfuric acid concentration and other ions on solubility of rare earth sulfates

Rare earth sulfates have decreased solubility in high sulfuric acid concentration due to the ‘common ion effect’. A solubility graph of Ce (III) ions in terms of sulfuric acid concentration clearly shows higher solubility at low acid concentration, and this is consistent at various temperatures (Figure 2-4).

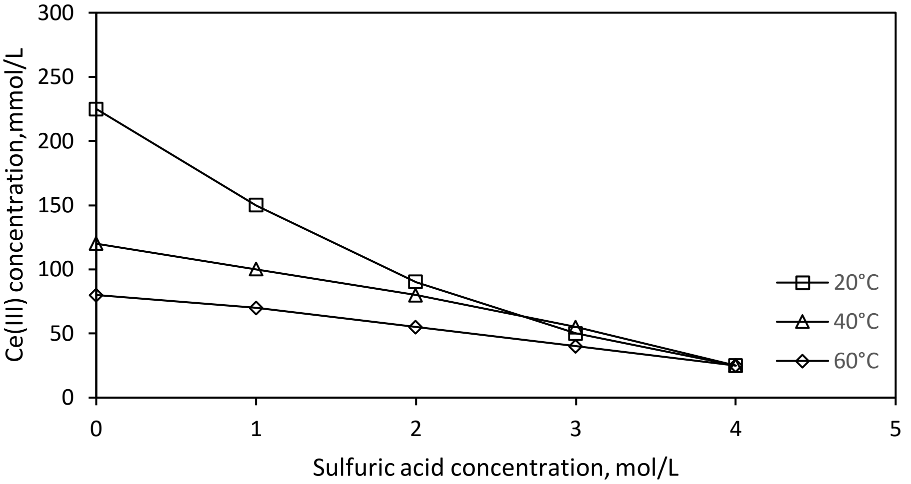


Figure 2-4: Solubility of Ce (III) ions in sulfuric acid at various temperatures (Paulenova, Creager et al. 2002)

This solubility pattern can change when rare earths are present in poly-component systems. For instance, in the presence of other lanthanide sulfates, La sulfates in octahydrate form $La_2(SO_4)_3.8H_2O$ were observed to have higher solubility in high sulfuric acid concentration at 64 °C as compared to 25 °C (Figure 2-5). On the other hand, Ce sulfate octahydrate $Ce_2(SO_4)_3.8H_2O$ has increased solubility in low sulfuric acid concentration at 64 °C as compared to 25 °C (Figures 2-5). Consistently, the solubility patterns of these hydrated La and Ce sulfates were observed in poly-component systems made up of calcium and lanthanide sulfates (Figure 2-6). The anomalous behaviour of La sulfate octahydrate was believed to be caused by hydroxylsulfate complexation reaction which has a different enthalpy of dissolution while that of Ce sulfate octahydrate is due to the formation of an isomeric series of mixed Ce and La sulfates that has higher solubility (Todorovsky, Milanova et al. 1993).

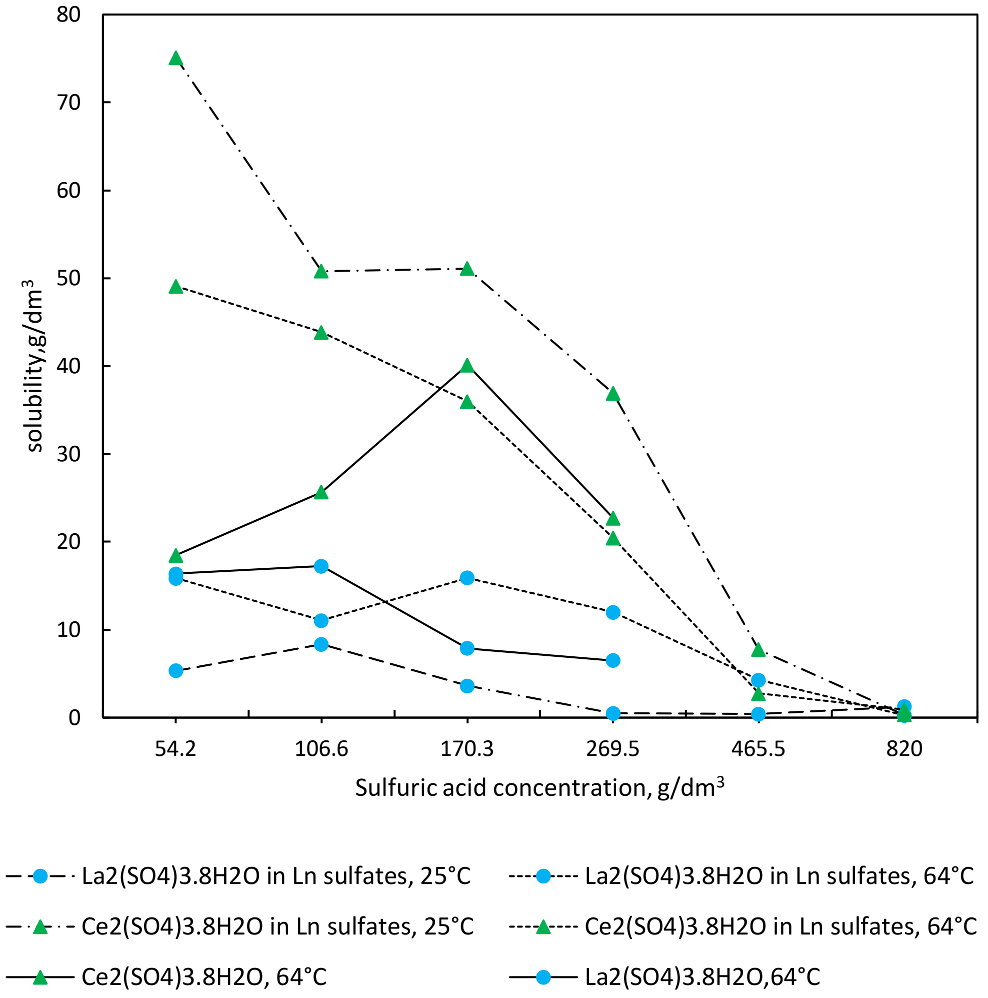


Figure 2-5: Solubility of La and Ce sulfate octahydrates in the presence of lanthanide (Ln) sulfates as a function of sulfuric acid concentration (Todorovsky, Milanova et al. 1993)

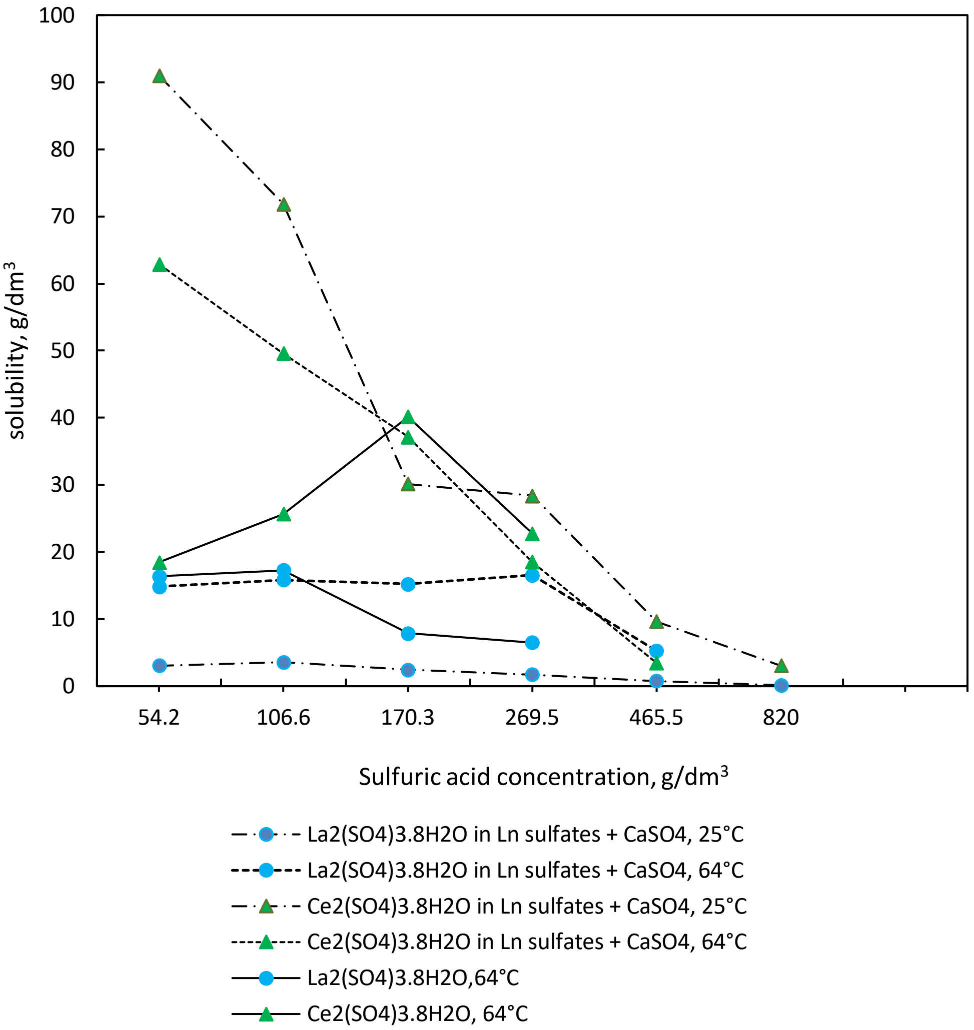


Figure 2-6: Solubility of La and Ce octahydrates in the presence of lanthanide and calcium sulfates as a function of sulfuric acid concentration (Todorovsky, Milanova et al. 1993)

Moreover, the presence of sodium sulfate Na_2SO_4 was reported to slightly increase the solubility of the hydrate form of $Y_2(SO_4)_3$ to a point where the solubility diminishes rapidly with the formation of double salt (Figure 2-7) (Little 1917). However, experimental data reported by Lebedev (2003), on the dissolution of REEs from eudialyte concentrate, showed a different result with a higher solubility of REEs in solution without the addition of Na_2SO_4 (Figure 2-8). While there was no explanation provided for this difference in behaviour, the decreasing patterns of solubility with the presence of Na_2SO_4 in the latter experiment could contribute to the presence of other REE sulfates in the solution, as compared to the sole presence of $Y_2(SO_4)_3$ in the earlier test.

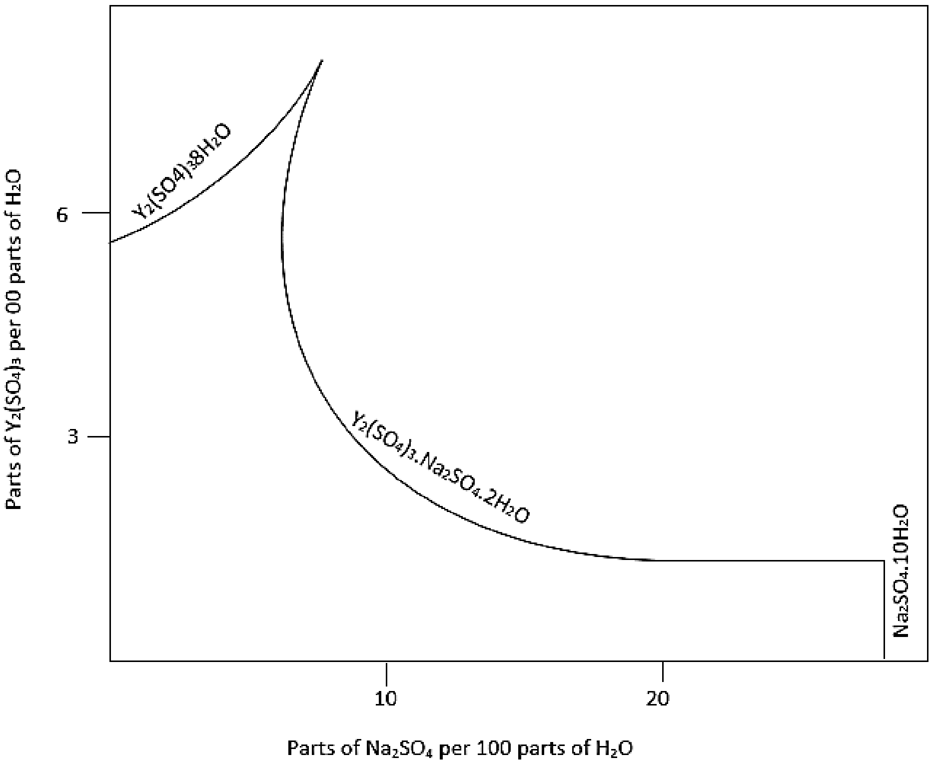


Figure 2-7: Solubility of Y octahydrate in sodium sulfate solution (Little 1917)

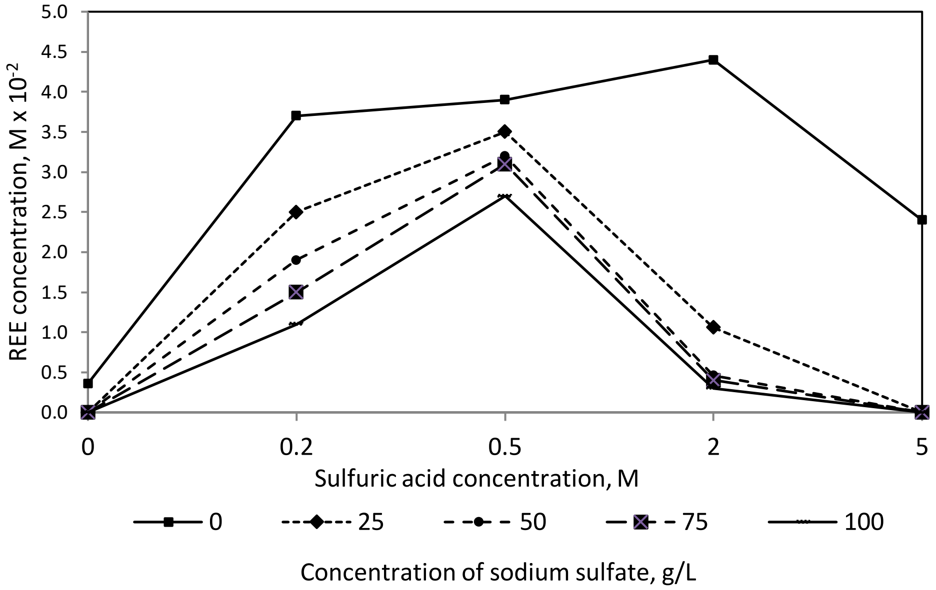


Figure 2-8: REE solubility in sulfuric acid at various sodium sulfate concentration, summarized from (Lebedev 2003)

It can be understood from the above discussion that rare earth sulfates chemistry is dominated by complex hydrated species. The solubility of these complexes generally decreases with increasing temperature and decreases with an increase in sulfuric acid concentration. The latter is due to the common ion effect. Higher REE solubility also results from conditions of high dilution and low pH. However, deviation from general solubility patterns is common for rare earth sulfates due to the formation of hydrated compounds which have different properties. The existence of various hydrated complexes in solution is brought about by the labile nature of rare earth sulfates chemistry. The complexity of solution chemistry of rare earth sulphates, which often results in high variability on leaching recoveries, motivated this research work to investigate the use of the organic complexing agent, citric acid, as an alternative lixiviant of sulfuric acid.

2.4 Sulfuric Acid Leaching of Rare Earths from Eudialyte

Earlier studies on the sulfuric acid leaching of eudialyte were made with an emphasis on Zr extraction from the mineral. This is understandable, as Zr is present in higher quantities relative to rare earths by as much as six fold in the mineral concentrate. Thus, there are few studies on sulfuric acid leaching of eudialyte primarily for the leaching of rare earths. The following review therefore looks at the co-leaching of REEs in the sulfuric acid leaching of eudialyte, as this is most relevant to this research work.

The first report on REE leaching from eudialyte was made by Motov and Leshtaeva (1966) where eudialyte was decomposed with 30-52 % sulfuric acid at 170 -200 °C followed by leaching with water. REE recovery in the wash solution was low at 15.1-23.7 %, with the majority retained in the insoluble residue. Y recovery was higher at 50 % at high dilution (Dibrov et al. cited in (Lebedev 2003). To increase REE recovery, the addition of 60 % ammonium sulfate in 50-100 % sulfuric acid was tested but failed to increase REE recovery in the leach solution (Ermakova, Kolenkova et al. 1985).

Conventional single stage treatment of eudialyte concentrate involves leaching at 40-90 °C using 2-4 M sulfuric acid (Lebedev 2002, Zakharov, Maiorov et al. 2011, Zakharov, Skiba et al. 2011). While REE extraction has largely been unmonitored, it can be deduced that for a single stage treatment of eudialyte, REE recovery is low in the leach solution. This is mainly because the high acidity requirement for increased Zr leaching promotes the precipitation of REEs as double sulfates. Thus, to increase REE recovery, a two-stage decomposition of eudialyte was designed (Lebedev 2003). In this procedure, REEs are recovered from the calcium-silica mass which is the leach residue retained after the second-stage leaching of eudialyte concentrate (Figure 2-9). A sodium sulfate background of 20-30 % concentration is maintained at a temperature of 10–20 °C to prevent re-dissolution of REEs into the leach solution (Lebedev 2003). REEs are then leached from the residue by calcium chloride or calcium nitrate for 3 h and filtered. REE leaching yield was reported to be 47-52 % (Lebedev 2002, Lebedev, Masloboev et al. 2012). Higher recovery at 80 % resulted from multiple stage leaching of eudialyte concentrate using recycled sulfuric acid (Lebedev, Shchur et al. 2003). The latter approach is expensive, given the amount of energy required to heat the bulk of the leach solution to recycle sulfuric acid and reconstitute it at the desired concentration (Figure 2-9).

Driven by recent increases in REE market prices, research on REE recovery from eudialyte has undergone a revival. Current investigations are commercially motivated and based on a conventional single stage treatment (Appendix B). A variant process, using sulfation baking at 200-250 °C, followed by water washing, was designed for some eudialyte deposits to maximise recovery of all metal values. Recovery of rare earths from a leach solution is usually obtained using solvent extraction methods, following the removal of major impurities (Schreiber, Marx et al. 2016). These projects report high recoveries, however, process details and parameters have been kept confidential.

Few recent technical studies have looked into the use of low temperature baking and leaching to take advantage of the easy leachability of eudialyte. Room temperature acid digestion of eudialyte concentrate using 10 M of sulfuric acid at 60 min digestion time, followed by water washing, resulted in 40 % LREE recovery and 62 % HREE recovery (Voßenkaul, Birich et al. 2016). The baking of eudialyte middling concentrate at 100-110°C using 2 M sulfuric acid at an L:S ratio of 4:1, followed by water washing at 30° C, provided a higher REE recovery at

90% (Davris, Stopic et al. 2016). REE leaching was instantaneous with 65 % recovery after 1 min, and an additional 30% recovery after 30 min, with recoveries of HREEs and LREEs favoured at a high dilution L:S ratio of 20:1. The high recoveries derived from the latter procedure can be explained by the lower Zr content of the middling concentrate used in the experiment.

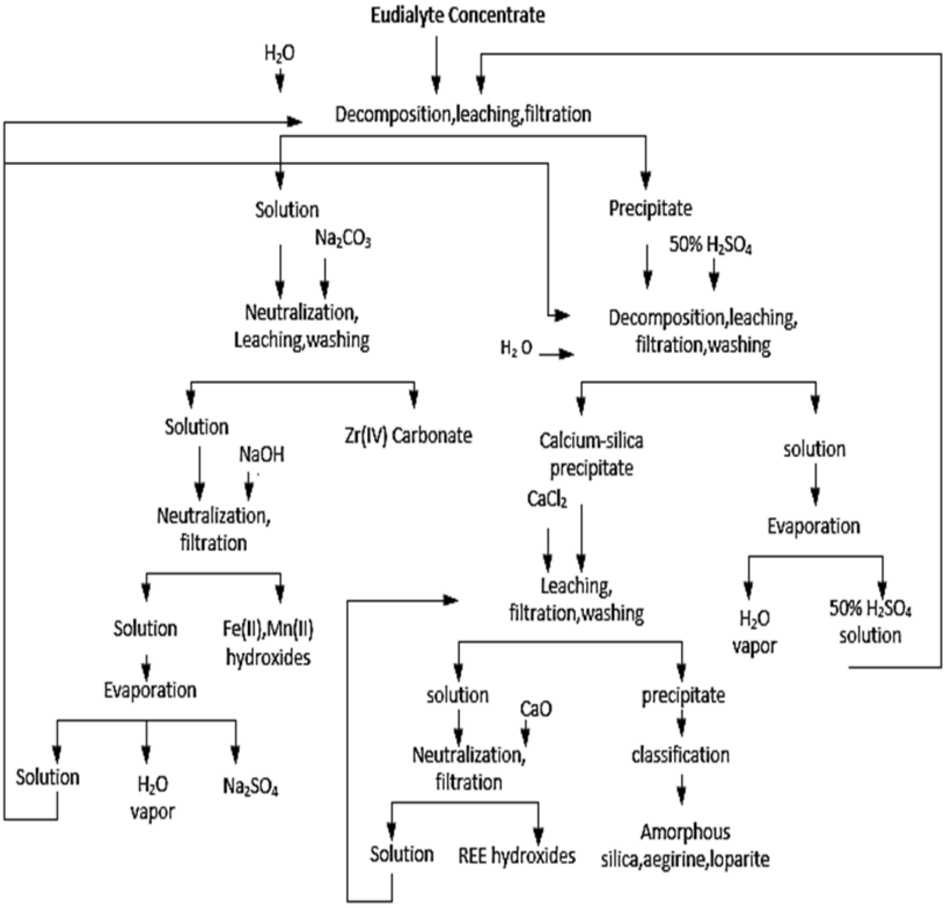


Figure 2-9: Schematic flowsheet for recovery of all metal values in eudialyte including that of REEs which are recovered via leaching of the calcium-silica precipitate (Lebedev 2003)

In summary, the results of early investigations showed that co-leaching of rare earths from single-stage sulfuric acid leaching of eudialyte resulted in low REE recoveries. This required multiple leaching stages of the mineral and the use of high dilution ratios during leaching. Such results are reasonable, considering that the conventional method of eudialyte leaching was designed for the extraction of Zr. In contrast, the few recent studies on REE leaching of eudialyte showed different results. This occurred as the procedures utilised, and the composition of eudialyte material differed. In all these studies, the leaching of rare earths from weathered fine-grained eudialyte minerals has been overlooked. Given the wide variability of eudialyte composition and mineralogy, more research is required to understand the leaching of rare earths, both from large-grained and fine-grained eudialyte minerals.

2.5 Solution Chemistry of Rare Earths in Citric Acid

Citric acid is a weak organic acid with a chemical formula $C_6H_8O_7$. Its IUPAC name is 2-hydroxypropane-1,2,3-tricarboxylic acid and its structural formula reflects a multi-dentate ligand (Figure 2-10). It is a natural food preservative occurring in citrus fruits. It is currently used industrially as a chelating agent as it readily forms complexes with various metal ions (Ozaki, Suzuki et al. 2006).

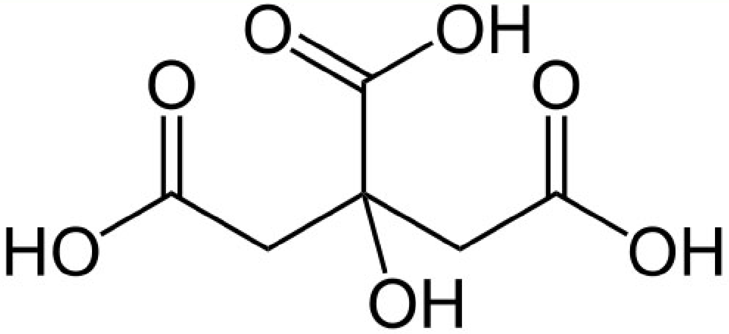


Figure 2-10: Structural formula of citric acid

The first utilisation of citric acid in REE extraction was as an eluting solution, to remove REEs from Amberlite ion exchange resin (Tompkins, Khym et al. 1947). This method paved the way for the separation and production of macro quantities of rare earths, specifically, Ce and Y (Spedding, Voigt et al. 1947). However, the low capacity of the ion exchange method discouraged its commercial application which led to its abandonment in favour of solvent extraction techniques (Kaczmarek 1981).

The solubility of REEs in citric acid is high and the complexes formed are highly stable (Ohyoshi, Ohyoshi et al. 1972, Wood 1993). This is evidenced by the application of citric-based separation of lanthanides from actinides in the partitioning of spent nuclear fuel (Del Cul, Toth et al. 1997).

2.5.1 Effect of pH and concentration

The complex formation of rare earths with citric acid proceeds according to the generalised Equation (2-5) (Brown, Gelis et al. 2012):

$$\boldsymbol{i}\mathrm{REE}^{3+} + \boldsymbol{j}\mathrm{H}^{+} + \boldsymbol{k}\mathrm{Cit}^{3-} \rightleftharpoons \mathrm{REE}_i\mathrm{H}_j\mathrm{Cit}_k{}^{3i+j-3k} \qquad (2\text{-}5)$$

Depending on pH and citric acid concentration, citric acid forms four complexes, namely: H_3Cit, H_2Cit^-, $HCit^{2-}$ and Cit^{3-} (Figure 2-11). Equilibrium studies carried out on ion exchange columns reported that only H_2Cit^- ions are responsible for effecting large separations of rare earths and optimising REE extraction. Separation should be made at pH level of 3.0-3.8 to minimise any interferences from $HCit^{-2}$ and Cit^{-3} ions (Tevebaugh 1947). At a higher pH than the levels mentioned, citrate forms complexes with rare earths, with dissociation constants smaller than complexes formed with H_2Cit^-, and as such the complexes formed are not stable. A summary of REE complexes formed at different ionic concentrations and pH is shown in Table 2-2. Potentiometric studies carried out on La citrates reported that the most stable complex for La citrate is $LaHCit_2^{2-}$, while the non-hydrated forms LaCit and $LaCit_3$ are less stable at pH 2-5 (Brown, Gelis et al. 2012). Different complexes were reported for pH 1.3-2.7 and include LaH_2Cit, LaHCit and LaCit (Barnes and Bristow 1970). These reports consistently noted decreasing stability of La citrates on increasing ionic strength.

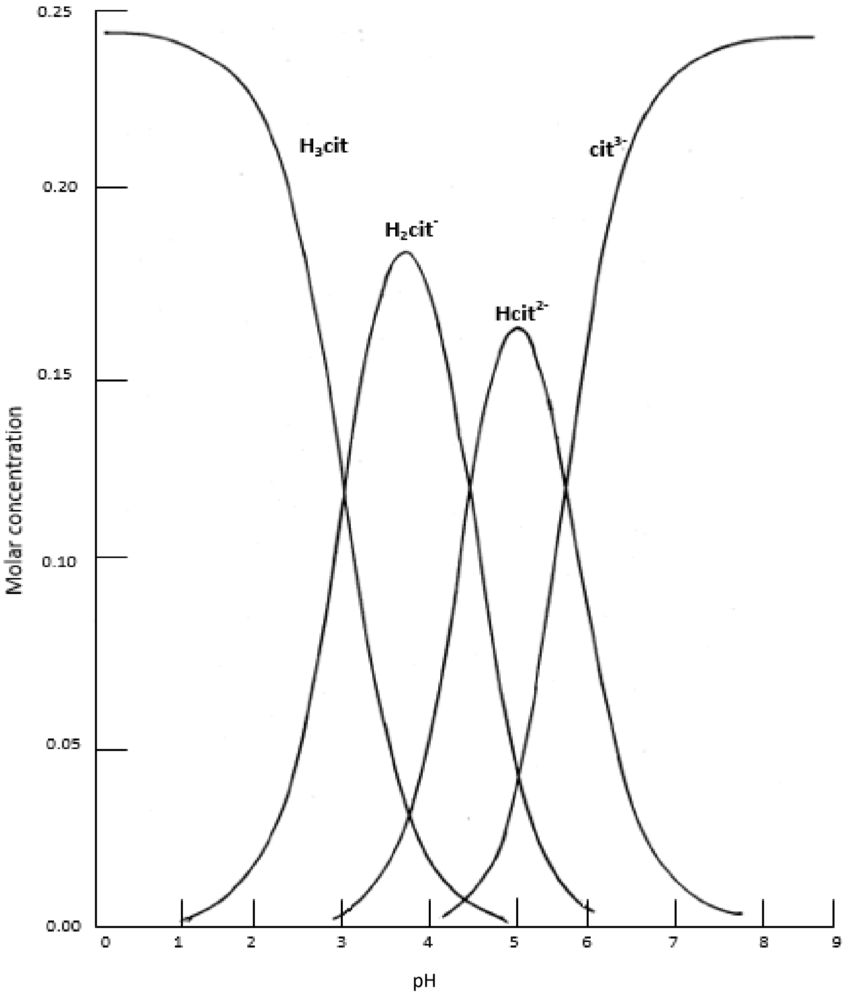


Figure 2-11: Stability graphs of various citrate complexes (H_3Cit, H_2Cit^-,$HCit^{2-}$ and Cit^{-3}) as a function of pH and citric acid concentration(Tevebaugh 1947)

Table 2-2: Summary of reported REE citrate complexes

Ionic strength at 25° C	pH	REE complexes	Reference
0.1-2.5 M	2-5	REECit, $REEHCit^+$, $REEHCit^{2-}$ and $REECit^{3-}$	Brown, Gelis et al. 2012
0.35 M	2.5-5.5	$REEHCit_2^{2-}$	Hubert, Hussonnois et al. 1973
0.1 M	2.0-4.4	REE_2Cit^{2+},$REEH_2Cit_2$, REEHCit, $REEHCit_2^{3-}$	Ohyoshi, Ohyoshi et al. 1972
1.0 M	1.3-2.7	$REEH_2Cit$, REEHCit,REECit	Barnes and Bristow 1970

Rare earth citrate complexes exhibit patterns of increased solubility on low pH, commencing at pH 2 to a maximum pH of 3. For instance, Ce was observed to have lower solubility in a pH solution of less than 2.81 (Spedding, Fulmer et al. 1947, Spedding, Voigt et al. 1947). At pH 3, Y citrate complex is more stable than La citrate (Tompkins and Mayer 1947). The high solubility of rare earths at low pH levels is supported by adsorption and desorption studies of REEs in soil, highlighting the decreased REE desorption at a pH of 3.0-6.5 (Shan, Lian et al. 2002).

2.5.2 Effect of temperature

A study on the solubility of citrate in water as a function of temperature showed that at a citric acid concentration greater than 0.08 M, and at temperatures higher than room temperature, citric acid exists as a hydrate, having increased solubility with increasing temperature (Figure 2-12) (de Kruif, van Miltenburg et al. 1982). Recent citric acid solubility studies support this claim (Oliveira, Malagoni et al. 2013). However, the solubility of rare earths in citric acid depends on the chemistry of the solution and is affected largely by pH and citric acid concentration and much less so by temperature (da Silva, Matos et al. 2008).

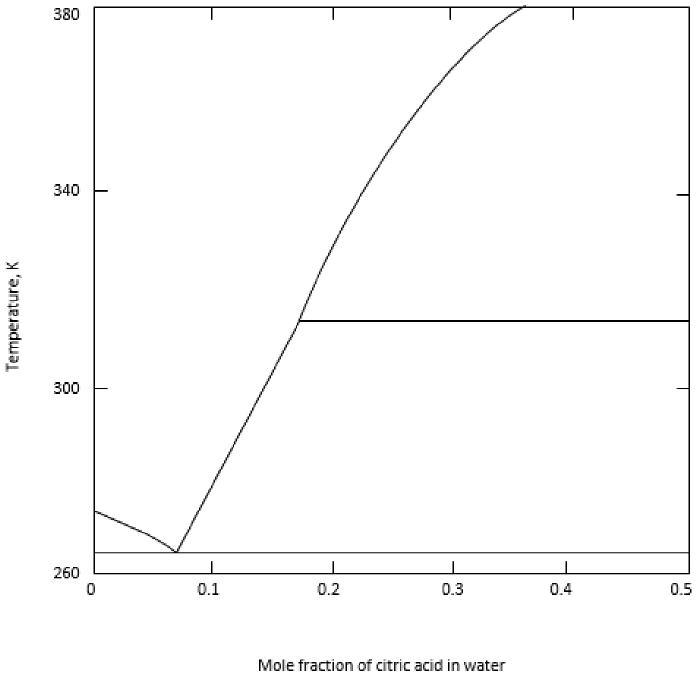


Figure 2-12: Phase diagram on solubility of citric acid (de Kruif, van Miltenburg et al. 1982)

2.6 Citric Acid Leaching of Rare Earths from Eudialyte

There are no known studies on citric acid leaching of REEs from eudialyte. The closest relevant studies are on the use of citric acid on the leaching of REEs from monazite $(La,Ce)PO_4$ and apatite $(Ca,REE)_5(PO_4)_3(OH,F,Cl)$. In these minerals, high REE yields result from the use of a low citric acid concentration of 10 mM (Goyne, Brantley et al. 2010). REE leaching was observed to be directly related to citric acid concentration. It was also reported that REE release is affected largely by the crystal structure of the minerals undergoing dissolution (Goyne, Brantley et al. 2010). However, another study on the use of citric acid on the leaching of monazite showed a contrasting result. Low REE leaching recoveries were reported, even with the use of a higher citric acid concentration of 1 M (Watts 2014). With no available information on its application on eudialyte minerals, but with viable reaction as supported by review of REE-citrate solution chemistry, it is interesting to investigate the potential use of citric acid as an alternative leaching agent to sulfuric acid on REE leaching from eudialyte.

2.7 Chapter Summary

Eudialyte is a zirconosilicate mineral which is characterised by an open crystal structure and by complex chemistry. In effect, rare earth cations easily substitute Na and Ca sites in the mineral crystal lattice. Eudialyte's open crystal structure also explains the inherent variability of its composition and structure and thus how it exists in many variants and textures.

The use of sulfuric acid for the leaching of eudialyte was originally used for the recovery of Zr, and thus REE leaching is poorly understood. There has been recent interest in the area but these studies are commercially driven and focus only on large-grained eudialyte minerals. There is therefore still a great lack of knowledge on REE leaching from fine-grained eudialyte minerals.

A review on REE sulfate solution chemistry showed that stable REE complexes exist in hydrolysed form. The solubility of these complexes is characterised by a positive correlation with dilution and a negative correlation with temperature, pH and sulfuric acid concentration. However, due to the labile nature of REE sulfates, deviation of these trends is common, due to the formation of different hydrolysis products with different solubility properties. These solubility trends will be considered in the design of leaching conditions for the extraction of rare earths from eudialyte.

The use of citric acid for the leaching of rare earths from eudialyte is a novel area of study. Citric acid was used in the early years of REE extraction and reviews of REE-citrate chemistry show that citric acid forms stable complexes with rare earths. The complexes formed can vary considerably depending on the solution pH and citric acid concentration. It has been tested in REE phosphate minerals with contradicting results. It is interesting to evaluate its potential for use as an alternative leaching agent to sulfuric acid in leaching of REEs from silicate minerals such as eudialyte.

Chapter 3

Literature Review Part II

Review of Studies on Leaching of Zirconium and Dissolution of Impurities from Eudialyte

3.1 Introduction

This chapter reviews existing studies on the leaching of Zr, and the co-leaching of rock-forming impurities, along with the deportment of radionuclides in the sulfuric acid leaching of eudialyte. As a major metal component in the mineral, it is important to understand the leaching behaviour of Zr during the sulfuric acid leaching of eudialyte particularly when conditions are modified to favour REE leaching.

The co-dissolution of acid soluble metals is inevitable in the acidic leaching of any mineral, and a review as applied to eudialyte leaching is provided for this purpose. As a major component in the mineral and its ores, emphasis is placed on silica, its co-dissolution and existing methods of management.

There are no known studies on the citric acid leaching of eudialyte. In this respect, the chemistry of Zr in citric acid and the solubility of silica in aqueous solution and in the presence of citric acid is discussed.

3.2 Sulfuric Acid Leaching of Zirconium from Eudialyte

Eudialyte is a minor mineral of Zr and has received attention due to its easy dissolution with mineral acids, as compared to the more refractory minerals of Zr, namely zircon and baddeleyite. Zirconium oxide content varies from 1-3 wt. % in ore to 9-16 wt. % in eudialyte concentrate (Deer, Howie et al. 1997, Lucas, Lucas et al. 2015). Sulfuric acid is the preferred lixiviant over other inorganic acids due to a higher recovery of Zr values (Zakharov, cited in (Lebedev 2003). The generic leaching procedure involves the slow uniform dosing of eudialyte concentrate to 1-4 M sulfuric acid at 40-90 °C, at a L:S ratio of 4:1 to 6:1, and a leaching time of 2-4 h (Dibrov, Chirkst et al. 1996, Lebedev 2003, Lebedev, Shchur et al. 2003, Zakharov, Maiorov et al. 2011, Zakharov, Skiba et al. 2011). Controlled mass loading of eudialyte concentrate into heated sulfuric acid is an important procedure for the prevention of silica gel formation.

Sulfuric acid digestion of unaltered eudialyte minerals occurs through the lixiviation of Zr in the form of Zr^{4+}, as brought about by the lower apparent activation energy of Zr leaching (Chizhevskaya, Chekmarev et al. 1994). Zr lixiviation proceeds at the same rate as silica dissolution, but its kinetics are highly dependent on the sulfuric acid concentration (Chelishchev, Motov et al. 1983). The solubility of Zr sulfate increases with increasing sulfuric acid concentration at high ionic strength due to the formation of various Zr sulfate compounds (Matijević, Watanabe et al. 1969). On low ionic strength however, the solubility of Zr sulfate decreases with increasing sulfuric acid concentration (Beyer 1955).

Although Zr forms various complexes with sulfate ions, these species, like any other Zr complex formed in aqueous solution, are highly sensitive to leaching conditions (Mukherji 1970). Thus, various compositions of Zr sulfate can form in a sulfate leach solution with a slight change in solution condition, and several hydrated forms of the general formula, $Zr(SO_4)_2.nH_2O$ are known to exist (Baes 1976, Rastsvetaeva and Chukanov 2013). The labile nature of Zr in solution also implies that Zr extraction processes are characterised by large variances in metal recovery. Moreover, Zr is prone to hydrolysis reactions owing to its high ionic charge in such a small atomic size (Baes 1976). The complexes formed on hydrolysis are polynuclear. Hydrolysis reactions also form insoluble metal hydroxides. The degree of hydrolysis is affected by pH, ionic concentration and temperature.

The first reported leaching of eudialyte was with the use of 30-52 % sulfuric acid and drying of the resulting gel at 170-200 °C, followed by washing with water where Zr was recovered with precipitation, using ammonium hydroxide (Motov and Leshtaeva 1966). Higher Zr recovery at 80 % resulted from the use of 8-10 folds of stoichiometric acid requirement (Tishchenko & Sidorkina, cited in Lebedev 2002), or the addition of fluoride ions (Motov and Leshtaeva 1966). The fluoride ions enhance the kinetics of Zr leaching. This is effected by converting Zr sulfate ions into Zr fluoride complexes which have a higher solubility in sulfate solution (Dibrov, Chirkst et al. 1996).

The complete digestion of eudialyte is hindered by a covering of dense silica layers on the eudialyte which prevents sulfuric acid diffusion into the mineral surfaces (Lebedev, Shchur et al. 2003). In addition, inherent to the chemical heterogeneity of eudialyte, the presence of refractory metals (Nb, Ta and Ti), as well as the presence of altered eudialyte, contributes to incomplete digestion of the mineral (Lebedev, Shchur et al. 2003, Zakharov, Maiorov et al. 2011). Thus, a single stage sulfuric acid leaching of eudialyte leaves 20-30 wt. % of undigested eudialyte. Use of rigorous leaching conditions with hydrofluoric acid, or sintering with alkali, results in more than 90 % Zr recovery (Zakharov, Maiorov et al. 2011). Alternatively, comparatively high recoveries ensued from multiple leaching with the use of 10-20 % sulfuric acid concentration for a first leaching of eudialyte concentrate, followed by the use of 50 % sulfuric acid concentration on a second leaching of the refractory portion (Lebedev 2003). Apart from this, a two-stage treatment based on continuous 16-18 h leaching at 80-95 °C has also been applied (Krebs and Furfaro 2014). In this method, the first leaching was carried out at pH 2-3 with less than 1 g/L of free sulfuric acid. The second leaching was conducted at a pH of less than 1 with 30-80 g/L of free acid. These techniques only describe Zr leaching from large-grained eudialyte, as Zr leaching from fine-grained eudialyte minerals has received scant attention.

The above discussion relates to favourable conditions for Zr recovery from the sulfuric acid leaching of eudialyte. When leaching conditions are modified to favour REE extraction, Zr recovery is relatively low. A leaching procedure which is based on baking eudialyte concentrate at 100-110 °C with an acid dosage of 0.4 g/g, followed by water leaching at 30 °C for 30 min with L:S ratio of 20:1, results in 58 % Zr recovery, with a reduced recovery of 38 % at a low L:S ratio of 2:1 (Davris, Stopic et al. 2016). More information is needed on how Zr leaching is affected on preferential leaching of REEs from eudialyte, both from large-grained and fine-grained variants.

As outlined above, the leaching of Zr from eudialyte by sulfuric acid is relatively straightforward, with high recoveries of 50-90 %. The major limitation is the effect of silica in forming gel in solution and its effect in hindering leaching reactions. The role of silica in eudialyte leaching is discussed in detail in the following section.

3.3 Citric Acid Leaching of Zirconium from Eudialyte

There are no known studies on the use of citric acid in the leaching of Zr from eudialyte, as the hydrometallurgical processing of the mineral has always been approached with the use of inorganic acid. This is due to the inherent refractoriness of Zr's major minerals. Citric acid has only been applied to the extraction of Zr from ion exchange resins where Zr forms anionic complexes with citric acid (Mukherji 1970). This process was carried out in the 1950s, following the successful application of the same technique in the production of rare earths (Oliver 1958). It was reported that maximum Zr recovery was achieved with 5 % citric acid at pH 1.8, with decreasing recoveries on increasing pH levels to a maximum tested pH of 6 (Brown and Rieman 1952). The change in the solubility of Zr in citric acid was a function of the active citrate complex present for a particular pH (Tompkins, Khym et al. 1947).

Similar to its application with rare earths production, ion exchange was abandoned in favour of the more cost-effective solvent extraction technique.

In acidic conditions, Zr forms a precipitate with carboxylic acids and its solubility is controlled by the precipitate (Kobayashi, Sasaki et al. 2008). In citric acid solutions, the reported Zr hydrolysis products include sol-gels (Zhang, Gao et al. 2015) and colloids (Venable and Lineberry 1922).

3.4 Silica Management in the Leaching of Eudialyte

The biggest concern in the hydrometallurgical treatment of any siliceous ore is the co-dissolution of large amounts of silica which readily form silicic acid. This can easily coagulate and precipitate out of solution. Silicic acid is known to have a deleterious effect on subsequent processes such as: a reduction in the filtration rate, decreased recovery of valuable metals by precipitation of silica on mineral surfaces thereby inhibiting surface reactions, and reduced solvent extraction efficiency due to the formation of interfacial films and/or stable emulsions (Ritcey 1980, Terry 1983a). In eudialyte processing, digestion is limited to 60-70 %, due to the incongruent dissolution of silica (Dibrov, Chirkst et al. 1996) and/or the covering of silica gel on eudialyte mineral surfaces (Zakharov, Maiorov et al. 2011).

The reactivity of silica during the leaching process of siliceous ore largely depends on silica structure, and the properties of metal cations associated with silica (Iler 1979). In the acidic leaching of siliceous ore for example, a complete breakdown of silicate structure, with accompanied polymerisation and gel formation, occurs in orthosilicates, pyrosilicates and cyclosilicates (Terry 1983a, Terry 1983b). Only partial dissolution of silica occurs in chain, sheet and framework silica. The difference in reactivity in different silicate structure is related to the easy dissolution of the smaller molecular units (and thus the relatively weaker strength of the Si-O bond) in the former silicate group, as compared to the longer silicate units in the latter (Murata 1943). In addition, the presence of substituting ions in silicate minerals weakens structural bonds and promotes silica dissolution (Murata 1943). As eudialyte has a cyclosilicate structure and contains an average of 23 % Si/mole (Johnsen, Grice et al. 2003), its acidic leaching is always accompanied by risk of silica gelatinisation. The control of silica in the hydrometallurgical treatment of eudialyte is therefore an important procedure in the processing of the mineral.

In the following sections, the solubility of silica, and factors affecting its solubility in sulfuric and citric acid is reviewed, along with the current practices of silica management in the processing of eudialyte.

3.4.1 The chemistry of siliceous species in solution

Silicate gangue minerals are co-dissolved in acid in the form of soluble silica, which is a generic term that includes silicic acid, silica polymers and colloidal silica. Initially, the dissolution of silica in aqueous solution results in the formation of monomeric silicic acid (monosilicic) $Si(OH)_4$ based on the fundamental equilibrium reaction in Equation (3-1) (Iler 1979):

$$SiO_2 + 2H_2O \leftrightarrow Si(OH)_4 \tag{3-1}$$

Sub-units of monosilicic acid are typically in the order of 0.4 nm in size and it only takes a few repeating steps to form oligomeric silicic acid (polysilicic or cyclic) by the polymerization of monosilicic acid, according to Equations (3-2) to (3-4) (Miller, Readett et al. 1997):

$$Si(OH)_4 + Si(OH)_4 \leftrightarrow (H_4SiO_4)_2 \tag{3-2}$$

$$Si(OH)_4 + (H_4SiO_4)_2 \leftrightarrow (H_4SiO_4)_3 \tag{3-4}$$

$$Si(OH)_4 + (H_4SiO_4)_3 \leftrightarrow (H_4SiO_4)_n \tag{3-5}$$

Depending on system conditions (pH, presence of salts, temperature), polysilicic acid grows in size according to the steps outlined in Figure 3-1(Iler 1979). Molecular silica can grow into colloids and then into free-settling size depending on the number of silica particles and the size of the particles (Figure 3-2). Colloidal silica is the most problematic form of colloid as it impedes solid-liquid separation by forming an array that blocks fine particles (1-5 µm) from settling (Iler 1979). The presence of colloidal forms of silica should be avoided, if not managed, in the leaching of eudialyte.

The above discussion provides an understanding on the dissolution of silica and its form in aqueous solution. It is important to review in depth the factors affecting silica solubility and chemistry in solution.

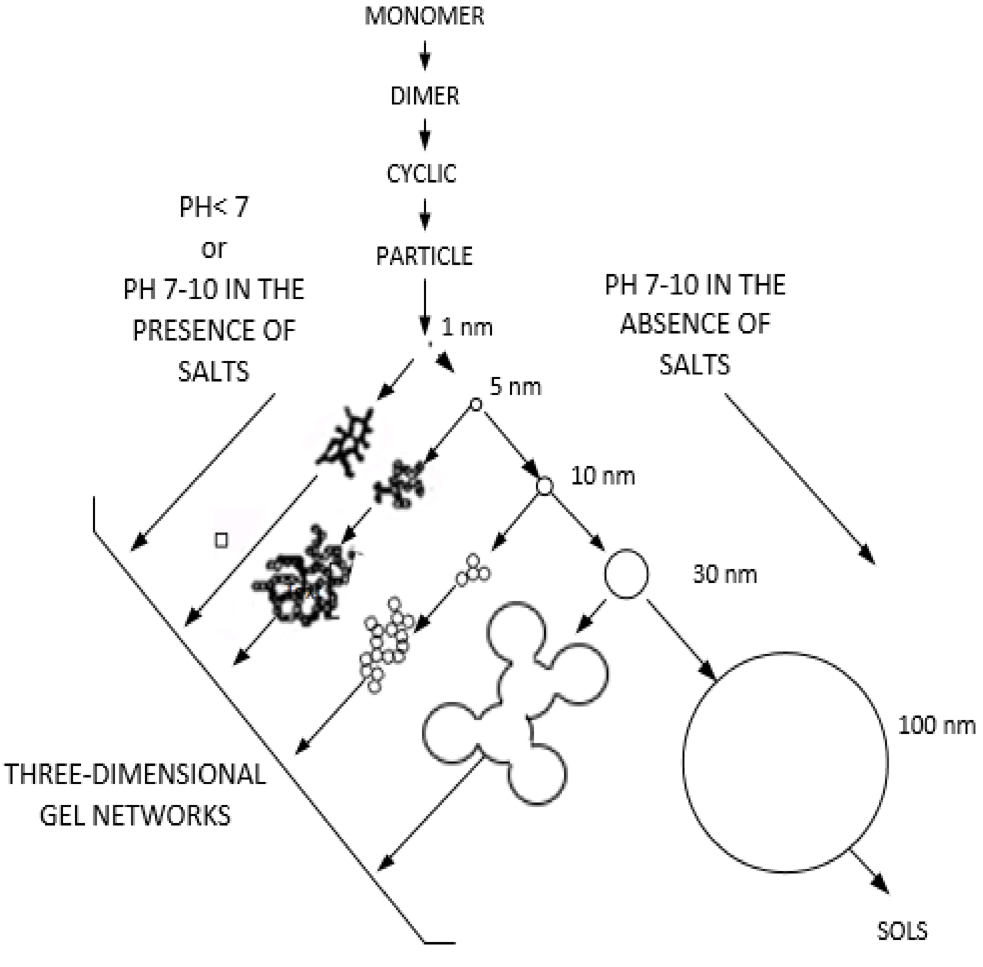


Figure 3-1: Stages of silica polymerisation in acidic and alkaline solution (Iler 1979)

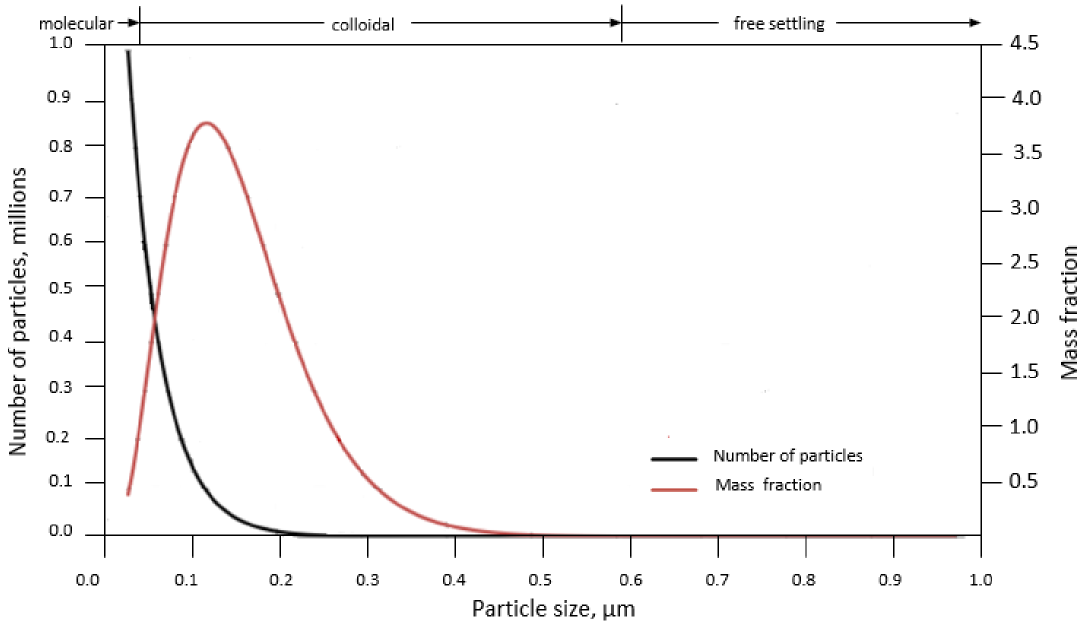


Figure 3-2: Forms of silica size as a function of particle size (Iler 1979)

3.4.2 Effect of factors affecting the solubility of silica

Factors affecting silica polymerisation are temperature, pH, time, agitation and the presence of metal ions which can easily promote polymerisation; e.g. Fe and Al (Murata 1943, Iler 1979). The effects of these factors are discussed below.

3.4.2.1 Effect of pH

The solubility graph of amorphous silica as a function of pH shows silica solubility in the range of 100-200 ppm at pH 1–8, with a marked increase at pH 9-10 (Figure 3-3). Improved silica solubility at high alkaline conditions is related to the formation of another silicate ion $Si(OH)_6^{2-}$ which has higher solubility properties than silicic acid (Alexander, Heston et al. 1954).

The degree of ionisation of silicic acid in solution affects polymerisation. Monosilicic acid exists in non-ionic form at acidic to neutral pH, after which ionisation commences past the neutral pH point. The degree of ionisation then increases from 10 % at pH 8, with silicic acid existing as $(HO)_3SiO^-$ ion, to 50 % at pH 10, with silicic acid converted to divalent anion $(HO)_2SiO_2^{2-}$ (Sheikholeslami, Al-Mutaz et al. 2002).

Colloidal silica is stable at a pH of 1.8-2.0 (Iler 1979). Above this range, colloidal silica grows by Ostwald ripening and below this pH, it grows by accretion and collision between particles (Iler 1979). Nucleation and growth by aggregation of silica particles generally increases with pH (Bałdyga, Jasińska et al. 2012).

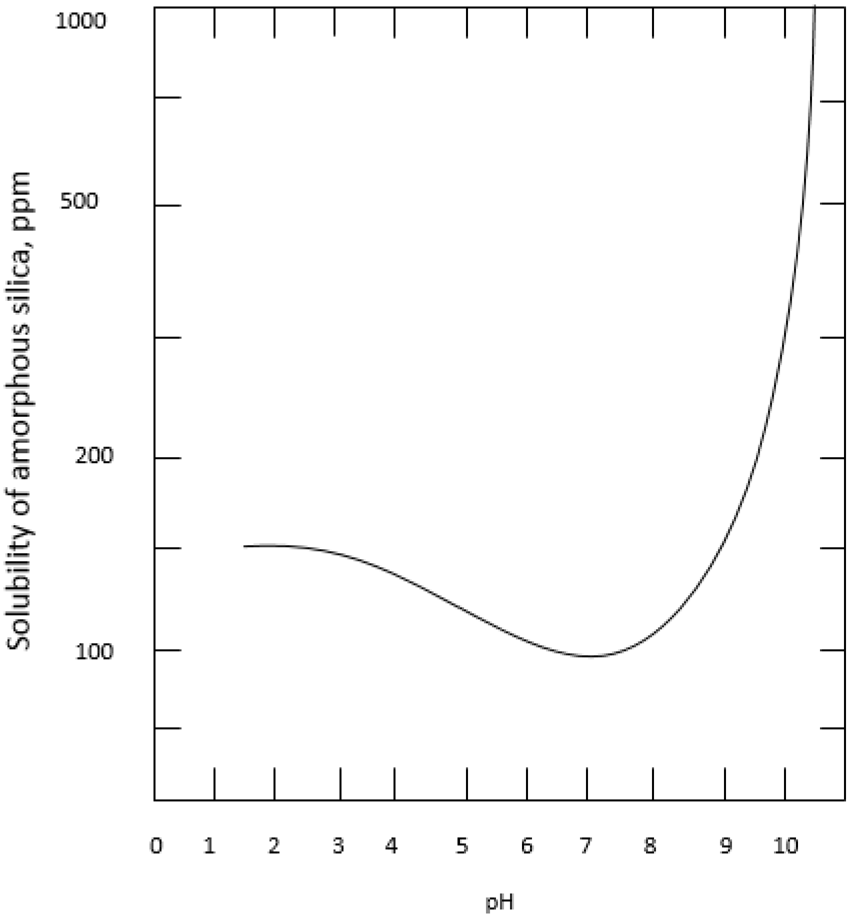


Figure 3-3: Solubility of silica as a function of pH at 25 °C (Alexander, Heston et al. 1954)

3.4.2.2 Effect of temperature

The solubility of amorphous silica increases with temperature, brought about by increased kinetic energy at higher temperatures (Figure 3-4) (Fournier and Rowe 1977). Silica polymerisation and nucleation is kinetically controlled with high rates of formation at high temperatures, compensated for by increasing solubility at high temperatures (Sheikholeslami, Al-Mutaz et al. 2002). The solubility of amorphous silica also increases with temperature at any pH range (Figure 3-5) (Okamoto, Okura et al. 1957).

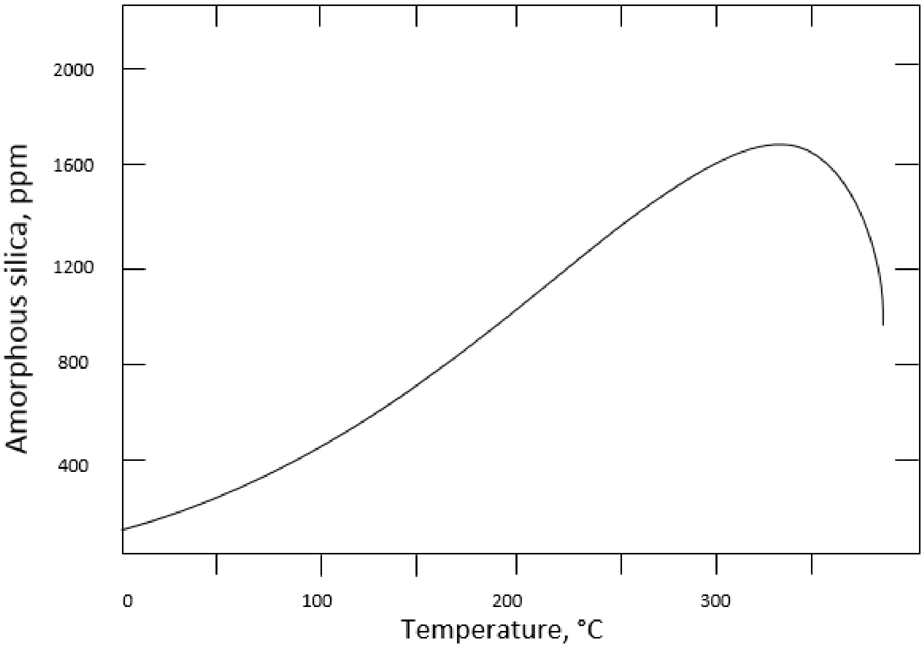


Figure 3-4: Solubility of amorphous silica as a function of temperature (Fournier and Rowe 1966, Fournier and Rowe 1977)

3.4.2.3 Effect of stirring

Depending on the ratio of vessel diameter:stirrer diameter and the design of the stirrer, stirring speed can affect silica form in solution. For example, mild stirring with the use of magnetic stirrers at a speed below 380 rpm at 25 °C does not cause stirring-induced aggregation of silica colloid, but it becomes noticeable at over 380 rpm (Li and Kaner 2005). At a low stirring speed, stirring increases the solubility of amorphous silica in the absence of salt ions, but this effect can reverse in its presence (Mustafa and Sheikholeslami 2003).

3.4.2.4 Effect of sulfurous ions

Silica dissolution and polymerisation is faster in sulfuric based solutions, compared to chloride and nitrate systems, as demonstrated by Iwasaki, Shimada et al. (1980). In their study, sulfate ions enhanced the dissolution rate of amorphous silica by reducing the zeta potential caused by the adsorption of sulfate ions onto the silica surface (Bai, Urabe et al. 2009). Among the sulfurous ions, bisulfite HSO_3^- and sulfite SO_3^{2-} anions have higher silica solubility compared to sulfate ions SO_4^{2-} . This is due to the "salting in" effect which results in the formation of stable sulphite-silica complexes (Marshall and Chen 1982, Gallup 1997, Bai, Urabe et al. 2009).

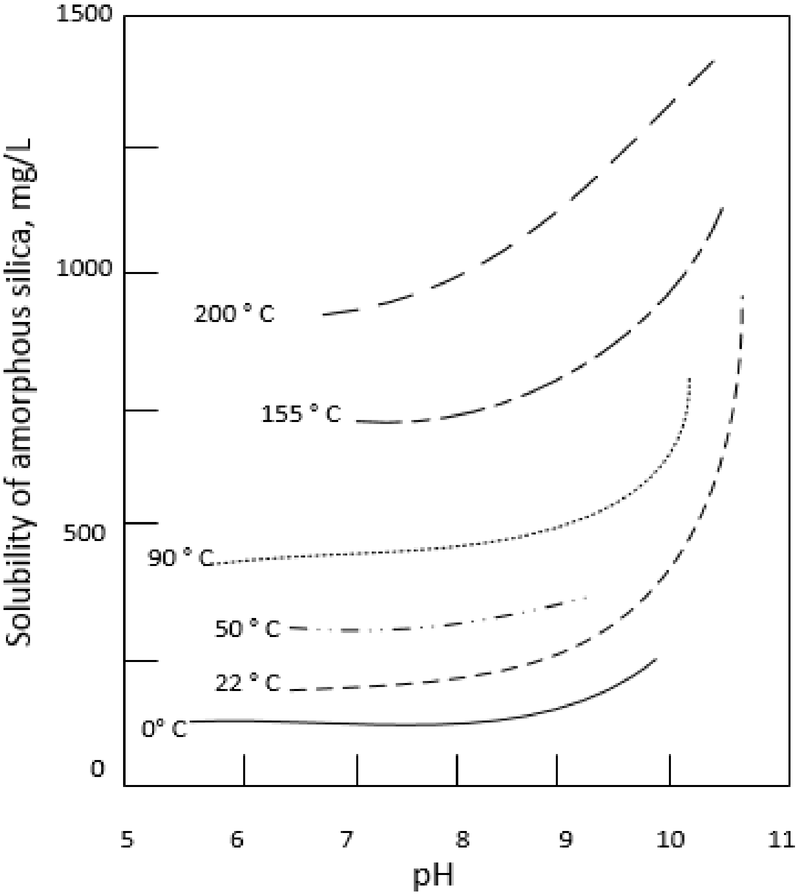


Figure 3-5: Solubility of amorphous silica at various temperatures as a function of pH (Okamoto, Okura et al. 1957)

3.4.2.5 Effect of citrate ions

The dissolution of silica by citric acid occurs by chelation with the carboxyl ion (-COOH) and the process is characterised by slow kinetic reactions (Kong, Huang et al. 2014). A leaching study supports this in that silica dissolution did not commence after 15 min, even at an elevated leaching temperature of 50° C (Umeda and Kondoh 2008).

The solubility of silica in citric acid is relatively low, as active citrate anions exist in a pH range where silicic acid also exists as anions (Plettinck, Chou et al. 1994).

3.4.3 Current practices of silica management in the sulfuric acid leaching of eudialyte

Eudialyte is a cyclosilicate mineral which readily decomposes in acid. During leaching, the silica fragments form a polycondensed gel with very long coagulation times. For example, eudialyte digestion ceased after 10 min while silica coagulation had not been achieved after 3 h (Chizhevskaya, Chekmarev et al. 1994). The rate of silica dissolution slows down over time (Chekmarev, Chizhevskaya et al. 1993). Thus, the classical method of managing dissolved silicic acid is to manage the polymerisation reactions such that the silicic acid formed can precipitate in filterable form. This approach is usually carried out by the control of mass loading. This is where eudialyte is gradually added into heated acid, while the pH is maintained at 1.0-1.9, to limit the amount of dissolved silica and to prevent the formation of colloidal silica (Lebedev 2003, Short, Apelt et al. 2015). Alternatively, the gradual dosing of acid may also be utilised to ensure that the rate of silica precipitation is faster than the rate of dissolution (Furfaro and Krebs 2014).

The same strategy with a different method may be used. One such method is the addition of acid in multiples of the stoichiometric requirement to increase nucleation sites for silicic acid formation, and facilitate silica dissolution at 40 °C (Lebedev, Shchur et al. 2003) or at ambient temperature (Voßenkaul, Birich et al. 2016). In cases where increased Zr recovery is required, the addition of F ions, known for their catalysing effect on silica dissolution (Mitra and Rimstidt 2009), is carried out at molar ratios of $F^-:Zr^{4+}=3$ (Dibrov, Chirkst et al. 1996).

However, this method suffers from safety issues related to the handling of highly corrosive hydroflouric acid.

Dehydration of sulfate mass is another technique used to limit silica dissolution. In this method, a gel is formed when eudialyte is mixed with acid. It is then heated until it dries, and washed with water (Motov and Leshtaeva 1966). This approach is effective in limiting silica dissolution, but it has high energy requirements.

The alteration of silica properties is another procedure used for the prevention of silica gel formation in solution. The digestion of eudialyte at 100 °C in the presence of 2 M sulfuric acid converts silica into insoluble secondary precipitate (Davris, Stopic et al. 2016). A similar effect is produced by the heat treatment of eudialyte at 1000-1400 °C, followed by air quenching and digestion with sulfuric acid (Friedrich, Hanebuth et al. 2016).

Overall, approaches to the silica management on sulfuric acid leaching of eudialyte involve a particular method or a combination of methods. These include: alteration of the leaching conditions; modification of silica properties; dehydration of silica by limiting the amount of water in the system, or utilising highly strong acidic leach solutions. The applicability of the approaches mentioned is dictated by the mineralogy of the eudialyte mineral used. For example, low temperature digestion of eudialyte which contains 20-30 % SiO_2 (Voßenkaul, Birich et al. 2016) was effective, but higher temperature digestion was applied for eudialyte which contained 50-60 % SiO_2 (Davris, Stopic et al. 2016). Where the abovementioned described methods do not suffice, a final silica removal step may be taken by the use of flocculants and/or coagulants. These can aggregate colloidal silica to free-settling size range, as in the proposed hydrometallurgical processing of eudialyte from Kvanefield deposits (Furfaro and Krebs 2014).

3.5 Co-dissolution of Impurities

Impurity management is a major consideration in the recovery of rare earths from eudialyte minerals. The acid leaching of rare earths is always associated with the co-dissolution of acid consuming species, mainly sodium aluminium silicates and Fe, Th and U. This is particularly true in the case of eudialyte which contains high levels of substituting Al and Fe. This weakens the Si-O bond and renders eudialyte susceptible to dissolution and gelatinisation (Murata 1943). Alkaline earth cations indirectly enhance the rate of dissolution by modifying the interfacial solvent structure via its associated waters of hydration in the order of $Ba^{2+}>K^{+}>Na^{+}>Li^{+}>Ca^{2+}>Mg^{2+}$ (Dove and Nix 1997). Ions that promote the polymerisation of silicic acid (Al,Ca,F,OH,Mo) also promote depolymerisation, once a solution has become unsaturated (Okamoto, Okura et al. 1957).

The major step in impurity removal is done at beneficiation, where a mineral concentrate is produced to separate eudialyte mineral from the bulk of the gangue minerals. In certain cases, physical beneficiation is used for the removal of main impurities, for instance, reverse flotation of aegirine from eudialyte in the processing of the Nora Karr deposit (Forrester, Reveley et al. 2015). On leaching, the conditions are well studied such that minimal impurity co-dissolution occurs.

Selective precipitation is a standard technique applied in the removal of large quantities of dissolved impurities. The solution pH is raised to less than 5.5, commonly 4.5, to precipitate impurities like Fe and Al (Cailly and Mottot 1991).

In some processes, differential solubility is used as a method of impurity management. In the leaching of steenstrupine and eudialyte minerals for example, LREEs' poor solubility in double sulfate solution provides its separation from Fe, Al, Mn and Zn. Though HREEs are less soluble in sulfate medium than LREEs, the leaching conditions are modified to slow down the kinetics of HREE leaching such that HREE is retained in the leach residue with the precipitated LREE to effect REE separation from dissolved impurities (Furfaro and Krebs 2014).

Further solution purification prior to final rare earths product precipitation can be effected through acid re-leaching. Hydrochloric acid re-leaching of metathesis precipitate is carried out at a pH of 3 to minimise Al and Fe re-dissolution (Furfaro and Krebs 2014). This procedure is usually performed in conjunction with solvent extraction, which is normally applied as a final impurity removal step. Th and U are removed via the latter technique (Lucas, Lucas et al. 2015). In the proposed commercial processing of eudialyte, these metals are neutralised from the barren leach solution and ends in the waste product (Chalmers 2016).

3.6 Chapter Summary

Eudialyte is a polymetallic mineral, valued primarily as a minor mineral of Zr. Hence, the approach to the leaching of eudialyte has been one where the recovery of Zr is the main metal of interest. Early investigations revealed that the leaching of large-grained eudialyte is preferably effected with the use of sulfuric acid. This is due to the higher recovery of Zr values at conditions of high acidity and low dilution. Currently, there is no information relating to the co-leaching behaviour of Zr when leaching conditions are modified to favour REE extraction.

The complete recovery of Zr from eudialyte is limited thermodynamically by the saturation of silica in solution or its precipitation on mineral surfaces. Thus, control of silica in the sulfuric acid processing of eudialyte is an important step in the hydrometallurgical processing of eudialyte. The conventional practice of silica management as applied to eudialyte leaching, is the control of mass loading to ensure that the rate of silica precipitation is faster than silica dissolution.

The co-dissolution of large amounts of acid-soluble impurities is an important consideration in eudialyte leaching. In sulfuric acid leaching, the removal of alkali and alkali-earth metals is carried out mainly by pH modification. Increasing the pH level to a near-neutral range precipitates major impurities.

The citric acid leaching of eudialyte is a novel area of research. Information on the co-dissolution of Zr, silica and other impurities on the citric acid leaching of eudialyte is non-existent. Despite this, a review of closely-related studies showed that citric acid forms anionic complexes with Zr at a low pH, and the solubility of silica in citric acid is low, with slow kinetics of dissolution.

The information gathered from this review of related studies will be used in the design of leaching conditions on preferential extraction of REEs from eudialyte.

Chapter 4

Characterisation of Eudialyte Ore Samples

4.1 Introduction

Extreme compositional variation is one of the salient characteristics of eudialyte minerals. This is not surprising given the open nature of eudialyte's crystal structure. Isomorphic substitution of cations and anions is easily facilitated, resulting in the formation of eudialyte variants. While the classification of variation is structural and compositional in nature, eudialyte variants can be texturally categorised as large-grained or fine-grained.

The mineralogical features of any mineral impact upon its leaching behaviour. This chapter aims to discuss the physical and chemical characteristics of the eudialyte ore samples used in this research work. Understanding the mineralogical features of the eudialyte samples will generate vital information relevant to this study. Firstly, the results derived from this material characterisation were used as a basis for the design of leaching, management of silica co-dissolution on leaching and other related procedures of this research work. Secondly, the results supplied useful information in understanding the leaching behaviour of rare earths, as well as the co-leaching behaviour of Zr and other impurities from the mineral. Lastly, ore characterisation findings will define the mineralogical variability of the eudialyte minerals in the ore samples.

4.2 Objectives of the Chapter

This chapter discusses investigations into the following :

- physical and chemical characterisation of REE and Zr mineralisation in the eudialyte samples;
- physical and chemical characterisation of rock-forming minerals in the eudialyte samples; and
- quantitative characterisation of the minerals and elemental components of the ore samples;

4.3 Materials & Methods

4.3.1 Eudialyte ore samples

There were two differently textured eudialyte ore samples used in this research work: (1) kakortokite ore from Kringlerne, Narsaq, Greenland (SG ore) which contained large-grained eudialyte minerals and (2) silicate ore from Dubbo-Toongi (DT ore), New South Wales, Australia which contained fine-grained eudialyte minerals.

4.3.2 Equipment and reagents

Equipment used for the test samples preparation consisted of a Contherm Thermotec 2000 drying oven, an Essa 8-pan rotary splitter, a Sepor riffle splitter (Jones type), an Essa disc pulveriser, a Rocklab ring mill, and a Selfrag laboratory fragmentator.

Laboratory grade sodium polytungstate, NaPT (2.9 g/cm^3, Imbros Pty Ltd), was used as a heavy medium for the separation of eudialyte from the gangue minerals in SG ore.

Analytical grade calcium fluoride, CaF_2 (99.99%, Sigma Aldrich) was used as an internal standard for XRD analysis.

4.3.3 Analytical equipment

Analytical equipment utilised for mineral identification and quantitative analyses was as follows: a Bruker D8 Advance X-ray diffractometer with copper target as an X-ray source, a JEOL JXA-8530F Hyperprobe electron probe microanalyser, an MS Agilent 7700 inductively coupled plasma mass spectrometer, a Panalytical MagiX Fast X-ray fluorescence analyser, a Resonetics M-50 laser ablation coupled to an MS Agilent 7700 plasma mass spectrometer, a TESCAN 3 FE GMU integrated mineralogy analyser with Pulse Tor 30 detector, and a Zeiss Evo 40 XVP scanning electron microscope with energy dispersive spectrometer equipped with a Keithley 480 digital picoammeter.

4.3.4 Preparation of test samples

The ore samples were dried overnight in a drying oven at 100°C. Mixing and splitting of the 20 kg head sample was carried out in an 8-pan rotary splitter. The split sample of 2.5 kg was divided further using a Jones-type riffle splitter. The split sample was mixed thoroughly and rolled in a sample mat where 16 increment samples were retrieved using a sampling scoop which constituted the 600-g final split sample (split A.1.1.1) (Figure 4-1). Intensive mixing and ore sample homogenisation was intended to ensure that representative test samples were produced for material characterisation, in consideration of the mineralogical heterogeneity of eudialyte.

As eudialyte minerals in SG ore were present in a coarsely-grained texture, pulverisation was performed with the use of a Selfrag pulse power fragmentator. This technique breaks rocks along grain boundaries and so minerals are liberated with minimal generation of fine particles (Arribas, Bonilla et al. 2014). The pulverised SG ore was subsequently screened. It was then beneficiated by heavy media separation, using sodium polytungstate as a medium, to produce a mineral concentrate (SG concentrate). Pulverisation of test samples for DT ore was carried out in a disc pulveriser for 3 min. This procedure was the final step of preparation for DT ore. A mineral concentrate could not be produced owing to its extremely fine mineralisation.

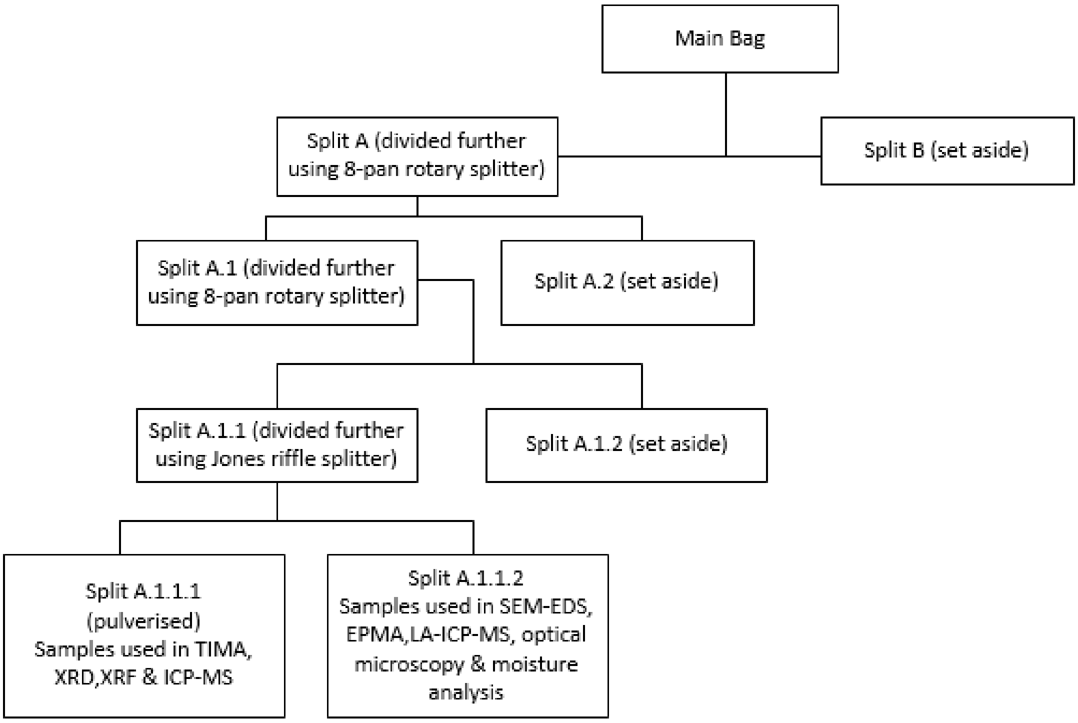


Figure 4-1: Sampling scheme utilized for the preparation of test samples from SG and DT ore

Consistent with the size and weight requirements for the physical and chemical characterisation test methods for the two ores, the pulverised samples from split A.1.1.1 (Figure 4-1) were the samples used for analysis by X-ray Diffraction (XRD), X-ray Fluorescence (XRF), TESCAN Integrated Mineral Analyser (TIMA) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The unpulverised split samples from split A.1.1.2 were used for analysis by Scanning Electron Microscopy – Energy Dispersive Spectroscopy (SEM-EDS), Electron Probe Microanalysis (EPMA), and Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) as well as for moisture analysis.

4.3.5 Physical characterisation of eudialyte ore samples

Hand-picked samples from split A.1.1.2 were mounted on polished sections and examined under a light microscope (Meiji MTL93) using 100-600x magnification lenses for characterisation of physical mineralogical features such as grain size, colour and evidence of alteration.

A 50 g sample of each eudialyte ore, taken from split A.1.1.2 was subjected to moisture analysis by heating the samples masses at 110 °C in a drying oven (Contherm Thermotec 2000) for 8 h.

4.3.6 Chemical and quantitative characterisation of eudialyte ore samples

Determination of rock-forming and REE-bearing minerals in SG ore and SG concentrate were carried out using XRD and SEM-EDS. Fewer analytical techniques were used for the chemical characterisation of SG ore and concentrate due its coarse-grained texture and the high mass content of REE both in the ore and in the mineral concentrate.

In contrast, a number of instrumental analytical techniques were utilised in the chemical characterisation of DT ore, owing to its fine-grained texture. These techniques included XRD, EPMA, SEM, LA-ICP-MS, and TIMA. XRD was used for the determination of rock-forming minerals, while the other four techniques were used for the determination of REE-bearing minerals. EPMA is an established method for compositional spot analysis on small volumes of geological samples (1-9 um^3) and an appropriate method for the detection of REE-bearing minerals in DT ore. However, the use of EPMA in combination with LA-ICP-MS is a recommended technique. This is because the use of the EPMA method alone can produce highly variable analytical results due to the instability of eudialyte under electron beams (Schilling, Wu et al. 2011, Atanasova, Krause et al. 2015). This methodological problem is further complicated by the presence of complex mineral zones in finely textured ore where there is usually overlapping and fusing of mineral grain boundaries (Chakrabarty, Pruseth et al. 2012, Atanasova, Krause et al. 2015). Quantitative analysis by LA-ICP-MS is a complementary technique used to check on EPMA results (Pyle, Spear et al. 2002, Atanasova, Krause et al. 2015). Characterisation of eudialyte minerals in DT ore was also supplemented with TIMA analysis.

Quantitative analysis of elemental composition for the two ore samples was carried out using XRF (PANalytical MagiX Fast). Table 4-1 presents a summary of the various techniques performed for the analysis of the two eudialyte ore samples.

Table 4-1: Summary of analytical techniques for of SG and DT ore

Characterisation test	Ore test sample		
	SG ore	SG concentrate	DT ore
Qualitative examination	Light microscope SEM	Light microscope SEM	Light microscope SEM
Quantitative analysis of rock-forming minerals	XRD	XRD	XRD TIMA
Quantitative analysis of REE- bearing minerals	XRD SEM-EDS	XRD SEM-EDS	EPMA SEM-EDS LA-ICP-MS TIMA
Quantitative elemental analysis	XRF ICP-MS	XRF ICP-MS	XRF ICP-MS

4.3.6.1 Chemical characterisation of rock-forming minerals in eudialyte ore samples

Test samples of SG ore, SG concentrate and DT ore were prepared separately by grinding 30 g of each material in a ring mill for 30 s. A mass of 0.33 g anhydrous calcium fluoride (99.99%, Sigma-Aldrich) was added as an internal standard, along with the addition of 8 mL of ethanol. This was followed by 1min of homogenisation in a microniser. The resulting slurry was then placed into a plastic container and dried at 60 °C. The dried sample was then pulverised manually, using a spatula, and packed into glass slides for mounting onto equipment. XRD analysis was performed on two replicates of each material using the following equipment settings: radiation by Cu$K\alpha$ (λ= 1.54 Å), an angular range of 7-120 ° 2θ, step size of 0.015 °, spinning for 2 s per revolution. The total scanning time was 90 min. Interpretation of XRD results was provided as a technical report by the Centre for Materials Research, Curtin University.

4.3.6.2 Chemical characterisation of REE-bearing minerals in eudialyte ore samples

Determination of REE-bearing minerals in SG ore was carried out with the use of XRD and SEM-EDS. XRD analysis was performed using the same procedure as described earlier in section 4.3.6.1. SEM-EDS analysis was conducted on two polished sections, which contained six pieces of 10-mm SG ore samples. SEM equipment settings were as follows: acceleration voltage of 30 kV, 409 Å spot size and 8.5 mm working distance. Electric current setting for the spectrometer was 100 pA and this was monitored by a digital picoammeter.

The determination of REE- bearing minerals for DT ore was conducted using SEM, EPMA, LA-ICP-MS, and TIMA. Three polished mineralogical sections, which contained nine pieces of handpicked 5-mm DT rock samples, were coated with 5 nm of carbon coating for SEM examination. During analysis, the SEM accelerating voltage was set at 20 kV, the beam spot size was 450 Å and a working distance of 8.5 mm was observed. SEM was utilised mainly to map the location of REE-bearing minerals in the polished section, in preparation for subsequent EPMA and LA-ICP-MS analysis.

The excitation voltage for EPMA analysis was 20 kV, the beam current was set at 50 nA, the beam diameter at 1 μm and the scanning time was 60 s. Wavelengths and standards used were: La $L\alpha$ (LaPO4),F $K\alpha$ (Durango apatite),Cr $K\alpha$ (Cr),Eu $L\alpha$ (REE1), Zr $L\alpha$ (Zircon),Ce $L\alpha$ (CePO4),Mg $K\alpha$ (springwater olivine),Er $L\alpha$ (ErPO4),Mn $K\alpha$ (Spessartine),Nb $L\alpha$ (CaNb2O6),Pr $L\alpha$ (PrPO4), Al $K\alpha$ (Corundum),Tb $L\alpha$(TbPO4),Fe $K\alpha$ (magnetite),Nd $L\alpha$ (NdPO4),Si $K\alpha$ (wollastonite),Tm $L\alpha$ (TmPO4),Dy $L\alpha$ (DyPO4),Th $M\alpha$ (ThO2),Sm $L\alpha$

(SmPO4),P (LaPO4),Yb $L\alpha$ (YbPO4),Hf $L\alpha$ (Zircon),Gd $L\alpha$ (GdPO4),Y $L\alpha$ (YPO4),Ho $L\alpha$ (HoPO4),Ca $K\alpha$ (wollastonite),Lu $L\alpha$ (REE2),Ti $K\alpha$ (rutile),K Kα (orthoclase),Na Kα (albite) and Zn $L\alpha$ (ZnO). The analysis of light anion F, and that of light cations K and Na, was carried out prior to the analysis of other elements. This procedure is recommended in order to minimise the errors associated with the diffusive volatility of light elements which commonly occurs in microprobe analysis (Goldstein, Newbury et al. 2003). The results were exported into MS Excel from the Probe Software (V.9.X) interphase.

A complementary technique for the determination of REE- bearing minerals of DT ore was devised using LA-ICP-MS. Measurements were performed on a 193-nm excimer laser ablation system, coupled to a mass spectrometer. Equipment was set to a frequency of 5 Hz and a spot size of 5 µm. The ablated material was analysed in low resolution mode with Ar as a carrier gas. The analysis time limit was set at 60 s which included 30 s of background time and 30 s of sample ablation time. An NIST 610 standard glass, using Si^{29} was used as an internal reference standard. Data was collected and exported to MS Excel.

An additional complementary technique used to determine REE-bearing minerals in DT ore was carried out by means of a TIMA with a Pulse Tor 30 detector. A liberation type of analysis was used in high resolution scanning mode, using 25000 eV beam energy, 5.81 nA beam current, 18.51 beam intensity, a spot size of 52.32 nm and a working distance of 15 mm. Data analysis was performed using TIMA software V.1.5. In this method, a mounted sample of DT ore was scanned under the conditions stated above and this created a reference profile of the eudialyte in DT ore.

4.3.6.3 Chemical analysis of eudialyte ore samples

The elemental components of the two ore samples were analysed by an independent laboratory, UltraTrace Pty Ltd (National Association of Testing Authorities member, Canningvale, Western Australia). Pulverised samples of SG ore, SG concentrate and DT ore from split A.1.1.1 (Figure 4-1) were sent to the commercial laboratory in which glass bead-

XRF was used for analysis of the following elements: Al_2O_3, CaO, Fe_2O_3, K_2O, MgO, MnO, Na_2O, Nb_2O_5, P_2O_5, SiO_2, Ta_2O_5, TiO_2 and ZrO_2 . Sodium peroxide fusion followed by ICP-MS was performed for the analysis of REEs.

4.4 Results and Discussion

4.4.1 Physical characterisation of eudialyte ore samples

SG ore was provided as 10-mm crushed high grade kakortokite ore (Figure 4-2, left photo). The ore had a moisture content of 0.1 % and contained coarsely textured eudialyte minerals which were easily beneficiated by heavy media separation. In this method, the ore was separated into three mineral fractions. White aegirine minerals with a density of 2.5-2.7 g/cm^3 floated and formed as the topmost fraction. Red eudialyte minerals with a density of 2.7-3.1 g/cm^3 remained as the middle fraction. Black arfvedsonite minerals with a density of 3.3 - 3.5 g/cm^3 sank and constituted the bottom fraction (Figure 4-3). The mineral fraction distribution after heavy media separation of the -540 µm screen lot was (wt. %): arfvedsonite 28, eudialyte 25 and feldspar 47.

Figure 4-2: Photo images of SG ore (left) and DT ore (right)

In contrast, DT ore was provided as 5-mm crushed ore (Figure 4-2, right photo) and was observed to be highly weathered. This was evidenced by the presence of altered feldspar minerals (e.g. traces of visible kaolinite). The ore appeared mottled - bearing green, black and pink spots and had fine-grained mineralisation such that beneficiation of its eudialyte minerals was not pursued. The ore contained 1% moisture.

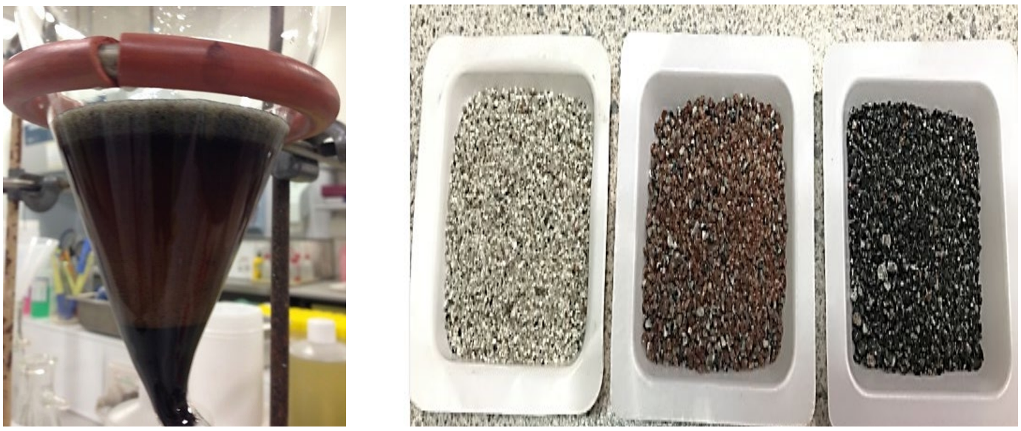


Figure 4-3: Photo images of SG ore beneficiated via heavy media separation (left) and mineral fractions recovered as red eudialyte minerals, black arfvedsonite minerals and white aegirine minerals (right)

4.4.2 Characterisation of rock-forming minerals in SG and DT ore

XRD analysis of SG ore showed that its rock-forming minerals were nepheline, acmite, albite and microcline (Table 4-2). The ore contained 85 % Si-bearing minerals, 11 % amorphous minerals and 4 % phosphate minerals. These were largely removed by heavy media separation such that the rock-forming minerals left in SG concentrate were acmite, mejillonesite and Na-Ca-Al sulfide silicates. These rock-forming minerals have densities close to eudialyte, hence their presence in SG concentrate. The amorphous content had doubled in the SG concentrate, attributable to both non-crystalline and unrecognised phases in the SG ore sample. The SG concentrate contained acid-consuming silicate minerals, dominated by a high Na content. The presence of these acid-soluble species is expected to affect the REE leaching of eudialyte, particularly in increasing the potential for silica polymerisation on leaching. Acmite, for instance, is a cyclosilicate which is known to decompose totally in acid (Terry 1983a).

Table 4-2: Comparative XRD analysis of SG ore, SG concentrate and DT ore

Mineral	**Chemical Formula**	**Average Phase Abundance, wt %**		
		SG ore	**SG con**	**DT ore**
Acmite	$NaFeSi_2O_6$	11.0	11.0	-
Aegirine	$NaFe^{+3}Si_2O_6$	-	-	8.2
Albite	$NaAlSi_3O_8$	9.0	-	40.5
Analcime	$NaAlSi_2O_6H_2O$	4.0	-	-
Anorthoclase	$NaAlSi_3O_8$	6.0	-	-
Ca-Aluminium Oxide	$Ca_{12}Al_{14}O_{32}$	-	-	0.5
Dolomite	$Ca_{1.14}Mg_{0.86}(CO_3)_2$	-	-	1.7
Eudialyte	$Na_{15}Ca_7Fe_3Zr_3Si(Si_3O_9)_2(Si_9O_{27})_2(OH)_2Cl_2$	17.5	55.5	nd*
Magnesio-arfvedsonite	$Na_3(Mg,Fe)_5Si_8O_{22}(OH)_2$	4.1	-	-
Mejillonesite	$Na_{0.93}Mg_{2.08}(PO_3OH)(PO_{4)1.06}(OH)_{0.86}0.95H_5O_2$	4.1	6.1	-
Microcline	$KAlSi_3O_8$	9.1	-	27.1
Na-Ca-Al Sulfide Silicate	$Na_{6.4}Ca_{1.4}Al_6(SiO_4)_6S_{1.6}$	11.0	4.1	-
Nepheline	$K_{1.43}Na_6(AlSiO_4)_8$	13.1	-	-
Omphacite	$NaCaMgAl(Si_2O_6)_2$	-	-	2.0
Quartz	SiO_2	-	-	17.1
Amorphous content		11.1	23.3	2.9

**not detected in the sample, eudialyte present in DT ore is not in the database and is an unkown variety of eudialyte and thus was reported as part of the amorphous material*

Visual examination through SEM showed that the rock-forming minerals in the SG concentrate were coarsely-textured with well-defined grain boundaries (Figure 4-4).

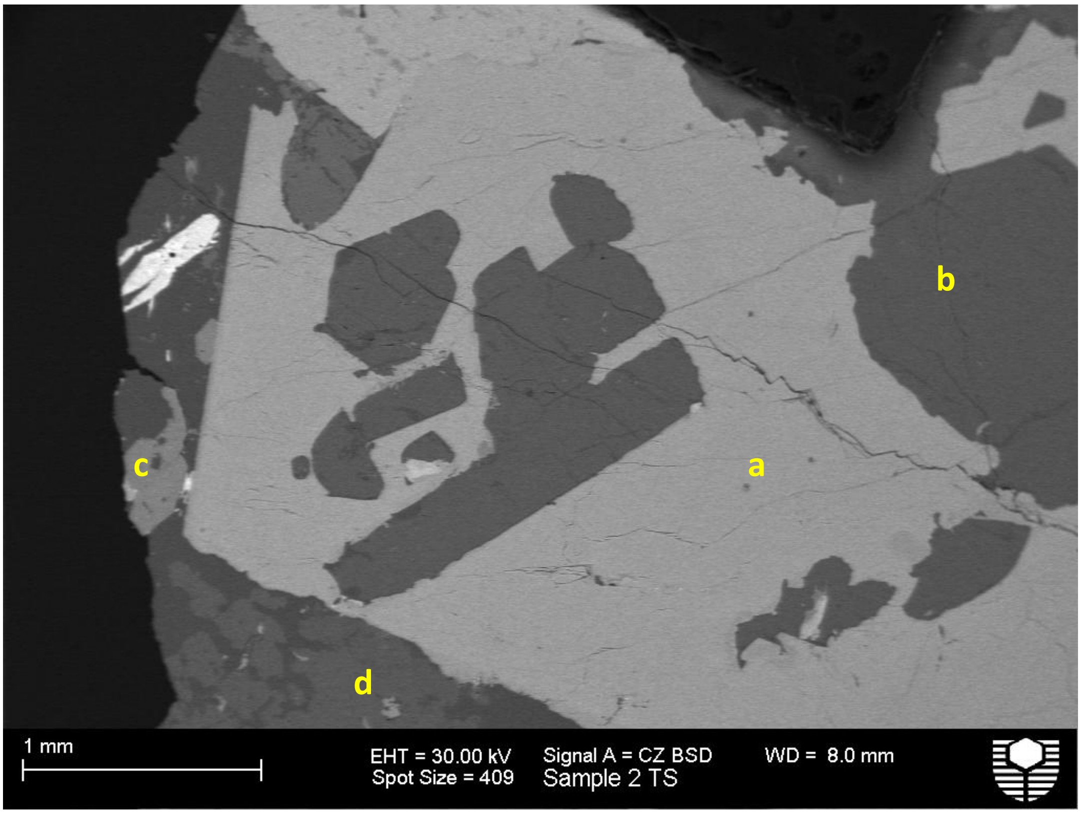


Figure 4-4: Backscattered electron image of SG ore showing (a) large eudialyte grains and major rock-forming minerals (b) nepheline, (c) albite and (d) microcline

XRD analysis of DT ore showed that its rock-forming minerals were albite, microcline and quartz (Table 4-2). The ore contained 95 % Si-bearing minerals and 3 % amorphous minerals, with the remainder being carbonate minerals. Thus, the DT ore contained more Si-bearing minerals than the SG concentrate, but with a lesser risk of silica polymerisation on the acidic leaching of DT ore. Albite, microcline and quartz are tectosilicates which only partially decompose under acid attack (Terry 1983a). The host rock minerals are shown in Figure 4-5 as dark-coloured components of the backscattered electron image of the DT ore sample.

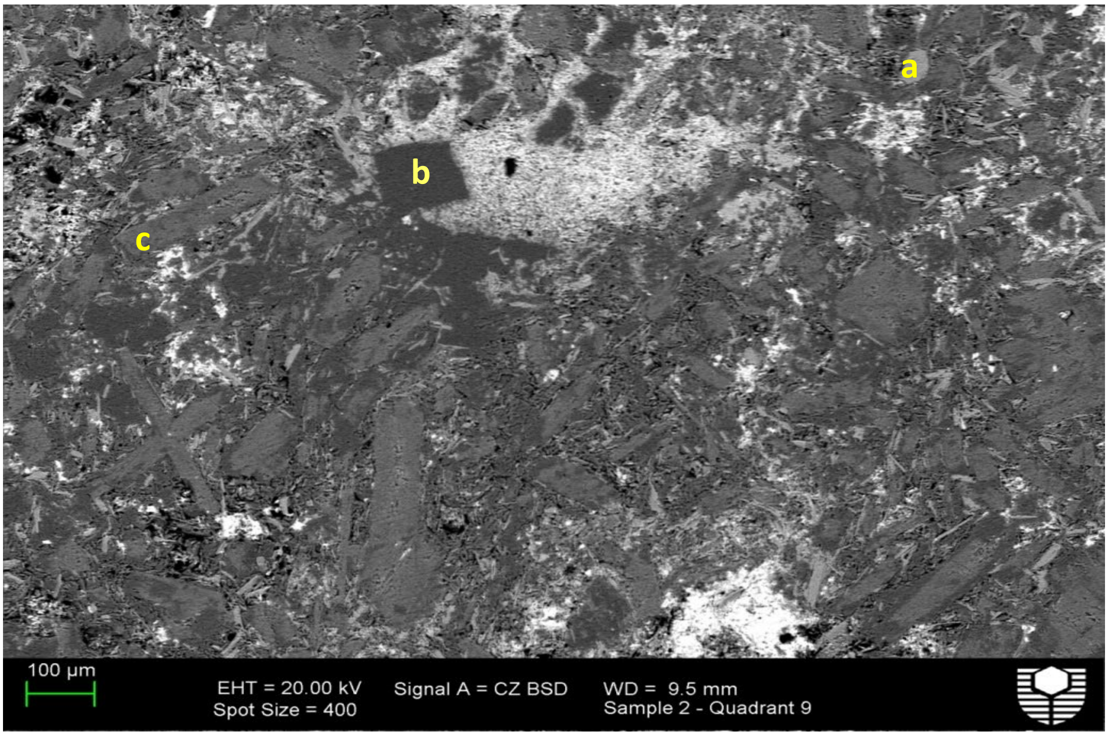


Figure 4-5: Backscattered electron image of DT ore showing rock-forming minerals (a) albite, (b) quartz and (c) microcline, shown as dark-coloured minerals in this micrograph

Qualitative SEM examination of mounted DT ore samples revealed scattered tabular grains of aegirine, prismatic microphenocrysts and noticeable incipient alteration of alkali feldspar to albite. DT ore was also observed to be highly altered, as evidenced by the display of complex mineral growth zones, overlapping grain boundaries and the presence of altered feldspar minerals (Figure 4-6). This evidence of alteration is consistent with geological reports of the deposit which noted that the trachyte base was severely weathered and altered (Love 1982, Warren, Barron et al. 1999). Furthermore, a recent study on the geology and genesis of the Dubbo-Toongi rare metal deposit confirmed the occurrence of mineral alteration in the deposit (Spandler and Morris 2016).

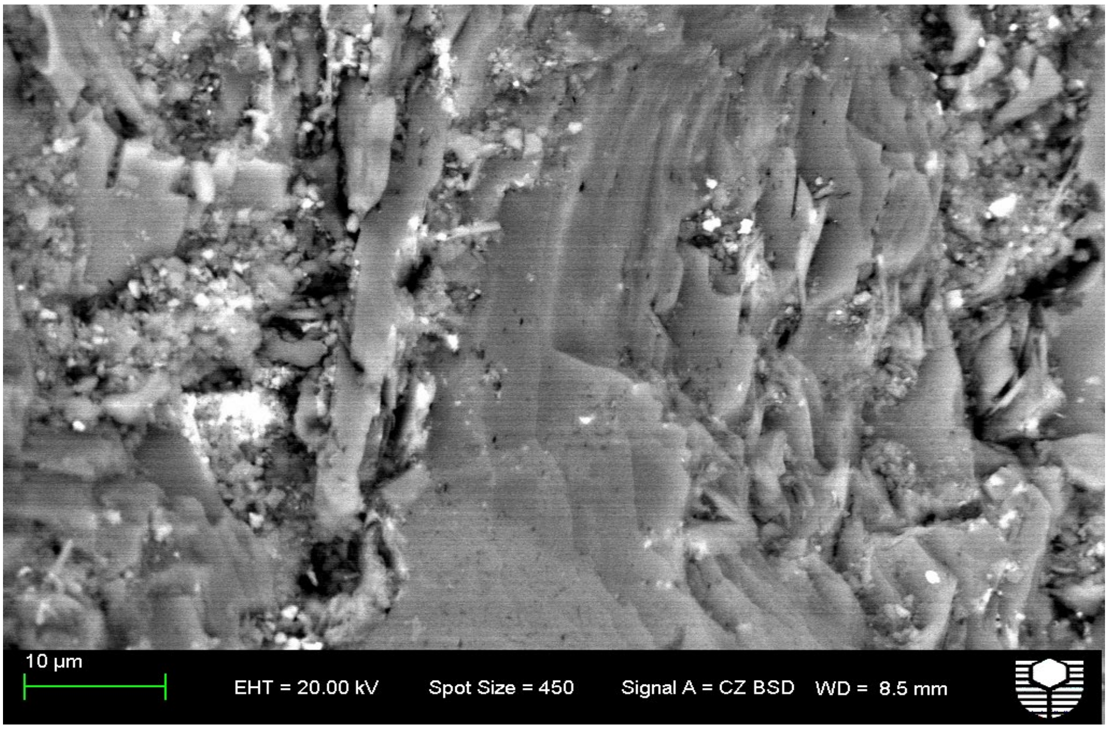


Figure 4-6: Backscattered electron image of DT ore showing complex growth zones and presence of fine clay minerals

4.4.3 Characterisation of eudialyte minerals in SG ore

Quantitative XRD analysis showed that SG ore contained 17 wt. % eudialyte, with increased concentration to 55 wt. % in SG concentrate (Table 4-2). XRD analysis indicated that the eudialyte mineral in SG concentrate has the chemical composition $Na_{15}Ca_7Fe_3Zr_3Si(Si_3O_9)_2(Si_9O_{27})_2(OH)_2(Cl,F)_2$ (Figure 4-7). The closest structural classification of this eudialyte variant is *eudialyte proper* (also known as primary eudialyte) as determined by the atomic ratio of Na:Ca:Fe:Si in the chemical formula. A typical ratio of Na:Ca:Fe:Si ~ 15:6:3:26 for *eudialyte proper* was reported by Golyshev, Simonov et al. (1971). Eudialyte structure of this type is one of the common variants of eudialyte (Appendix C). It is generally characterised by Fe dominating the *M(2)* site and REE substituting Na, Ca and Fe atoms (Rastsvetaeva and Chukanov 2013). *Eudialyte proper* is a cyclosilicate in which the silicate framework readily dissolves in mineral acids (Voßenkaul, Birich et al. 2016). This finding means that the potential of silica polymerisation of SG concentrate on acidic leaching is high.

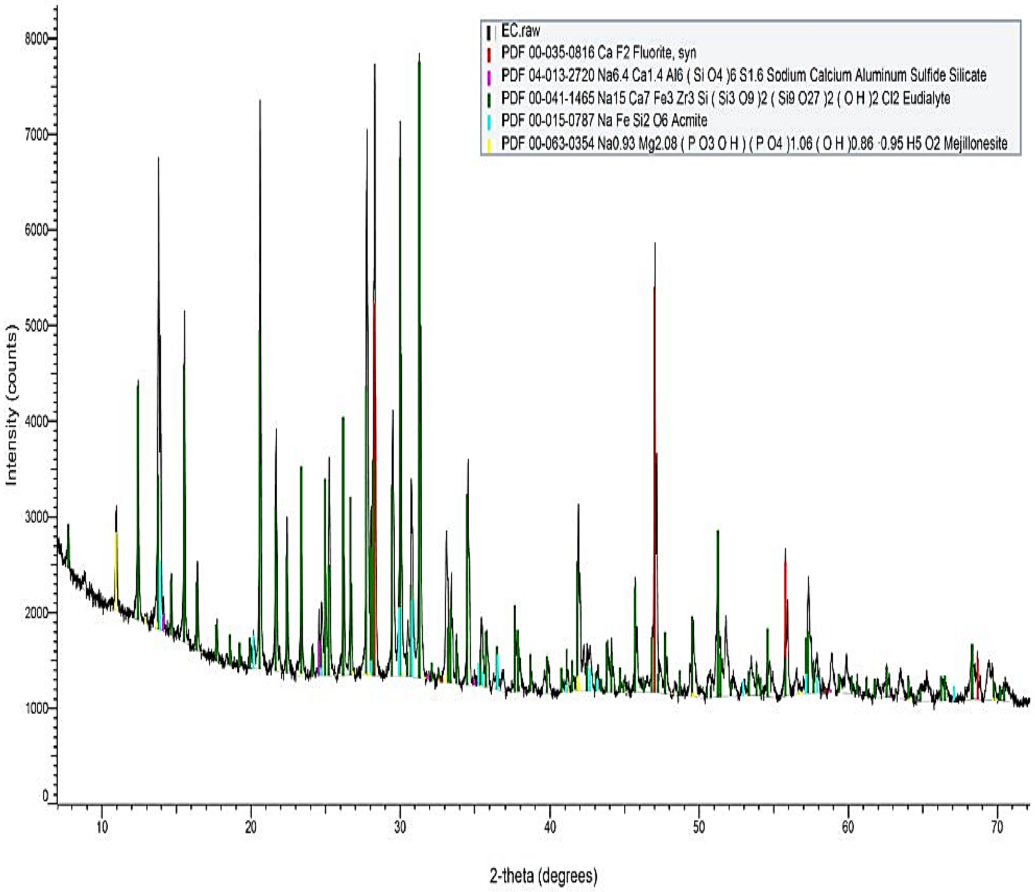


Figure 4-7: Results of XRD analysis of SG concentrate

The eudialyte grains were visible to the naked eye in their classic pink-red colour. In the samples examined under SEM, the eudialyte grains had well-defined grain boundaries, occurring as large crystals greater than 1 mm in dimension (Figure 4-8). There were minor mineral phases Ca-Fe-Al-Na fluorosilicates of unknown chemical composition, also occurring as large grains with an average dimension of 0.3 mm. These unknown phases formed part of the reported amorphous content from the XRD analysis of SG ore. Consistent with other geological investigations from the Greenland deposit, these unknown mineral phases were reported as new minerals. These were derived from a slight alteration of a eudialyte deposit in the Kringlerne locality of the Illimaussaq region of South Greenland (Karup-Moller, Rose-Hansen et al. 2010). REE was mainly hosted in these slightly altered eudialyte phases while Zr was largely found on unaltered eudialyte grains (Figure 4-9).

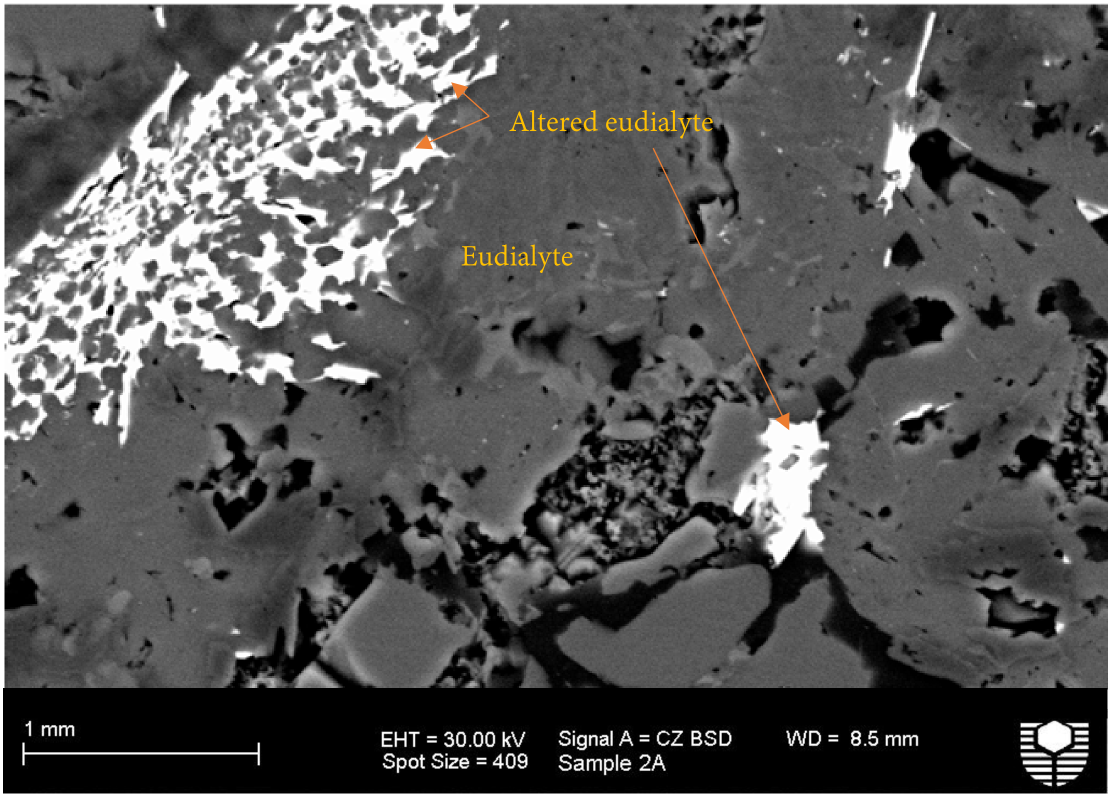
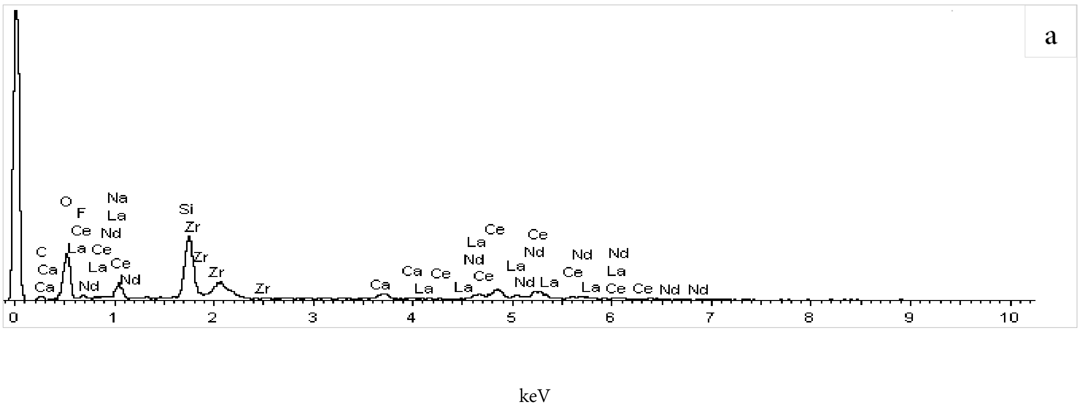


Figure 4-8: Backscattered electron image of SG ore showing unaltered and altered eudialyte grains, REEs were hosted in the latter (Lim, Ibana et al. 2016)



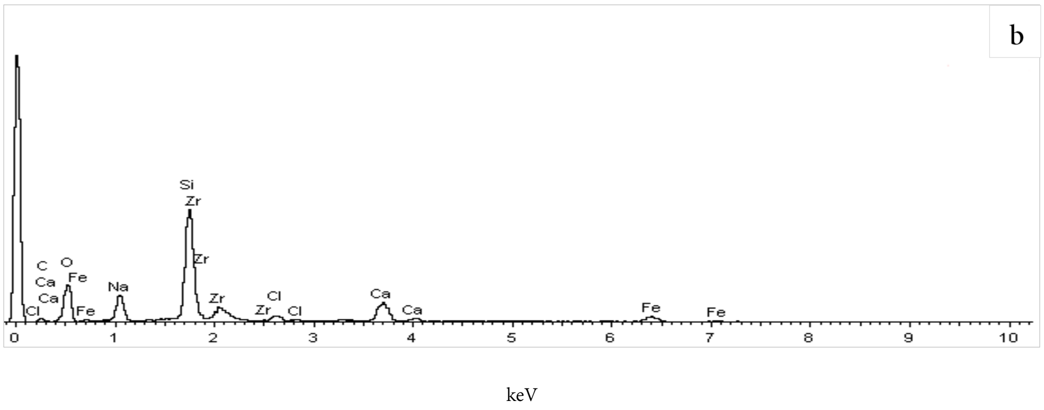


Figure 4-9: EDS spectrum of (a) altered and (b) unaltered eudialyte phases

4.4.4 Characterisation of eudialyte minerals in DT ore

XRD analysis of DT ore was not able to detect eudialyte minerals in the ore, mainly as the detected Na-Ca-Zr phases were not present in the available mineral databases. This is a common difficulty in characterisation of eudialyte minerals, as new variants are always added (Rastsvetaeva and Chukanov 2013) and there is usually a degree of alteration which makes characterisation challenging (Schilling, Wu et al. 2011, Atanasova, Krause et al. 2015).

A combination of supplementary analytical techniques were further utilised for characterisation of REE minerals in DT ore. Qualitative examination by SEM revealed that the Na-Ca-Zr phases in DT ore existed in complex mineral phases which were finely textured at less than 5 µm (Figure 4-10). Examination through an electron microprobe revealed that these Na-Ca-Zr minerals were present as dispersed submicron grains. Some formed porous shapeless aggregates which were interstitial with the neighbouring feldspar and aegirine minerals (Figure 4-11). These fine aggregates were characterised by overlapping grain boundaries and in some cases, the fusing of grain boundaries was observed.

Microprobe analysis also showed that these complex Na-Ca-Zr mineral phases had variable contents of Na, Ca, Mn, Fe, REE, Zr and Nb (Appendix D). The average atomic ratio of Si:Zr was 7. A Si:Zr atomic ratio of 7-10 is characteristic of eudialyte minerals (Schilling, Wu et al. 2011). These Na-Ca-Zr mineral aggregates had a relatively high content of Nb, Mn and Fe as compared to SG ore. A high content of rare metals is an indication of alteration in eudialyte minerals (Coulson 1997).

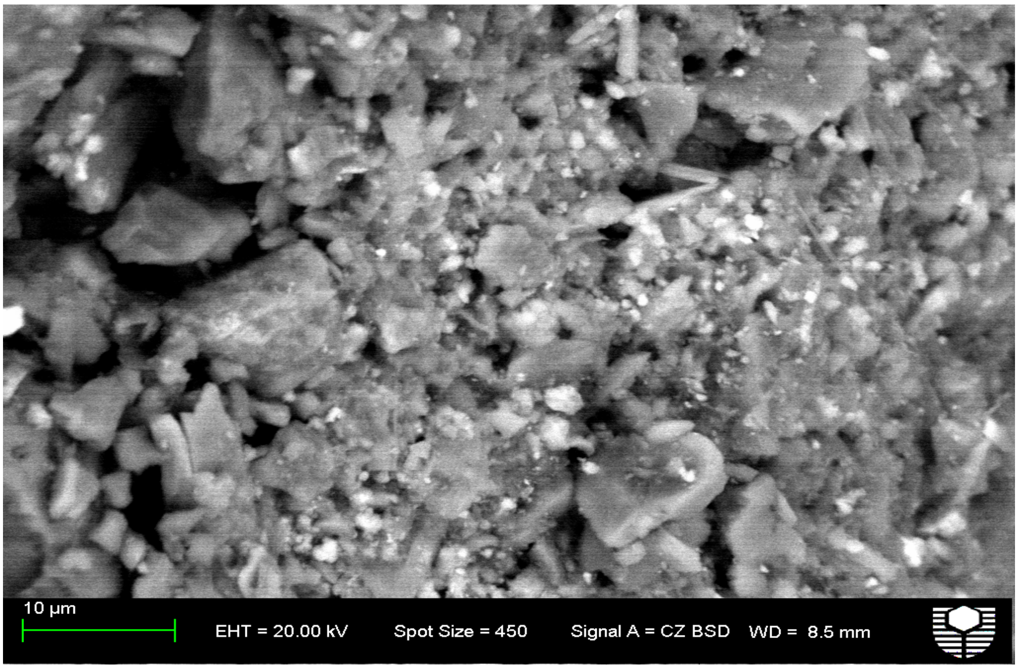


Figure 4-10: Back-scattered electron micrograph of DT ore showing fine-grained complex eudialyte phases (Lim, Ibana et al. 2016)

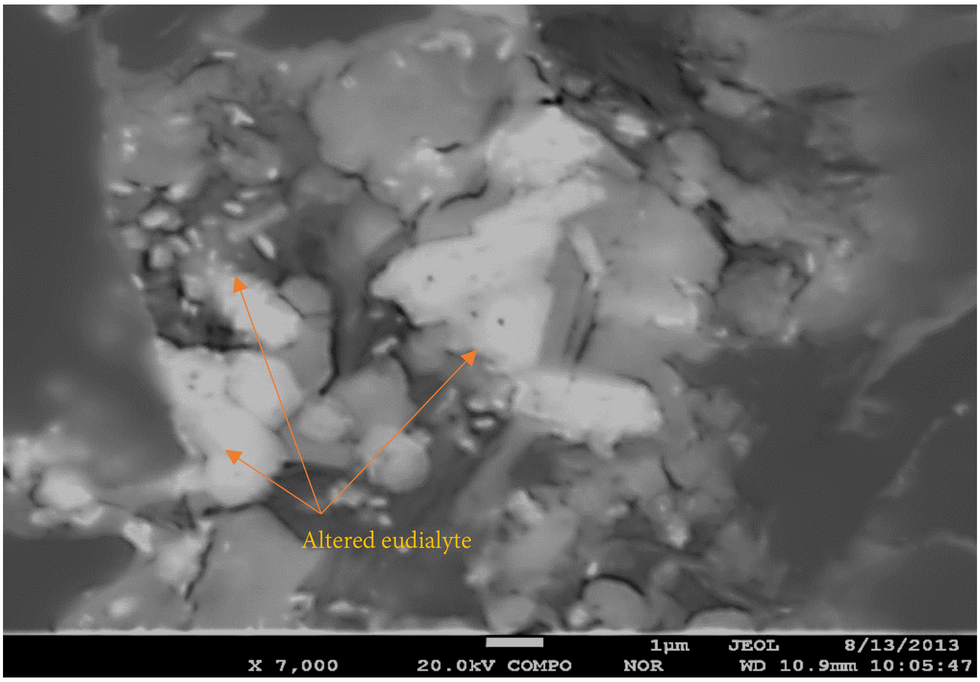


Figure 4-11: Electron microprobe image of DT ore showing fine-grained interstitial eudialyte mineral grains and aggregates (light grey) with undefined grain boundaries

The presence of alteration minerals in a new chemical compositional variety is common for eudialyte minerals. Large eudialyte deposits in Greenland have reported such cases where alteration minerals of unknown composition were found along with the eudialyte minerals (Karup-Moller, Rose-Hansen et al. 2010, Borst, Waight et al. 2014). Similar cases have also been reported for eudialyte deposits in Sweden (Sjöqvist, Cornell et al. 2013), Antartica (Harris and Rickard 1987) and India (Chakrabarty, Pruseth et al. 2012).

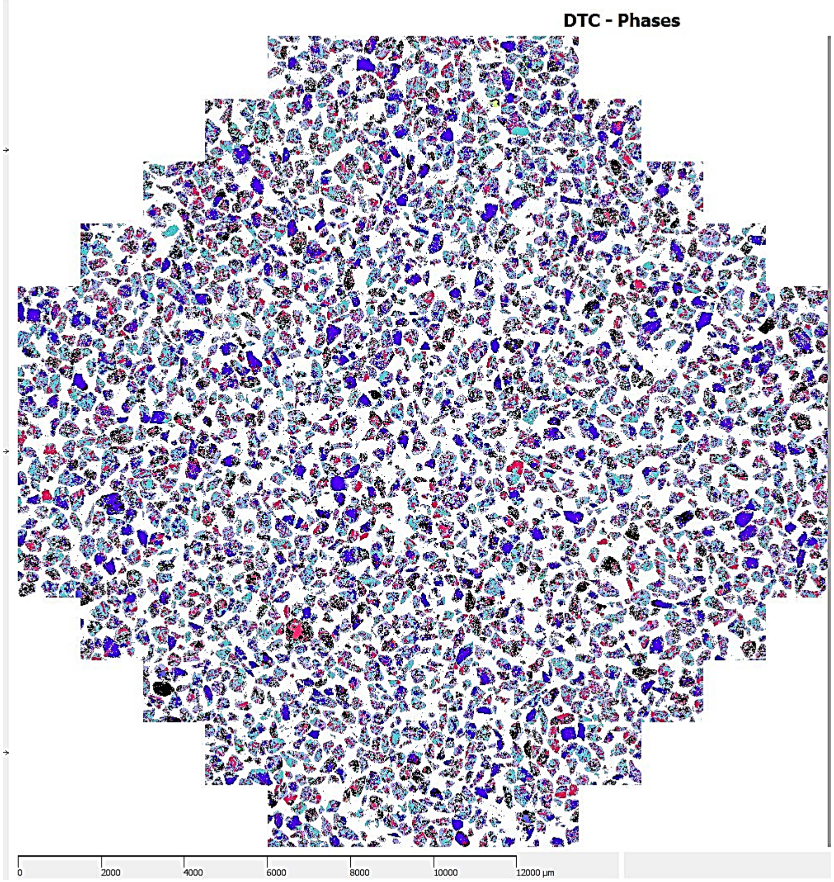
With microprobe analysis, rare earths were detected in these finely textured Na-Ca-Zr phases in mass concentration as follows (%): 0.1-0.7 (Y), 0.2-2.3 (La) and 0.2-3.5 (Ce). The wide range of REE content in Na-Ca-Zr minerals was brought about by the inherent variability in its chemical composition. This was also due to poor spatial resolution owing to the characteristic complex zoning of its finely textured phases. Supplementary analysis carried out by means of LA-ICP-MS showed comparative quantitative results (Table 4-3).

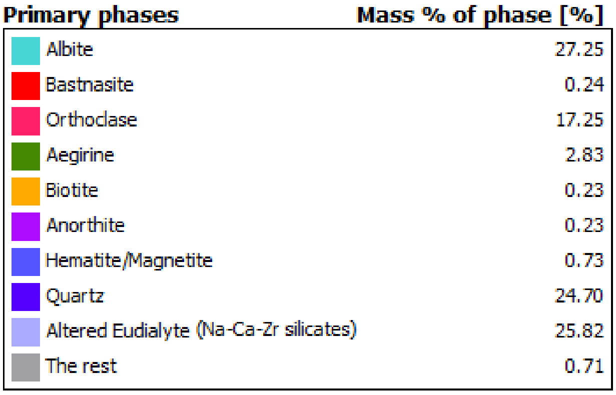
Table 4-3: Comparative EPMA and LA-ICP-MS analysis of REE content in eudialyte minerals of DT ore

REE element	**EPMA analysis (wt. %)**	**LA-ICP-MS analysis (wt. %)**
Y	0.16	0.15
La	0.46	0.37
Ce	0.85	0.61

The chemical composition of Na-Ca-Zr minerals in DT ore did not match any of the known eudialyte minerals. The same conclusion has been reported from the recent geology and ore genesis investigation of the Toongi rare metal deposit (Spandler and Morris 2016). It is an altered eudialyte of unknown composition, characterised by fine-grained mineralisation, and will be generally referred to in this report as Na-Ca-Zr silicate.

A semi-quantitative determination (based on method described in Section4.3.6.2) by TIMA-liberation-type of analysis showed that the altered eudialyte phases in DT ore hosted the majority of REE and Zr values (Figure 4-12). Catapleiite $(Na,Ca,REE)_2ZrSi_3O_9.2(H_2O)$ and bastnasite $(La,Ce)CO_3F$ were determined as minor REE-bearing minerals as determined by microprobe and TIMA respectively.





Primary phases	Mass % of phase [%]
🟦 Albite	27.25
🟥 Bastnasite	0.24
🟥 Orthoclase	17.25
🟩 Aegirine	2.83
🟧 Biotite	0.23
🟪 Anorthite	0.23
🟦 Hematite/Magnetite	0.73
🟪 Quartz	24.70
🟪 Altered Eudialyte (Na-Ca-Zr silicates)	25.82
⬜ The rest	0.71

Figure 4-12: Mineral composition analysis of DT ore by TIMA technique

4.4.5 Quantitative characterisation of eudialyte ore samples

XRF analysis indicated that SG ore contained 0.58 % REO and 3.1 % ZrO_2. Beneficiation of eudialyte minerals by heavy media separation increased the REO content to 1.93 % and ZrO_2 content to 11.1 %. This resulted in a concentration of REO three times that of the original material. LREEs constituted 70 % of the total REO, with Ce being the highest component at 33 % followed by La at 17 %. Y was the major HREE component at 19 % mass concentration.

In contrast, DT ore contained 1 % REO with 81 % LREEs mainly La and Ce, and the remaining 19 % were HREEs, mainly Y. The ZrO_2 content was 1.38 % and silica was the major impurity (Figures 4-13 & 4-14).

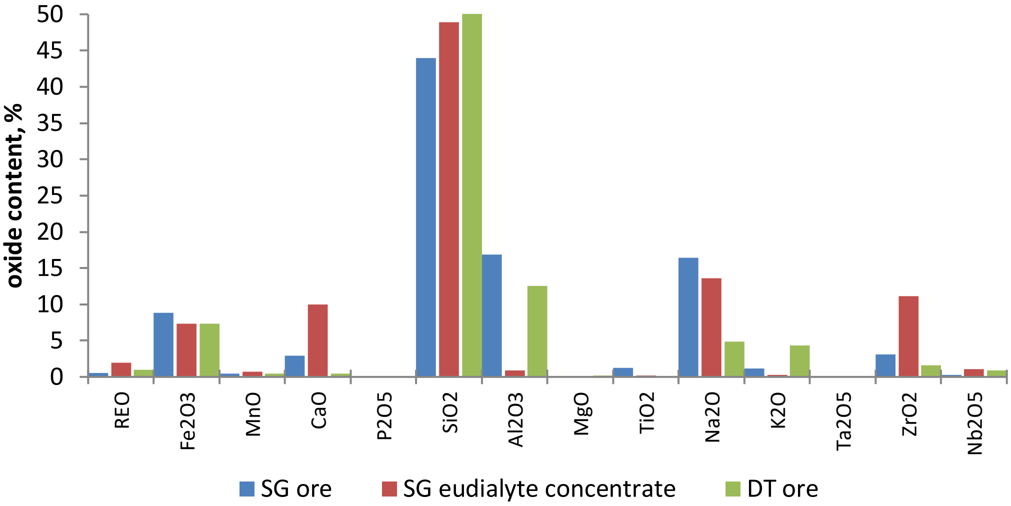


Figure 4-13: Comparative XRF analyses of SG ore, SG concentrate and DT ore

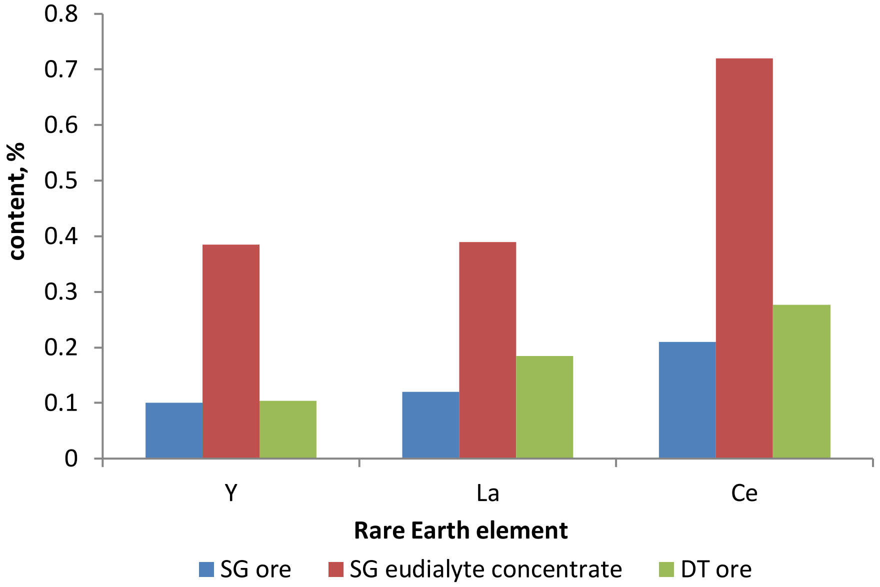


Figure 4-14: Comparative REE content of SG ore, SG concentrate and DT ore

The silica content in DT ore was higher at 64%, compared to SG ore and SG concentrate which were 44 % and 49 % respectively. Against the high content of silica in DT ore, there is a lesser risk of silica gel formation with acidic leaching of DT ore. This is because the major silicate minerals in DT ore were albite and microcline. These silicate minerals only undergo partial decomposition on acid attack (Terry 1983a). The content of potassium oxide was also higher in DT ore by 4 %, compared to SG ore. This could potentially impact REE solubility. K readily forms alkali silicates or alkali sulfates which could produce floating films or trigger REE precipitation by the formation of double salts (Little 1917).

After the beneficiation of SG ore, there was a significant reduction in the amount of aluminium oxide, sodium oxide and iron oxide. However, there was an increase in silica and calcium oxide content in the SG concentrate. The amount of calcium oxide was significantly higher at 10 %, as compared to 0.46 % in DT ore (Figure 4-14). Like many of the alkaline earth metals, Ca reacts with sulfuric acid on leaching and forms partially soluble sulfates, e.g.

gypsum. This can lower REE solubility by co-precipitation of REE with gypsum formation. Notably, the SG concentrate contained Ta and Ti oxides. These compounds are normally refractory to acid attack.

4.6 Chapter Summary

The material characterisation tests carried out on the eudialyte ore samples used in this research work showed that:

- Eudialyte minerals in SG ore existed as large crystals with well-defined grained boundaries. The eudialyte had the chemical composition of $Na_{15}Ca_7Fe_3Zr_3Si(Si_3O_9)_2(Si_9O_{27})_2(OH)_2(Cl,F)_2$ and based on the stoichiometric ratios of the framework elements Na:Ca:Zr:Si which were 15:7:3:25, it closely classified as *eudialyte proper*. For this type of eudialyte variant, REEs are substituting elements in Na, Ca and Fe sites. Thus, it is expected that REE leaching will be accompanied by the co-leaching of these three impurity elements. *Eudialyte proper* variants are cyclosilicates, known to dissolve easily in acid. As a consequence, there is a high potential of silica gel formation on acidic leaching of SG concentrate. Measures for limiting co-dissolution of large amount of silica will be considered as part of the design of the leaching procedure for this material.

- Eudialyte in DT ore occurred in an extremely fine-grained mineralisation of less than 5 μm. The eudialyte minerals were found in complex morphologies, composed of fused and overlapping grain boundaries. It was also found to be altered as evidenced by the high content of rare metals. The atomic ratio of Si:Zr of 7 indicated that it is a eudialyte mineral but the varying content of REEs in the mineral grains could not be used to determine its chemical composition. Thus, it was generally classified as Na-Zr-Si eudialyte. Due to the ultra-fine mineralisation of eudialyte minerals in DT ore, it will be leached as a whole-of-ore. The complex morphologies of these fine-grained eudialyte phases are seen to impact the leachabililty of REEs. For example, it is expected that more rigorous conditions will be required for its leaching compared to SG concentrate in which the eudialyte grains were well-defined.

- REEs were hosted mainly in flourosilicates phases while Zr was hosted in the unaltered eudialyte grains in SG concentrate. The fluorosilicate phases were believed to be products of the slight alterion of eudialyte minerals in SG concentrate. In DT ore, the altered fine-grained Na-Zr-Si eudialyte phases hosted both REEs and Zr. The presence of minerals is common in eudialyte minerals. Such occurrence adds up to the chemical inhomogeneity of eudialyte minerals.
- SG ore contained 0.6 % total REO and 2.3 % ZrO_2 but was easily beneficiated to produce a mineral concentrate with 2 % REO and 11 % ZrO_2. The REO content in SG concentrate contained 36 % Ce, 20 % La and 20 % Y. DT ore contained 1% total REO and 1.4 % ZrO_2. The REO content in DT ore was 28 % Ce, 18 % Ce and 10 % Y. Consistent with the textural differences of the eudialyte minerals in the ore samples, different leaching conditions will be used for each material. For instance, requirements for grind size and acid dosage will be considered appropriately.
- The major rock-forming minerals in SG ore were nepheline, acmite, albite and microcline. The major rock-forming minerals in DT ore were quartz, microcline and albite. The potential for silica gel formation on acidic leaching of SG concentrate is increased further by the presence of its residual rock-forming minerals. Acmite, for example, is another cyclosilicate which totally dissolves on acid attack. In contrast, against the larger sample mass of DT ore on its use as whole-of-ore, there will be lesser chances of silica gel formation. Quartz, microcline and albite are tectosilicates which only partially decomposes on acid attack. Thus, there will be more requirement for silica management on leaching of SG concentrate.
- The larger sample mass of DT ore will mean that it will have higher content of impurity metals Na, Ca, K, Al and silica. This is expected to increase the acid requirements on

leaching. The subsequent co-dissolution of these non-desirable components might affect the leaching responses of REE and Zr due to the estimated higher ionic strength of the leach solutions of DT ore leaching compared to SG concentrate. It was learned in reviews of literature in Chapter 2 that REE sulfate solubility and stability are affected by the presence of other ions.

Chapter 5

Sulfuric Acid Leaching of Rare Earths from Eudialyte

5.1 Introduction

Sulfuric acid leaching is the generic procedure used for the hydrometallurgical processing of eudialyte minerals. The primary metal of interest on leaching of eudialyte is Zr; rare metals and REE are regarded as secondary values. The general practice is to leach large-grained eudialyte minerals with the use of heated or non-heated sulfuric acid. A variant to this procedure, as applied to large-grained eudialyte minerals with a high content of refractory metals, e.g. Nb and Ti, is the inclusion of a sulfation baking step prior to leaching (Cox, Moreton et al. 2010). On baking, excess amounts of concentrated sulfuric acid are used to digest and induce thermal cracking of the mineral matrix. This effects the sulfation reactions necessary to facilitate the recovery of valuable metals in the subsequent water leaching step. Reported conditions for eudialyte leaching in Lebedev (2002, 2003) were 15-50 % sulfuric acid, leaching for 2-4 h at 40-230 °C at a liquid:solid (L:S) ratio of 3-6 mL:g. It is not currently known how leaching conditions are modified to maximize rare earth recovery. Further, regarding the mineralogical variety of eudialyte minerals, no studies has been found on the application of sulfuric acid to REE leaching from finely-textured eudialyte.

This chapter discusses experimental results of the sulfuric acid leaching of rare earths from eudialyte. In particular, it focuses on the comparative leaching of rare earths from coarsely textured and finely textured eudialyte. A discussion on the effect of each significant leaching factor is also provided.

5.2 Aims of the Chapter

This chapter discusses investigations into the following:

- sulfuric acid leaching of rare earths from a (a) large-grained and (b) fine-grained eudialyte mineral;
- comparative leaching behaviour of HREEs and LREEs including the determination of conditions for the optimal leaching of HREEs in the sulfuric acid leaching of the large-grained eudialyte mineral;
- comparative leaching behaviour of HREEs and LREEs including the determination of conditions for the optimal leaching of HREEs in the sulfuric acid leaching of the fine-grained eudialyte mineral; and
- causes of incomplete leaching of rare earths in the sulfuric acid leaching of the two differently textured eudialyte minerals

5.3 Materials & Methods

5.3.1 Eudialyte ore samples

Two differently textured eudialyte minerals were used in the leaching test: large-grained eudialyte minerals in SG ore and finely-textured eudialyte in DT ore.

5.3.2 Reagents and equipment

Leaching tests made use of the following reagents: sulfuric acid (Analar, 98 %), sodium hydroxide pellets (Rowe Scientific, 40.00 g/mol) and deionized water.

The following equipment were used in the leaching test: Thermo Fisher Scientific 2200 hotplate (0-350 °C), 3-L IEC magnetic stirrer hot plates with PTFE top, 14-L Ratek OM11 shaker with thermal control, glass thermometer (0-110 °C), PTC Instruments 314C surface-type thermometer (0- 500 °C), 307 ECE digital temperature scanner (0-800 °C) and TPS Aqua pH meter.

5.3.3 Preparation of test samples for leaching

SG and DT ore were prepared according to the procedures detailed in *Preparation of test samples* in Section 4.3.4. In the procedures mentioned, SG ore was beneficiated to produce SG concentrate while DT ore was pulverised and used as whole-of-ore.

Leaching experiments were conducted using test sample mass of 1.0 g for SG concentrate and 20.0 g for DT ore.

5.3.4 Analytical techniques

Analysis of leach solutions from SG concentrate leaching was carried out by Agilent 735ES ICP-OES. Analysis of leach solutions derived from DT ore leaching was performed by means of an Agilent 7700 ICP-MS. The choice of analytical technique was made with due consideration to the concentration of REEs in the leach solution. The analysis of leach solutions was conducted by external laboratories Ultra Trace Pty Ltd (Canningvale, Western Australia) and the Commonwealth Scientific and Industrial Research Organization (CSIRO) Mineral Resources (Waterford, Western Australia) respectively.

The analysis of leach residues was performed using PANalytical X'Pert Pro PW3040 XRD, along with a TESCAN 3 FE GMU integrated mineralogy analyser with Pulse Tor 30 detector. Analysis work on leach residues was sourced from Ultra Trace Pty Ltd (Canningvale, Western Australia) and from the Material Characterisation Laboratory of John de Laeter Center, Curtin University (Bentley, Western Australia).

Thermal analysis of DT ore was conducted using Perkin Elmer STA6000 Differential Scanning Calorimetry - Thermal Gravimetric Analysis (DSC-TGA) and data was analysed using Perkin Elmer Pyris Analysis Software V8. This analysis was undertaken at Chemistry and Mathematical Sciences at Murdoch University, Murdoch, Western Australia. A 50-mg sample was heated from 50 °C to 20 °C at a heating rate of 10 °C/min with Ar as a carrier gas.

5.3.5 Leaching procedure

Leaching of rare earths from SG concentrate was conducted with the use of heated sulfuric acid. A pre-treatment step was carried out prior to leaching to minimise the risk of solution polymerisation. In this procedure, SG concentrate was boiled with 0.1 % sulfuric acid, without any stirring, to remove aluminium silicates (Figure 5-1a). An Al:Si ratio greater than 4:3 enhances silica polymerization in aqueous solution (Murata 1943).

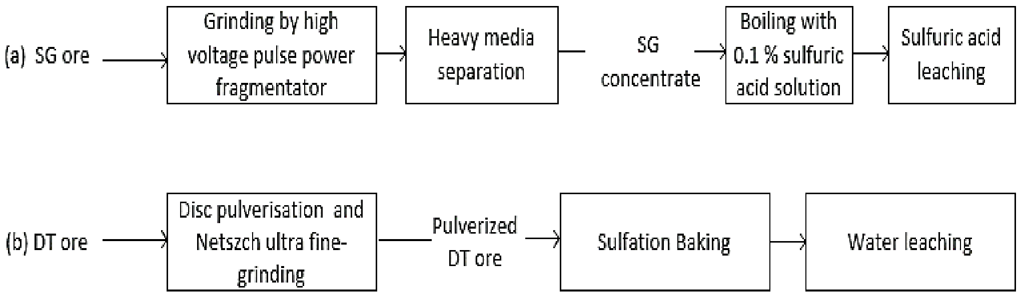
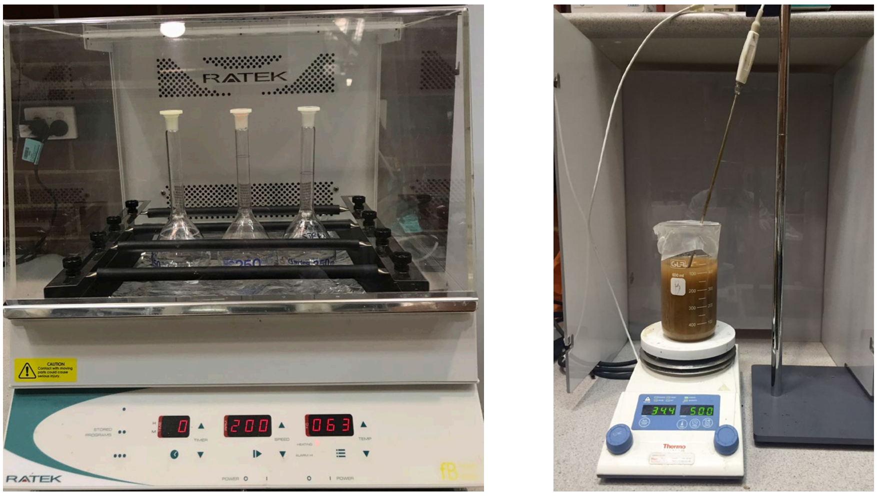


Figure 5-1: Sample preparation and leaching method applied for (a) SG ore and (b) DT ore

Leaching tests for SG concentrate were carried out using 100-mL round-bottom flasks placed in a temperature controlled-shaker (Figure 5-2a). Non-contact stirring, with the use of the shaker, further minimised silica gel formation. A stirring speed greater than 340 rpm was reported to cause early silica coagulation and enhance gel formation in solution (Li and Kaner 2005). Depending on the solution volume, the shaking speed was maintained at between 200-300 rpm.

In contrast, the leaching of rare earths from DT ore was carried out via a sulfation-baking and water leaching procedure (Figure 5-1b). Results of exploratory tests showed that there were nil leaching recoveries for rare earths when DT ore was leached directly with sulfuric acid. It was also determined that leaching of DT ore via this procedure did not result in silica gel formation. Details of the exploratory test for both ores are provided in Appendix E.



(a) (b)

Figure 5-2: Laboratory set-up for the leaching of (a) SG concentrate and (b) DT ore

Sulfation baking of DT ore was carried out using a 100-mL beaker placed on a hotplate and use of 98 % sulfuric acid, calculated base on stoichiometric requirement. Temperature measurement was performed with the use of dial-type surface thermometers placed on the hotplate surface. Temperatures were validated using a digital thermal scanner with hourly readings taken for temperature monitoring. The subsequent water leaching for DT ore was carried out using 500-mL beakers mounted on 3-L capacity heater-stirrer plates (Figure 5-2b). In this leaching method, the stirring speed was held constant at 300 rpm for leaching conditions at low volume conditions, and 500 rpm for leaching run at high volume conditions.

5.3.6 Acid stoichiometric equivalent

Sulfuric acid stoichiometric requirements were calculated based on sulfation reactions for REEs, Zr, Nb and for the impurities of Al, Ca, Fe, K, and Na. The proposed generalised sulfation reaction is as follows:

$$M_xO_y + nH_2SO_4 \rightarrow M_x(SO_4)_y + nH_2O \tag{5-1}$$

where M represents the cations enumerated earlier;

This value was calculated to be 494 mg (270 μL) of 98 % sulfuric acid/g of SG concentrate and 396 mg (216 μL) of 98 % sulfuric acid/g of DT ore.

5.3.7 Design of experiment

In this research work, the leaching test was approached using statistical methodology to create a cost-effective experimental plan. The main criterion for choosing which statistical experimental design to use for the leaching of each ore was decided based on the number of factors relevant to the leaching procedure. This was determined by prior exploratory tests and from information gathered from related studies.

5.3.7.1 Fractional factorial experimental design for the leaching of SG concentrate

The leaching of rare earths from SG concentrate was conducted using a fractional factorial experimental design for five factors at two levels, or $2v^{5-1}$ *resolution five* design. Factors monitored were as follows: grind size, leaching temperature, leaching time, sulfuric acid concentration and L:S ratio. The low and high settings for each factor were determined empirically. For example, the high level setting for acid concentration was decided not only on stoichiometric requirements but also on the occurrence of silica polymerisation in solution. The use of 15 wt. % acid resulted in immediate silica gelling (Appendix E). Thus, the highest sulfuric acid concentration used was 10 wt. %. It was also learned from reviews of related studies that high dilution promotes REE solubility (da Silva, Ogasawara et al. 1996, Dibrov et al. cited in (Lebedev 2003)). Hence, L:S ratios used in the leaching test were higher than normally used in the leaching of Zr from eudialyte.

The experimental plan table was generated using DOE++ V9 software and involved 16 different sets of leaching conditions (Table 5-1).

Table 5-1: Fractional factorial experimental design table for the leaching of eudialyte minerals in SG concentrate

Factors	Experimental setting per factor		Run number															
	low level (-)	high level (+)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Grind size, µm	149-212	300-420	-	+	-	+	-	-	+	-	+	+	-	-	-	+	+	+
Leaching time, h	2	6	+	-	-	+	-	-	-	+	-	+	+	+	-	+	-	+
Leaching temp,^{0}C (+/-5^{0}C)	20	60	+	-	+	-	-	+	-	+	+	-	-	-	-	+	+	+
Sulfuric acid concentration, wt. %	1	10	+	-	+	+	-	-	+	-	+	-	-	+	+	+	-	-
L:S ratio, mL:g	50	100	-	-	+	-	+	-	+	+	-	+	-	+	-	+	+	-

5.3.7.2 Taguchi experimental design for leaching of DT ore

The leaching of rare earths from DT ore was conducted using Taguchi's method of experimental design on seven factors, at two levels, or *$L_{8,}$ (2^7) resolution seven* design. This design was chosen to accommodate the higher number of factors associated with treatment procedures for DT ore, enumerated as follows: baking temperature, baking time, acid:ore ratio, leaching temperature, leaching time, L:S ratio, and grind size (Table 5-2). The low and high experimental settings of each factor were determined empirically. For instance, the acid dosage for DT ore was designed to ensure that there was sufficient wetting of the finely pulverized DT ore. The higher acid dosage of 3.2 g acid/g ore is eight times higher than the stoichiometric acid requirement for DT ore. This is the recommended acid dosage for the leaching of Lovozero eudialyte concentrate to increase metal recoveries (Lebedev 2003).

The experimental plan table was generated using DOE++ V9 software and involved eight different sets of leaching conditions. In consideration of the reduced number of tests with this type of experimental design, two experimental runs were done for each set of leaching conditions (Table 5-2).

Table 5-2: Taguchi experimental design table for the leaching of DT ore

Factors	Experimental setting per factor		Run number							
	Low level (-)	High level (+)	1	2	3	4	5	6	7	8
Baking temperature, °C (+/- 20 °C)	200	320	-	-	-	-	+	+	+	+
Baking time, h	1	3	-	-	+	+	-	-	+	+
Acid-ore ratio, g/g	0.4	3.2	-	-	+	+	+	+	-	-
Leaching time, h	1	3	-	+	-	+	-	+	-	+
Leaching temperature, °C (+/- 5 °C)	20	60	-	+	-	+	+	-	+	-
L:S ratio, mL:g	5	20	-	+	+	-	-	+	+	-
Grind size, µm	10 (D_{90})	300-420	-	+	+	-	+	-	-	+

5.3.7.3 Optimisation test for leaching of SG concentrate and DT ore

The determination of significant factors for the leaching of rare earths from SG concentrate and DT ore carried out using an Analysis of Variance (ANOVA) at 95 % confidence level. Statistical analysis and optimisation were performed using DOE++ V9 (Reliasoft Corporation) and Minitab 17.1 (Minitab Inc.) software. The statistically optimised condition was validated in laboratory. Further optimisation was conducted by varying one factor at a time at the optimal leaching condition of Y lixiviation. Y was chosen as it is a more economically significant REE than La and Ce.

5.3.8 Analysis and presentation of data

In this research, the response variable for leaching is the individual metal yields of Y, La and Ce, where the desired quality characteristic is the highest leaching recovery (R_i) of the REEs mentioned. This is calculated based on the following equation:

$$R_i = \frac{V.C_i}{M_{SA}C_{iSA}} = 1 - \frac{M_{SB}C_{iSB}}{M_{SA}C_{iSA}} \qquad (5\text{-}2)$$

where V is the volume of the leach solution, C_i is the concentration of rare earth element ***i*** in solution, M_{sA} is mass of the initial sample and C_{isA} is the concentration of rare earth element ***i*** in the initial sample, M_{sB} is the mass of the leach residue and C_{isB} is the concentration of rare earth element ***i*** in the leach residue;

These three REEs were chosen as they comprised more than 80% of the total REO content of the ore samples. Y was used as an index of HREE leaching response, while La and Ce were used as indicators of LREE leaching responses.

Leaching recoveries were analysed using Minitab 17.1 software in which results were presented in Main Effects and Cube plots.

5.3.8.1 Main Effects plot

The Main Effects plot was used to graphically display which factors have the highest impact on the leaching recoveries of each REE. The plot provides a linear presentation of the data means of leaching recoveries at a low (-1) and a high (1) level setting for each factor (Figure 5-3). The length of the line is a visual measure of how each factor affects the independent variable. The middle horizontal line represents the average value of all the experimental results.

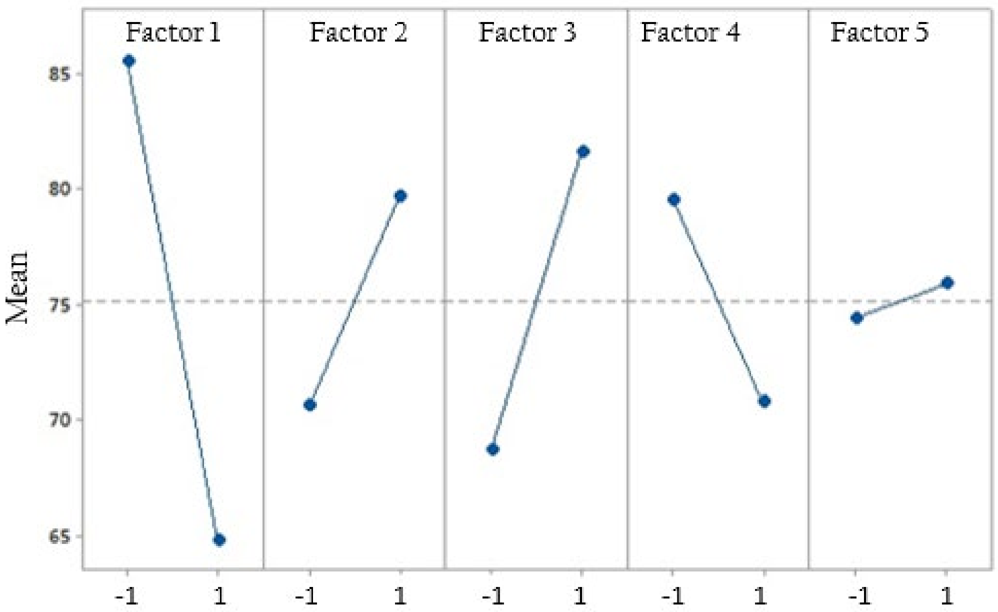


Figure 5-3: Example of Main Effects plot showing factors and factor effects line

5.3.8.2 Cube plots

The data from the SG concentrate leaching was presented in cube plots. A cube plot is a graphical method of displaying results where the axes of the cubes represent a factor with its low and high level setting. A sample cube plot, as applied to the leaching of SG concentrate, is shown in Figure 5-4. The same figure is provided in Appendix G, with information provided on how this type of graph is read.

In contrast, as the leaching of DT ore involved more factors, data results were presented in a simple table format, as cube plots could not be applied to present data for a seven-factor test from a Taguchi design.

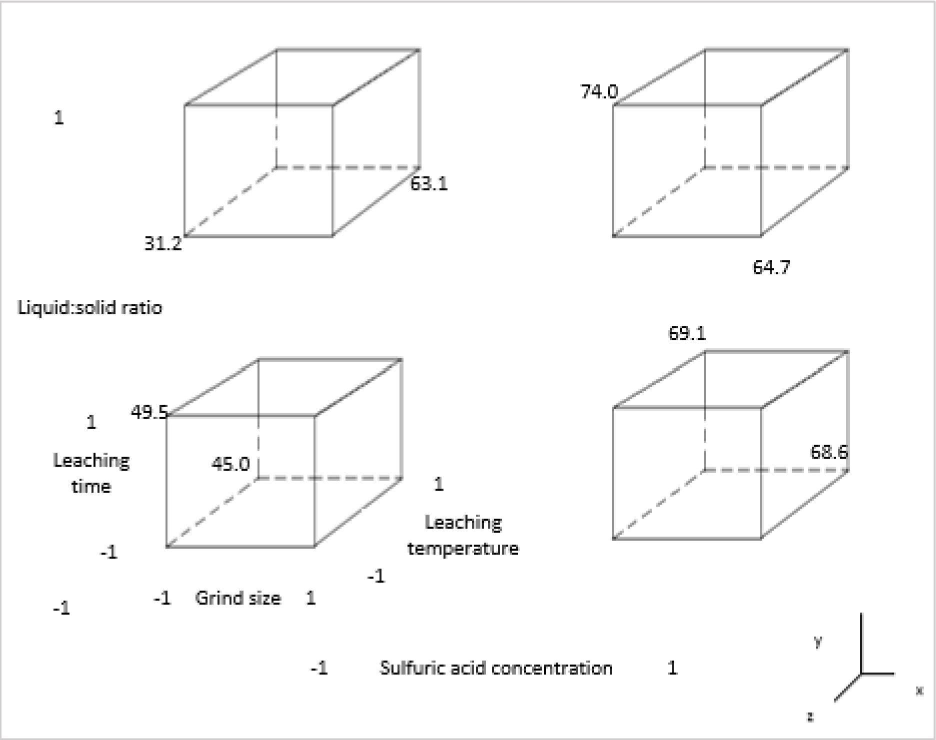


Figure 5-4: A sample Cube plot showing leaching factors as applied to SG concentrate leaching

5.4 Results and Discussion

5.4.1 Leaching of rare earths from eudialyte

In the sulfuric acid leaching of large eudialyte grains from SG concentrate, the proposed reaction is as follows (Equation 5-3):

$$Na_{15}Ca_7Fe_3Zr_3Si(Si_3O_9)_2(Si_9O_{27})_2(OH)_2Cl_2 + 20H_2SO_4 \rightarrow 7.5Na_2SO_4 + 7CaSO_4 + 3FeSO_4 + 3ZrOSO_4 + 25SiO(OH)_2 + 2HCl \quad (5\text{-}3)$$

In *eudialyte proper*, REE are substituting elements in Na, Ca and Fe sites (Rastsvetaeva and Chukanov 2013). Thus, REE leaching from *eudialyte proper* in SG concentrate was believed to occur on the dissolution of framework elements Na, Ca and Fe.

The comparative conditions on the highest and lowest REE leaching recoveries is summarised in Table 5-3 from results shown in Figure 5-5. These results indicated that two factors were significantly influencing REE leaching: sulfuric acid concentration and temperature. However, a survey on the leaching recoveries as shown in Figure 5-5 clearly showed that leaching done on conditions of 10 wt. % acid concentration have higher REE leaching recoveries compared to leaching done on conditions of 60 °C. This finding highlighted the significance of sulfuric acid concentration in influencing REE leaching. Analysis of leaching recoveries by the ANOVA method confirmed this finding (Figure 5-6). ANOVA analysis also showed that sulfuric acid concentration was the only significant factor affecting the leaching of REE from large eudialyte grains in SG concentrate (Figure 5-6).

Table 5-3: Summary of leaching conditions on highest and lowest REE recoveries on sulfuric acid leaching of SG concentrate

Factors	Leaching conditions at highest REE yield (recovery at 82%)	Leaching conditions at lowest REE yield (recovery at 33 %)	
Leaching temperature, °C	60	20	20
Leaching time, h	2	2	2
Sulfuric acid concentration, wt. %	10	1	1
L:S ratio, mL:g	100	100	50
Grind size, µm	149-212	149-212	300-420

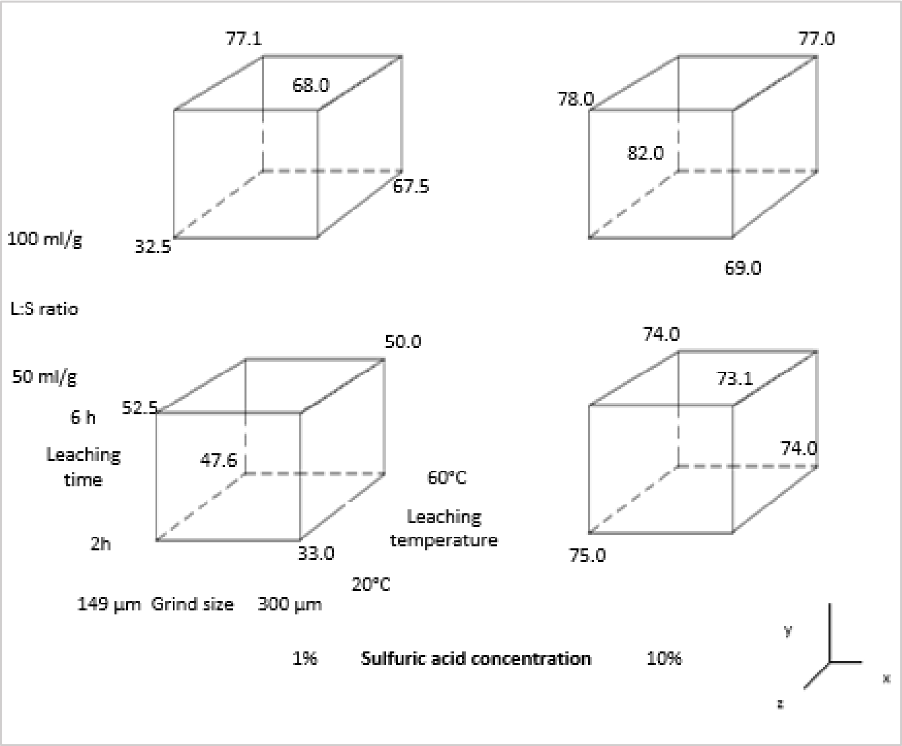


Figure 5-5: Cube plot for the leaching recoveries of REE from SG concentrate

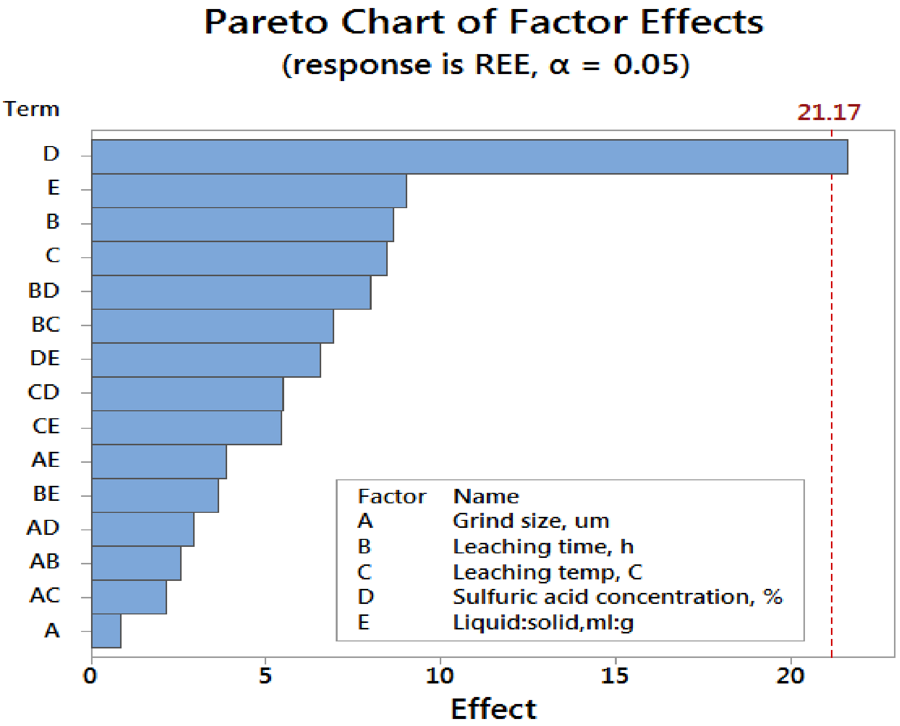


Figure 5-6: Pareto Chart of Factors Effects on sulfuric acid leaching of SG concentrate

The findings on conditions for preferable leaching of REEs from SG concentrate showed that comparably high leaching recoveries of REEs at 82 % can be achieved with a single stage treatment of large-grained eudialyte minerals. Previous investigations into sulfuric acid leaching of eudialyte reported a high recovery of REEs at 90 %. This was only after multiple leaching of eudialyte at the following reported leaching conditions: use of 5-21% sulfuric acid concentration, 40-90 °C leaching temperature, 2-4 h leaching time and L:S ratio of 4:1– 6:1 mL:g (Lebedev 2003).

The results of this current study also indicated that a 45 % higher REE leaching recoveries were attainable with the use of 10 wt. % sulfuric acid and 100 mL:g dilution. This was as compared to room temperature leaching of large-grained eudialyte middling concentrate using 50 % sulfuric acid and L:S ratio of 2.5, as studied by Voβenkaul et al. (2016). The striking differences in the leaching conditions of this current investigation, compared to earlier studies, were the lower sulfuric acid concentration and large dilution. The identified contrast in the leaching conditions strongly suggested that high acidity requirements for REE leaching can be compensated for by high dilution. Thus, comparatively high REE lixiviation can be achieved, even with a single stage treatment of large eudialyte minerals using a high 20 fold dilution, but with half the acid concentration (as previously used in earlier studies by Lebedev et al.). In these conditions, the chemical reaction in Equation (5-3) is inclined to proceed to the right, by the formation of stable hydrolysed REE sulfates on high dilution. Hydrolysis enhances the stability of REE complexes (Moeller, Martin et al. 1965). Also, losses by co-precipitation of REE double sulfate were believed to be minimal due to the lesser influence of the common sulfate ion effect on large dilutions. Going against the reduced treatment steps, the main drawback of this approach was the low concentration of REE in solution. At the highest leaching recovery rate of REE at 82 %, the concentrations of REE in solution were as follows (mg/L): 36 (Y), 30 (La) & 57 (Ce). Further, the use of dilute acid concentration will increase the aqueous waste streams. With this consideration, the effect of L:S ratio becomes significant.

The leaching of REE from large-grained eudialyte in SG concentrate was higher by 9 % on leaching at 60 °C, compared to leaching at 20 °C (with other factors held constant, Figure 5-5). This was believed to be caused by the kinetics of eudialyte decomposition which were influenced strongly by sulfuric acid concentration and temperature. In the present study, the lowest leaching recoveries of 33 % resulted from two tests carried out by leaching at 20 °C with 1 wt. % sulfuric acid (Figure 5-5). The leaching residues from these tests were characterised by the presence of non-digested eudialyte.

In contrast, leaching of rare earths from fine-grained eudialyte in DT ore required more rigorous conditions, as compared to the leaching of large eudialyte grains. The rare earths in the complex Na-Ca-Zr silicates were converted to sulfates in the sulfation-baking step and solubilised in the succeeding water leaching step (Equation 5-4) as follows:

$$REE_2(SO_4)_3 + xH_2O \rightleftarrows REE^{3+}(H_2O)_xSO_4^{2-} \qquad (5\text{- }4)$$

The above treatment procedure resulted in an average of 80 % REE leaching recovery, from the 16 tests conducted (Appendix H). The treatment conditions for the highest and lowest REE leaching yields are summarised in Table 5-4 (from data in Appendix H). These results indicate that REE leaching from DT ore was promoted on use of a higher acid dosage of 3.2 g/g on baking, but with a lower leaching temperature of 20 °C (Appendix H, run 6), or on the use of a lower acid dosage of 0.4 g/g on baking but with a higher leaching temperature of 60 °C (Appendix H, run 7). These results also suggest the significant effect of baking temperature and grind size on influencing REE lixiviation. Analysis by ANOVA method confirmed these findings (Table 5-5). Leaching temperature were also determined as a significant factor.

The results of the ANOVA analysis also highlighted that the sulfation-baking step was a significant step in the treatment procedure. As indicated in the p-values of the three factors in the sulfation baking step, baking temperature was the most significant factor having the least p-value. It is believed that the effect of baking temperature was to promote thermal cracking of the fused phases of complex Na-Ca-Zr silicates. The increased corrosivity of sulfuric acid and the increased porosity of the mineral matrix at elevated temperatures both

Table 5-4: Summary of leaching conditions on highest and lowest REE recoveries on sulfuric acid leaching of DT ore

Factors	Leaching conditions on highest REE yield (recovery at 91%)		Leaching conditions on lowest REE yield (recovery at 65 %)
Baking temperature, °C	320	320	200
Baking time, h	1	3	1
Acid:ore ratio, g:g	3.2	0.4	0.4
Leaching temperature, °C	20	60	60
Leaching time, h	3	1	3
L:S ratio, mL:g	20	20	20
Grind size, µm	10 (D_{90})	10 (D_{90})	300-420

Table 5-5: ANOVA test of REE yields on leaching of DT ore, significant factors shown in italics, $\alpha = 0.05$

Factors	p-value	Factors	p-value
Baking temperature	***0.000***	Leaching time	0.794
Baking time	***0.002***	Leaching temperature	***0.040***
Acid: ore dosage	***0.021***	L:S ratio, mL:g	0.230
Grind size	***0.000***		

facilitated the sulfation reactions necessary for thermal cracking. Porosity of mineral matrices can be increased at relatively low temperatures of 100-400 °C by removal of water or by promoting heat-induced structural changes. These mechanism were believed to be happening during sulfation baking of DT ore. DSC-TGA analysis of DT ore strongly supported the evidence of water removal as indicated by the endothermic reaction at 50-130 °C and the associated enthalphy change (Figure 5-7). Oxidation reactions occurring on sulfation baking was also believed to be the major contibutor to the exothermic reactions determined at 130-350 °C. These oxidation reactions can effect structural changes. For instance, the onset of oxidation of Fe in some eudialyte variants occurs at 275 °C (Khomyakov, Korovushkin et al. 2010). The ferrous-ferric oxidation was followed by structural re-arrangement of Fe sites resulting to minor crystal lattice expansion.

In summary, the leaching of rare earths from eudialyte minerals was dictated largely by eudialyte mineralogy. A high REE leaching yield of 82 % was achieved with a single stage leaching of large-grained eudialyte in SG concentrate in conditions of a high dilution of 100 mL:g and a lower sulfuric acid concentration of 10 wt. %. In contrast, direct leaching of DT ore yielded nil recoveries but leaching using rigorous conditions base on sulfation baking – water leaching yielded a high leaching yield of 91%. With this information at hand, it is of interest to investigate the differences in leaching responses of HREEs and LREEs in the sulfuric acid leaching of eudialyte.

5.4.2 Leaching responses of heavy and light rare earths in sulfuric acid leaching of large-grained eudialyte in SG concentrate

It was demonstrated in previous section that leaching of REEs in large-grained eudialyte minerals in SG concentrate yielded leaching recoveries of 82 % on conditions of high dilution of 100 mL:g, elevated leaching temperature of 60 °C and acid concentration of 10 wt. %. By ANOVA method, acid concentration was identified as the only significant factor in the leaching process.

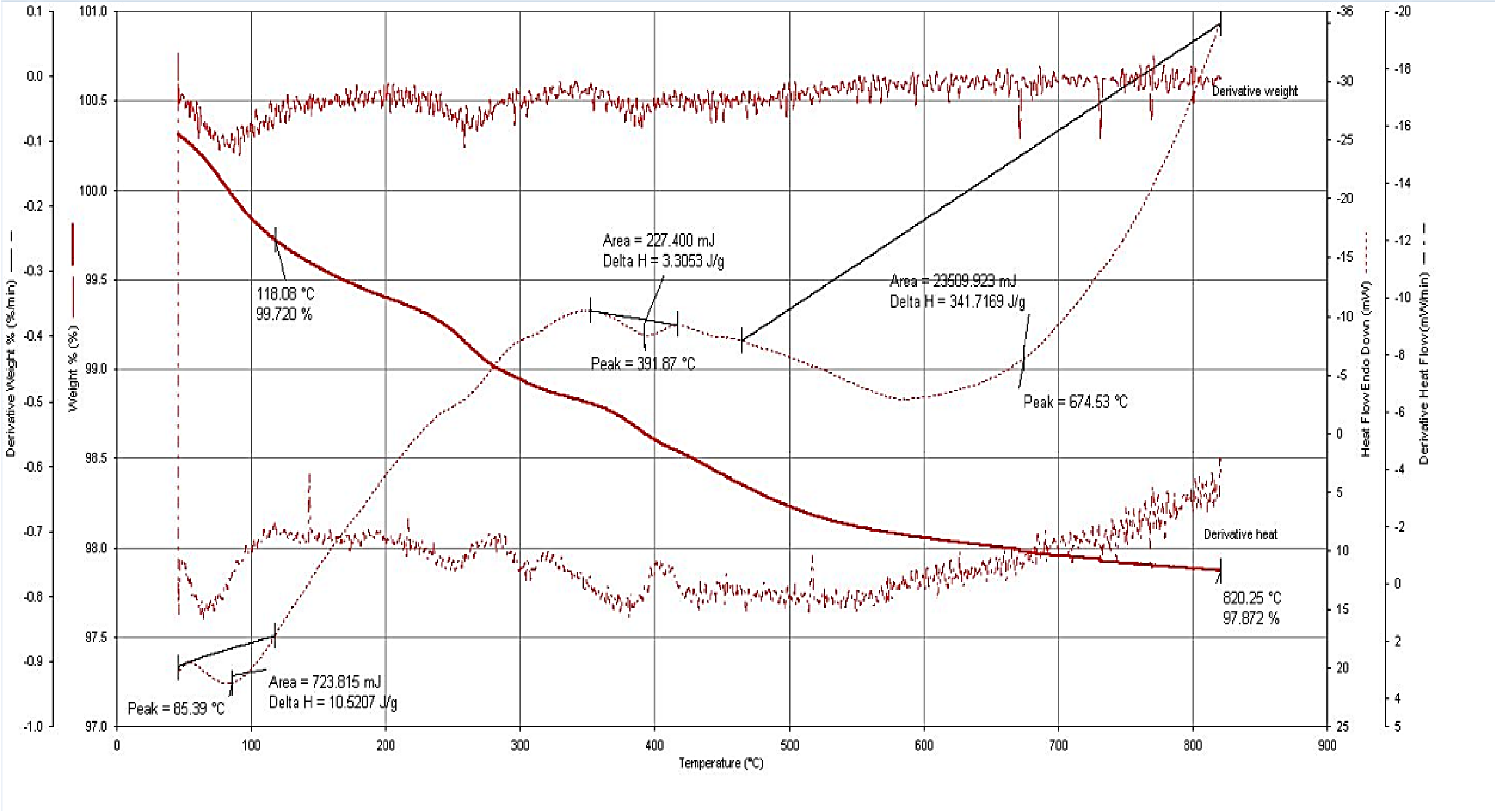


Figure 5-7: DSC-TGA results of DT ore

A summary of means on leaching recoveries showed that comparatively, Y was leached favourably on leaching at 60 °C for 6 h using 10 wt.% acid at an L:S ratio of 100 mL:g and 300-420 µm grind size (Figure 5-8; for raw data, see Appendix G-2). LREEs La and Ce were leached favourably, with leaching at 60 °C for 6 h using 10 wt. % sulfuric acid at an L:S ratio of 100:1 mL:g and 149-212 µm grind size (Figure 5-9; for raw data, see Appendices G 2.2 & 2.3). The only difference in the favourable leaching conditions between the two REE group s was the grind size: Y leaching yield was slightly higher by 1% on leaching using 300-420 µm than 149-212 µm grind size. However, the effect of grind size was the least among the factors considered, as shown in the Main Effects plots in Figures 5-8 & 5-9. Given the small difference in leaching yield of Y as influenced by the relatively insignificant effect of grind size on leaching of SG concentrate, it can be deduced that there is no difference in the leaching responses of HREEs and LREEs in the sulfuric acid leaching of large-grained eudialyte in SG concentrate.

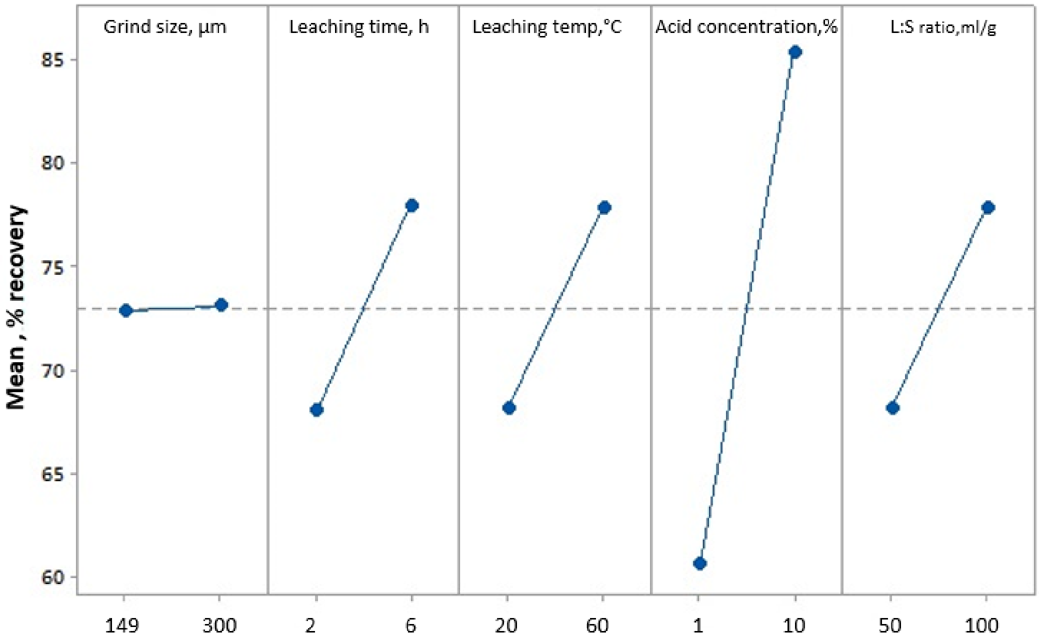


Figure 5-8: Main Effects plot for Y leaching from SG concentrate indicating sulfuric acid concentration as the main factor affecting Y leaching

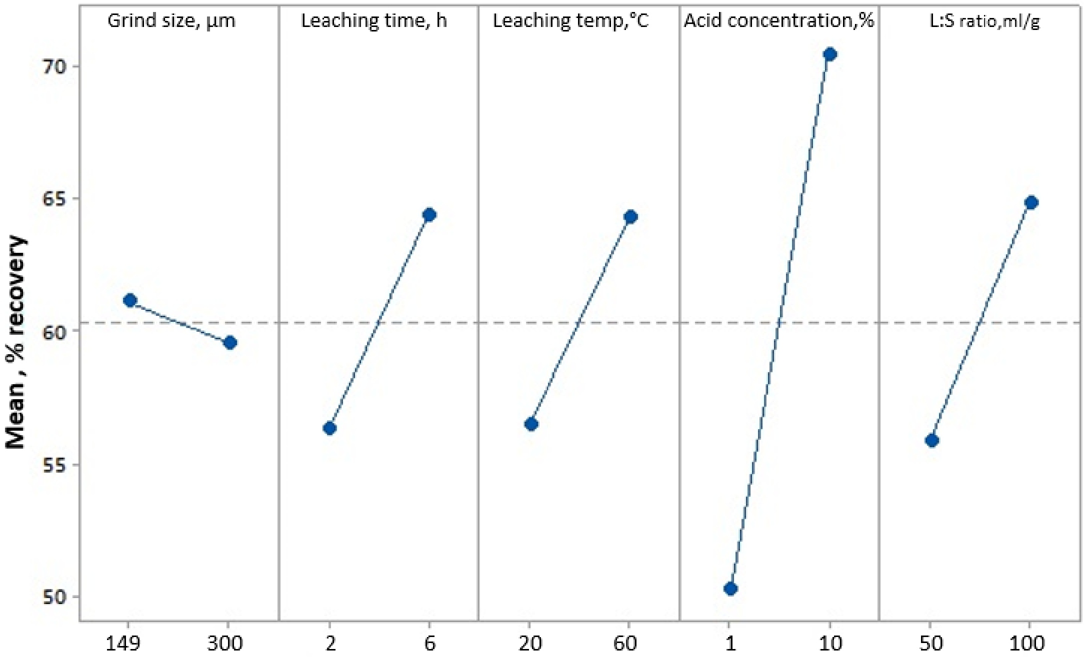


Figure 5-9: Main Effects plot for La and Ce leaching from SG concentrate, sulfuric acid is the main factor affecting leaching process.

The effect of acid concentration was clearly the main factor largely affecting the lixiviation of both Y and LREEs La and Ce as shown by the length of effects line for sulfuric acid concentration in the Main Effects plots (Figures 5-8 & 5-9). From the 16 tests conducted, there was a 15-20 % difference in the average leaching recovery of rare earths from the use of 10 wt. % sulfuric acid concentration, as opposed to the use of 1 wt. % sulfuric acid concentration. Analysis of leaching recoveries by the ANOVA method supported this finding (Table 5-6). The sulfuric acid concentrations used in this leaching test were comparatively lower than those used in earlier investigations.

Results of optimisation tests on sulfuric acid concentration showed that there was no significant difference in leaching recovery from the use of 5 wt. % sulfuric acid concentration against higher concentrations of up to 25 wt. %, as evidenced by the nil increase of REE recovery with increased acid concentration (Figure 5-10). On acid concentrations of more than 10 wt. %, the polymerisation of silica in solution was progressively evident and with 25 wt. % acid, silica gel formed on the cooling of the leach solution. In reference to the above results, and in consideration of a weaker acid concentration being preferred for cost benefit, the optimal acid strength for use in the leaching of SG concentrate was 5 wt.%.

Table 5-6: ANOVA table highlighting significant factor (italicized) for the leaching of Y, La and Ce from SG concentrate

	p-value		
Factors	Y	La	Ce
Grind size	0.972	0.807	0.750
Leaching time	0.121	0.124	0.125
Leaching temperature	0.127	0.129	0.134
Sulfuric acid concentration	***0.002***	***0.002***	***0.002***
L:S ratio	0.127	0.110	0.091

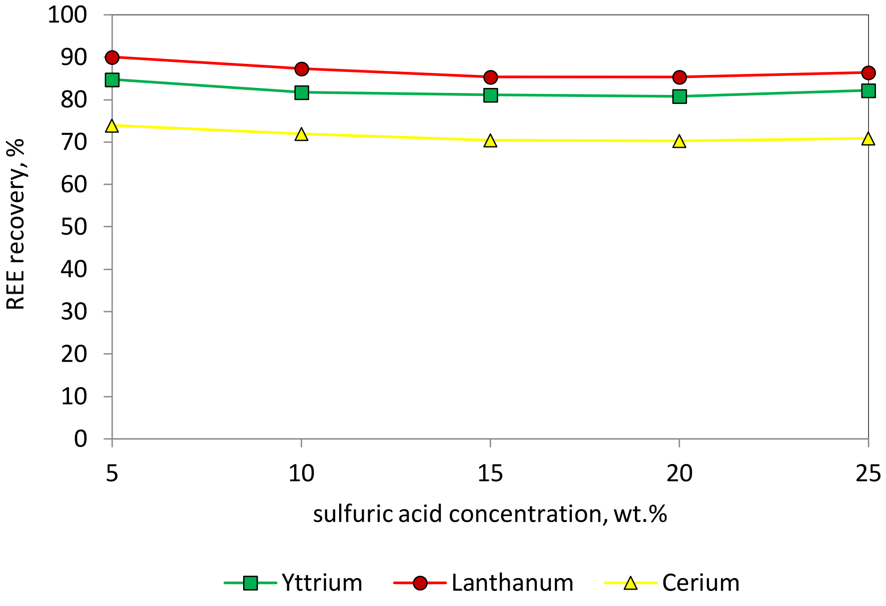


Figure 5-10: Effect of sulfuric acid concentration on REE leaching from SG concentrate; leaching conditions: 6 h leaching at 60 ° C on L:S ratio of 100:1 mL:g and 300-420 µm grind size

In light of the above findings, the conditions for optimal REE leaching from large-grained eudialyte minerals in SG concentrate was determined as follows: leaching at 60 °C for 2 h using 5 wt. % sulfuric acid concentration at an L:S ratio of 100 mL:g and grind size of 300-420 µm. These leaching conditions were validated in a leaching test. The results yielded the following recoveries (%): 93 (Y), 88 (La) & 76 (Ce). Y recovery was 10 % higher than the leaching recovery derived from non-optimal leaching conditions.

5.4.3 Leaching responses of heavy and light rare earths in the sulfuric acid leaching of fine-grained eudialyte in DT ore

It was noted in an earlier section of this chapter that the leaching of rare earths from fine-grained eudialyte in DT ore requires harsher conditions due to the complex mineralogical features of the ore. Analysis of leaching by the ANOVA method reflected the statistical significance of the sulfation-baking step in REE leaching.

A summary of means indicated that leaching of HREE Y from fine-grained eudialyte in DT ore was favoured in the following conditions: baking at 320 °C for 3 h with an acid dosage of 3.2 g/g, followed by water leaching at 20 °C for 1 h at 20 mL:g L:S ratio and 300-420 µm grind size (Figure 5-11). Baking temperature was evidently the main factor affecting the leaching of Y. Of the 16 tests conducted, baking at 320 °C yielded an average leaching recovery of 80 % while baking at 200 °C resulted in a lower recovery of 45 %. This finding is supported by results of supplementary test conducted to further investigate the effect of baking temperature. Results confirmed the strong positive correlation of Y leaching and baking temperature (Figure 5-11). This was believed to be due to a relatively intense thermal cracking on the fused Na-Zr-Si phases at a higher baking temperature. The effect of thermal cracking was only evident on Y leaching as Y was mainly hosted in these fused phases. The concurrent presence of La and Ce in bastnasite minerals might have overshadowed this trend on the leaching responses of LREEs. Bastnasite is a La and Ce carbonate mineral. This is believed to be the reason why La and Ce showed easy lixiviation even at room temperature curing (Figure 5-12).

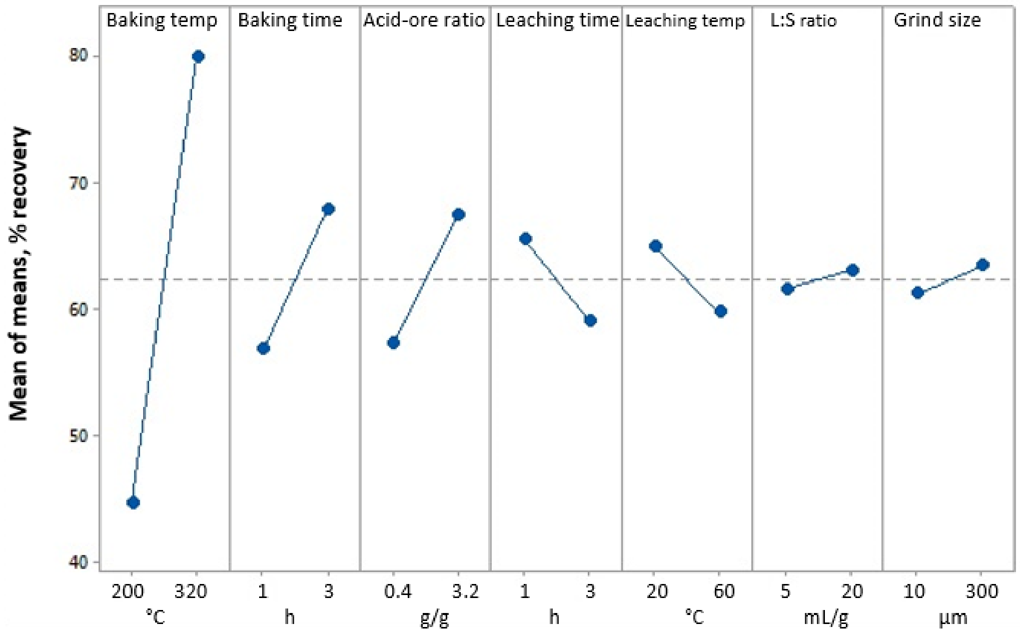


Figure 5-11: Main Effects plot leaching of Y from DT ore highlighting the effect of baking temperature as the main factor affecting leaching of Y

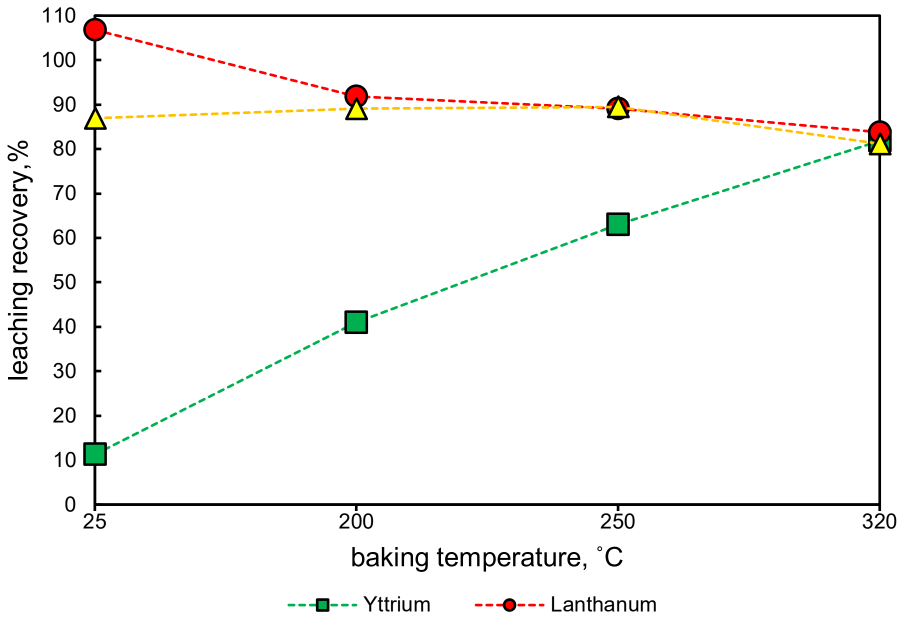


Figure 5-12: Effect of baking temperature on the leaching of REEs from DT ore (Lim, Ibana et al. 2016)

The leaching of LREEs La and Ce from fine-grained eudialyte minerals in DT ore was largely affected by grind size, in which 96 % leaching recovery resulted from the use of 10 µm (D_{90}) grind size ore. A lower recovery rate of 80 % resulted from the use of 300-420 µm grind size ore (Figures 5-13 & 5-14). The effect of grind size on promoting the lixiviation of LREEs could be attributed to bastnasite content in DT ore. Bastnasite minerals occur as large acicular grains of 100 µm (Figure 5-15). Fine grinding would favour the liberation and easy leaching of LREEs from bastnasite minerals. While a parallel analogy would similarly favour the liberation of REE values from fine-grained eudialyte on fine grinding, in reality this was not the case, particularly for Y. Y recovery was 37 % lower than that of LREEs La and Ce at a 10 µm (D_{90}) grind size (Figure 5-16). Fine grinding at 10 µm might have caused structural and chemical changes in DT ore, as evidenced by a pronounced colour change in the ore when pulverized to 10 µm or less (Figure 5-17). Over grinding can effect crystal changes in some silicate materials with adverse impact on leaching behaviour (Chizhevskaya, Chekmarev et al. 1994). At leaching conditions for the optimal recovery of Y, the use of a 10 µm grind size (D_{90}) resulted in a low recovery rate of 50 % (Figure 5-16).

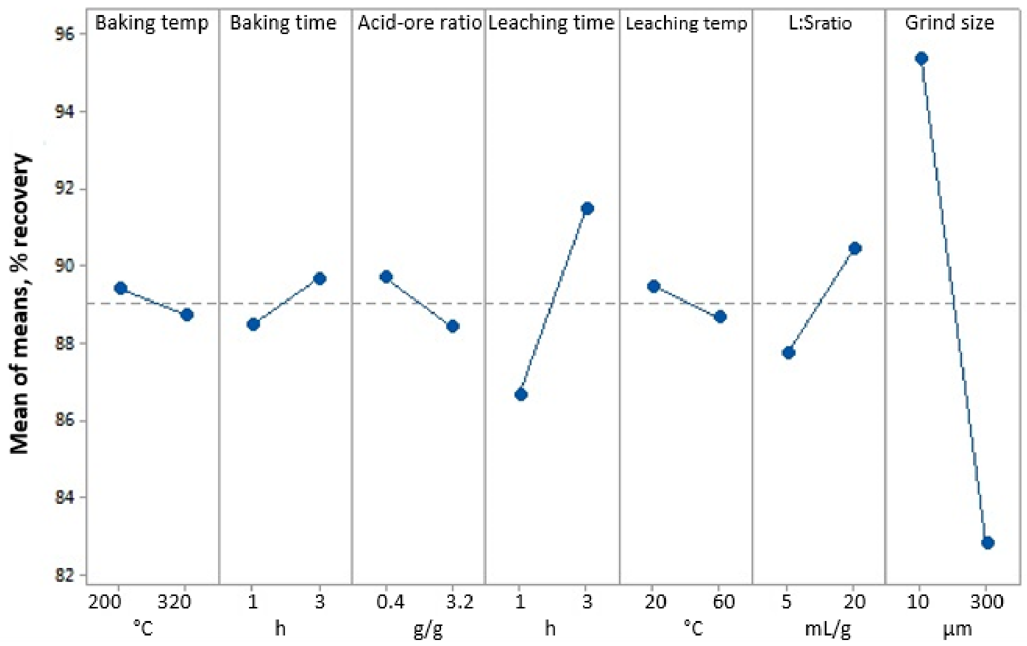


Figure 5-13: Main Effects plot for the leaching of La from DT ore

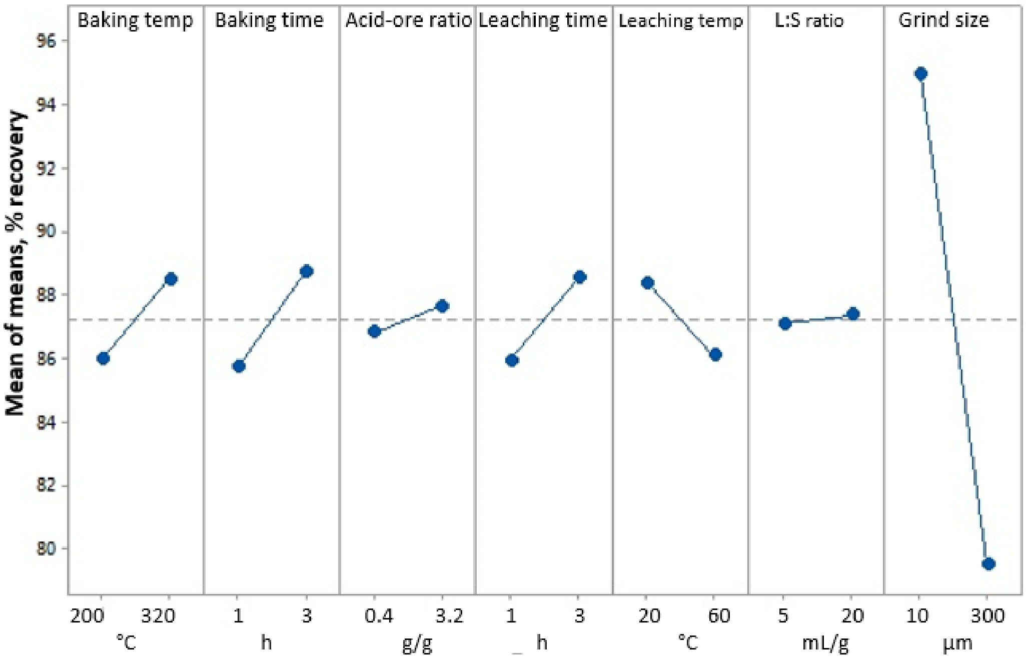


Figure 5-14: Main Effects plot for the leaching of Ce from DT ore

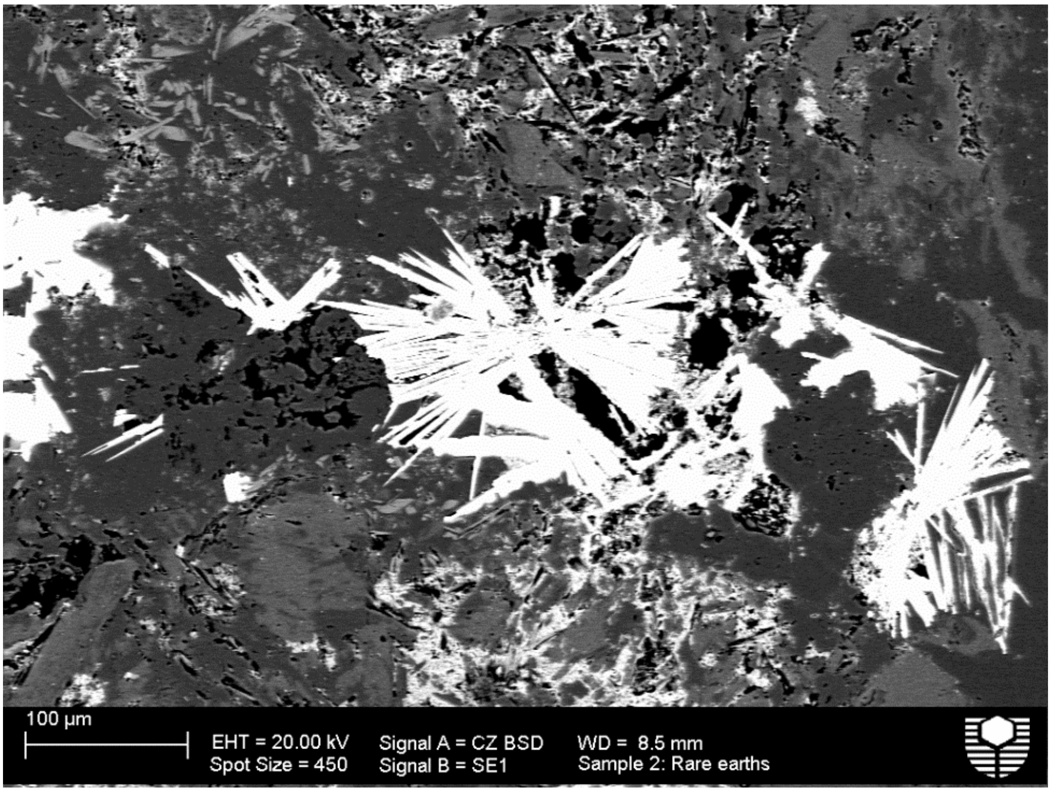


Figure 5-15: Micrograph of acicular bastnasite grains

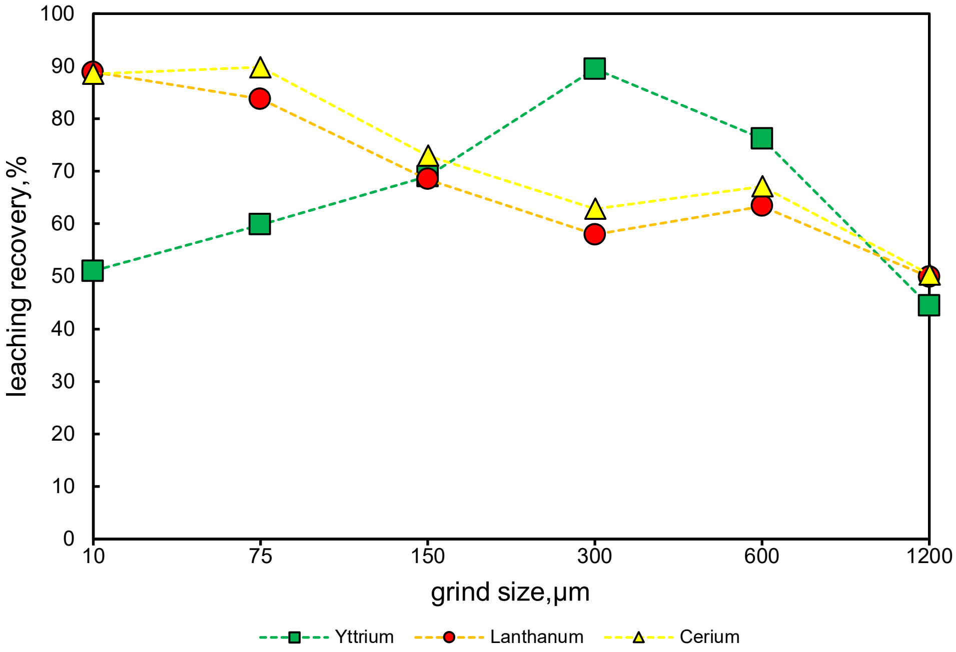


Figure 5-16: Effect of grind size on sulfuric acid leaching of REE. Test was conducted at sulfation-baking at 320 °C, 3 h and 3.2 g/g acid followed by water leaching at 20° C for 1 h on 20mL:g L:S ratio (Lim, Ibana et al. 2016)

Figure 5-17: DT ore changed in colour from brown at 53 µm (rightmost) to brown-grey at 10 µm (middle) to light grey at 5 µm (leftmost)

Analysis of leaching results by the ANOVA method showed that the significant factors affecting the leaching of REEs from fine-grained eudialyte minerals in DT ore varied considerably (Table 5-7). The leaching of Y was affected significantly by the sulfation-baking step, leaching temperature and leaching time. Other than the effect of the baking temperature which was mentioned earlier, the effect of the acid dosages (Fig 5-18b), and the effect of the leaching temperature (Fig. 5-18c) showed a marked influence on Y leaching. The graphs indicate that higher Y recovery was favoured with the use of 3.2 g/g acid, baking at 320 °C and a leaching temperature of 60 °C. These rather rigorous treatment conditions suggest the relative refractoriness of fine-grained eudialyte and explain why Y leaching recoveries were consistently lower compared to the leaching of LREEs La and Ce, which were also present in minor phases of bastnasite minerals. While there was a slight increase in Y yield as leaching time was increased, a leaching time of more than 12 h was accompanied by the formation of floating calcium sulfates (Figure 5-19). Thus the recommended leaching time was 3 h. There was only 3 % rise in Y recovery on 12 h leaching time.

Table 5-7: ANOVA analysis showing significant factors affecting leaching of REE from sulfuric acid leaching of fine-grained eudialyte minerals in DT ore

	p-value		
Factor	Y	La	Ce
Baking temperature	***2.50E-07***	0.4998	***0.0330***
Baking time	***0.0011***	0.2565	***0.0160***
Acid-ore dosage	***0.0019***	0.2274	0.4228
Leaching time	***0.0196***	***0.0011***	***0.0298***
Leaching temperature	***0.0479***	0.4273	***0.0479***
L:S ratio	0.5399	***0.0235***	0.7904
Grind size	0.3471	***1.17E-06***	***2.62E-07***

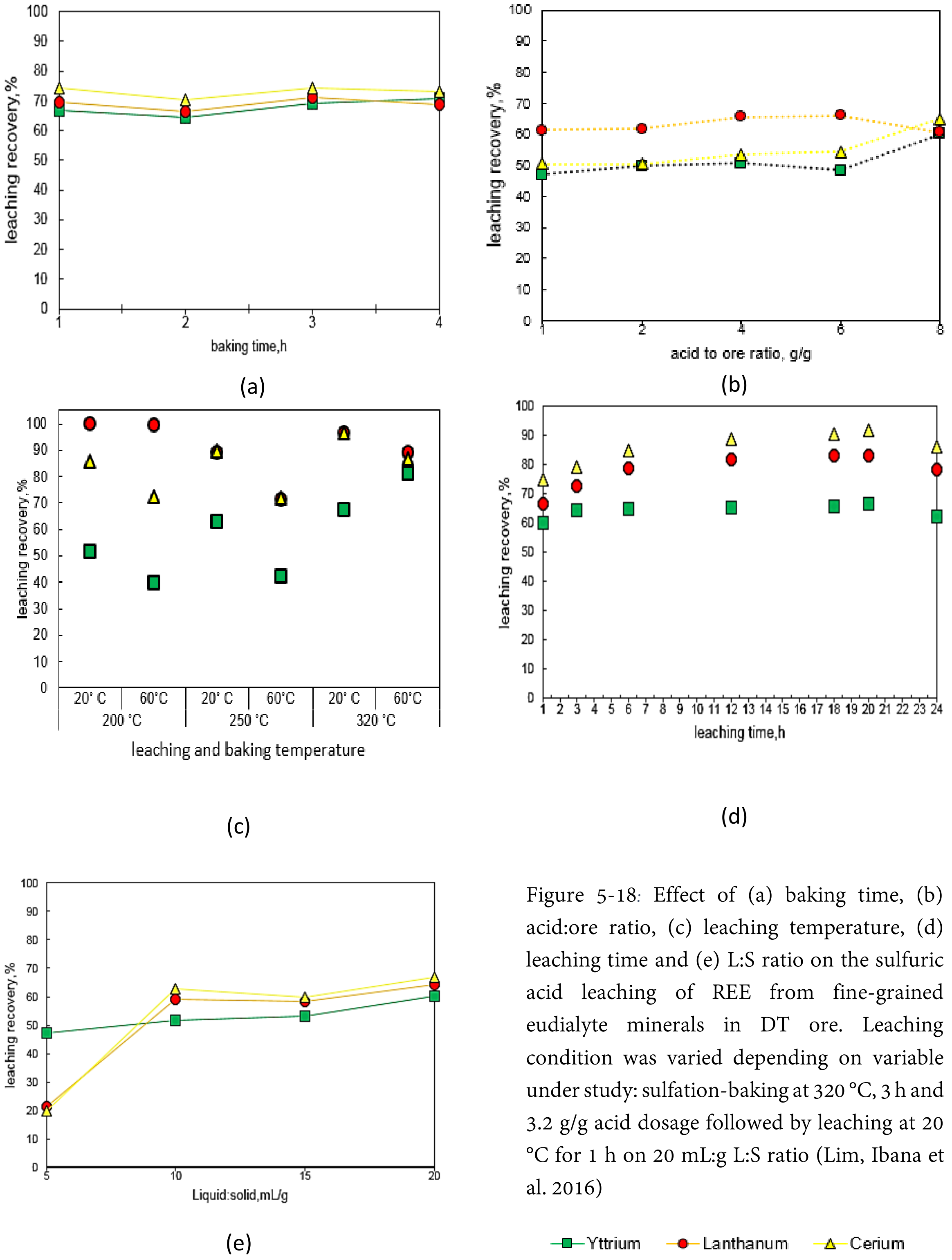


Figure 5-18: Effect of (a) baking time, (b) acid:ore ratio, (c) leaching temperature, (d) leaching time and (e) L:S ratio on the sulfuric acid leaching of REE from fine-grained eudialyte minerals in DT ore. Leaching condition was varied depending on variable under study: sulfation-baking at 320 °C, 3 h and 3.2 g/g acid dosage followed by leaching at 20 °C for 1 h on 20 mL:g L:S ratio (Lim, Ibana et al. 2016)

The leaching of Ce was also significantly affected by the sulfation-baking step. At a baking temperature of 320 °C and a baking time of 3 h, the heated ore mass underwent a colour change, believed to be associated with the oxidation of trivalent Ce to a tetravalent state. Tetravalent Ce is more soluble than trivalent Ce (Paulenova, Creager et al. 2002). On leaching, the leach solution turned pale yellow. Tetravalent Ce has a distinct yellow colour in solution (Gschneidner 2006).

The leaching of La suggested its relatively easy lixiviation. Grind size, leaching time and L:S ratio were the significant factors affecting its lixiviation.

Figure 5-19: Floating calcium sulfates scales observed on prolonged leaching of DT ore (Lim, Ibana et al. 2016)

Given the above results, the leaching of REE from fine-grained eudialyte minerals in DT ore was optimised, based on the optimal leaching of Y. The conditions were as follows: sulfation baking at 320 °C for 3 h at 3.2 g/g acid dosage, followed by water leaching at 60 °C for 3 h at an L:S ratio of 20 mL:g and 300-420 μm grind size. These leaching conditions were tested in a laboratory and provided the following recovery rates (%): 91 (Y), 94 (La) & 93 (Ce). The assays of REE in solution were (ppm): 290 (Y), 659 (La) & 986 (Ce). At this level of concentration, REE recovery can be effected using a standard solvent extraction technique after leach solution purification (Xie, Zhang et al. 2014).

5.4.4 Factors limiting rare earths leaching

In the sulfuric acid leaching of REEs from large-grained eudialyte minerals in SG concentrate, mass balances on XRF analysis indicated that 20-25 % of eudialyte mass was left unleached (Appendix M). Optical microscopy examination revealed that there was a dense silica layer on the undecomposed eudialyte grains (Figure 5-20). This may have limited the complete leaching of REE. Furthermore, XRD analysis of the leach residue showed a lower Na and Zr content as determined from the chemical composition of the eudialyte as $Na_4(Ca, Ce)_2(Fe^{2+}, Mn^{2+}, Y)ZrSi_8O_{22}(OH, Cl)_2$. (Table M-1 Appendix M, Figure 5-21). These results reflect a similarity to previous investigations. In the sulfuric acid leaching of Lovozero eudialyte, the eudialyte had not completely decomposed due to two main factors: (1) the silica covering on the eudialyte grains and (2) the conversion of eudialyte into wadeite, a refractory Zr silicate (Lebedev 2003, Lebedev, Shchur et al. 2003, Zakharov, Maiorov et al. 2011).

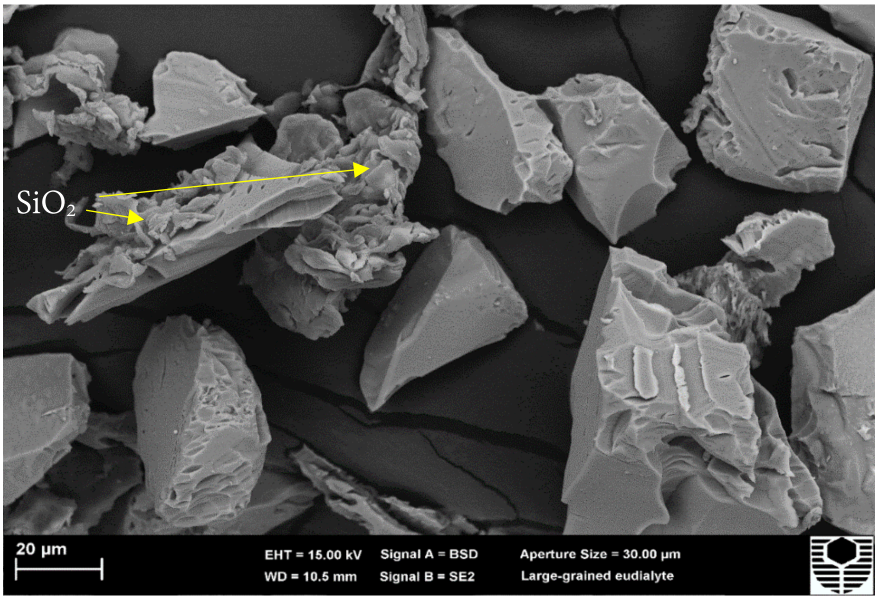


Figure 5-20: Mixed back-scattered and secondary electron image of SG concentrate leach residue

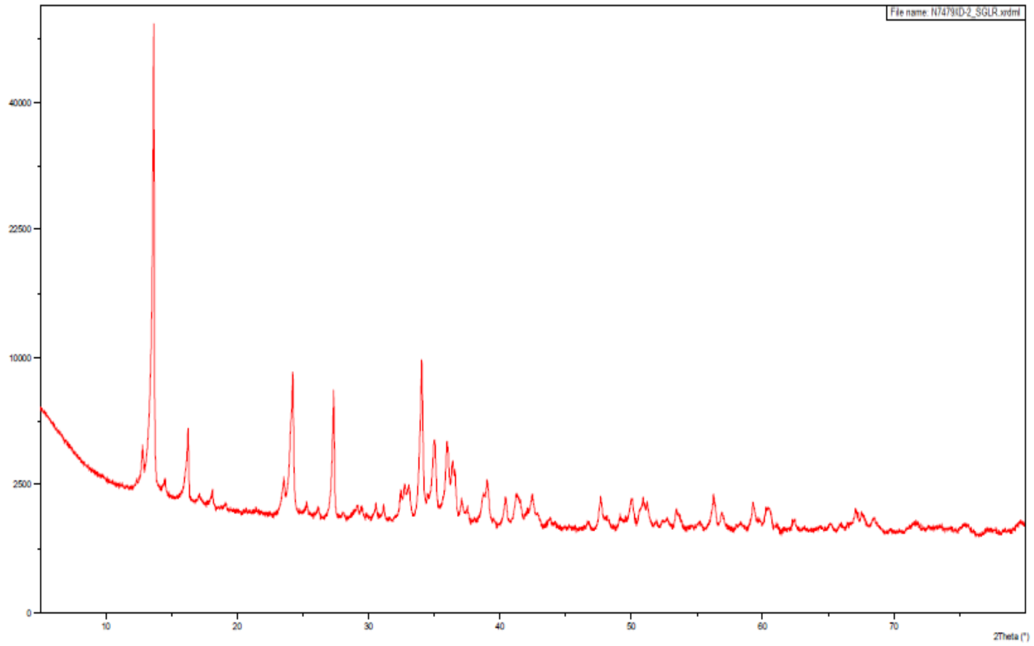


Figure 5-21: XRD diffractogram of SG concentrate leach residue

In the case of fine-grained eudialyte minerals in DT ore, no significant silica precipitation on eudialyte surfaces was observed. SEM-EDS examination of the leach residue showed the thinning of fine eudialyte grains, with no detectable level of REEs (Figure 5-22). The non-dissolution of feldspar minerals and quartz was also evident in the micrograph. Results of TIMA analysis on these leach residue showed similar findings in which fine-grained eudialyte paled out while quartz and feldspar were only partially decomposed (Figure 5-23).

These findings support earlier findings on higher REE recovery from DT ore compared to SG concentrate.

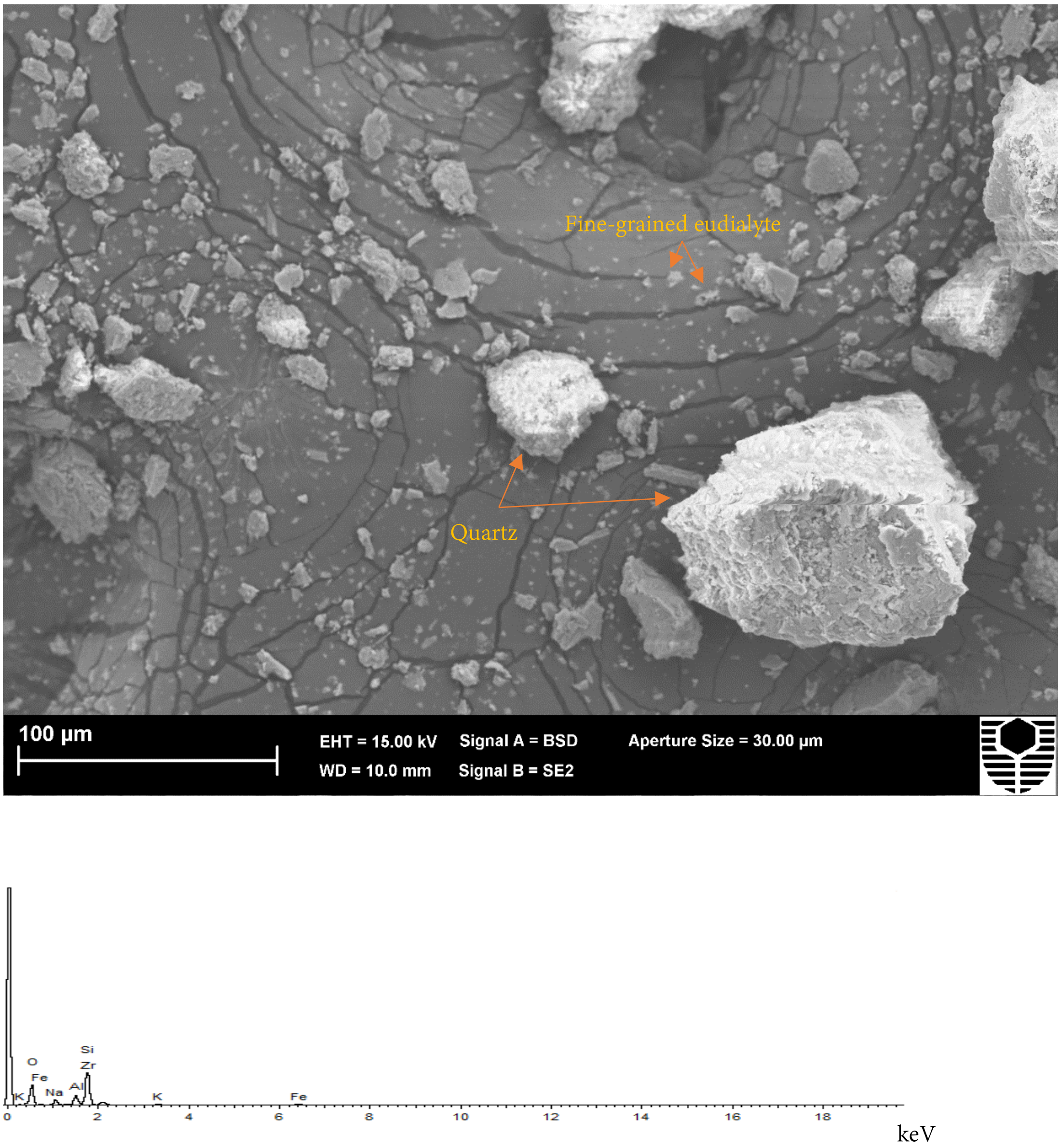
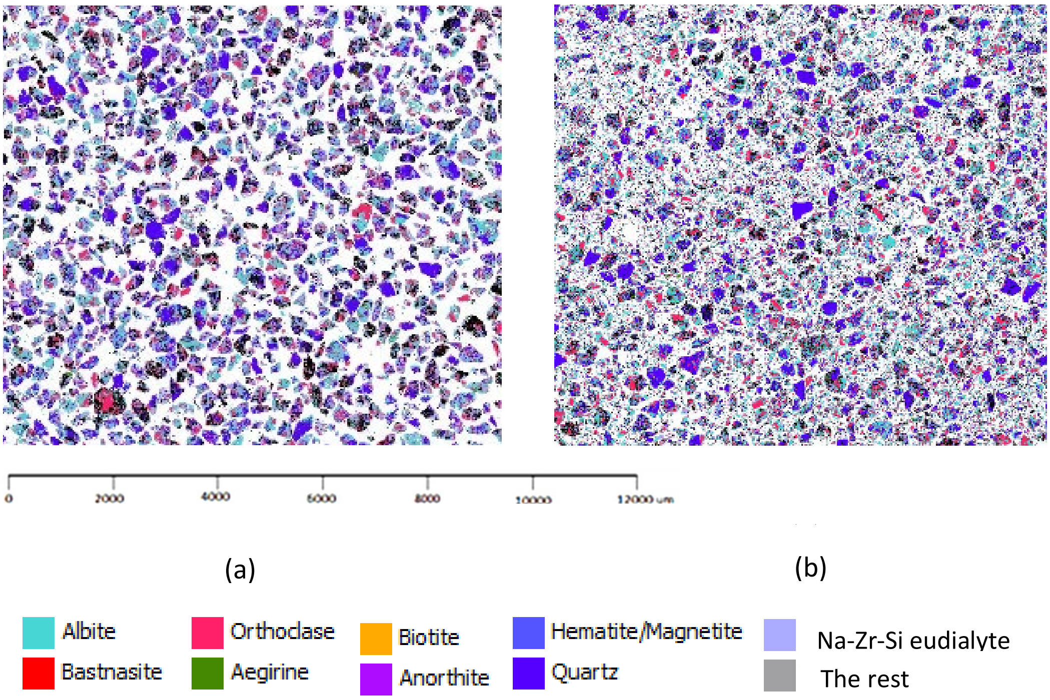


Figure 5-22: Photomicrograph of DT ore leach residue after sulfuric acid leaching showing residual fine-grained eudialyte (top); EDS of fine-grained eudialyte indicated Zr content only and no detectable concentration of REEs on EDS analysis (bottom)



(a)

(b)

Figure 5-23: Mineral liberation analysis on (a) DT ore sample, 300-420 µm grind size and (b) DT leach residue after sulfuric acid leaching showing the thinning out of Na-Zr-Si eudialyte phases

5.5 Chapter Summary

This chapter has shown that the leaching of rare earths from eudialyte, using sulfuric acid as a lixiviant, required a different set of conditions compared to conventional leaching of the mineral. Although the leaching procedure and conditions were highly dictated by mineralogy, the leaching conditions for rare earth lixiviation were characterised by a high L:S ratio. With increased water addition, the sulfuric acid concentration was reduced considerably, with the added benefit of a reduced risk of silica gel formation on leaching.

In this chapter, it was found that large-grained eudialyte in SG concentrate responded well to direct lixiviation with heated sulfuric acid. This resulted to high REE leaching recoveries of 82 %. The optimal leaching of Y occurred with leaching at 60 °C for 2 h with 5 wt. % sulfuric acid, at an L:S ratio of 100 mL:g and grind size of 300-420 µm. The optimal lixiviation of LREEs La and Ce was found from the same leaching conditions except that these elements had higher recovery rates on using a finer grind size of 149-212 µm but the effect of grind size on REE recoveries was found to be insignificant. Sulfuric acid concentration was the only significant factor. Thus, the leaching responses of HREEs and LREEs were similar in the sulfuric acid leaching REEs from large-grained eudialyte in SG concentrate. The high REE recoveries achieved with single stage leaching of eudialyte minerals were comparable to REE recoveries derived from previous techniques of multiple leaching of eudialyte. This finding provides a new approach to processing eudialyte mainly for REE recovery.

This chapter has also shown that leaching REE from fine-grained eudialyte in DT ore requires more rigorous treatment. Sulfation baking was a significant preparatory procedure for REE lixiviation. In particular, the baking temperature had a strong influence in effecting thermal cracking of the fused and complex morphology of fine-grained eudialyte in DT ore. As such, the optimal leaching of Y was with sulfation baking at 320 °C for 3 h at 3.2 g/g acid dosage, followed by water leaching at 60 °C for 3 h at an L:S ratio of 20 mL:g and 300-420 µm grind size. The optimal leaching of La and Ce required differing temperatures and acid dosages on sulfation baking. However, a generalisation cannot really be made, as the leaching of these LREEs were also influenced by the co-leaching of bastnasite minerals in DT ore. The above findings on the conditions for preferable leaching of REEs from fine-grained eudialyte provided new information on how similar materials can be processed.

It was determined that the main limitation on the complete leaching of REEs from large-grained eudialyte was the covering of dense silica layers on its surface. This effect was minimal in fine-grained eudialyte, as the silicate bearing minerals in DT ore had only undergone partial decomposition. The low effect of silica in the leaching of DT ore may explain its higher REE leaching recovery of 91%. These findings emphasised the significant effect of silica in limiting REE lixiviation.

Chapter 6

Citric Acid Leaching of Rare Earths from Eudialyte

6.1 Introduction

The sulfuric acid leaching of eudialyte suffers a cost disadvantage due to the large volume of chemicals needed for leaching and the cost of subsequent waste neutralisation. It is therefore worthwhile to explore low-cost alternative leaching agents for rare earth leaching from eudialyte.

Citric acid is an inexpensive weak organic acid. As a carboxylic acid, it forms strong metal complexes. Reviews of REE-citrate solution chemistry indicate that the solubility of rare earths in citric acid is high. However, there are no studies that report the application of citric acid as a leaching agent for the extraction of rare earths from eudialyte minerals. Hence, this study was initiated to address this gap.

This chapter discusses investigations into the citric acid leaching of rare earths from two differently textured eudialyte minerals. The approach to the leaching test is statistical in nature, owing to the lack of sufficient pertinent information.

6.2 Aims of the chapter

This chapter discusses investigations into the following:

- citric acid leaching of rare earths from a (a) large-grained and (b) fine-grained eudialyte mineral;
- comparative leaching behaviour of HREEs and LREEs including the determination of conditions for the optimal leaching of HREEs in the citric acid leaching of large-grained eudialyte;
- comparative leaching behaviour of HREEs and LREEs including the determination of conditions for the optimal leaching of HREEs in the citric acid leaching of fine-grained eudialyte; and
- causes of incomplete leaching of rare earths in the citric acid leaching of the two differently textured eudialyte minerals

6.3 Materials and Methods

6.3.1 Eudialyte ore samples

Two differently textured eudialyte minerals were used in the leaching test: large-grained eudialyte minerals from South Greenland (SG ore) and finely-textured eudialyte from Dubbo, New South Wales (DT ore).

6.3.2 Reagents and equipment

Reagent grade citric acid (Rowe Scientific, 192.12g/mol), sodium hydroxide pellets (Rowe Scientific, 40.00g/mol), hydrochloric acid (Rowe Scientific, 32%) and deionized water were used in the leaching test.

Equipment utilised for leaching was as follows: 14-L Ratek OM11 shaker with thermal control, glass thermometer (0-110 °C), 307 ECE digital temperature scanner (0-800 °C) and TPS Aqua pH meter with Ag/AgCl reference electrode.

6.3.3 Analytical equipment

The analysis of the leach solution was conducted by means of Agilent 735ES ICP-OES and performed externally by the CSIRO Mineral Resources Laboratory (Waterford, Western Australia).

Analysis of leach residues was performed using PANalytical X'Pert Pro PW3040 XRD, PANalytical MagiX Fast XRF, and a TESCAN 3 FE GMU integrated mineralogy analyser with a Pulse Tor 30 detector. XRD and XRF analysis work on eudialyte ore samples was carried out at the John de Laeter Centre at Curtin University (Bentley, Western Australia) while the analysis on the leach residue was outsourced to Ultra Trace Pty Ltd (Canning Vale, Western Australia).

6.3.4 Leaching test sample preparation

SG and DT ore were prepared according to the procedures described in *Preparation of test samples* in Section 4.3.4. In these procedures, SG ore was beneficiated to produce SG concentrate while DT ore was pulverised and used as whole-of-ore. The sample preparation utilised for each ore was decided from the texture of the mineralisation of the eudialyte minerals in the ore samples.

Leaching experiments were conducted using a test sample mass of 1.0 g for SG concentrate and 20.0 g for DT ore.

6.3.5 Leaching procedure

SG concentrate and DT ore were leached using a direct leaching method with the use of citric acid as direct leaching manifested to be a cost-effective procedure amongst the explored treatment procedures for both ores (Appendix I). Prior to citric acid leaching, SG concentrate was firstly subjected to a pre-treatment procedure where it was boiled without any stirring action, using 0.1% sulfuric acid to remove aluminium silicates (Figure 6-1a). This reduced the risk of silica gel formation on leaching. The presence of Al in silicate minerals increases the potential for gel formation on leaching (Terry 1983a). Gel formation was observed in exploratory test for SG concentrate (Appendices E & I).

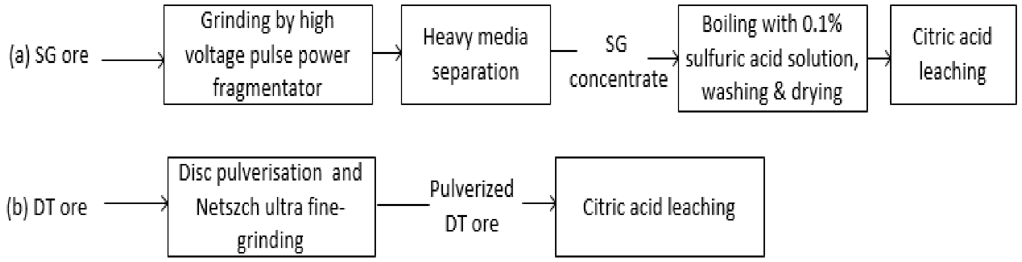


Figure 6-1: Schematic diagram of sample preparation and leaching method for (a) SG concentrate and (b) DT ore

In contrast, the leaching of DT ore was effected after the ore was pulverised at the desired grind size (Figure 6-1b).

Leaching tests for SG concentrate and DT ore were carried out in round-bottom flasks placed in a temperature controlled-shaker. The shaking speed was 200 rpm for 50-mL solution volume and 300 rpm for 200-mL solution volume. Shaking speed of more than 340 rpm had been identified to contribute to early silica coagulation (Li and Kaner 2005).

The solution temperature of the leaching was monitored with the use of a thermal scanner. Measurements of pH were taken with a Ag/AgCl reference electrode, calibrated from standard solutions. Solution pH was adjusted using NaOH. Filtration was carried out with the use of a 0.45 μm acetate filter.

6.3.6 Citric acid stoichiometric requirement

Citric acid stoichiometric requirements were calculated based on the reactions for REEs, Zr, Nb, and for the impurities Al, Ca, Fe, K, and Na. The proposed generalised reaction for the citric acid was as follows:

$$aM^{z+} + bC_6H5O_7^{-3} \rightarrow M_a(C_6H_5O_7)_b \qquad (6\text{-}1)$$

where M represents the cations enumerated earlier;

The stoichiometric amount of citric acid required was calculated to be 233 mg/g for SG concentrate and 217 mg/g for DT ore.

6.3.7 Design of experiment

The leaching of rare earths from eudialyte minerals in SG concentrate and DT ore was approached with the use of a statistical experimental design based on a 2^{6-2} fractional factorial design which denotes 2 levels of 6 factors, at two replicates. Leaching factors were: grind size, leaching time, leaching temperature, citric acid concentration, pH and L:S ratio. Citric acid concentration and pH were considered as separate factors. The type of citrate complex is dictated by both factors (Tevebaugh 1947). The low and high experimental settings for each factor were designed based on empirical tests and information gathered from related studies. For example, as DT ore was used as a whole-of-ore leach, a higher citric acid dosage and a larger dilution ratio were required, consistent with the larger mass sample of DT ore. Further, the grind size chosen for the leaching test differed from that of SG concentrate, in consideration of the fine mineralisation of DT ore. Statistical software (Minitab 17.1) was used to generate the experimental plan table which consisted of 16 different sets of leaching conditions, at two replicates for the leaching test of SG concentrate (Table 6-1) and DT ore (Table 6-2).

Table 6-1: Experimental plan table for the citric acid leaching of rare earths from SG concentrate

Factors	low setting (-)	high setting (+)	Run number																															
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
Grind size,µm	75-106	212-300	+	-	+	+	+	-	-	-	+	+	-	+	+	-	+	+	-	-	+	-	+	+	+	-	+	-	-	-	-	-	+	-
Leaching time, h	5	8	-	-	+	+	-	-	+	+	-	-	-	-	-	+	+	+	+	+	-	-	-	+	+	-	+	-	+	-	+	+	+	-
Leaching temp, °C	20	60	+	-	-	+	-	+	-	+	-	+	-	-	+	-	+	+	+	+	-	-	+	-	-	+	+	-	-	+	-	+	-	+
Citric acid, M	0.3	0.8	-	+	-	+	-	-	+	-	+	+	-	+	+	-	-	-	+	+	-	+	-	-	+	+	+	-	-	-	+	-	+	+
L:S ratio, mL:g	50	100	+	+	+	+	-	+	-	-	+	-	-	+	-	+	-	-	+	+	-	+	+	+	-	-	+	-	+	+	-	-	-	-
pH	2-3	6-7	-	-	-	+	+	+	+	-	+	-	-	+	-	+	+	+	-	-	+	-	-	-	-	+	+	-	+	+	+	-	-	+

Table 6-2: Experimental plan table for the citric acid leaching of rare earths from DT ore

Factors	low setting (-)	high setting (+)	Run number																															
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
Grind size,µm	10 (D_{90})	212-300	-	-	-	+	+	+	-	+	+	-	-	+	-	-	-	-	+	-	-	+	+	+	+	+	+	-	-	+	-	+	+	-
Leaching time, h	5	8	+	+	+	-	-	-	+	+	+	-	-	-	-	-	-	-	+	+	+	-	+	+	+	-	-	+	-	+	-	+	-	+
Leaching temp, °C	20	60	+	-	-	-	-	+	+	-	-	-	-	+	+	+	+	+	+	-	-	+	-	-	+	+	-	+	-	+	-	+	-	+
Citric acid, M	0.1	0.3	+	+	-	-	-	+	-	-	-	-	-	+	-	-	+	+	+	-	+	-	+	+	-	-	+	+	+	+	+	-	+	-
L:S ratio, mL:g	50	200	-	-	+	+	+	-	+	-	-	-	-	-	-	-	+	+	+	+	-	+	+	+	-	+	-	-	+	+	+	-	-	+
pH	2-3	6-7	+	-	+	-	-	-	-	+	+	-	-	-	+	+	-	-	+	+	-	+	-	-	-	+	+	+	+	+	+	-	+	-

6.3.8 Optimization test for leaching of SG concentrate and DT ore

The determination of significant factor/s for leaching of rare earths from SG concentrate and DT ore involved use of an Analysis of Variance (ANOVA) at a 95 % confidence level. Statistical optimisation was performed using DOE++ V9 (Reliasoft Corporation) and Minitab 17. 1 (Minitab Inc.) software. Optimal leaching conditions for REE extraction were determined statistically and validated in a laboratory leaching test. Further optimisation was carried out by varying one factor at a time. Conditions were those for the optimal leaching of Y, it being a more economically significant REE than La and Ce.

6.3.9 Analysis and presentation of data

For the leaching tests, the response variables were the individual metal yields of Y, La and Ce, calculated using Equation 5-2 (Chapter 5). The desired outcome would be the highest leaching recovery of rare earths. Results of the leaching test are presented in Main Effects and Cube plots.

6.4 Results and Discussion

6.4.1 Citric acid leaching of rare earths from eudialyte

The lixiviation of rare earths on citric acid leaching of eudialyte proceeds according to the general chemical reaction first described in Equation 2-5 (Brown, Gelis et al. 2012):

$\boldsymbol{i}\mathrm{REE}^{3+} + \boldsymbol{j}\mathrm{H}^{+} + \boldsymbol{k}\mathrm{Cit}^{3-} \rightleftharpoons \mathrm{REE}_i\mathrm{H}_j\mathrm{Cit}_k{}^{3i+j-3k}$

The results of the leaching tests showed clearly that REE lixiviation from citric acid leaching of large-grained eudialyte in SG concentrate was promoted in a low pH of 2-3. An average leaching recovery of 73 % resulted from the 32 tests conducted, compared to nil REE leaching at a pH of 6-7 (Figure 6-2). At a pH of 2-3, leaching recovery was 17 % higher on leaching at 60 °C, compared to leaching at 20 °C. In the same pH range, leaching recovery was 8 % higher with 0.8 M citric acid at an L:S ratio of 100 mL:g, compared to leaching with 0.3 M citric acid at an L:S ratio of 50 mL:g. The effect of grind size and leaching time showed comparable leaching recovery rates.

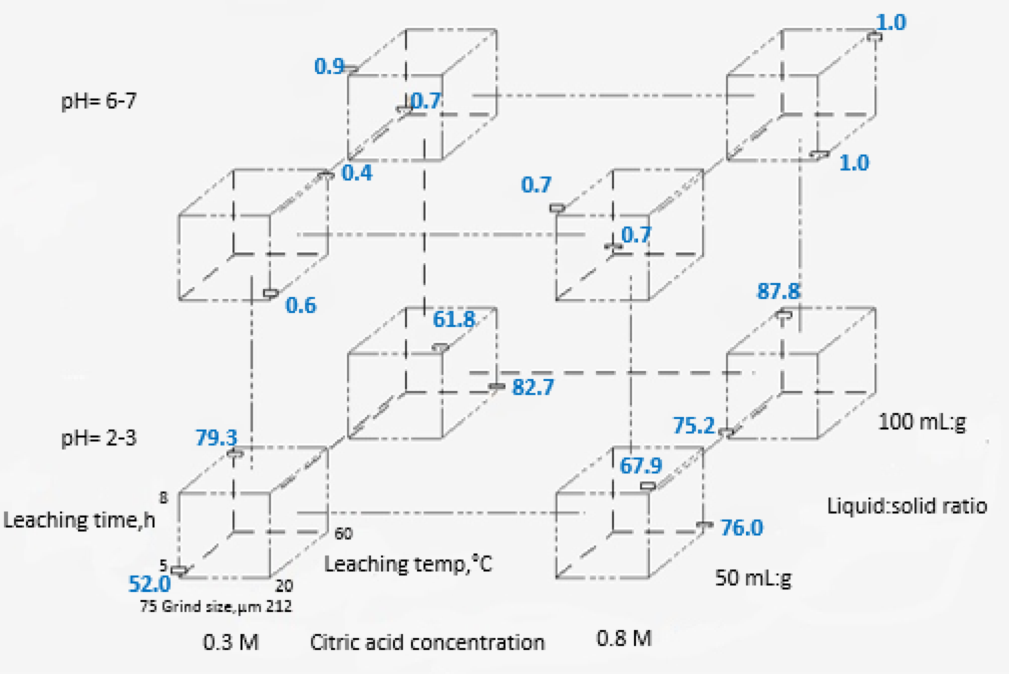


Figure 6-2: Cube plot for citric acid leaching of REE from eudialyte in SG concentrate indicating high recoveries on leaching at low pH of 2-3

The above results highlight the effects and importance of pH and temperature. Analysis of leaching recoveries by the ANOVA method supported this finding. This indicates that pH and leaching temperature were the only significant factors affecting the leaching of rare earths from large-grained eudialyte minerals in SG concentrate (Table 6-3). The highest leaching recovery was 88 % in the following conditions: leaching at 60 °C for 8 h using 0.8 M citric acid concentration at a pH of 2-3, L:S ratio of 100mL:g and 75-106 µm grind size. Under these conditions, the rare earths concentration in solution were as follows (mg/L): 32 (Y), 41 (La) & 58 (Ce).

Table 6-3: ANOVA results on leaching recoveries from citric acid leaching of rare earths from SG concentrate; pH and temperature were the significant factors (italicized)

Factor	**p-value**	**Factor**	**p-value**
Grind size	0.781	Citric acid concentration	0.100
Leaching time	0.544	pH	***0.000***
Leaching temperature	***0.001***	L:S ratio	0.085

The high lixiviation of rare earths at a low acidic pH is consistent with similar studies on using citric acid as an eluting agent for rare earths separation from ion-exchange resins. These studies reported the high uptake of REE by citric acid at a pH of 2–4. This was brought about by the presence of H_2cit^- ions, known to form more stable REE citrate complexes than other citrate ions (Spedding, Fulmer et al. 1947, Tevebaugh 1947). However, in this present study, it was believed that the use of a high L:S ratio of 100 mL:g promoted the existence of REE citrates as hydrated complexes, and the effect of temperature was to increase the solubility of these complexes. This rationale runs in agreement with REE citrate solubility studies citing REE hydrate formation on citric acid molar concentrations greater than 0.1 M and its increased solubility with increased solution temperature (de Kruif, van Miltenburg et al. 1982, Oliveira, Malagoni et al. 2013).

In contrast, the leaching of rare earths from fine-grained eudialyte in DT ore resulted into poor leaching yields (Figure 6-3). The effect of pH on the leaching of REE was not significant, as evidenced by comparably low leaching recoveries both from leaching at a pH of 2-3 and a pH of 6-7. The highest leaching recovery was only 8 % which resulted from leaching at pH 2-3 at 60 °C for 8 h using 0.1 M citric acid concentration and 10 μm (D_{90}) grind size. Analysis of leaching test results by the ANOVA method showed that unlike the leaching of rare earths from large-grained eudialyte in SG concentrate, the leaching of rare earths from fine-grained eudialyte minerals in DT ore was significantly affected by grind size and leaching temperature (Table 6-4).

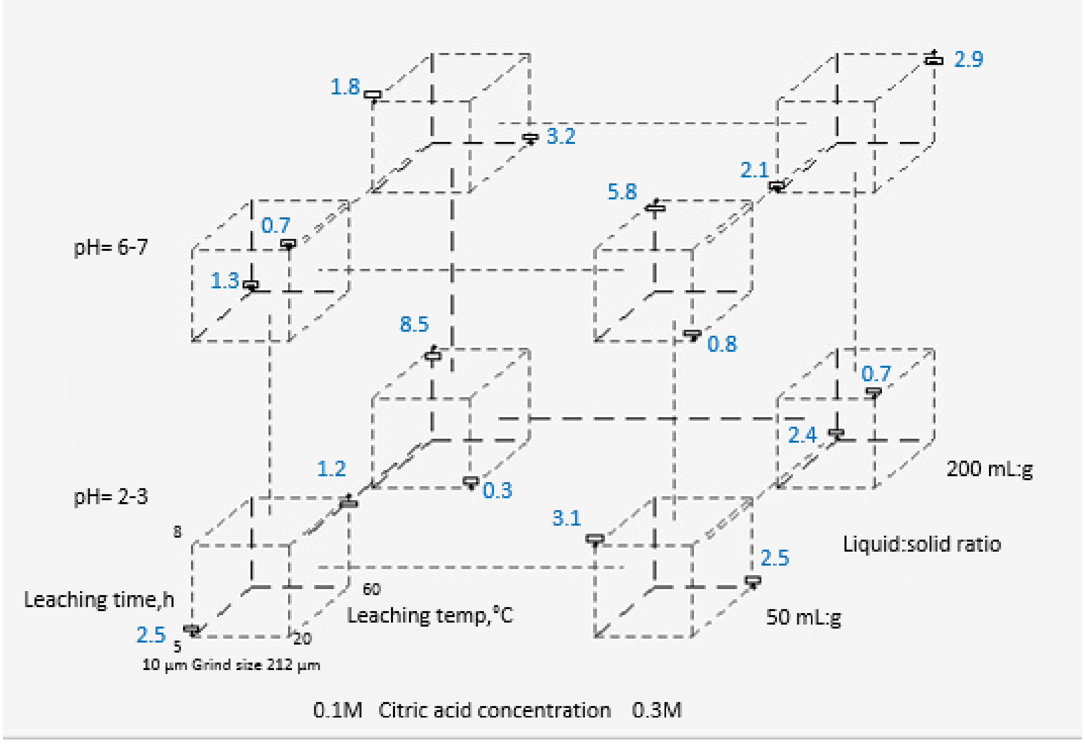


Figure 6-3: Cube plot for citric acid leaching of REE from eudialyte in DT ore

Table 6-4: ANOVA results of leaching recoveries on citric acid leaching of rare earths from DT ore, pH and temperature were the significant factors (italicized)

Factor	**p-value**	**Factor**	**p-value**
Grind size	***0.003***	Citric acid concentration	0.851
Leaching time	0.042	pH	0.570
Leaching temperature	***0.002***	L:S ratio	0.397

Additional leaching tests carried out to investigate further the poor leaching of REE from fine-grained eudialyte minerals showed that while grind size and temperature were significant factors, the kinetics of REE lixiviation were slow. The highest leaching recovery was 8 % on leaching for 8 h using 10 µm (D_{90}) grind size, both on leaching at 25 °C and 70

°C (Figure 6-4). Extended leaching times of 50 h yielded only comparably low leaching recoveries as with leaching for 8 h. However, a leaching time of 100–200 h showed progress, with recovery increasing four fold to 42 % (Figure 6-5). Further increases in leaching times showed erratic results: leaching recoveries dropped to 25 % at 300 h leaching and increased up to 37 % at 400 h. These behaviours could be attributed to co-precipitation of rare earths onto floating calcium citrates and its re-dissolution with a longer leaching time.

Furthermore, the possibility of preg-robbing phenomena was also looked into to investigate the poor leaching recovery of REE from fine-grained eudialyte minerals in DT ore. Preg-robbing is the immediate precipitation of leach species by adsorption into ore surfaces, a popular scenario in fine-grained silicate minerals (Mohammadnejad 2014). However, results of a preg-robbing test showed that this phenomena was non-existent, as evidenced by the slight increase in REE concentration over time (Appendix J).

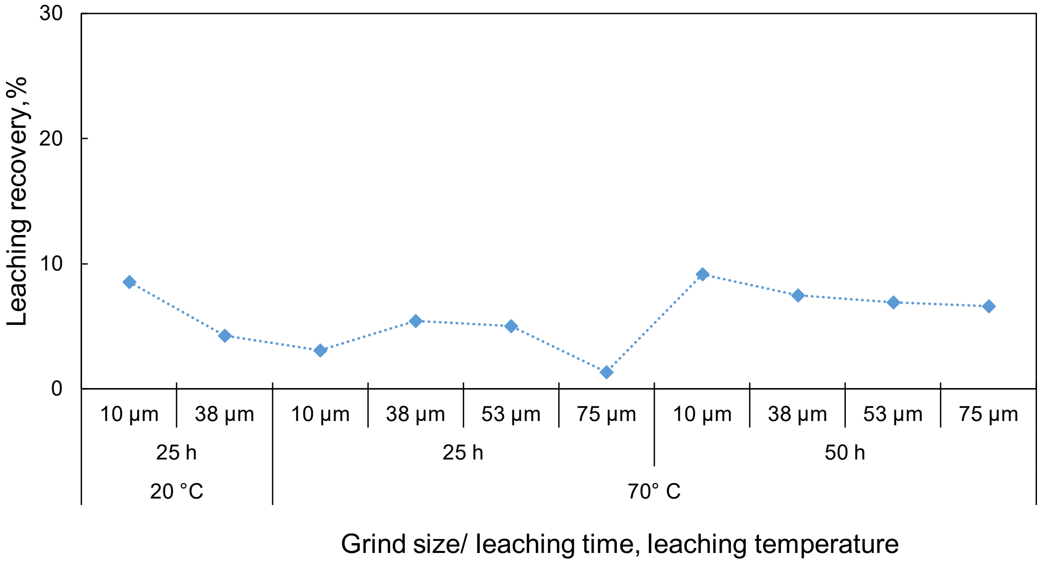


Figure 6-4: Effect of grind size, leaching time (25-50 h) and leaching temperature on citric acid leaching of rare earths from fine-grained eudialyte minerals in DT ore

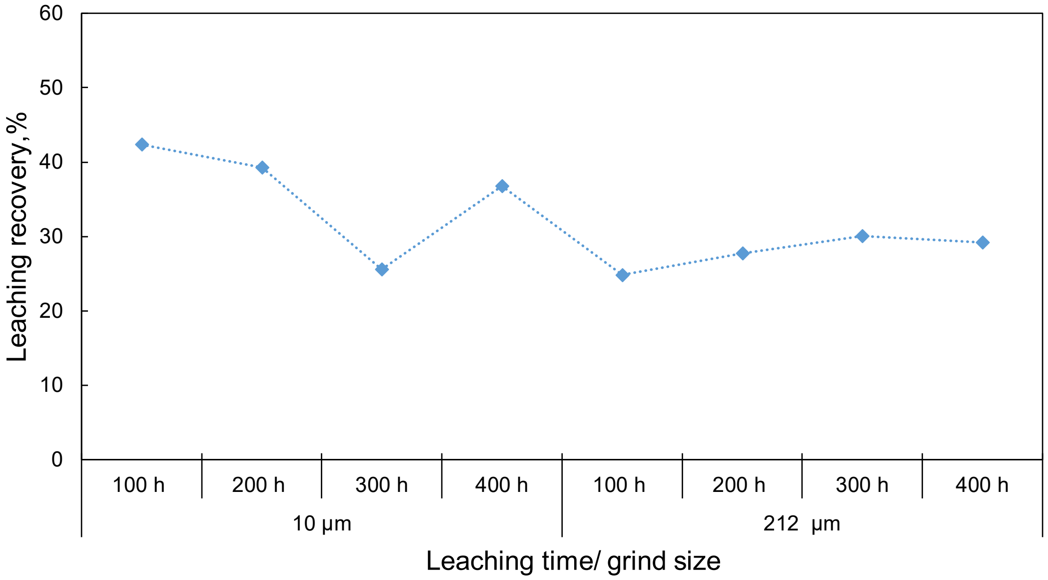


Figure 6-5: Effect of longer leaching time (100-400 h) and grind size on citric acid leaching of rare earths from fine-grained eudialyte minerals in DT ore

Thus, the differences in leachability of rare earths from the two differently-textured eudialyte minerals used in this research work can be attributed largely to mineralogical differences. Large-grained eudialyte in SG concentrate yielded to leaching with citric acid, and pH was found to be the most significant factor, while leaching temperature enhanced leaching kinetics. On the other hand, the complex mineralogy of fine-grained eudialyte mineral phases in DT ore would not render to easy lixiviation with citric acid. The direct leaching method yielded only slow kinetics. Due to the lack of practicality of exploring further the comparative leaching behaviour of HREEs and LREEs in DT ore, this objective was only explored with SG concentrate.

6.4.2 Leaching responses of heavy and light rare earths in large-grained eudialyte in SG concentrate

Results of leaching tests showed that Y lixiviation was favoured in the following leaching conditions: use of 212-300 μm grind size, 8 h leaching at 60 °C at pH 2-3, 0.8 M citric acid concentration and 100 mL:g L:S ratio (Figure 6-6). On the other hand, the leaching of LREEs La and Ce were favoured in the following conditions: use of 75-106 μm grind size, leaching for 8 h at 60° C at pH 2-3, 0.8 M citric acid concentration and 100 mL:g L:S ratio (Figures 6-7 & 6-8). From the 32 tests conducted, it can be seen that both the lixiviation of Y and LREEs La and Ce were largely affected by solution pH, as exhibited by the resulting average leaching recovery of 75 % on leaching at pH of 2-3 conducted, while there was nil for leaching of REE on pH of 6-7. The favourable grind size on leaching varied between Y and LREEs La and Ce but the influence of grind size was the least among the factors. Hence, the leaching behaviour of HREE Y and LREEs La and Ce were comparably similar, as exhibited in the resulting Main Effects plots of the leaching results (Figures 6-6 to 6-8). As presented earlier, analysis of leaching test results by the ANOVA method showed that pH and leaching temperature were the only significant factors affecting the leaching of Y, La and Ce (Table 6-3). These factors were further investigated to learn more on the comparative optimal leaching conditions for HREEs and LREEs. Although the influence of the L:S ratio was not significant, this factor was also investigated, owing to the economic impact of increasing mass loading on leaching.

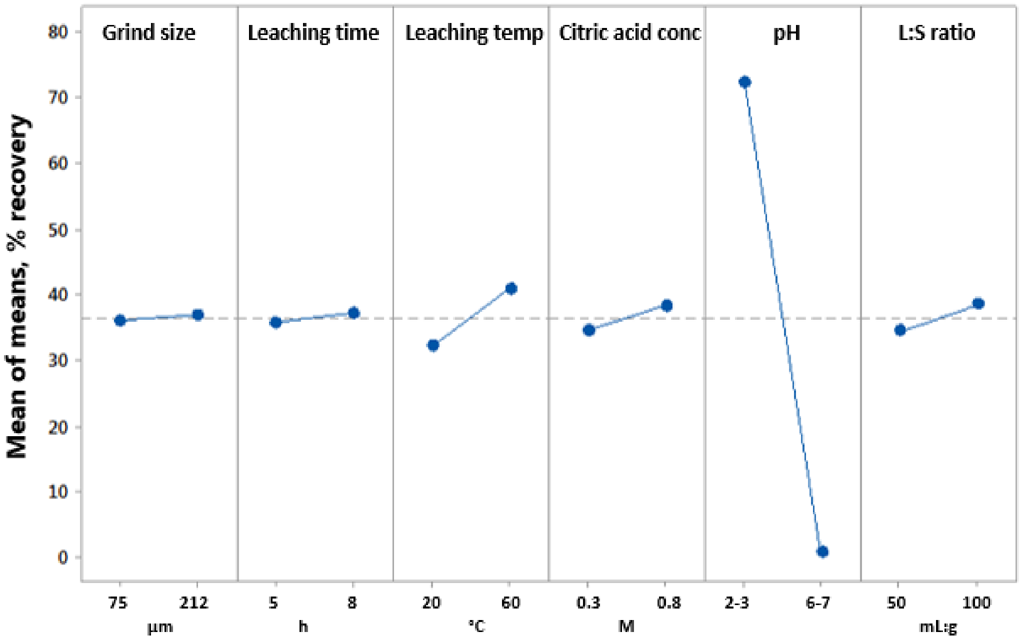


Figure 6-6: Main Effects plot for Y recovery on citric acid leaching of large-grained eudialyte in SG concentrate

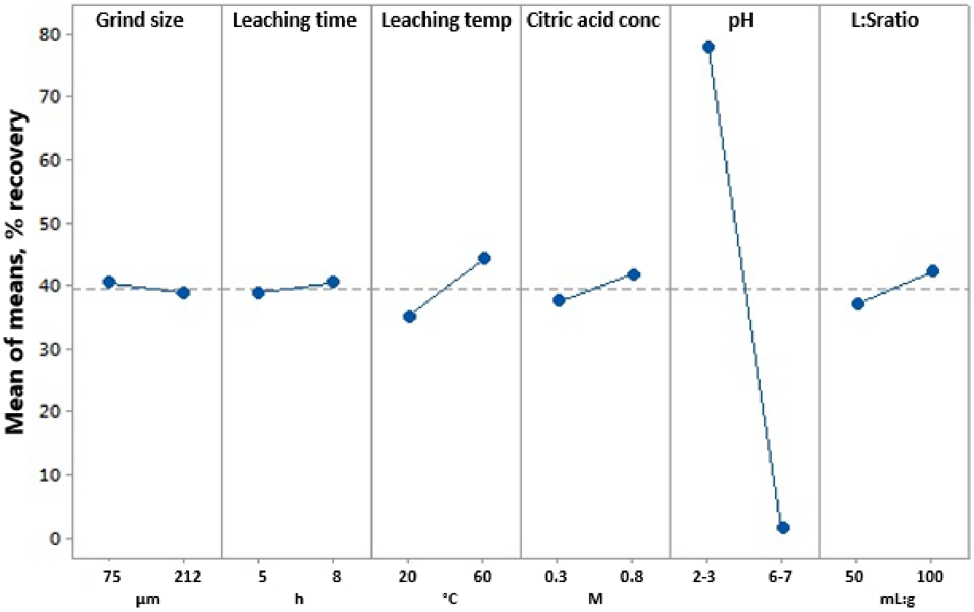


Figure 6-7: Main Effects plot for La leaching from large-grained eudialyte minerals in SG concentrate

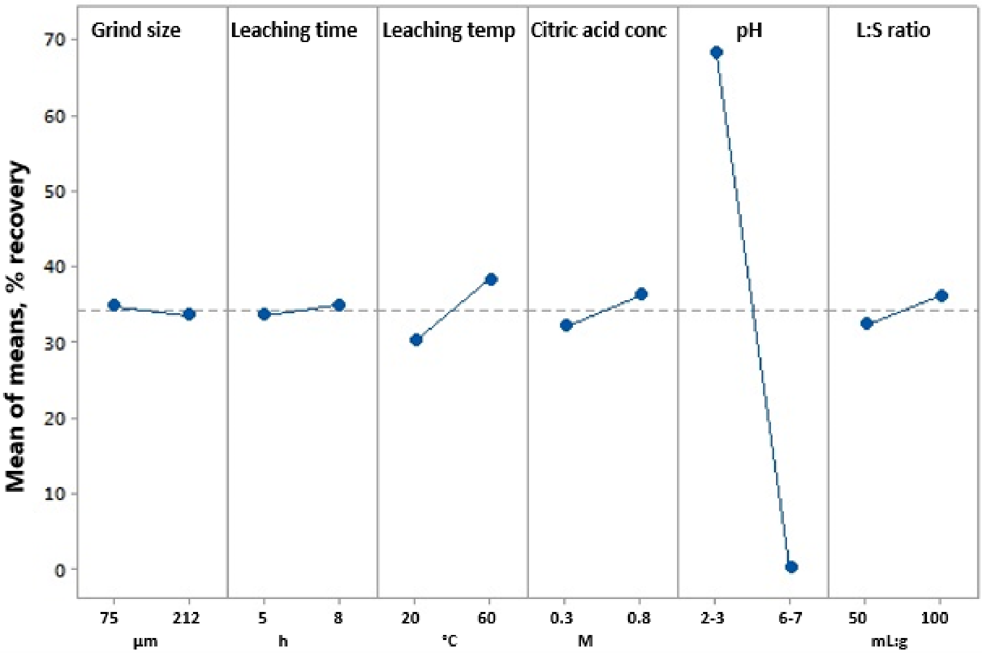


Figure 6-8: Main Effects plot for Ce leaching from large-grained eudialyte minerals in SG concentrate

6.4.2.1 Effect of pH

Optimisation tests on the effect of pH showed that slightly higher leaching recoveries were attainable at a lower pH of 1-2 (Figure 6-9).With the change in pH, it is not fully known what the dominant REE citrate complex in the solution was, as the literature has contradicting views on this. Tevebaugh (1947) reported that the prevalent citrate complex at pH 1 is H_2cit. Barnes and Bristow (1970) on the other hand, reported a combination of complexes: H_2cit and Hcit. Nonetheless, increased leaching kinetics were observed at pH 1; eudialyte digestion was completed in half the time required to fully digest it on leaching at pH 2. Precipitation of silica in a filterable form was also observed on leaching at pH 1. This resulted in easy filtration of the pregnant leach solution.

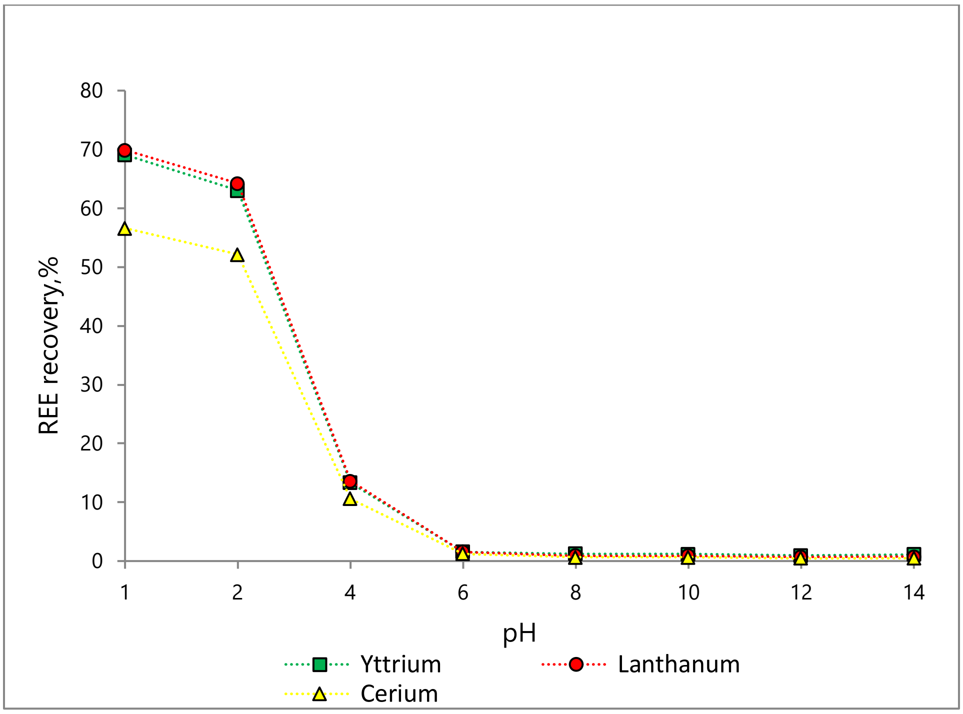


Figure 6-9: Effect of pH on citric acid leaching of rare earths from large-grained eudialyte minerals in SG concentrate

6.4.2.2 Effect of temperature

Results of optimisation tests showed clearly the effect of temperature in increasing leaching kinetics. After an hour of leaching, there was a significant increase in the average[4] REE yield from a recovery of less than 10 % at room temperature leaching, to a recovery of 70 % on leaching at 100 °C (Figure 6-10). The highest leaching recoveries were derived from leaching using a heated citric acid solution.

Results also showed that at room temperature leaching, REE yield increased with time after 5 h when the metal yield for the three REEs dropped. This was believed to be aused by the saturation of solution, as evidenced by the formation of silica and calcium precipitates,w hich

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[4] average of the leaching recovery of Y, La & Ce

caused co-precipitation of REEs. At the end of 8 h leaching, undecomposed eudialyte minerals were found along with the undigested minerals arfvedsonite and feldspar.

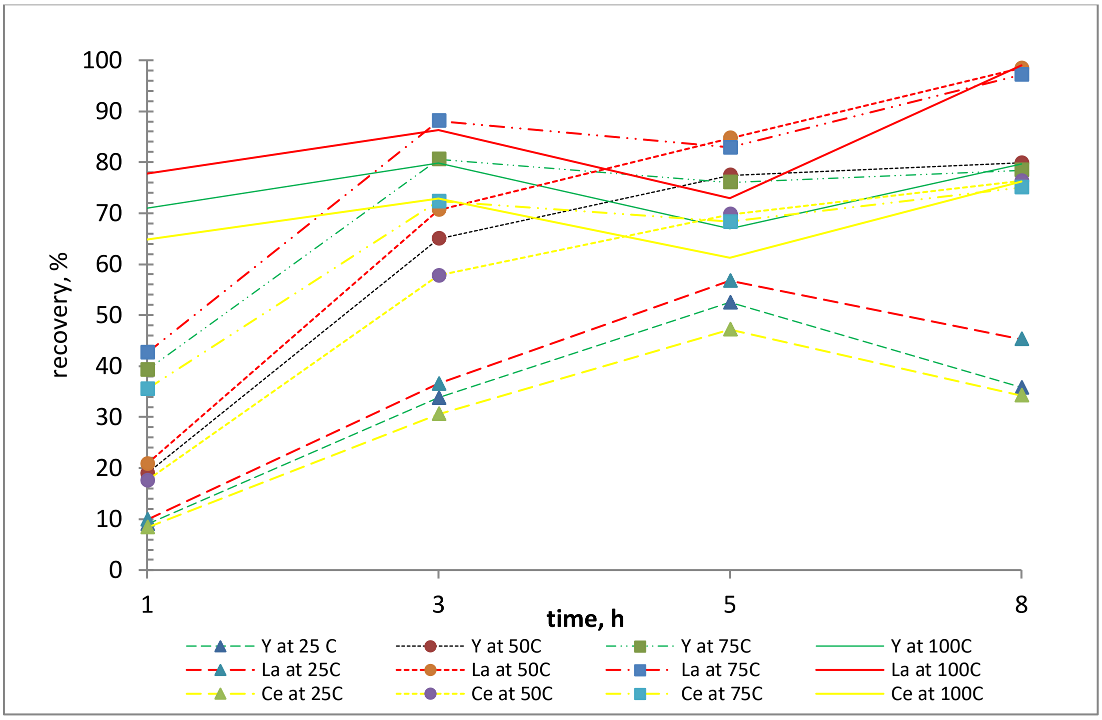


Figure 6-10: Effect of leaching temperature on the citric acid leaching of rare earths from SG concentrate

On leaching at 50 °C, REE leaching recoveries improved considerably, as shown by the leaching isotherms in Figure 6-10. The kinetics of REE leaching were highest in the first 3 h, they continued to increase after 2 h, with the highest recovery attained for La, while Y and Ce experienced relatively slower kinetics.

The 75 °C and 100 °C isotherms showed similar responses at which the recoveries were the same at 3 h leaching, they dropped at 5 h leaching and then started to increase for up to 8 h. La had the highest recovery. It was believed that the reduction in metal yield was related to co-precipitation of REE on silica films formed on the colder sides of the beaker; these re-dissolved on prolonged leaching.

6.4.2.3 Effect of liquid: solid ratio

Results of leaching tests carried out to ascertain the effect of L:S ratio showed that leaching recoveries of REE decreased by 23 % with a ten-fold decrease in L:S ratio (Figure 6-11). At the lowest L:S ratio of 10, the assays in solution were (mg/L) : 219 (Y), 282 (La) and 400 (Ce). These concentrations were seven fold compared to assays on 100 mL:g L:S ratio but the silica content was high at 20 g/L. Although the solution did not form a gel on cooling, it did so after a week in temperature-controlled storage.

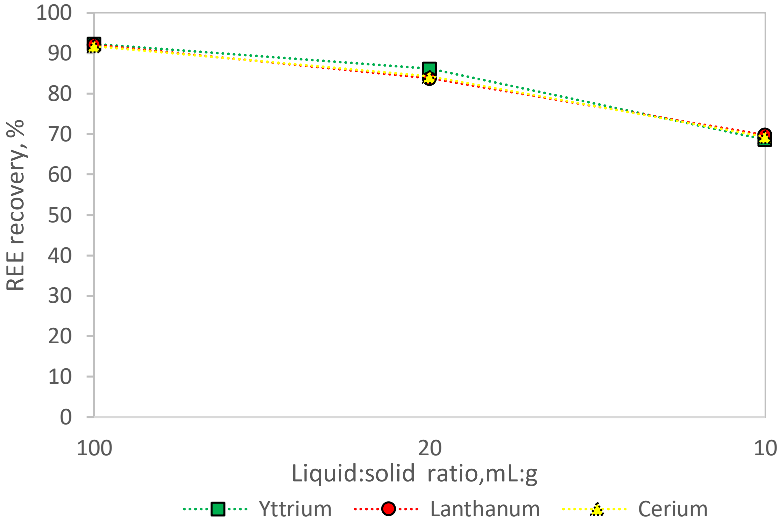


Figure 6-11: Effect of L:S ratio investigated at 0.5 M citric acid, using 100 mL, 60 °C for 8 h leaching with the solid content varied accordingly

An exploratory test carried out to test the direct precipitation method of recovering REEs from solution showed promising results in which 99 % of the REEs precipitated as oxalates (Appendix K). The REE oxalates have high content of co-precipitated iron and a test on the recyclability of citric acid showed poor recovery rates (Appendix L) due to high residual silica in the barren leach solution. Thus, further investigations on the removal of impurities prior to REE precipitation will enhance the economic attractiveness of the method.

In consideration of the above factors, the optimal leaching of Y was at pH 1, leaching at 60 °C for 4 h, with 0.8 M citric acid, 100 mL:g L:S ratio and 75-106 μm grind size. Recoveries under these conditions were as follows (%): 78 (Y), 72 (La) & 70 (Ce). There was a high variance in recovery values owing to the co-precipitation of rare earths with Zr hydrolysis products (Appendix P).

6.4.3 Factors limiting rare earths leaching

Mass balance calculations showed that at the optimal citric acid leaching of large-grained eudialyte, 20-30 % of the SG mineral concentrate was left undecomposed. SEM-EDS analysis of leach residue showed that undecomposed grains were covered with silica particles and Zr hydrolysis products (Figure 6-12) which might have hindered leaching kinetics and the complete decomposition of eudialyte.

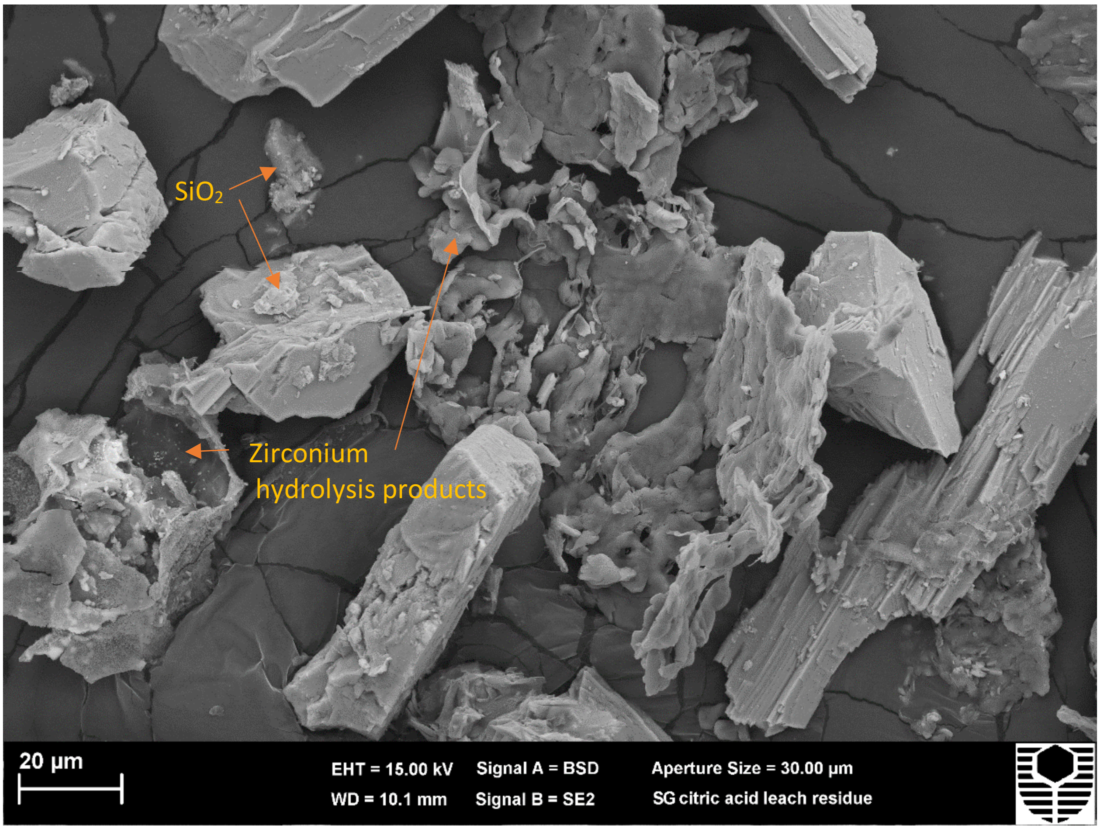
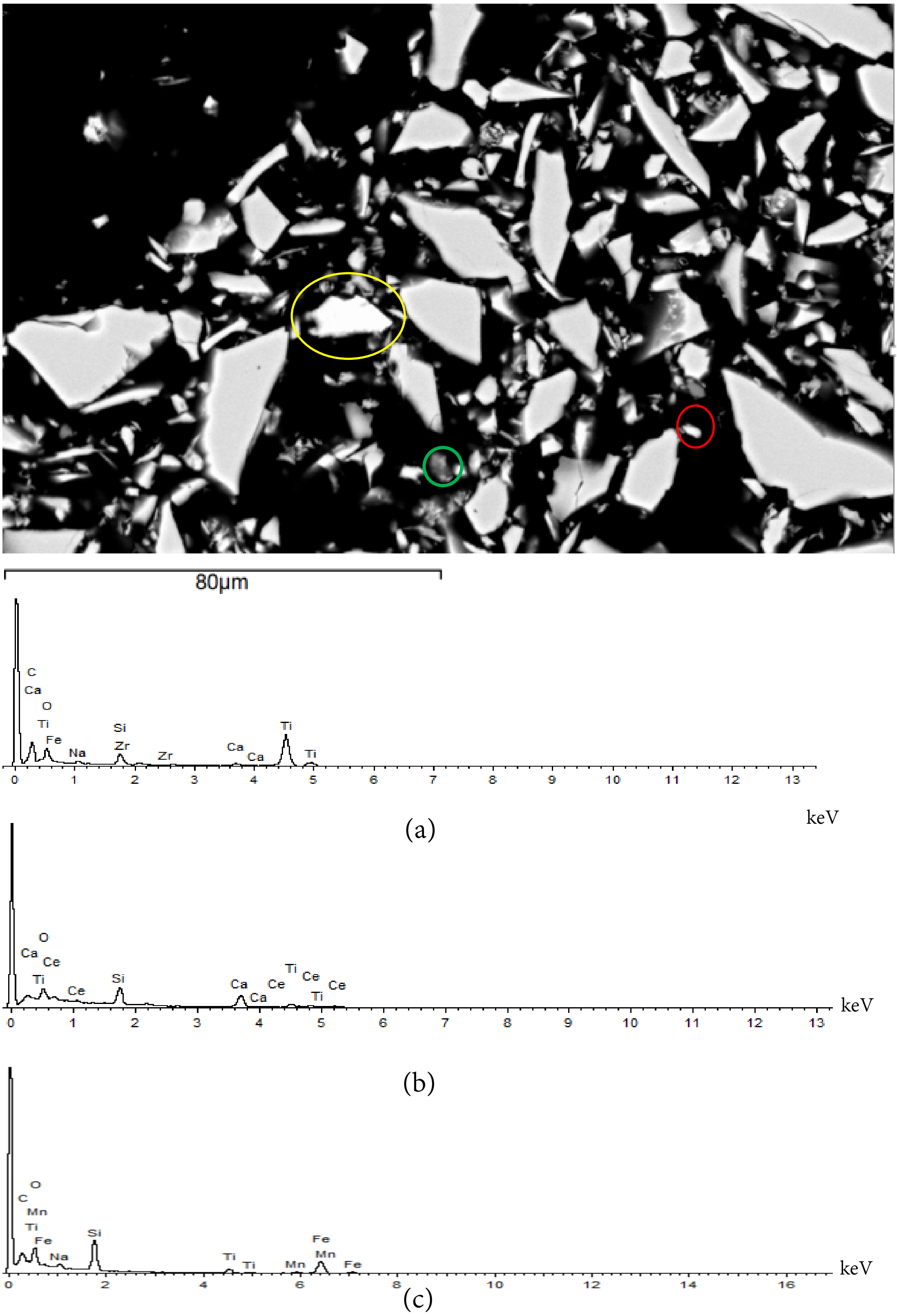


Figure 6-12: SEM micrograph showing precipitated Zr hydrolysis products and silica precipitates covering on some eudialyte grains

SEM-EDS analysis also showed that some undecomposed eudialyte grains contained Fe-Ti-Zr, Ti-Ce and Fe-Mn-Zr values (Figure 6-13). It was believed that the non-dissolution of these elements contributed to the incomplete leaching of REE from eudialyte in SG concentrate. Ti forms stable complexes with citrate ions only at a higher pH of 3-8 (Collins, Uppal et al. 2005). Complete Fe dissolution from eudialyte grains was limited with saturation of Fe in the pregnant leach solution (Appendix M). As REEs were present in the eudialyte matrix as substitution elements of framework elements Na, Ca and Fe, their lixiviation were affected by the leaching responses of these elements.

In contrast, SEM-EDS analysis of the leach residue of DT ore indicated that rare earths remained in the fine-grained eudialyte minerals (Figure 6-14). The non-dissolution of the fine-grained Na-Zr-Si eudialyte phases in DT ore was also observed on examination of the leach residue by TIMA equipment (Figure 6-15). As highlighted in Chapter 5, the lixiviation of rare earths in fine-grained eudialyte in DT ore was highly dependent on baking treatment, in particular, on baking temperature, in effecting thermal cracking of the fused complex phases of Na-Zr-Si eudialyte minerals. The use of a high baking temperature of 320 °C could not be paralleled with use of citric acid, owing to the lower decomposition temperature of the organic chemical at 175 °C. Further, the decomposition products of citric acid on heating above 175 °C are carbon dioxide and acetonic acid $C_6H_6O_6$ (Wyrzykowski, Hebanowska et al. 2011). The latter decomposition product is a much weaker organic acid with no known solubilities of REE. Other methods of thermal cracking will need to be explored for fine-grained eudialyte minerals.

Hence, the above findings derived from the examination of DT ore leach residue supported earlier findings on the slow kinetics of DT ore leaching as discussed in Section 6.4.1 of this chapter.



(a)

(b)

(c)

Figure 6-13: SEM-EDS of SG concentrate leach residue showing EDS spectra of grains containing (a) Ti-Zr, circled in red, (b) Ti-Ce, circled in yellow and (c) Fe-Mn-Zr, circled in green

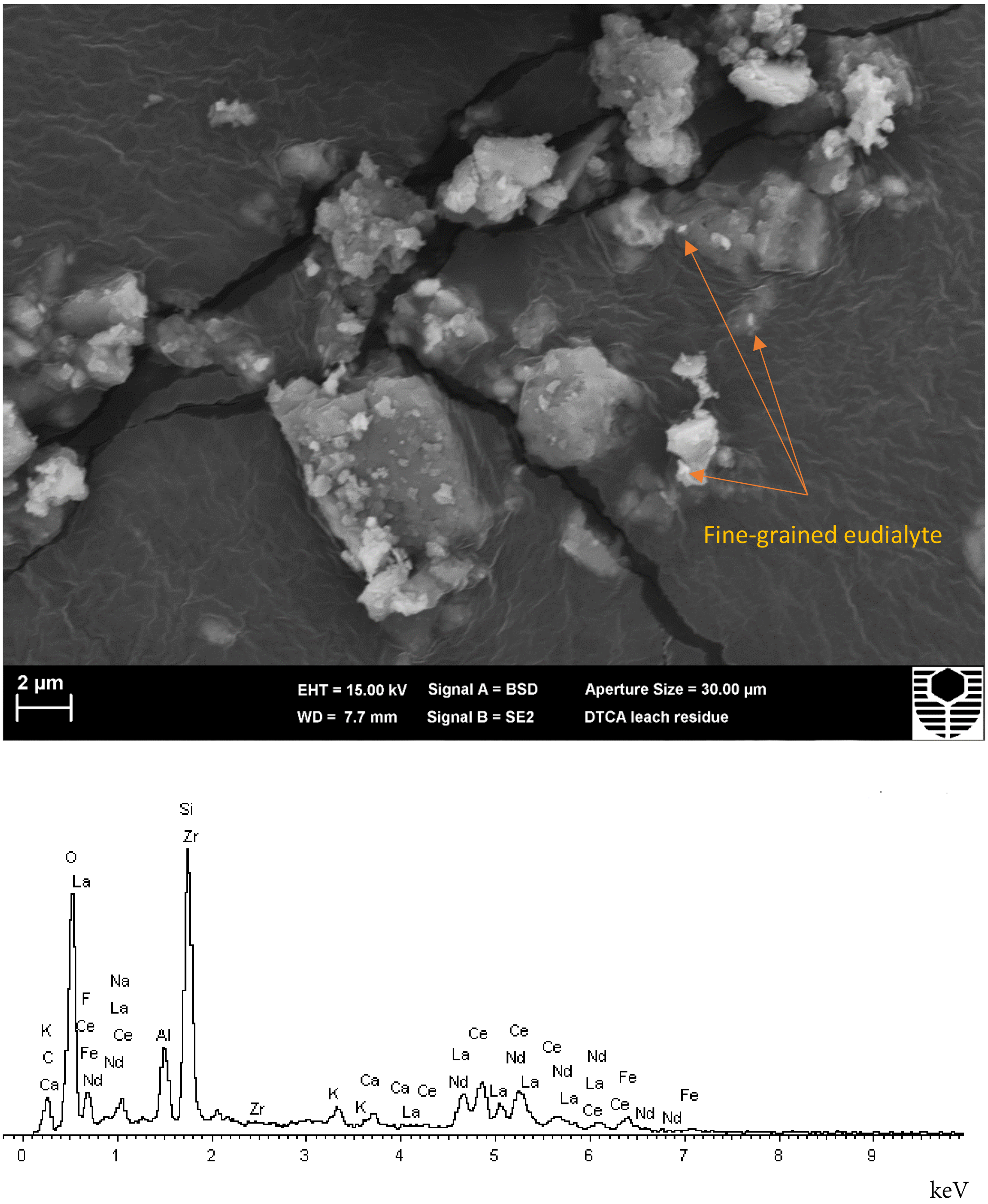
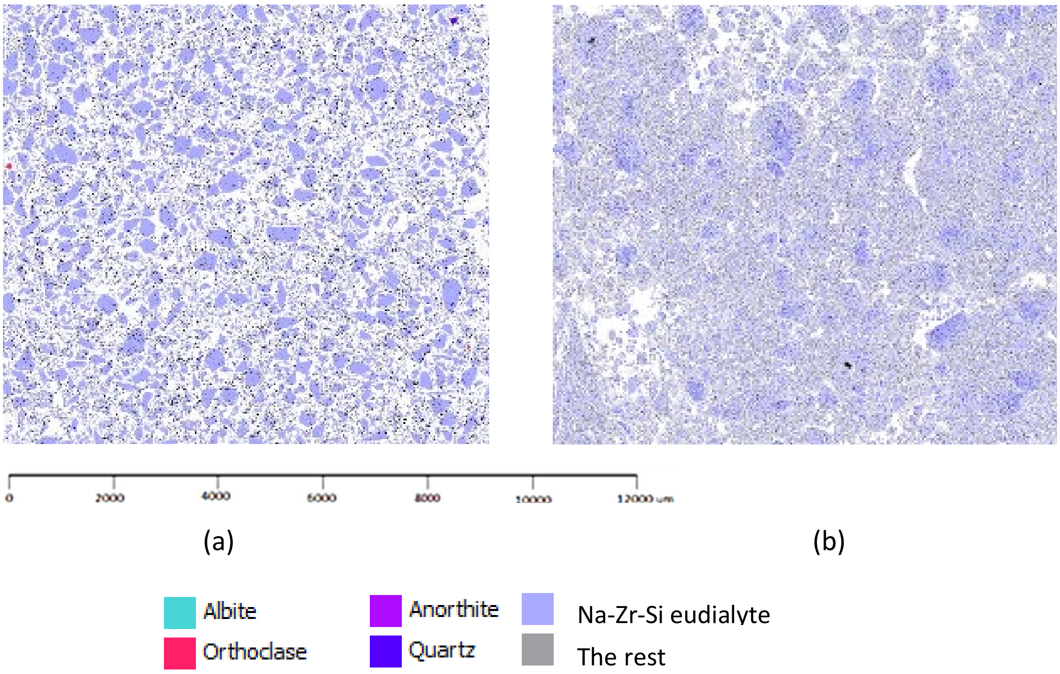


Figure 6-14: Back-scattered photomicrograph of DT ore leach residue after citric acid leaching (top) and EDS spectrum of unleached fine-grained eudialyte (bottom)



(a) (b)

Figure 6-15: Mineral liberation analysis on (a) DT ore sample at 10 µm (D_{90}) grind size and (b) DT leach residue after citric acid leaching showing the thinning out of impurities and non-dissolution of Na-Zr-Si eudialyte phases

6.5 Chapter Summary

The main findings of this chapter showed that the use of citric acid in the leaching of rare earths from large-grained eudialyte in SG concentrate yielded high leaching recoveries of 70-80 %. These were comparable recoveries to those normally achieved with conventional leaching using sulfuric acid. The optimal conditions for the leaching of Y were: a pH of 1, leaching at 60 °C for 4 h with 0.8 M citric acid, a L:S ratio of 10 mL:g and 75-106 µm grind size. Comparatively, the leaching conditions of Y and LREEs La and Ce were the same, except that Y leaching recovery was slightly higher on use of 212-300 µm grind size compared to 75-106 µm. This difference though is insignificant. ANOVA test showed that only pH and leaching temperature were the significant factors affecting the leaching of REEs from large-grained eudialyte in SG concentrate.

Examination of the leach residue indicated complete leaching of REEs was limited due to the covering of precipitated Zr hydrolysis products unto eudialyte grains, covering of silica precipitates unto some eudialyte grains, non-dissoluton of refractory element Ti and over saturation of Fe in the leach solution.

The above findings on the citric acid leaching of REEs from large-grained eudialyte highlighted the potential of citric acid as an alternative leaching agent to sulfuric acid. The new information generated will provide directions for further studies.

Other findings of this chapter showed that the use of citric acid in the leaching of rare earths from fine-grained eudialyte in DT ore yielded a low recovery rate of less than 10 %. The complex mineralogy of fine-grained eudialyte required rigorous conditions which were not really possible to achieve due to the low decomposition temperature of citric acid. Thus, the citric acid leaching of rare earths from fine-grained eudialyte was characterised by slow kinetics and yielded 10 % recovery on 8 h leaching, and 40 % leaching recovery with an extended leaching time of 400 h. This means that other procedures for surface preparation will need to be explored for fine-grained eudialyte minerals. For example, the use of microwave heating has been effective for some silicate ores. Alternatively, the slow kinetics of REE leaching on use of citric acid in fine-grained eudialyte may have potential application for heap leaching methods.

Chapter 7

The Leaching Responses of Zirconium and Impurities in the (a) Sulfuric and (b) Citric Acid Leaching of Rare Earths from Eudialyte

7.1 Introduction

One of the findings of this study, as presented in Chapter 5, was that the sulfuric acid leaching of rare earths from eudialyte was favoured in conditions of high dilution and lower sulfuric acid concentration. This is as compared to the previously reported conditions on eudialyte leaching intended for Zr extraction. It is not known how such differences in leaching conditions would affect the co-leaching of Zr in the sulfuric acid leaching of eudialyte. More interestingly, the citric acid leaching of Zr from eudialyte is an unexplored area of research. There is a significant amount of Zr content in eudialyte minerals, 1-2 % in ore and 8-12% in concentrate. This has led to academic and economic interest in investigating the co-leaching of Zr from (a) sulfuric acid leaching and (b) the citric acid leaching of rare earths from eudialyte.

Eudialyte also contains significant amounts of impurities in the form of silica, alkali, alkaline earth elements and radionuclides. These elements normally co-dissolve with the acidic leaching of eudialyte. The major component is silica; the average content in eudialyte is 50-60 % in ore or 40 % in concentrate. The effect of silica on the leaching of rare earths from eudialyte has been emphasised in this research work. Minimal co-dissolution of silica was one of the major objectives considered in the design of the leaching procedures.

This chapter presents investigations into the co-leaching responses of Zr and impurities in the sulfuric acid and citric acid leaching of two texturally different variants of eudialyte. Among the non-desired components, emphasis is placed upon the co-leaching of silica, given its substantial effect on the leaching process.

7.2 Aims of the Chapter

This chapter discusses investigations into the following:

- co-leaching of Zr in the sulfuric acid leaching of rare earths from a (a) large-grained and (b) fine-grained eudialyte mineral;
- effect of significant factors in the co-leaching of Zr in the sulfuric acid leaching of rare earths from a (a) large-grained and (b) fine-grained eudialyte mineral;
- co-leaching of Zr in the citric acid leaching of rare earths from a (a) large-grained and (b) fine-grained eudialyte mineral;
- effect of significant factors in the co-leaching of Zr in the citric acid leaching of rare earths from a (a) large-grained and (b) fine-grained eudialyte mineral;
- leaching responses of silica in the (a) sulfuric acid leaching and (b) citric acid leaching of the two differently textured eudialyte minerals; and
- leaching responses of other impurities Ca, Na, K, Fe, Al, Mn, Ti and radionuclides Th and U in the (a) sulfuric acid leaching and (b) citric acid leaching of the two differently textured eudialyte minerals

7.3 Materials & Methods

The materials and methods used to study the co-leaching of Zr and impurities are as described in Chapter 5, Section 5.3 (Materials & Methods in Sulfuric acid leaching of rare earths from eudialyte) and in Chapter 6, Section 6.3 (Materials & Methods in citric acid leaching of rare earths from eudialyte). The leach solutions derived from the conduct of leaching tests from the procedures described in Sections 5.3 & 6.3 were analysed for Zr, Si, Na, K, Al, Ca, Fe, Mn, Ti, Th and U content using ICP-OES.

Additional leaching tests were conducted to investigate significant factor/s which affect Zr co-leaching. Liquid test samples of these optimisation tests were dissolved with 0.5 M HCl (AR grade, Sigma-Aldrich). HCl reduces the effect of hydrolysis on Zr (Lister and McDonald 1952).

Data results were analysed using the same statistical software, Minitab 17.1 (Minitab Inc.).

7.4 Results and Discussion

7.4.1 Co-leaching of zirconium in the sulfuric acid leaching of rare earths from eudialyte

Results of the leaching tests showed that Zr co-leached at an average recovery of 75 % from large-grained eudialyte minerals in SG concentrate and at an average recovery of 56 % from finely-textured eudialyte minerals in DT ore (Figures 7-1 & 7-2). The differences in leaching responses can be attributed to both the differences in mineralogy and the nature of the Zr hydrolysis reaction.

With direct sulfuric acid leaching of large-grained eudialyte in SG concentrate, the co-leaching of Zr was promoted in the following conditions: use of 149-212 μm grind size and leaching at 60 °C for 6 h with 1 wt. % sulfuric acid concentration at an L:S ratio of 100 mL:g (Figure 7-1). High Zr lixiviation with the use of 1 wt. % sulfuric acid was in contradiction to results of previous investigations by Lebedev (2003) and Zakharov et al. (2011). In those investigations, Zr leaching from large-grained eudialyte was promoted in the highly acidic conditions provided by the use of 5-25 % sulfuric acid or at acid dosages eight times those of the stoichiometric requirements. This discrepancy can be explained by the large differences in the L:S ratios used. This present study used 25 times the L:S ratio of previous investigations.

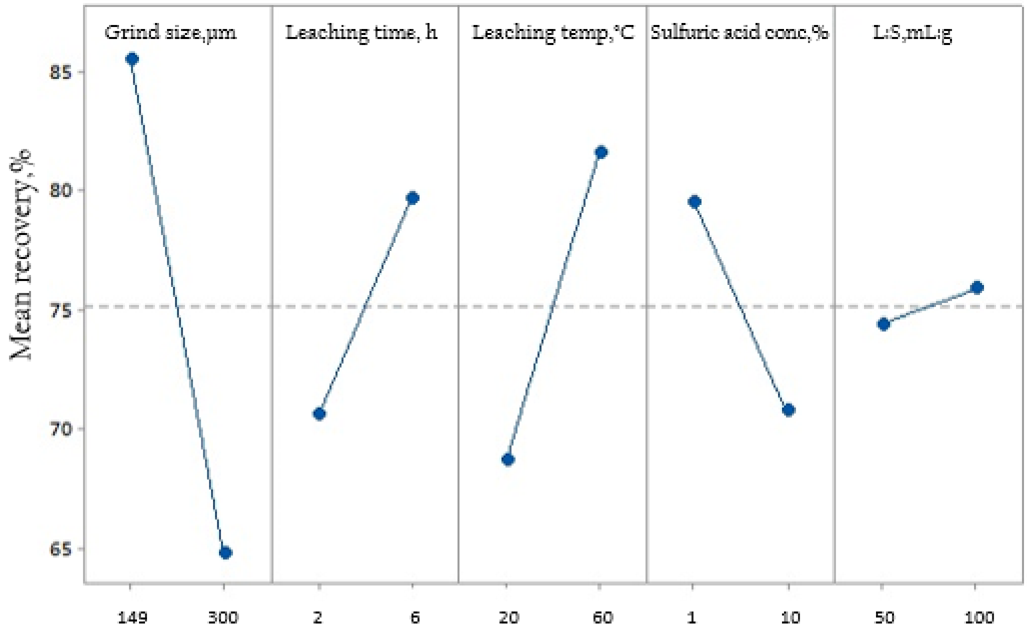


Figure 7-1: Main Effects plot showing average leaching recoveries of Zr on sulfuric acid leaching of SG concentrate

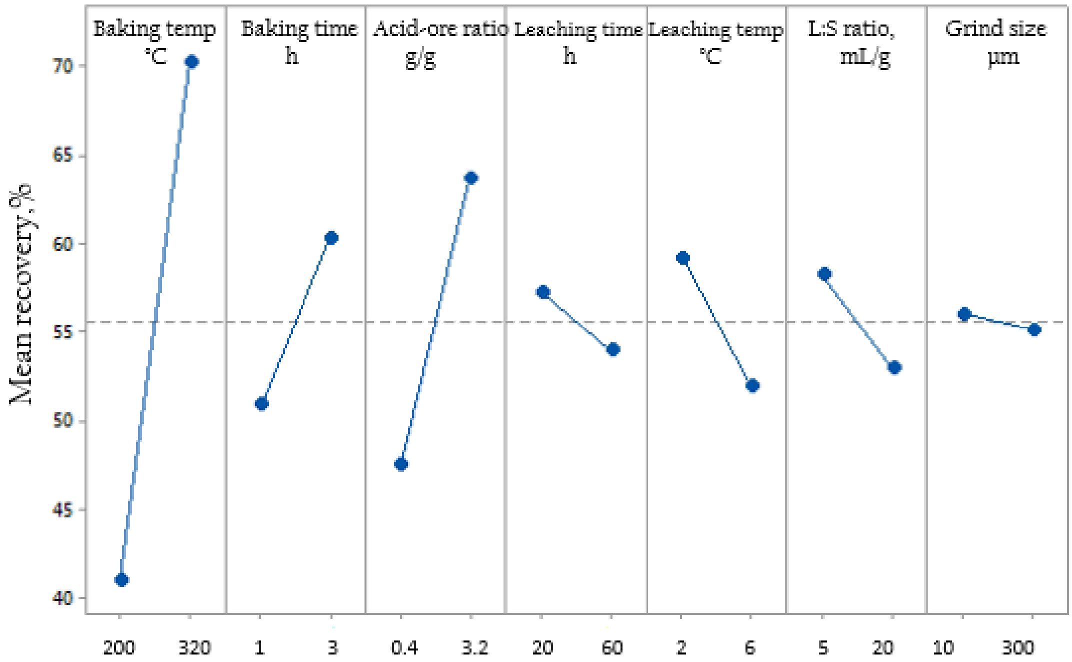


Figure 7-2: Main Effects plot showing average leaching recoveries of Zr on sulfuric acid leaching of DT ore

The higher lixiviation of Zr at a reduced acid concentration was believed to be caused by the formation of stable hydrolysis products on high dilution. Against the labile nature of Zr ion in solution, stable basic Zr sulfates are known to exist in low sulfuric concentration (Squattrito, Rudolf et al. 1987). Further, a high L:S ratio may have lowered the common ion effect with regard to competing sulfate complexes which resulted in enhanced Zr solubility on the leaching of SG concentrate. Thus, at the high dilution of 100 mL:g used in the present study to promote rare earths solubility, there was significant co-leaching of Zr, with average recoveries of 75 % (Figure 7-1). The obvious drawback was the lower concentration of Zr in solution. At the highest leaching recovery point of 99 % (Appendix N), Zr assay in solution was only 1.4 g/L.

Grind size has a stronger influence on the co-leaching of Zr, compared to the influence of sulfuric acid concentration. The use of 149-212 µm grind size led to recoveries 20 % higher than leaching at 300-420 µm grind size, while the effect of sulfuric acid concentration caused a smaller difference in leaching recovery of 10 % (Figure 7-1). This effect was clearly related to the faster leaching kinetics associated with leaching using finer grind size material. These two factors showed the highest influence on Zr co-leaching, as shown in the Main Effects plot in Figure 7-1 although results of ANOVA test of leaching results showed that these factors were not significant (Table 7-1).

In contrast, the co-leaching response of Zr to the sulfuric acid leaching of fine-grained eudialyte minerals in DT ore resulted in a 20 % lower leaching recovery rate. This is as compared to the leaching of Zr from large-grained eudialyte minerals, as brought about by complex mineralogy of DT ore. The leaching of Zr from DT ore was favoured under the following conditions: use of 300-420 µm grind size ore, baking at 320 °C for 3 h with 3.2 g/g acid dosage followed by 1 h leaching at 20 °C with 5 mL:g water dosage (Figure 7-2). The sulfation baking step was a significant procedure in Zr lixiviation (Table 7-1). On water leaching, Zr leaching was favoured at a low L:S ratio of 5 mL:g and a shorter leaching time of 2 h. As DT ore was processed via a whole-of–ore leach, the high solids content translated to high ionic strength resulting from the co-dissolution of impurities. Such conditions were believed to result in the formation of unstable Zr hydrolysis products. A repeat quantitative analysis of leach solutions, carried out over a span of one month, provided evidence on the drastic reduction of Zr concentration in leach solutions from DT ore leaching, as compared to SG concentrate leaching (Appendix O).

Table 7-1: ANOVA results on leaching recoveries on sulfuric acid leaching of SG concentrate and DT ore, significant factors italicised; α = 0.05

Factors	p-value	
	SG concentrate	DT ore
Baking temperature	NA	***0.000***
Baking time	NA	***0.001***
Acid dosage	NA	***0.001***
Leaching time	0.401	***0.035***
Leaching temperature	0.237	0.059
Acid concentration	0.417	NA
L:S ratio	0.888	0.878
Grind size	0.071	0.137

In summary, the prioritised leaching of rare earths from eudialyte affected the co-leaching of Zr differently in each eudialyte mineral. The co-leaching of Zr with sulfuric acid leaching of large-grained eudialyte in SG concentrate yielded an average 75 % leaching recovery rate. The high dilution used to promote rare earths lixiviation resulted in the formation of relatively stable Zr hydrolysis reactions. On the other hand, there was a lower co-leaching of Zr, at a 55 % average recovery rate with sulfuric acid leaching of fine-grained eudialyte. As DT ore was processed via a whole-of-ore leach owing to the fineness of its mineralisation, the co-dissolution of large amounts of impurities resulted in the formation of unstable hydrolysis products.

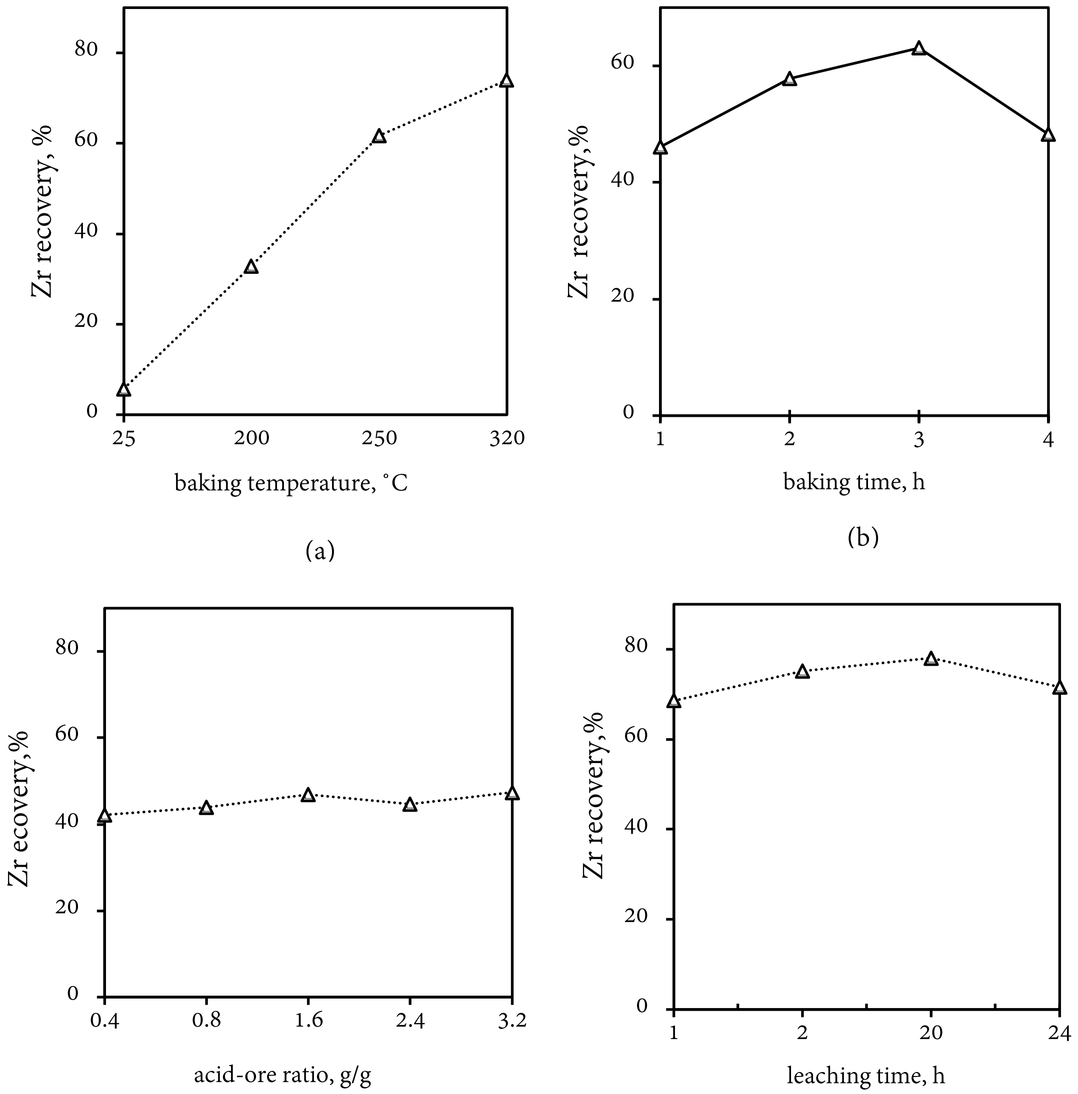
Analysis of leaching test results by the ANOVA method highlighted the mineralogical differences between the two eudialyte minerals. There were no significant factors in the leaching of Zr from large-grained eudialyte, which suggested the easy lixiviation of Zr with sulfuric acid. The sulfation baking step was determined as a significant procedure in the leaching of Zr from fine-grained eudialyte minerals in DT ore (Table 7-1). These significant factors are investigated further in the following section.

7.4.2 Effect of significant factors in the co-leaching of zirconium in the sulfuric acid leaching of rare earths from fine-grained eudialyte minerals

The co-leaching responses of Zr, as influenced by the significant factors of baking temperature, baking time, acid dosage and leaching time are shown in Figure 7-3. The baking temperature produced the highest effect, with a marked increase in Zr recovery with an increase of temperature (Figure 7-3a). These plots were observed to mirror the leaching responses of Y in the sulfuric acid leaching of rare earths (Chapter 5, Section 5.4.1.2). However, the Zr recovery values were lower, understandably, as the leaching conditions sought were for the favourable lixiviation of REE. This finding relates back to the mineralogy of Y and Zr as discussed in Chapter 4, Section 4.4.4. Y and Zr were mainly hosted in the fine-grained Na-Ca-Zr silicates or fine-grained eudialyte minerals in DT ore and thus, the leaching responses of both metals were similar.

7.4.3 Co-leaching of zirconium in the citric acid leaching of eudialyte

The results of the leaching test showed that the use of citric acid resulted in a lower Zr recovery of 33 % compared to 75 % with the sulfuric acid leaching of large-grained eudialyte in SG concentrate (Figure 7-4). Nil recoveries resulted from the leaching of fine-grained eudialyte minerals in DT ore (Figure 7-5).



(a)

(b)

(c)

(d)

Figure 7-3: Effect of significant factors on Zr co-leaching from sulfuric acid leaching of REE from fine-grained eudialyte minerals in DT ore: (a) effect of baking temperature, (b) effect of baking time, (c) effect of acid dosage and (d) effect of leaching time

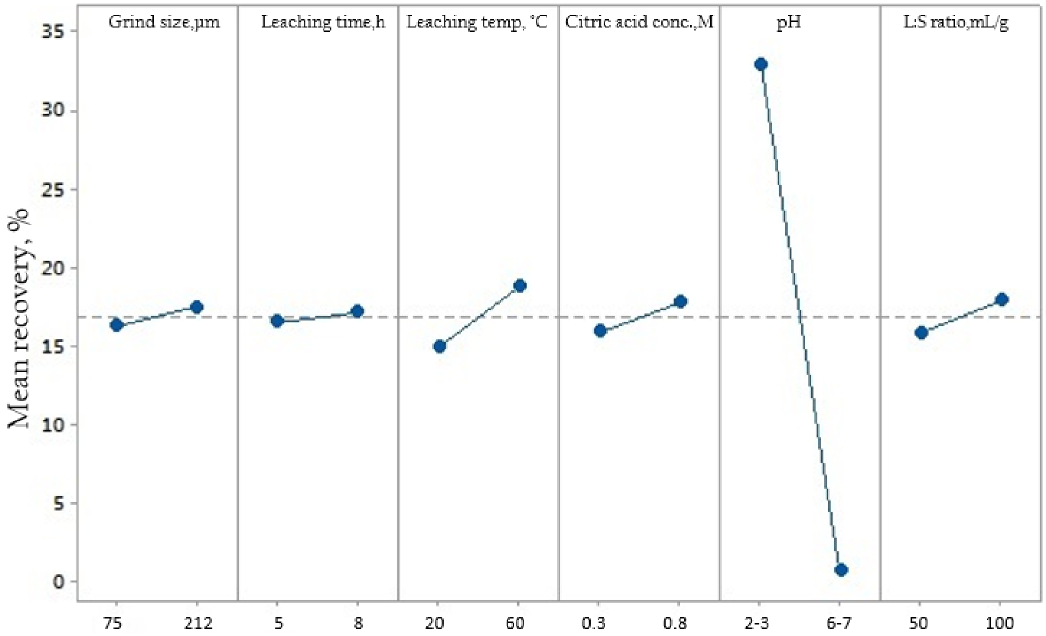


Figure 7-4: Main Effects plot for the co-leaching of Zr in the citric acid leaching of rare earths from large-grained eudialyte minerals in SG concentrate

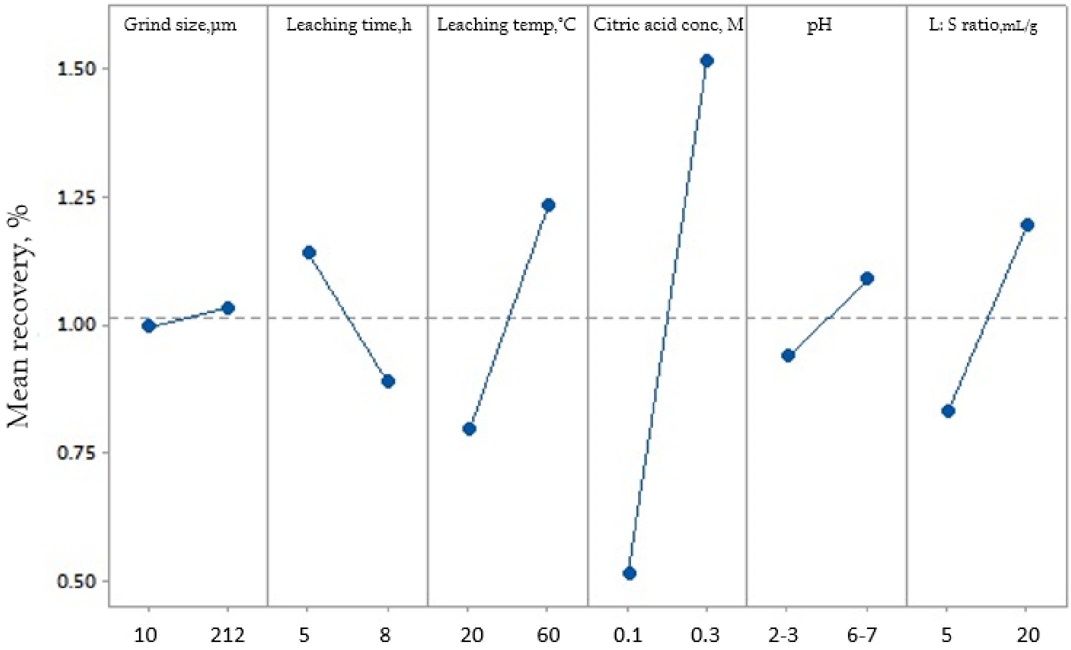
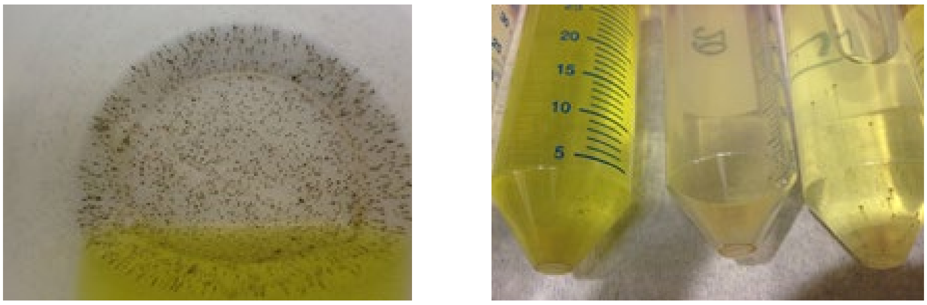


Figure 7-5: Main Effects plot for the co-leaching of Zr in the citric acid leaching of rare earths from fine-grained eudialyte minerals in DT ore

As applied to this work, Zr co-leaching from large-grained eudialyte was favoured with the use of a coarser grind size of 212-300 µm, leaching for 8 h at 60 °C using 0.8 M citric acid at a pH of 2-3 and an L:S ratio of 100 mL:g (Figure 7-4). Such low recoveries were believed to be caused by the precipitation of unstable hydrolysis products, as evidenced by the observed precipitation in the leach solution containers (Figure 7-6a). An analysis of the precipitates confirmed the presence of Zr values (Appendix M). Comparative analysis of the leach solution indicated that the precipitated Zr hydrolysis products contained Zr assays equivalent to half of the original content in the leach solutions. Restated, half of the Zr values were reported in the precipitate.



(a) (b)

Figure 7-6: Precipitation observed on leach solution from citric acid leaching of (a) SG concentrate and (b) DT ore

In contrast, the co-leaching of Zr from the citric acid leaching of fine-grained eudialyte in DT ore showed nil recoveries. As explained earlier in Chapter 6, the kinetics of citric acid leaching of fine-grained eudialyte minerals was slow. Further, the loss of metal values on the precipitation of hydrolysis products was also observed in DT ore citric acid leaching (Figure 7-6b). This was confirmed by the analysis on the precipitate recovered from leach solution of DT ore leaching (Appendix M). Against the differences in concentration of metal values in leach solutions of SG concentrate and DT ore, the analysis of the precipitates showed relatively similar assays. This suggests that the Zr hydrolysis products formed were the same.

The analysis of leaching results by ANOVA test shows that significant factors for the co-leaching of Zr from large-grained eudialyte minerals in SG concentrate were pH and leaching temperature (Table 7-2). There were no significant factors for the co-leaching of Zr from fine-grained eudialyte minerals in DT ore (Table 7-2). Due to the lack of practicality in pursuing further investigations into the co-leaching of Zr in DT ore, only the leaching responses of Zr in SG concentrate were studied further, based on the effect of significant factors.

Table 7-2: Summary of ANOVA table for the citric acid leaching of Zr from eudialyte minerals; significant factors italicised

Factors	SG concentrate	DT ore
Citric acid concentration	0.105	0.543
pH	***0.000***	0.414
Leaching temperature	***0.002***	0.070
Leaching time	0.572	0.785
Liquid: solid ratio	0.076	0.220
Grind size	0.308	0.951

7.4.4 Effect of significant factors on co-leaching of zirconium in the citric acid leaching of eudialyte from SG concentrate

Further investigations into the effects of pH showed that the leaching responses of Zr were comparable with those of the leaching responses of rare earths in a citric acid medium. Higher leaching recoveries were derived with an increased acidity of pH of 1-2, dropping significantly as the pH increased (Figure 7-7). The leaching recoveries reflected higher values on the modification of the test sample preparation. Leaching temperatures clearly propelled kinetics with the increased decomposition of eudialyte (Figure 7-8). The main drawback with the use of a high leaching temperature was the high co-dissolution of silica and the increased precipitation of hydrolysis products. Thus, the recommended leaching temperature was 50 °C. At this leaching temperature, the formation of observed hydrolysis products was at minimum.

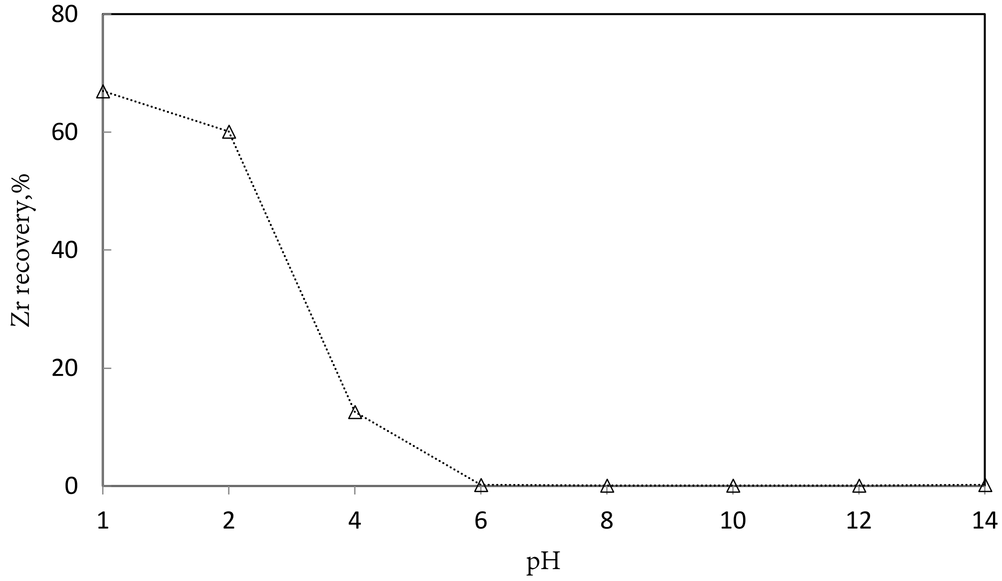


Figure 7-7: Effect of pH on the co-leaching of zirconium in the citric acid of eudialyte from SG concentrate

These findings showed favourable results. The optimal leaching of Zr resulted from leaching conditions at a pH of 1-2 and a temperature of 50 °C. This pH range was the same optimal pH for the citric acid leaching of rare earths from the same material (Chapter 6, Section 6.4.2). Although the optimal temperature for rare earths leaching was higher at 75 °C, an intermediate temperature of 60 °C can be observed for the optimal recovery of both REE and Zr. The addition of a dilute solution of HCl as a pH modifier was also observed to minimise the progressive hydrolysis of Zr.

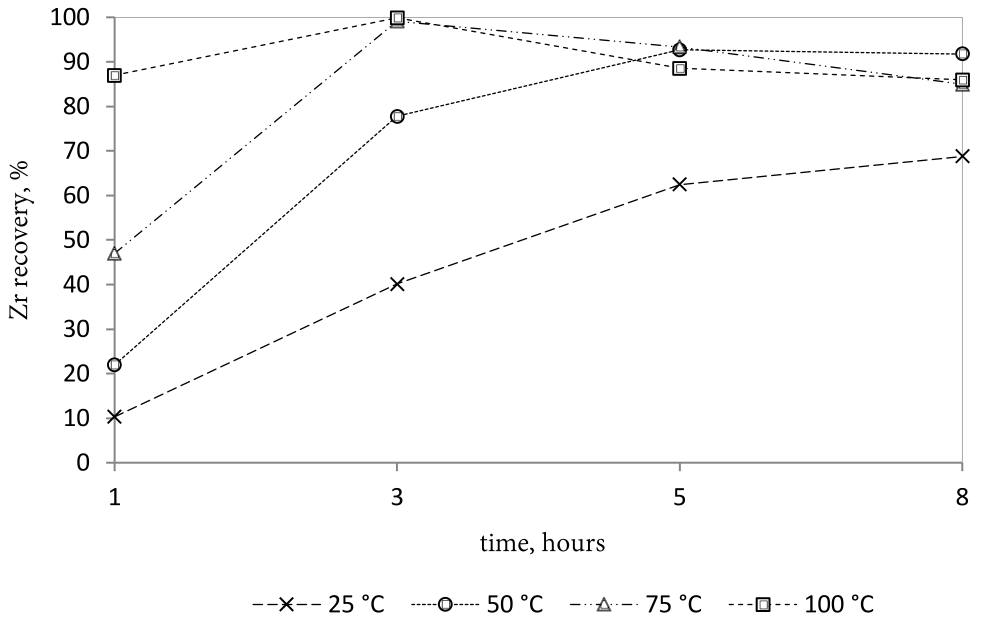


Figure 7-8: Effect of temperature on co-leaching of zirconium in the citric acid leaching of eudialyte in SG concentrate

7.4.5 Leaching responses of silica in the sulfuric acid leaching of eudialyte

In the leaching of large-grained eudialyte in SG concentrate, the mineral concentrate was pre-treated by boiling the concentrate in 0.1 % sulfuric acid solution. This method reduced the amount of Al in the material (Appendix F) and reduced the risk of silica polymerisation on leaching. The shaking speed on leaching was controlled below 300 rpm to reduce the potential of silica coagulation, which easily occurs on use of a stirring speed of more than 300 rpm (Li and Kaner 2005). Leaching test results showed that Si co-dissolves to a greater extent from large-grained eudialyte than from fine-grained eudialyte - the former yielded an average Si dissolution of 63 % (Figure 7-9) but the latter's average Si co-dissolution was lower at 18 % (Figure 7-10). The difference in leaching responses of Si was mainly brought about by the differences in mineralogy of the eudialyte ore samples. The eudialyte in the SG concentrate was classified as *eudialyte proper*, a known cyclosilicate, which readily undergoes congruent dissolution on acidic attack. On the other hand, eudialyte minerals in

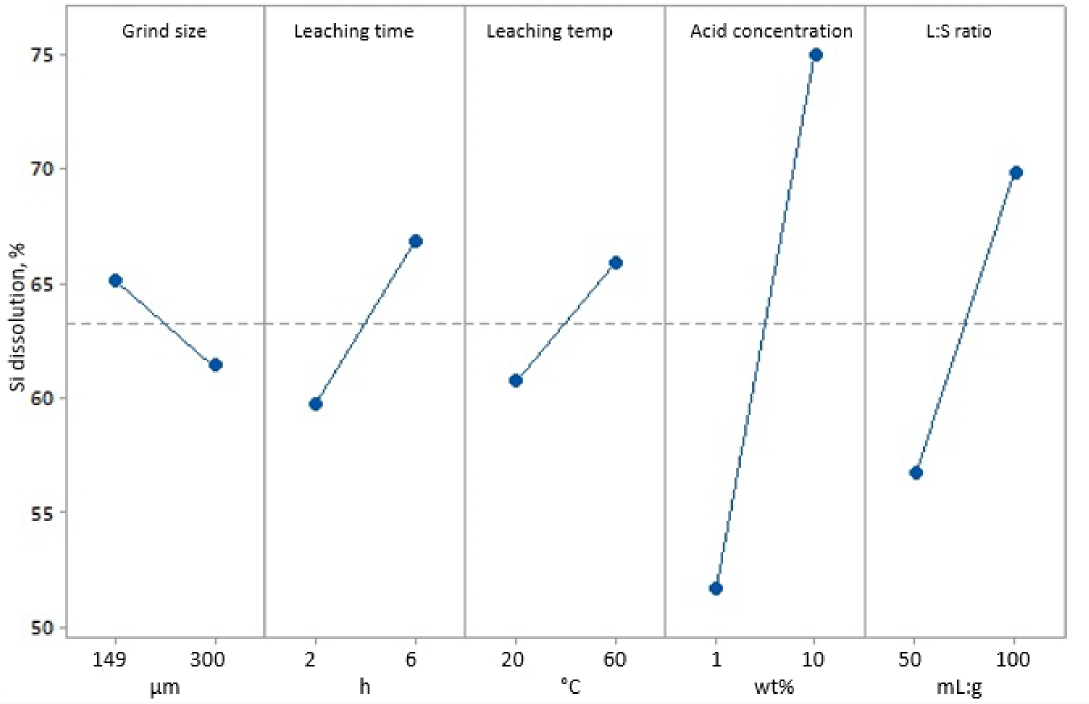


Figure 7-9: Main Effects plot for Si dissolution on sulfuric acid leaching of large-grained eudialyte; sulfuric acid concentration was the major factor affecting Si co-dissolution

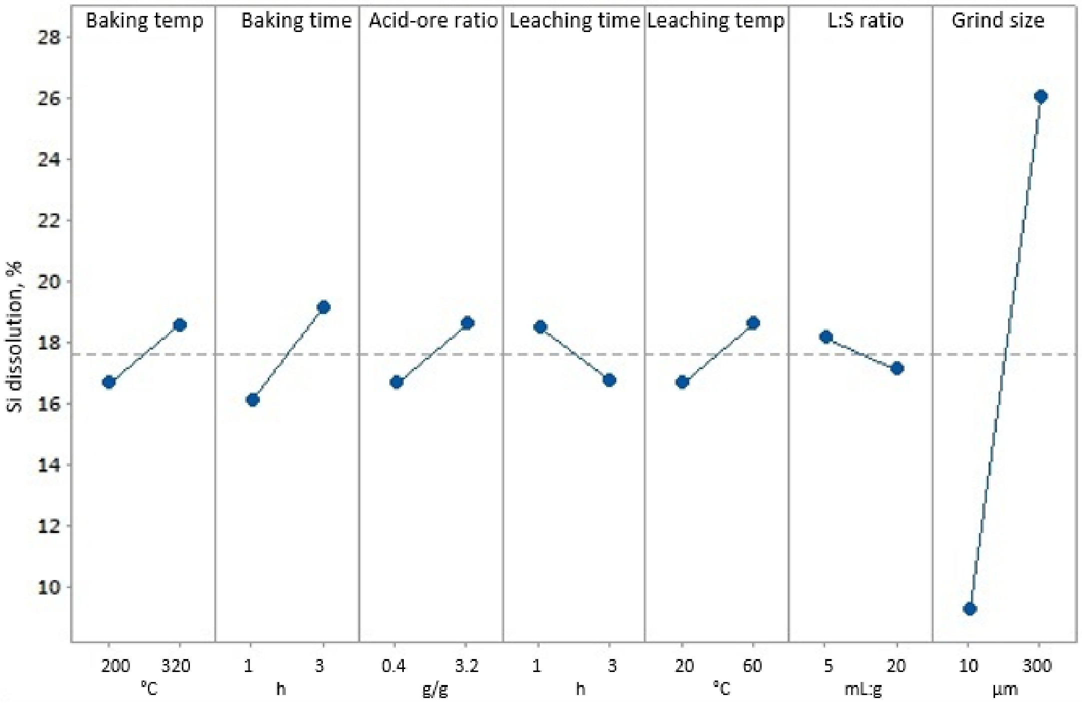


Figure 7-10: Main Effects plot for Si dissolution on sulfuric acid leaching of fine-grained eudialyte; grind size was the main factor affecting the co-dissolution of Si on leaching

DT ore, though chemically unclassified as they are of new composition, were observed to behave like clay minerals, as evidenced by the poor dissolution of silica on ambient leaching of DT ore (Appendix Q). Furthermore, though DT ore was used as a whole-of-ore leach, the other silica-bearing minerals in it were feldspar and quartz minerals. These minerals are tectosilicates which only partially decomposed on acid attack (Terry 1983a).

The co-dissolution of Si from large-grained eudialyte minerals was highly influenced by the sulfuric acid concentration (Figure 7-9). There was a 25 % increase in Si dissolution with an increase in acid concentration from 1 to 10 wt. %. This leaching response was expected, as sulfate ions are known to enhance the dissolution rate of silica (Bai,Urabe et al. 2009). The highest co-dissolution of Si was in conditions of 10 wt. % acid and an L:S ratio of 100 mL:g. These conditions were similar to conditions of favourable REE and Zr leaching. At the highest co-dissolution, the silicon concentration was 3.5 g/L (equivalent of 5.4 g/L SiO_2), which is the lower limit for silica gel formation (Iler 1979). However, no gel formation was observed on leaching by keeping the pH at 1.8-2.0 or by leaching at pH 1 at a low shaking speed of 200 rpm. Silica is stable at pH 2.0 (Iler 1979) while in the latter scenario, silica precipitation was faster than silica dissolution.

In the leaching of eudialyte in SG concentrate, the co-leaching response of Si mirrored that of Zr co-dissolution, in that both were strongly influenced by acid concentration. In conditions of the highest Si dissolution of 10 wt. % acid and 100 ml:g L:S ratio, REE and Zr co-leaching were at the highest. This finding was consistent with previous studies. Silica co-dissolution follows that of Zr co-leaching (Chelishchev, Motov et al. 1983).

In contrast, Si co-dissolution was influenced mainly by grind size in the leaching of fine-grained eudialyte minerals in DT ore, in which Si dissolution was highest with the use of a grind size of 212-300 μm (Figure 7-10). Ultra-fine grinding to 10 μm (D_{90}) may have incurred structural and chemical changes in eudialyte which affected its leaching behaviour. This phenomenon is common in silicate minerals in which there is reduced leachability on overgrinding as brought about by the conversion of crystalline phases to amorphous on severe mechanical action (Chizhevskaya, Chekmarev et al. 1994) or the oxidation of silicate phases (Bowden and Thomas 1954, Reay 1981). This was evidenced further by low Si dissolution with a finer grind size at ambient leaching (Appendix Q). Thus, the formation of silica gel was not a problem in the sulfuric acid leaching of fine-grained eudialyte minerals in DT ore. In conditions of optimal REE lixiviation, Si co-dissolution was 26 % and the concentration of silicon in solution was 215 mg/L which was below the critical concentration for polymerisation to occur.

7.4.6 Leaching responses of silica in the citric acid leaching of eudialyte

Consistent with the results of REE leaching, the dissolution of Si in the citric acid leaching of eudialyte was high in large-grained eudialyte and nil in fine-grained eudialyte (Figure 7-11). The dissolution of Si from large-grained eudialyte ranged from 40-50 % and was influenced by the leaching factors considered, as shown in Figure 7-11.

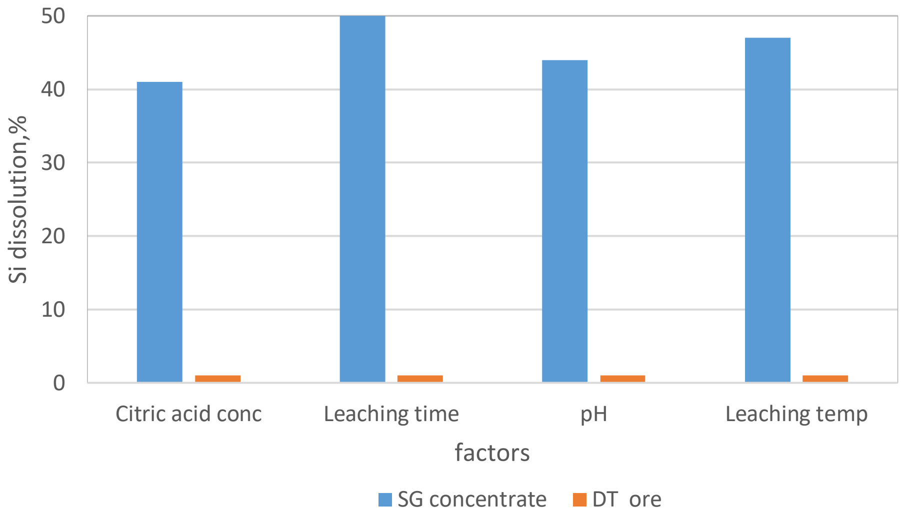
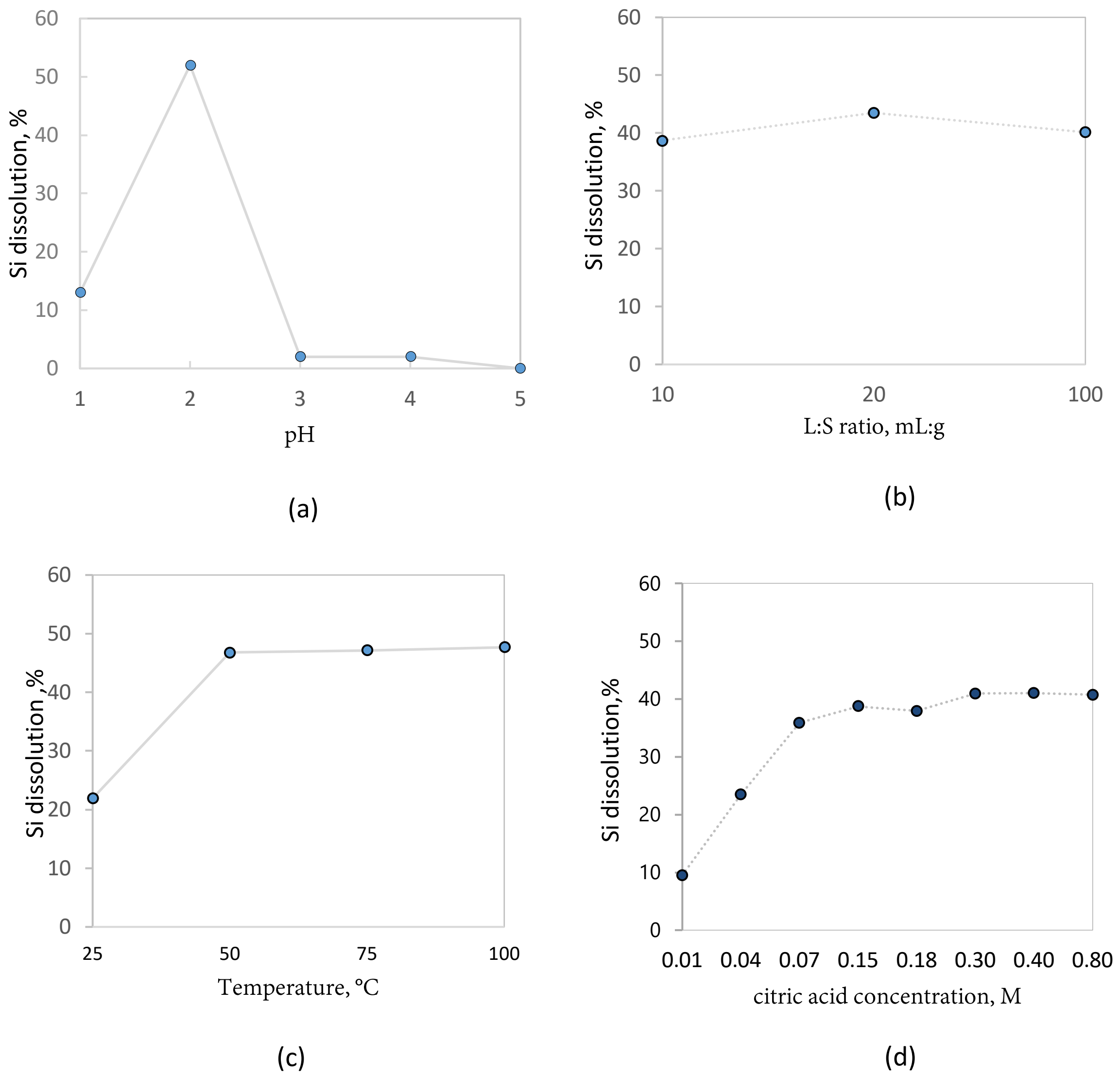


Figure 7-11: Comparative Si dissolution from eudialyte on citric acid leaching; test done on 0.8 M citric acid, 8 h leaching time at 60 °C and pH of 2

The results of additional leaching tests for SG concentrate showed that Si co-dissolution was highest at pH 2, but this was reduced with optimised leaching at pH 1 (Figure 7-12a). There was precipitation of filterable form of silica observed on leaching at pH 1 and this resulted in easy filtration of the leach solution. The low dissolution of silicon at pH 3-5 was caused by the non-dissolution of eudialyte with citric acid at these pH ranges. At L:S ratios of 10–100 mL:g, Si dissolution was at 40 % (Figure 7-12b). Comparable Si dissolution occurred on leaching at temperatures of 50-100 °C as a concurrent result of the acid digestion of eudialyte (Figure 7-12c). There was a positive correlation between Si dissolution and citric acid concentration (Figure 7-12d), believed to be related to the increased digestion of eudialyte and the release of Si into the solution with increased citric acid concentration.

7.4.7 Leaching responses of other impurities in the sulfuric acid leaching of eudialyte

The comparative profile of impurity distribution in the sulfuric acid leaching of eudialyte showed that there was a higher co-dissolution of impurities Na, Ca, K, Al, Mn, Fe and Th from large-grained eudialyte in SG concentrate than from fine-grained eudialyte in DT ore (Figure 7-13 & Table 7-3). This was largely influenced by mineralogy. It was emphasised earlier that the silicate-bearing minerals in SG concentrate were prone to congruent dissolution with acid attack, hence, the high dissolution of impurities. The low dissolution of Ti was a consistent result with a high residual Ti content in SG concentrate leach residue, previously determined to be one of the main reasons for the incomplete decomposition of eudialyte. Although the concentrations of the impurity in leach solution were low at less than 1 g/L (Table 7-3), these values would increase with increased mass loading of eudialyte concentrate. With 70-100 % dissolution of alkali impurities in the SG concentrate, the purification of the leach solution is a necessary step prior to REE recovery by standard solvent extraction methods.



(a)

(b)

(c)

(d)

Figure 7-12: Effect of factors on silicon co-dissolution: (a) pH, (b) L:S ratio, (c) temperature and (d) citric acid concentration; tested by varying one factor at a time on pH of 2, temperature of 60 °C, leaching time of 8 h, L:S ratio of 100 mL:g, grind size of 149-212 μm and citric acid concentration of 0.80 M

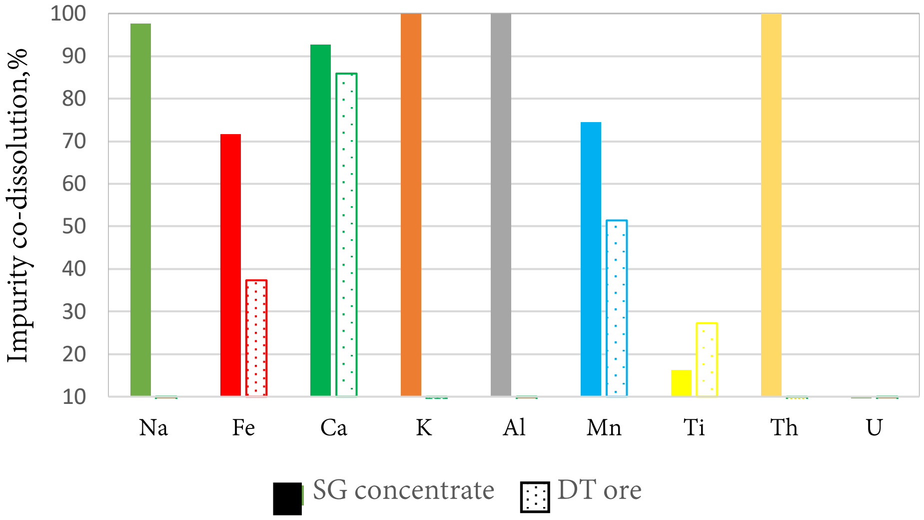


Figure 7-13: Profile of impurity co-dissolution on sulfuric acid leaching of rare earths

Table 7-3: Concentration of impurities in solution in sulfuric acid leaching of eudialyte

Sample	Elemental assay in solution, g/L								
	Na	Fe	Ca	K	Al	Mn	Ti	Th	U
SG concentrate	0.95	0.05	0.66	0.04	0.01	0.04	0.004	0.001	<0.001
DT ore	0.09	1.0	0.14	0.02	0.19	0.09	0.008	0.013	0.002

For the sulfuric acid leaching of eudialyte in DT ore, only Ca,Fe and Mn dissolved significantly (Figure 7-13), with the concentration of Fe and Mn comparatively higher than the leach solution from SG concentrate leaching (Table 7-3). The nil dissolution of both Th and U from DT ore leaching produced a favourable result in that these radionuclides remained in the leach residue. Thus, the sulfuric acid leaching of fine-grained eudialyte in DT ore was more “attractive” from the point of view of lower impurities dissolution.

In the citric acid leaching of large-grained eudialyte in SG concentrate, a similar pattern was observed for impurity co-dissolution wherein there was dissolution of alkali elements although the degree of dissolution was lower by 20 % compared to leaching with sulfuric acid

(Figure 7-14 & Table 7-4). Investigations related to the removal of these impurities, and subsequent REE recovery are of interest in bringing this study forward. In contrast, there was 100 % dissolution of Ca and Mn in the citric acid leaching of fine-grained eudialyte in DT ore and a slight dissolution of less than 20 % for Fe, Al and K (Figure 7-14 & Table 7-4). In summary, there was a higher dissolution of impurities with the citric acid leaching of fine-grained eudialyte. In consideration of the low REE and Zr leaching from the material, this leaching method is deemed to be impractical.

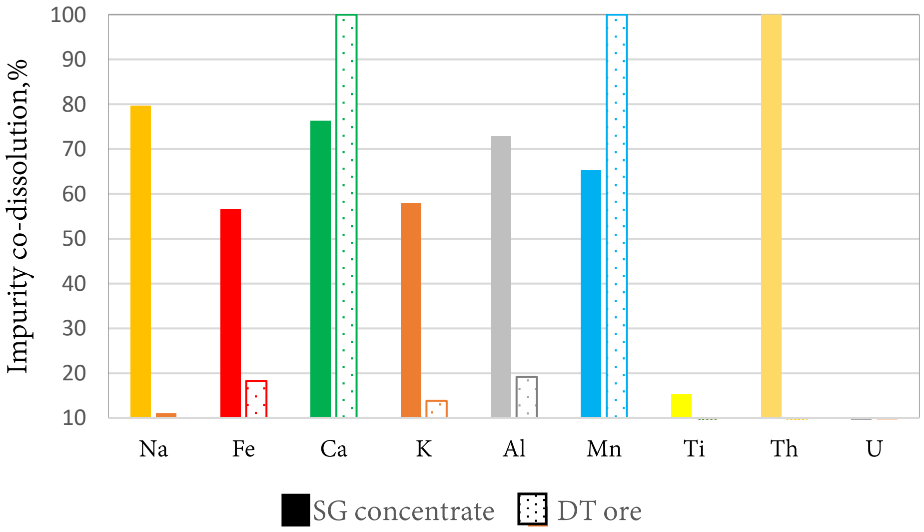


Figure 7-14: Profile of impurity co-dissolution on citric acid leaching of rare earths

Table 7-4: Concentration of impurities in solution on citric acid leaching of eudialyte

Sample	Elemental assay in solution, g/L								
	Na	Fe	Ca	K	Al	Mn	Ti	Th	U
SG concentrate	0.86	0.41	0.60	0.02	0.05	0.03	0.004	0.002	<0.001
DT ore	0.10	0.23	0.17	0.13	0.32	0.12	0.000	0.003	<0.001

7.4 Chapter Summary

This chapter showed that the co-leaching of Zr in sulfuric acid and citric acid was affected by the ore mineralogy and hydrolysis reactions of Zr. In particular, this chapter made the following findings:

- In the preferential leaching of rare earths from large-grained eudialyte using sulfuric acid, the co-leaching of Zr yielded comparable recoveries of 75 % to that of the conventional leaching of eudialyte. Conditions of a high dilution of 100 mL:g used to promote REE lixiviation also promoted Zr lixiviation;
- In the preferential leaching of rare earths from fine-grained eudialyte using sulfuric acid, the co-leaching of Zr yielded a lower recovery of 56 % brought about by the lower L:S ratio of 20 mL:g used in the leaching of DT ore;
- In the preferential leaching of rare earths from large-grained eudialyte using citric acid, the co-leaching of Zr was 65 % but this was reduced to 33 % due to the hydrolysis of Zr and the precipitation of the hydrolysis product. Hydrolysis was minimised with the use of HCl as a pH modifier;
- There was nil leaching of Zr with the citric acid leaching of fine-grained eudialyte in DT ore, consistent with the results of REE leaching from the material;

The above findings on the co-leaching of Zr in the sulfuric acid leaching of REEs from eudialyte showed that the comparably high Zr recoveries will provide an economic advantage on its recovery as a valuable by-product in the preferential leaching of REE from the mineral. This will be particularly relevant on high REE market prices. In the case of fine-grained eudialyte, more studies are needed to address the minimization of Zr hydrolysis.

This chapter has also shown that the dissolution of impurities on the leaching of eudialyte was significant with regard to large-grained eudialyte. The main findings with regards to dissolution of non-desirable components were as follows:

- The dissolution of silica and impurities was higher in large-grained eudialyte as brought about by the silicate structure of silica-bearing minerals in SG concentrate. This was true for both sulfuric and citric acid leaching scenarios. With a high dissolution of Si at 63 % in SG concentrate, the formation of silica gel on leaching was avoided by controlling the pH at 1-2.
- Impurity dissolution including that of radionuclides Th and U was not an issue in the sulfuric acid leaching of fine-grained eudialyte, making it a more attractive material compared to large-grained eudialyte;

Chapter 8

Conclusions and Recommendations

The aims of this thesis were to:

- characterise and discuss the physical and chemical features of two textural types of eudialyte minerals;
- identify and investigate the statistically significant factors affecting the leaching of rare earths by sulfuric acid, from two differently textured types of eudialyte;
- identify and investigate the statistically significant factors affecting the leaching of rare earths by citric acid, from two textural classes of eudialyte;
- determine the optimal conditions for the leaching of HREE by (a) sulfuric and (b) citric acid from two textural classes of eudialyte;
- investigate the co-leaching of Zr in the leaching of REE by (a) sulfuric and (b) citric acid from two differently textured types of eudialyte; and
- investigate the co-leaching of silica and the deportment of impurities in the leaching of REE by (a) sulfuric and (b) citric acid from two differently textured types of eudialyte

Conclusions made in the pursuit of achieving the above objectives are discussed in detail in the following sections. Recommendations are also provided for potential future research on this subject.

8.1 Characterisation of Eudialyte Minerals

Material characterisation was a vital aspect in the present study particularly in defining the variability of the two textural classes of eudialyte used in this research work. Eudialyte is a complex zirconosilicate mineral and exist in many variants.

The large-grained eudialyte ore samples in this research work existed in well–defined grains of chemical composition $(Na,REE)_{15}(Ca,REE)_7(Fe,REE)_3Zr_3Si(Si_3O_9)_2(Si_9O_{27})_2(OH)_2(Cl,F)_2$. It classified under the variant *eudialyte proper*, from the stoichiometric ratios of the framework elements Na:Ca:Zr:Si. This type of eudialyte is characterised by high co-dissolution of Si on acid leaching. These grains hosted mainly Zr values, while rare earths were hosted in slightly altered fluorosilicate phases. The presence of alteration minerals is common in eudialyte and intensifies its chemical and mineralogical variability. The large-grained eudialyte was easily beneficiated to a mineral concentrate.

A textural variant of eudialyte was also the subject of this present investigation. A fine-grained Na-Ca-Zr eudialyte of unknown chemistry was characterised in the present study. Not only did the Na-Ca-Zr silicate differ mineralogically and texturally from large-grained eudialyte, but the eudialyte clusters were found to differ considerably in chemical composition. REEs and Zr were hosted in these complex micro-phases. The average grain size of fine-grained eudialyte was less than 5 μm and thus it was used as a whole-of-ore.

The textural differences of these eudialyte variants reflected their leaching responses. Rare earths were extracted easily from large-grained eudialyte using the direct leaching method, with leaching recoveries of 70-80 % on use of either sulfuric or citric acid. On the other hand, the leaching of rare earths from fine-grained eudialyte minerals required more rigorous conditions. Such conditions could be due to the requirement for thermal cracking of the complex and ultrafine texture of eudialyte minerals, as well as the overlapping of grain boundaries of the fine eudialyte masses. This was evidenced by the strong influence of high temperature baking on effecting high recoveries of 80-90 % with the use of sulfuric acid.

However, the low decomposition temperature of citric acid and its low corrosiveness prevented its application in creating a similar effect. Hence, the citric acid leaching of rare earths from fine-grained eudialyte minerals suffered from low kinetics and resulted in poor recoveries of less than 10 %.

While the effect of textural differences on the leaching responses of eudialyte can be clearly differentiated, the optimal leaching conditions for recovery of HREEs over LREEs, which was one of the objectives of this research, cannot really be generalised to apply to similar eudialyte variants, owing to the inherent variability in eudialyte composition. The findings of the present study have shown that the optimal conditions for HREE leaching were affected significantly by mineralogy.

The effect of differences in impurity content, and the content of other REE –bearing minerals, has made a significant contribution to differences in leaching conditions. In the leaching of rare earths from large-grained eudialyte, the speed of agitation, acid concentration and pH were kept low to avoid the formation of silica gel on leaching. On material characterisation, it was determined that leaching of SG concentrate was highly prone to the formation of coagulated silicic acid. This was due to the silica-bearing minerals in SG concentrate being cyclosilicates, which are known to decompose congruently on acid attack. This was not the case for DT ore, as the silica-bearing minerals were tectosilicates which are known to only partially decompose on acid leaching. To this effect, there was a higher dissolution of impurities in the leaching of large-grained eudialyte than in fine-grained eudialyte.

8.2 Sulfuric Acid Leaching of Rare Earths from Eudialyte

The use of sulfuric acid in the leaching of rare earths from eudialyte was characterised by a high recovery of more than 70 %. The main contributory factor in the high recovery rate was the leaching procedure applied, relative to the textural differences of eudialyte ore samples.

A leaching recovery rate of 70-80 % resulted from the direct leaching of large-grained eudialyte, while an 80-90 % recovery rate resulted from the sulfation baking- water leaching procedure applied to fine-grained eudialyte samples.

This study has showed that high recoveries of 70-80 % in the single stage sulfuric acid leaching of rare earths from large-grained eudialyte minerals can be achieved. The conditions for leaching were: a high dilution of 100 mL:g with a low acid concentration of 5 wt. %. In previous investigations, high recoveries of REE at 80-90 % could only be achieved with multiple leaching of eudialyte with 5-21 % acid at 4:1 to 6:1 mL:g dilution. Obviously, the slight differences in recovery do not compensate for the longer processing time used in previous work. This finding provided new information on process conditions for preferential leaching of REE from large-grained eudialyte.

The optimal leaching of HREEs as applied to SG ore, devised as a result of this study, were: leaching at 60 °C for 2 h using 5 wt. % sulfuric acid at a L:S ratio of 100 mL:g and 300-420 µm grind size. HREE lixiviation showed a slight improvement with the use of a coarser grind size of 300-420 µm. The main drawback of the high dilution used was the low concentration of REE in solution.

The leaching of large-grained eudialyte left 20-30 % of leach residue. The reasons for this were covering of precipitated silica particles on eudialyte surfaces, and the presence of the refractory metals Nb and Ti in the residual masses. The significant influence of silica in limiting the total decomposition of eudialyte was consistent with findings of previous studies. This highlighted the role of silica in eudialyte processing and thus, further improvements in increasing REE recoveries should be directed towards addressing silica management on leaching or with the use of non-aqueous based lixiviants. The chemical composition of eudialyte changed from $(Na,REE)_{15}(Ca,REE)_7(Fe,REE)_3Zr_3Si(Si_3O_9)_2(Si_9O_{27})_2(OH)_2(Cl,F)_2$ in the mineral concentrate to $Na_4(Ca, Ce)_2(Fe^{2+}, Mn^{2+}, Y)ZrSi_8O_{22}(OH, Cl)_2$ in the leach residue.

The change in chemical composition clearly indicated the reduced REE and Zr content in undigested eudialyte.

In contrast, the recovery of HREEs from fine-grained eudialyte minerals was approached using a two-stage process, which included thermal cracking followed by water leaching. The sulfation baking step was a significant step in the extraction of Y. The optimal leaching conditions for the leaching of HREEs were: baking at 320 °C for 3 h using 3.2 g/g sulfuric acid, and water leaching for 3 h at 20 °C on 20 mL:g using 300-420 μm grind size. Examination of the leach residue of fine-grained eudialyte showed that the chemical composition shifted to low Na-Zr silicates with most of the Zr and Ca being dissolved from the grains. By mass balance, there was only 10 % unleached REE in the DT ore. The high lixiviation of REEs from fine-grained eudialyte was believed to be caused by the low effect of silica on leaching, as brought about by the slight dissolution of silica-bearing minerals in DT ore.

The finding on sulfuric acid leaching of fine-grained eudialyte minerals provided detailed information on processing conditions for preferential REE leaching from the material. This information is currently not available in public domain.

8.3 Citric Acid Leaching of Rare Earths from Eudialyte

The use of citric acid proved to be a promising alternative leaching agent for rare earth leaching from large-grained eudialyte but not for fine-grained eudialyte. Recoveries of 70 % resulted from the optimal leaching of REEs in the following conditions: use of 75-106 μm grind size, leaching for 4 h at 60 °C at pH 1, 0.8 M citric acid concentration and a L:S ratio of 10 mL:g. For these leaching conditions, the concentration of REE was 60 mg/L (which can be precipitated with oxalic acid).

The main limitation on the complete decomposition of large-grained eudialyte under citric acid leaching was covering on eudialyte surfaces of silica and precipitated Zr hydrolysis products. The presence of Ti, Mn and Fe was also a contributory factor. The first two elements form citrate complexes at a pH of 3-8, which is a higher pH range than was used in this leaching study. The limited dissolution of Fe was brought about by the saturation of Fe in solution. The co-leaching of Zr was 65 % but this decreased to 33 % due to hydrolysis and its precipitation out of solution. This also affected the leaching of eudialyte, as some grains were found covered with hydrolysed Zr films.

In contrast, the leaching of rare earths from fine-grained eudialyte was characterised by slow kinetics in that only 8 % leaching recovery resulted with 8 h leaching and 35 % recovery on extended leaching of 400 h. The complex mineralogy of fine-grained eudialyte required rigorous conditions which could not be achieved with the use of citric acid, owing to the low decomposition temperature and low corrosiveness of citric acid.

The use of citric acid in leaching of REEs from eudialyte is a novel method. The findings derived from such use will open up new approaches to eudialyte processing.

8.4 Leaching Responses of Zirconium & Impurities in the Leaching of Eudialyte

In the preferential leaching of rare earths from eudialyte using sulfuric acid, the co-leaching of Zr yielded comparable recoveries of 55-75 % to that of the conventional leaching of eudialyte. The conditions of a high dilution of 100 mL:g used to promote REE lixiviation in large-grained eudialyte in SG concentrate resulted to higher co-leaching of Zr at 75 % while a lower recovery of 56 % was believed to brought about by the lower L:S ratio of 20 mL:g used in the leaching of fine-grained eudialyte in DT ore.

In the preferential leaching of rare earths from eudialyte using citric acid, the co-leaching of Zr was highly variable due to Zr hydrolysis. For example, in the citric acid leaching of large-grained eudialyte, the co-leaching of Zr was initially 65 % but this was reduced to 33 % on precipitation of Zr hydrolysis products. There was nil leaching of Zr with the citric acid leaching of fine-grained eudialyte in DT ore, consistent with the results of REE leaching from the material. Precipitation of Zr hydrolysis products was also observed in the leaching of fine-grained eudialyte.

The above findings on the co-leaching of Zr in the sulfuric acid leaching of REEs from eudialyte showed that the comparably high Zr recoveries will provide an economic advantage on its recovery as a valuable by-product in the preferential leaching of REE from the mineral. This will be particularly relevant on high REE market prices. In the case of fine-grained eudialyte, more studies are needed to address Zr hydrolysis.

The leaching resposes of silica and impurities Na, Ca, K, Al, Mn, Fe and Th were as expected from the findings of the material characterisation results. There was higher dissolution of impurities on sulfuric acid leaching of large-grained eudialyte as brought about by the silicate structure of silica-bearing minerals in SG concentrate. With a high dissolution of Si at 63 % in SG concentrate, the formation of silica gel on leaching was avoided by controlling the pH at 1 - 2 .In contrast, impurity dissolution including that of radionuclides Th and U was not an issue in the sulfuric acid leaching of fine-grained eudialyte, making it a more attractive material compared to large-grained eudialyte. A similar pattern of impurity dissolution was observed in the citric acid leaching of eudialyte.

8.5 Recommendations

The sulfuric acid leaching of eudialyte, as applied to this work, focused on a reverse scenario where rare earth leaching was preferentially leached over Zr. Thus, the conditions for optimal recovery of REEs, devised as a result of the present study will provide useful information for eudialyte processing in a scenario with highly attractive REE market prices. Future work should include investigations related to the purification of the leach solution and REE recovery by solvent extraction techniques. These studies will provide useful information needed for the economic evaluation on preferential REE leaching from eudialyte.

The use of citric acid in the leaching of rare earths from large-grained eudialyte is a promising alternative method to the use of sulfuric acid. Further study on the use of two-stage citric acid leaching of large-grained eudialyte is highly recommended. The aim would be to increase Zr recovery and enhance the integrated recovery of metal values from eudialyte leaching. In addition, more studies are required on the applicability of citric acid leaching to fine-grained eudialyte. The relative insensitivity to grind, but sensitivity to leaching time of citric acid leaching of fine-grained eudialyte may lend itself to heap leaching methods of rare earths extraction. Alternatively, investigation into the use of surface preparation techniques on opening complex mineral morphologies, e.g. the use of microwave heating, is recommended. These procedures have reported success in enhancing leaching kinetics in low-Fe content minerals. Moreover, it is of interest to study solution purification and REE recovery from citric acid solution.

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Appendix A. Abbreviations & Acronyms

Abbreviations

con	concentrate
conc.	concentration
temp.	temperature
wt.	weight

Acronyms

ANOVA	Analysis of Variance
CSIRO	Commonwealth Scientific and Industrial Research Organization
DT	Dubbo-Toongi
HREE	Heavy Rare Earth Element
L:S	Liquid : Solid
LA-ICP-MS	Laser ablation- inductively coupled plasma-mass spectrometry
LREE	Light Rare Earth Element
REE	Rare Earth Element
REO	Rare Earth Oxide
SEM-EDS	Scanning Electron Microscopy- Energy Dispersive Spectroscopy
SG	South Greenland
TIMA	TESCAN Integrated Mineral Analyser
XRD	X-ray Diffraction
XRF	X-ray Flourescence

Appendix B. List of Industrial Projects on REO Production from Eudialyte Minerals

Company	Location	Mineral/s	Company website
Alkane	Dubbo,Australia	Eudialyte	http://www.alkane.com.au/projects/current-projects/dubbo/project-overview
Avalon	Nechalacho,Canada	Eudialyte	http://avalonadvancedmaterials.com/nechalacho/nechalacho_overview/ http://www.geotop.ca/pdf/Gestion_Documents/Memoires/Memoire_Emma_Sheard.pdf
Greenland Mining	Kvanefjeld,Greenland	Steenstrupine Eudialyte	http://www.ggg.gl/projects/specialty-metals-kvanefjeld/
Metamec	Kipawa, Canada	Eudialyte	http://www.matamec.com/vns-site/page-energy_kipawa-en.html
Quest	Strange Lake,Canada	Eudialyte	http://www.questrareminerals.com/strange_lake.php
Tanbreez	Tanbreez,Greenland	Eudialyte	http://tanbreez.com/en/the-tanbreez-licence-geology/
Tasman	Nora Karr, Sweden	Eudialyte	http://www.tasmanresources.com.au/
Tantalus Rare Earths AG	Madagascar	Zircon, Eudialyte	http://www.tre-ag.com/~/media/Files/T/Tantalus-Rare-Earths/Attachments/pdf/2013_01_21_ES7520_SRKES_Tantalus%20CPR_Final_English.pdf

Appendix C. Eudialyte Variants

Table C.1: Structural classification of eudialyte and it variants (Rastsvetaeva and Chukanov 2013)

12-layer structures (Z=Zr)								**24-layer structures**			
1. Eudialyte-type structures					2. Oneillite-type structures			3. Structures of low-hydrous Na> H_2O + H_3O			4. Structures of high – hydrous members Na< H_2O + H_3O
1.1 Variant (T + T)	1.2 variant (T+M)	1.3 Variant (M+M)	1.4 Variant (□+T)	1.5 Variant (□+□)	2.1 Variant (T+T)	2.2 Variant (□+T+M)	2.3 Variant (□+T)	3.1 Variant $Z_{Ti} + Z_{Ti}$	3.2 Variant $Z_{Zr} + Z_{Ti}$	3.3 Variant $Z_{Zr} + Z_{Zr}$	4.1 Variant, Hydrated eudialyte

where T is the tetrahedron in the center of nine-membered ring eudialyte

M is the octahedron in the center of nine-membered ring eudialyte

□ is the vacancy in the center of nine-membered ring eudialyte

Z_{Zr} is the zirconium analog of the Z position

Z_{Ti} is the titanium analog of Z position

Appendix D. Microprobe Analysis of DT Ore

D:\UserData\HLim\20130812_REE.MDB

UWA CMCA JEOL 8530F Electron microprobe | Average Si/Zr atomic | 7

SAMPLE DESCRIPTION	LINES	ATOMIC %																															
		La	Ce	Eu	Y	Dy	Pr	Nd	Er	Sm	Gd	Yb	Cr	Tb	Ho	Lu	Tm	Th	Nb	Ti	Zr	Hf	Zn	Mn	Mg	Al	Fe	Ca	K	Si	O	P	F
Un 2 mount 1_phase1	156-159	0.0	0.0	0.0	0.1	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	15.1	1.3	0.3	0.0	0.2	1.3	0.0	1.0	9.9	0.1	0.4	5.2	64.9	0.0	0.1
Un 3 mount 1_phase2	160-164	7.0	13.5	0.0	0.0	0.0	1.3	4.5	0.0	0.7	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.1	0.1	0.5	0.9	2.1	0.0	2.6	50.5	0.0	15.7
Un 4 mount 1_phase3	165-169	7.1	14.6	0.0	0.2	0.1	1.5	5.2	0.0	0.9	0.5	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.1	0.4	0.0	0.4	0.7	2.4	0.0	0.3	50.4	0.0	14.9
Un 5 mount 1_phase4	170-172	0.5	0.8	0.0	0.0	0.0	0.1	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.7	0.2	1.5	0.0	0.2	0.1	0.2	5.9	3.0	0.4	0.2	21.3	63.8	0.2	0.6
Un 6 mount 1_phase4_1	173-175	5.0	7.6	0.0	0.2	0.1	0.8	2.6	0.0	0.4	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.6	0.1	5.3	0.0	0.1	0.7	0.1	0.8	1.1	1.5	0.1	7.1	57.7	0.2	7.4
Un 7 mount 1_phase5	176-180	1.1	1.4	0.0	0.0	0.0	0.1	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	9.4	0.0	1.0	0.0	0.1	1.6	0.0	3.5	0.8	1.1	0.7	12.5	65.3	0.6	0.6
Un 8 mount 1_phase6	181-185	0.7	1.5	0.0	0.0	0.0	0.1	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	14.5	1.1	0.1	0.0	0.2	1.1	0.0	0.2	10.6	0.3	0.0	1.1	64.8	2.8	0.3
Un 9 mount 1_phase7	186-189	7.4	14.8	0.0	0.0	0.1	1.5	5.2	0.0	0.8	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.3	0.0	0.2	0.4	2.4	0.0	1.2	51.9	0.0	13.0
Un 10 mount 1_phase8	190-194	3.7	6.8	0.0	0.0	0.0	0.7	2.3	0.0	0.4	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	1.1	0.0	0.0	0.1	0.1	0.9	5.1	1.0	0.0	12.4	56.5	0.1	8.3
Un 11 mount 1_rock 2_phase9	195-197	7.5	13.7	0.0	0.1	0.1	1.4	4.6	0.0	0.7	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.2	0.1	0.4	0.0	0.0	0.0	0.0	0.1	1.8	2.5	0.0	0.9	50.7	0.1	14.7
Un 13 mount 1_rock 2_phase11	203-205	0.0	0.0	0.0	0.1	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	18.7	0.9	0.1	0.0	0.2	2.0	0.0	0.2	11.6	0.1	0.0	1.0	65.1	0.0	0.0
Un 14 mount 1_rock 2_phase12	206-209	5.0	9.2	0.0	0.2	0.1	1.0	3.5	0.0	0.6	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.2	2.1	0.2	1.1	0.0	0.2	0.2	0.0	0.7	7.0	2.0	0.0	3.2	55.3	0.1	7.6
Un 15 mount 1_rock 2_phase13	210-212	6.8	11.4	0.0	0.0	0.0	1.0	3.3	0.0	0.3	0.1	0.0	0.1	0.0	0.0	0.0	0.0	0.2	0.2	0.1	1.6	0.0	0.1	0.0	0.0	0.4	3.6	2.1	0.0	2.4	50.6	0.1	15.4
Un 16 mount2rock 1_phase 1	213-215	4.4	7.8	0.0	0.0	0.1	0.8	2.6	0.0	0.4	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.0	0.5	0.0	0.1	0.0	0.3	1.7	2.5	1.6	0.0	9.3	51.5	0.1	16.1

Appendix E. Exploratory Test on Sulfuric Acid Leaching of Eudialyte

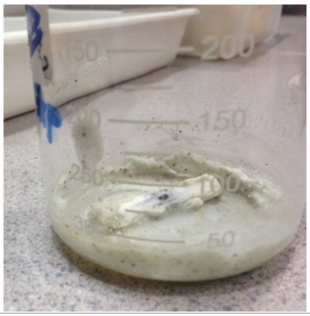
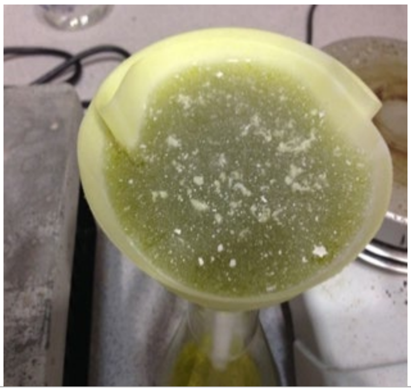
E-1. Exploratory test on sulfuric acid leaching of REE from SG concentrate

Objective The main purpose of this exploratory test was to determine which treatment procedure would be favorable for the recovery of REE from SG concentrate. Due to the high content of silica in the mineral, one of the considerations for method selection was the minimization if not the avoidance of silica polymerization in solution.

Procedure Several treatment procedures using various sulfuric acid concentration were explored (Table E-1). Visual observations were noted for polymerization, difficulty in filtration and leachability. The last criterion was determined from the color of the resulting leach solution. Base on empirical observation, high REE content in leach solution was evident by resulting yellow-green coloration of the liquid solution. Quantitative analysis was conducted for leach solutions with promising results.

Outcome Results of this exploratory test showed that use of 33 wt% sulfuric acid on direct leaching at 100 °C resulted to gelling of leach solution while the use of 10 wt% sulfuric acid on sulfation baking followed by water leaching resulted to difficulty in filtration. The most promising treatment was with the use of 5 wt% sulfuric acid on direct leaching of the mineral concentrate. In this treatment procedure, eudialyte was dissolved in a reasonable amount of time and filtration was manageable. Thus, this procedure was chosen as treatment method for REE recovery from SG concentrate.

Table E-1: Summary of exploratory test on sulfuric acid leaching of SG concentrate

Leach solution	Procedure	Results
33% sulfuric acid, 10 ml	2 g leached at 100° C for 1 h	Solution turned into gel on cooling below 50 °C 
15% sulfuric acid, 10 ml	2 g baked at 320 °C followed by leaching for 3 h at 70 °C	Eudialyte was partially dissolved, leach solution was difficult to filter
10% sulfuric acid, 15 ml	2 g acid baked at 320 °C followed by leaching for 3 h at 70 °C	Eudialyte was dissolved but the leach solution could not be filtered due to silica polymerization. 
5% sulfuric acid, 15 ml	Direct leaching at 25 °C	Eudialyte was partially dissolved, filtration was manageable
5% sulfuric acid, 15 ml	Direct leaching at 70 °C	Eudialyte was totally dissolved and filtration was manageable. Recoveries were 80 % for REE and 43 % for Zr.

E-2. Exploratory test on sulfuric acid leaching of REE from DT ore

Objective The purpose of this exploratory test was to determine which lixiviants could be used to leach REE from DT ore. Results of this exploratory test would determine which treatment procedure will be explored further in the succeeding leaching study. The co-leaching of Zr and silica was also monitored.

Procedure Exploratory leaching tests were conducted using 50 g of 312 µm of DT ore, leached for 4 h at 100 °C using the following solution (in % volume, unless stated otherwise): 12 % HCl, 20 % (wt) NaOH, 50 % HNO_3, and 50 % H_2SO_4. Sulfation baking was also tested on two test samples by heating one sample at 150 °C for 3 h with acid dosage of 0.4 g/g followed by water leaching at 100 °C. Another sample was heated at the same condition but was water leached at 25 °C.

Outcome Results of exploratory test showed that the most promising treatment procedure was with the use of sulfation baking followed by water leaching as evidenced by the relatively higher Y and zirconium recovery as compared to the leaching results derived from direct leaching using various inorganic acids (Figure E-2). Results also showed that water leaching done at room temperature has higher Y and zirconium recovery as compared to water leaching at elevated temperature. The use of direct leaching with HCl, HNO_3 and H_2SO4 may be explored further for REE recovery but given that high zirconium co-leaching was an important consideration in the leaching objective, sulfation baking following by water leaching was the preferred treatment procedure.

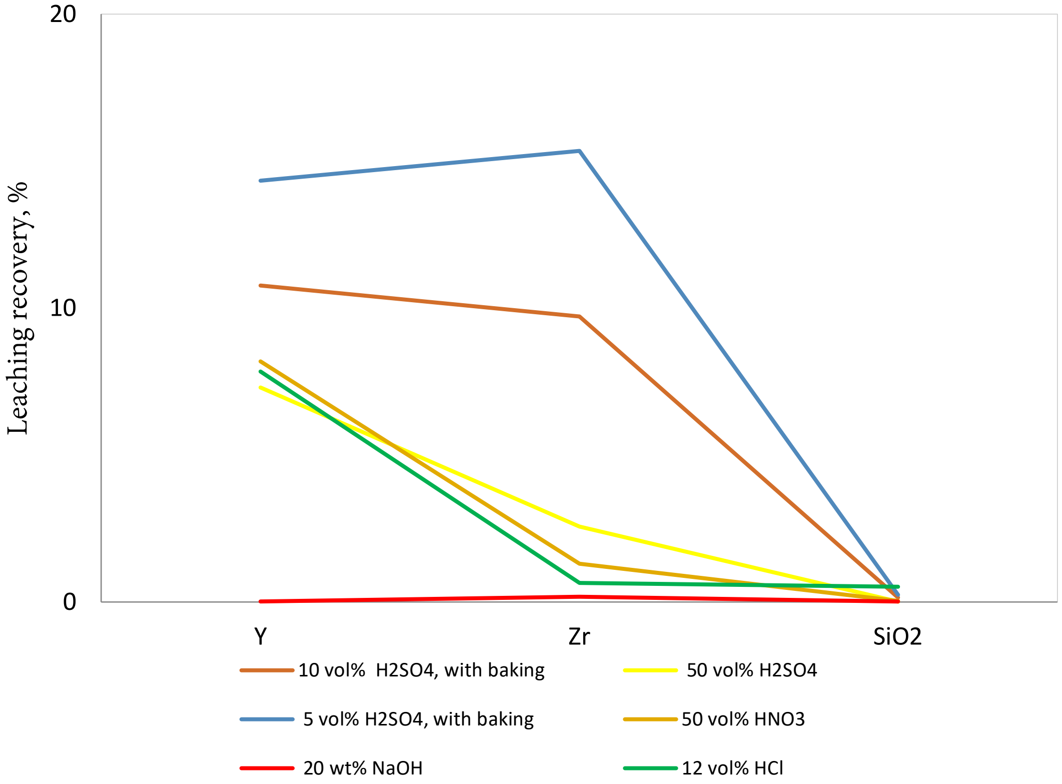


Figure E-2: Graph showing results of exploratory test on sulfuric acid leaching of DT ore; promising results on sulfation baking -water leaching approach (blue and brown line graphs)

Appendix F. Boiling of SG Concentrate for the Removal of Aluminum Silicates

Procedure: Pre-treatment of SG concentrate was carried out by boiling the concentrate in 0.1% sulfuric acid solution for 5 h at 100 °C, without any stirring.

Outcome: As shown in Figure F, boiling of SG concentrate in 0.1% sulfuric acid removed largely aluminum oxide, potassium oxide and sodium oxide. Aluminum has known effect in increasing the polymerization of silica in solution(Terry 1983a). After boiling, the content of REO and Zr has relatively increased in the concentrate as an effect of the reduced total oxide content in the material.

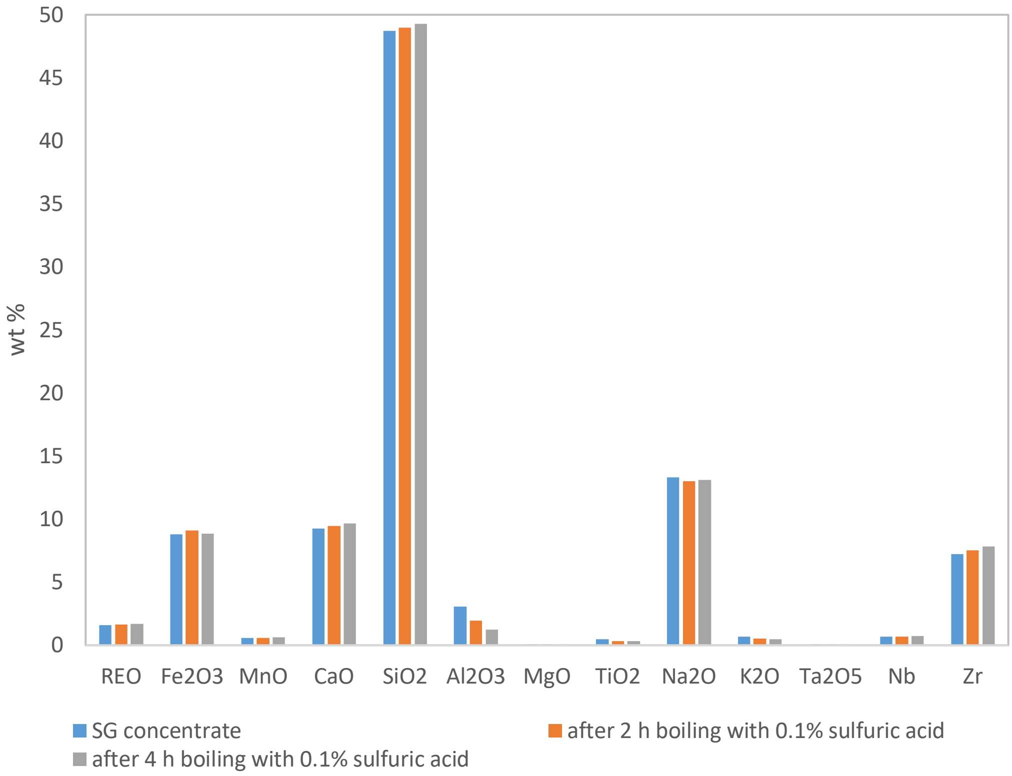


Figure F: Analysis of SG concentrate before and after boiling with 0.1% sulfuric acid

Appendix G. Cube Plots on Sulfuric Acid Leaching of Eudialyte from SG Concentrate

G-1. Procedure on how to read a Cube plot

A Cube plot is a graphical method of displaying results in which the axes of the cubes represent a factor with its low and high level setting. A sample Cube plot, as applied to the leaching of SG concentrate, shows four cubes in which the two cubes at the left side display the leaching recoveries on use of sulfuric acid concentration at low level setting (-1) while the two cubes at the right side show leaching recoveries at sulfuric acid concentration at high level setting (+1) (Figure G-1). The two upper cubes present results on leaching at high dilution (+1) while the two bottom cubes display results of leaching done on low dilution (-1). In each cube, -x axis represents condition on the use of fine grind size SG concentrate while +x axis represents condition on use of coarser grind size. Similarly, -y axis represents condition of shorter leaching time while + y axis represents condition of longer leaching time. Likewise, - z axis represents condition of lower leaching temperature while + z axis represents condition of higher leaching temperature.

To illustrate this configuration using the data shown in Figure G-1, the value of 31.2 at the top left cube represents the calculated recovery from leaching done at lower sulfuric acid concentration, high dilution, finer grind size, lower leaching temperature and shorter leaching time. To illustrate further, the value of 68.6 at the right bottom cube represent a leaching recovery data at conditions of higher sulfuric acid concentration, low dilution, coarser grind size, higher leaching temperature and shorter leaching time.

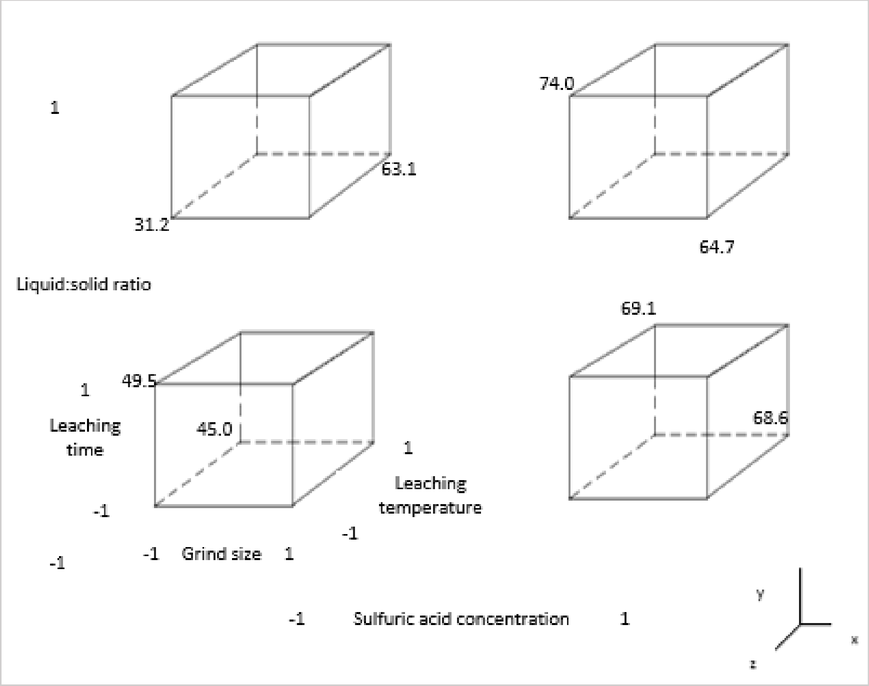


Figure G-1: An example of Cube plot showing leaching factors as applied to SG concentrate leaching

G-2. Cube plots on sulfuric acid leaching of REE from eudialyte

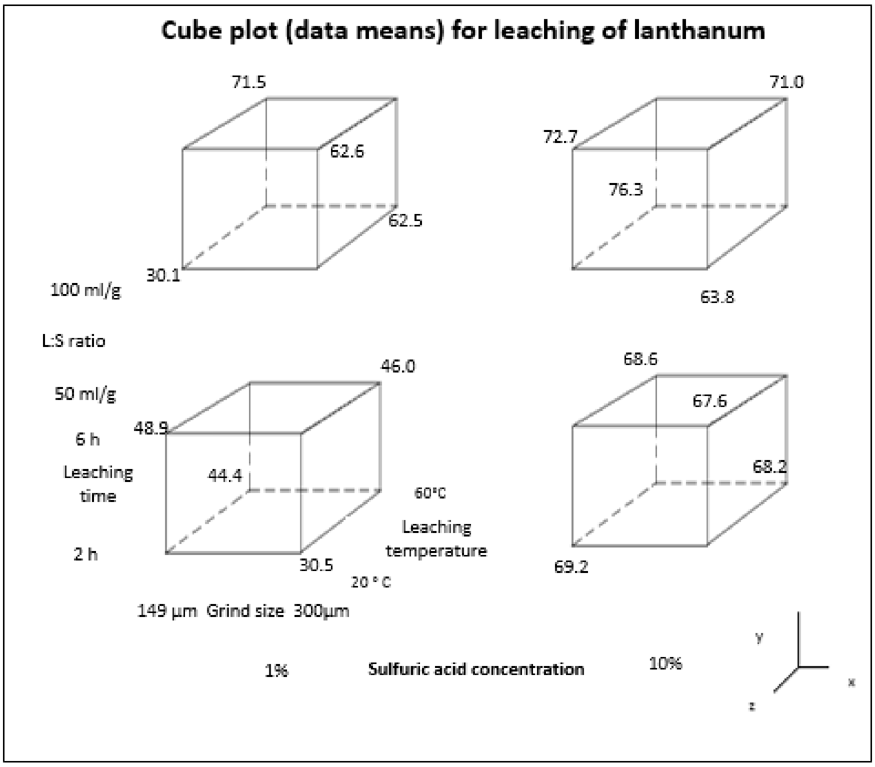


Figure G-2.1: Leaching recovery of La from sulfuric acid leaching of SG concentrate

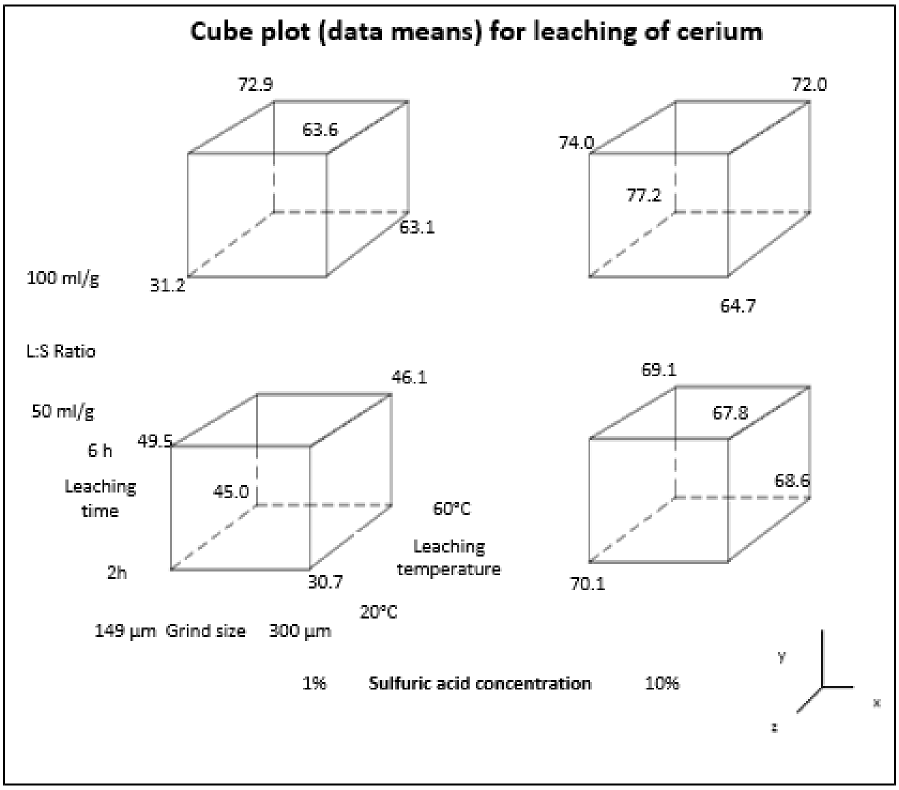


Figure G-2.2: Leaching recovery of Ce from sulfuric acid leaching of SG concentrate

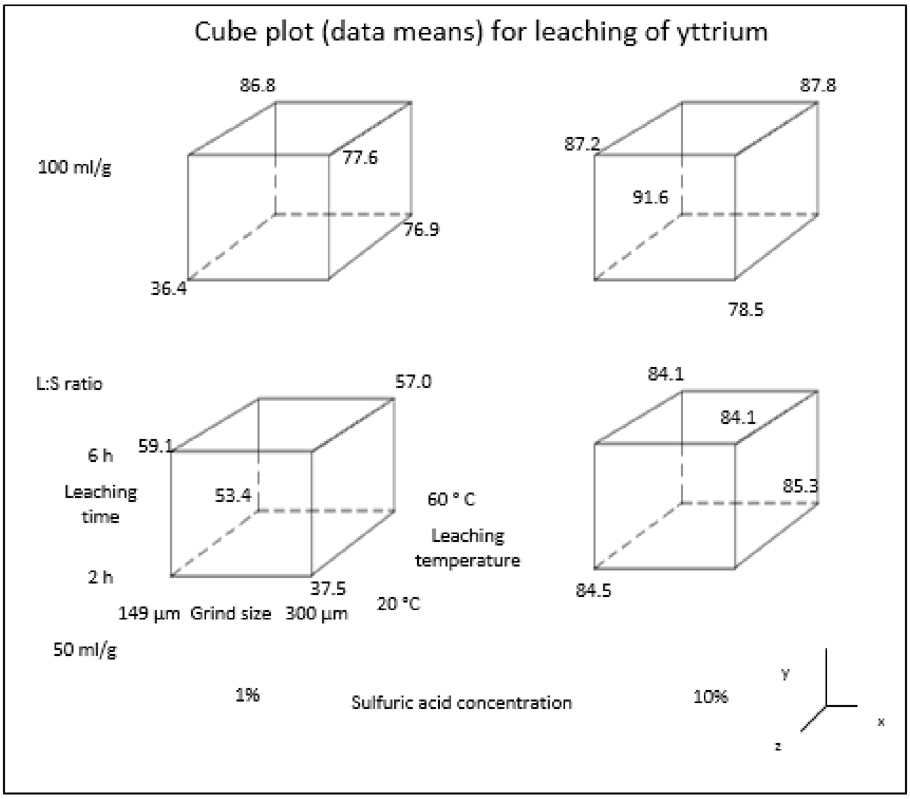


Figure G-2.3: Leaching recovery of Y from sulfuric acid leaching of SG concentrate

Appendix H. Test Results on Sulfuric Acid Leaching of REE from DT Ore

As the leaching of DT ore involved more factors compared to the leaching of SG concentrate, data results were presented on a table format (Table H) as Cube plots could not be applied to graphically present data for a seven-factor test from a Taguchi design.

Table H: Test results on sulfuric acid leaching of REE from DT ore

Leaching conditions								Leaching recoveries, %			
Run No	Grind size (μm)	Baking temp (^{0}C)	Baking time (h)	Acid-ore ratio (g /g)	Leaching temp (^{0}C)	Leaching time (h)	Liquid: solid ratio (mL:g)	Y	La	Ce	Average REE recovery
1-1	10*	200	1	0.4	20	1	5	36.06	91.97	90.92	72.98
1-2	10	200	1	0.4	20	1	5	40.05	92.73	92.11	74.96
2-1	300[88]	200	1	0.4	60	3	20	32.41	87.05	78.03	65.83
2-2	300	200	1	0.4	60	3	20	27.67	85.92	75.16	62.92
3-1	300	200	3	3.2	20	1	20	64.16	81.32	79.58	75.02
3-2	300	200	3	3.2	20	1	20	61.57	83.53	80.65	75.25
4-1	10	200	3	3.2	60	3	5	54.06	96.29	95.83	82.06
4-2	10	200	3	3.2	60	3	5	41.06	96.20	95.44	77.57
5-1	300	320	1	3.2	60	1	5	81.94	80.63	80.60	81.06
5-2	300	320	1	3.2	60	1	5	79.00	73.49	73.58	75.36
6-1	10	320	1	3.2	20	3	20	73.78	97.31	97.13	89.41
6-2	10	320	1	3.2	20	3	20	83.00	98.46	98.34	93.27
7-1	10	320	3	0.4	60	1	20	80.21	94.39	94.87	89.82
7-2	10	320	3	0.4	60	1	20	80.97	95.08	95.15	90.40
8-1	300	320	3	0.4	20	3	5	78.68	85.29	84.12	82.70
8-2	300	320	3	0.4	20	3	5	81.53	84.90	84.15	83.53

*10 μm (D_{90}), ** 300-420 μm(for all grind sizes) Over-all average REE recovery: 79.51%

Appendix I. Exploratory Test on Organic Acid Leaching of REE from Eudialyte

I-1. Exploratory test on organic leaching of REE from SG concentrate

Objective: The main purpose of this exploratory test was to evaluate which organic acid can be used to alternatively leach REE from eudialyte minerals.

Procedure: Table I. 1 and Table I.2 present a summary of procedures on exploratory tests to evaluate which organic acid can be used as an alternative lixiviant to sulfuric acid in leaching SG concentrate.

Outcome: Results presented in Table I.1 showed clearly that citric acid has the most favourable result on REE and Zr leaching from eudialyte in SG concentrate. This was evident with the high average leaching recoveries of metals at 65% compared to less than 10% leaching recoveries with the use of glycine or acetic acid and nil recovery with the use of sodium sulfate. This test also showed that silica co-dissolution on citric acid leaching presented a problem on the filterability of the liquid component.

Results of additional exploratory test as presented in Table I.2 showed that the use of citric acid alone has comparative leaching recoveries compared to the use of both citric and sulfuric acid. Relative to test results summarized in Table I.1, results in Table I.2 showed that baking large-eudialyte minerals prior to citric acid leaching caused increase in REE recovery but has the opposite effect to Zr recovery. The particular behaviour hinted the significant effect of temperature on REE recovery. In consideration of the high energy requirement on baking, direct leaching at elevated temperature will be tested in the leaching test.

Table I.1:Summary of leaching test done on SG concentrate with the use of various organic acid

Leaching solution	Procedure	Results
Citric acid	1g of SG concentrate was leached with 0.7 M citric acid for 18 h at 25 °C	Eudialyte was totally dissolved giving a yellow leach solution but filtration was observed to be slower compared to glycine solution; recoveries were 40% for REE and 78% for Zr
Glycine	1 g of SG concentrate was leached with 1.3 M glycine for 18 h at 25 °C	Eudialyte was partially dissolved giving an orange leach solution but recoveries for REE and Zr were low at less than 10%
Acetic acid	1 g of SG concentrate was leached with 17.4 M acetic acid for 18 h at 25 °C	Eudialyte was partially dissolved giving colorless leach solution; leaching recoveries were low at 2% for REE and 1.4 % Zr ; solution after leaching had a very pungent smell
Sodium sulfate	1 g of SG concentrate was leached with 0.7 M sodium sulfate solution for 18 h at 25 °C	Eudialyte was undissolved

Table I.2: Summary of exploratory test on use of citric and sulfuric acid for REE leaching from SG concentrate

Leaching solution	Procedure	Results
Sulfuric & citric acid	2 g of SG concentrate reacted with 1 ml of concentrated sulfuric acid and baked at 300 °C followed by citric acid leaching at 70 °C for 5 h	REE recovery was 63 % and 26 % for Zr
Sulfuric acid	2 g of SG concentrate mixed with 1 ml of concentrated sulfuric acid and baked at 300 °C for 3 h followed by water leaching for 5 h	REE recoveries were low at 6 % and Zr 1%
Citric acid	2 g baked at 300 °C followed by citric acid leaching at 70 °C for 3 h	REE recovery was 75 % and 33 % for Zr

I-2. Exploratory test on organic leaching of REE from DT ore

Objective: The main purpose of this exploratory test was to evaluate which organic acid and which procedure is best to use on REE leaching of eudialyte from DT ore

Procedure: In consideration of the results from organic leaching of SG concentrate, only glycine and citric acid were tested on DT ore. Table I.3 presents a summary of the test procedures done.

Outcome: Leaching test results (Table I.3) showed that both citric acid and glycine were poor lixiviants of REE from DT ore. High leaching recoveries only resulted from the use of sulfation baking in combination with organic acid leaching. The use of thermal treatment by heating the ore at 320 °C prior to citric acid leaching still resulted to poor recoveries. As the use of sulfation baking is not an alternative method, the use of citric acid was still explored in the leaching of DT ore.

Table I.3: Summary of exploratory test organic leaching of REE from DT ore

Leaching solution	Procedure	Results
Citric acid, 50 ml	10 g of 150 µm was added with 4 ml of 98 % H_2SO_4 and baked for 2 h at 320 °C followed by 1 h leaching with 0.8 M citric acid on pH 1	Recoveries were as follows: 49 % REE and 57 % Zr
Citric acid, 50 ml	10 g of 150 µm was leached for 1 h at 25 °C using 1.2 M citric acid on pH 3	REE and Zr recovery were less than 1%
Citric acid, 50 ml	10 g of 150 µm was baked at 320 °C for 2 h and leached for 1 h using 1.2 M citric acid on pH 3	REE and Zr recovery were less than 5 %
Citric acid, 50 ml	10 g of 150 µm was added with 20 ml of 1.2 M citric acid and baked at 100 °C for 2 h followed by water leaching for 1 h at 25 °C	REE and Zr recovery were less than 3 %
Glycine, 50 ml	10 g of 150 µm was added with 4 ml of 98 % H_2SO_4 baked for 2 h at 320 °C followed by leaching for 1h using 1.2 M glycine on pH 1	Recoveries were as follows: 47 % REE and 40 % Zr
Glycine , 50 ml	10 g of 150 µm was leached for 1h using 2.8 M of glycine on pH 9	Nil recoveries for both REE and Zr

Appendix J. Determination of Preg-robbing Occurrences

Objective: This test was conducted to determine if the low recoveries derived from the citric acid leaching of DT ore was due to preg-robbing phenomena. Preg-robbing refers to the immediate removal of leached constituents, normally through adsorption mechanism from leach solutions into preg-robbing components which includes organics, silicates, and sulphides among others. Pregrobbing occurrences can be easily detected through the decreased metal assays in the pregnant leach solution over time.

Procedure: A liter of starting solution of known REE content was added with 20 g of 37-44 μm grind size. A 10-ml sample solution was retrieved every 15 min for REE analysis.

Outcome: Results of this test showed that preg-robbing occurences was unlikely the cause of poor REE recovery on citric acid leaching of DT ore as evidenced by the slight increase of REE content in the final leach solution (Figure J).

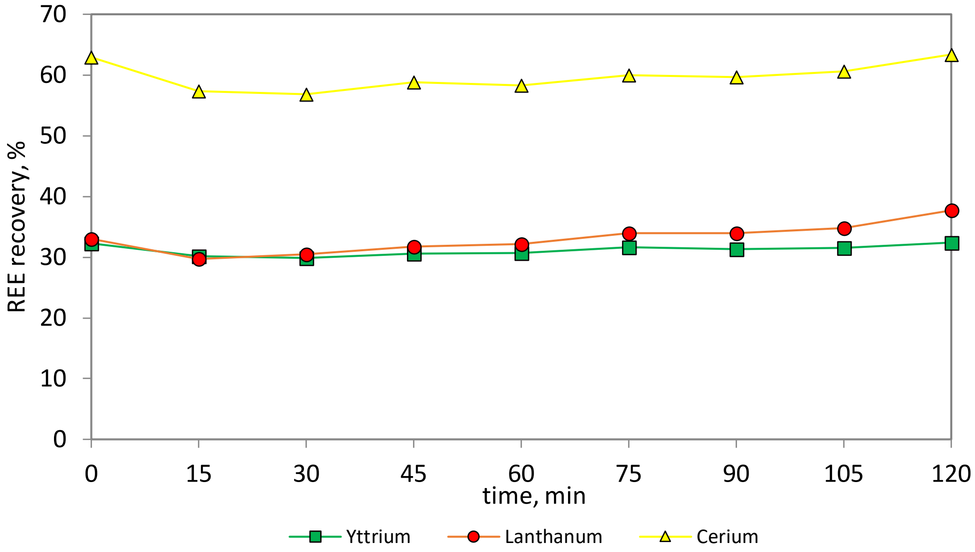


Figure J: Results of preg-robbing test done on DT ore

Appendix K. Precipitation of REE Citrates using Oxalic Acid

Objective: The purpose of this test was to try the use of oxalic acid in recovering REE from citric acid solution.

Procedure: A volume of 87 ml of pregnant leach solution was retrieved and added with 1.2 g of oxalic acid, manually shaken for 5 min and centrifuged for 10 min at 7830 rpm. Metal recoveries were calculated from analysis of leach solutions.

Outcome: Results of this trial indicated that oxalic acid can be used to precipitate REE as shown by the low content of REE in the barren leach solution (Table K). However, this method is not selective as there was a significant amount of Zr co-precipitation at 70%. To increase selectivity, it would be best to remove Zr first from the leach solution through established methods of solvent extraction. Silicon was not removed by oxalic acid from the solution.

Table K: Analysis of leach solution before and after the addition of oxalic acid

Scenario	Analysis of leach solution, mg/L				
	Y	La	Ce	Zr	Si
Before precipitation with oxalic acid	29	31	46	755	2006
After precipitation with oxalic acid	0.2	0.05	0.4	221	2089
Recovery in precipitate, %	99.3	99.8	99.2	70.7	-

Appendix L. Test on Citric Acid Recycling

Objective: The aim of this test was to determine the recyclability of citric acid solution and its leaching capacity when re-used as a leaching agent.

Procedure: A 100-ml barren citric acid solution produced from test detailed in Appendix K was recycled for use as the initial leach solution. A 2 g sample of pre-boiled SG concentrate of 212-300 μm grind size was leached using recycled citric acid solution. Leaching was conducted at 70 °C for 8 h at pH 2. Leaching recoveries were calculated from relative assays of the initial and final leach solution

Outcome: Results of this exploratory test showed that the use of recycled citric acid, produced from removing REE by precipitation with oxalic acid, could not be used directly as a leaching solution. This is shown clearly by the low REE recoveries as displayed in Table L. The recycled citric acid solution needs to be re-adjusted to its strength prior to re-use. Alternatively, the silica needs to be removed from the recycled citric acid solution.

Table L: Analysis of barren and pregnant leach solution using recycled citric acid

Scenario	Analysis of leach solution, mg/L			
	Y	La	Ce	Zr
Barren leach solution	0.2	0.05	0.4	221
Pregnant leach solution with re-use of citric acid solution	1.5	1.8	2.7	474
Recovery, %	3.2	4.6	2.9	11

Appendix M. Analyses of Leach Residues

Table M-1: XRD analysis of SG concentrate leach residue after sulfuric acid leaching

SG concentrate			Leach residue		
Mineral	Chemical composition	Wt%	Mineral	Chemical composition	Wt%
Eudialyte	$Na_{15}Ca_7Fe_3Zr_3Si(Si_3O_9)_2(Si_9O_{27})_2(OH)_2Cl_2$	56	Eudialyte	$Na_4(Ca,Ce)_2(Fe^{2+},Mn^{2+},Y)ZrSi_8O_{22}(OH,Cl)_2$	11
Acmite	$NaFeSi_2O_6$	11	Gypsum	$CaSO_4.2H_2O$	65
Mejillonesite	$Na_{0.93}Mg_{2.08}(PO_3OH)(PO_{4)1.06}(OH)_{0.86}0.95H_5O_2$	6	Pyroxene group[1]	ABZ_2O_6	18
Na-Ca-Al Sulfide Silicate	$Na_{6.4}Ca_{1.4}Al_6(SiO_4)_6S_{1.6}$	4	Aenigmatite group[2]	$A_2B_6X_6O_{20}$	6
Amorphous content		11			

[1] A=Ca,Fe^{2+},Li,Mg,Mn^{2+},Na,Zn;B= Al, Cr^{3+},Fe^{2+},Fe^{3+},Mg,Mn^{2+}, Sc,Ti,V^{3+}; Z= Al,Si

[2] A=Ca,Na;B=Al,Cr^{3+},Fe^{2+},Fe^{3+},Mg,Sb^{5+},Ti;X=Al,B,Be,Si

Table M-2.: XRF analysis of SG concentrate leach residue after citric acid leaching

Sample/ Units	SiO2	Fe2O3	MnO	MgO	P2O5	K2O	Na2O	TiO2	Ta2O5	CaO	Al2O3	ZrO2	Nb2O5	REO	Y	La	Ce
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	ppm	ppm	ppm
Eudialyte concentrate	49.00	7.30	0.73	0.06	0.05	0.27	13.60	0.20	0.08	10.00	0.87	11.10	1.09	1.93	3850	3900	7200
Leach residue, citric acid leaching	33.82	16.17	0.46	0.05	0.05	0.16	7.83	1.43	0.03	15.50	0.57	3.04	0.31	NA	1020	1120	2050

Table M-3: XRF analysis of DT ore leach residue

Sample/ UNITS	SiO_2	Fe_2O_3	MnO	MgO	P_2O_5	K_2O	Na_2O	TiO_2	ZrO_2	La_2O_3	CeO_2	Nb_2O_5	CaO	Al_2O_3	Y	La	Ce	Nd	Dy
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	ppm	ppm	ppm	ppm	ppm
DT raw material	63.36	7.30	0,46	0.22	0.09	4.37	4.86	0.09	1.62	0.18	0.28	0.86	0.46	12.6	1000	1800	2800	NA	200
DT ore leach residue after sulfuric acid leaching	69.98	2.21	0.02	0.02	0.021	4.58	4.57	0.03	0.17	0.003	0.007	0.06	0.04	12.4	67.2	33.9	45.5	16	9.93
DT ore leach residue after citric acid leaching	68.23	3.47	0.13	0.03	0.045	4.62	4.78	0.05	0.498	0.037	0.069	0.25	0.06	12.3	218	309	564	204	39.3

Appendix N. Co-leaching of Zirconium

N-1. Co-leaching of zirconium in sulfuric acid leaching of rare earths from SG concentrate

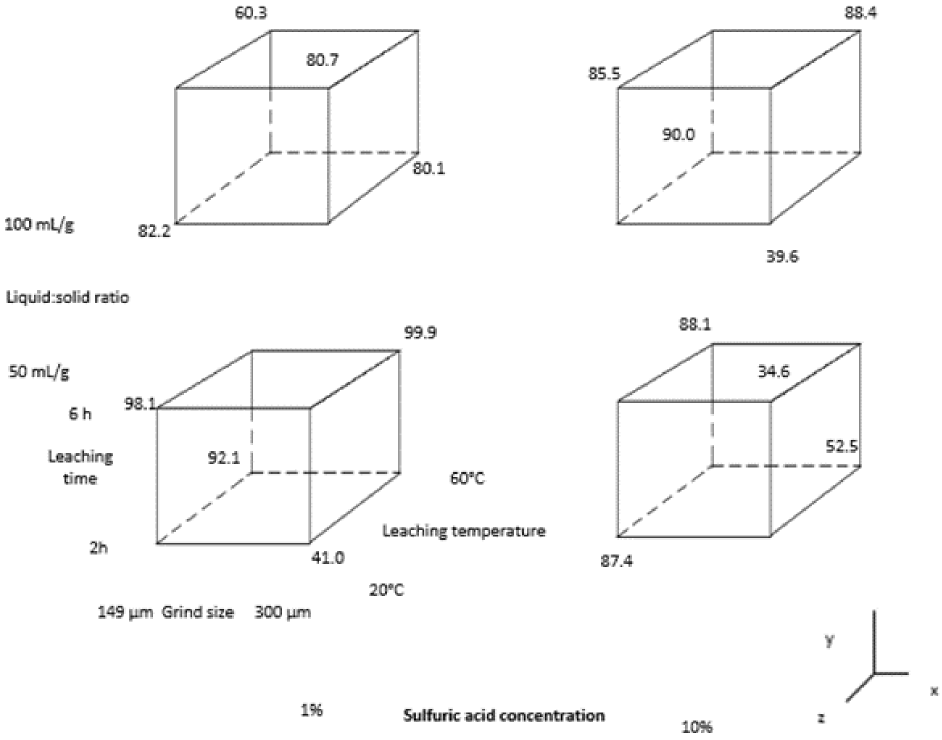


Figure N-1.1: Co-leaching recoveries of zirconium on sulfuric acid leaching of REE from large-grained eudialyte minerals in SG concentrate

Table N-1: Co-leaching recoveries of zirconium in the sulfuric acid leaching REE from fine-grained eudialyte minerals in DT ore

Run No	Leaching conditions							Zirconium leaching recovery,%
	Grind size (μm)	Baking temp (^{0}C)	Baking time (h)	Acid-ore ratio (g /g)	Leaching temp(^{0}C)	Leaching time(h)	Liquid-solid ratio (mL:g)	
1-1	10*	200	1	0.4	20	1	5	29.11
1-2	10	200	1	0.4	20	1	5	28.77
2-1	300**	200	1	0.4	70	3	20	25.53
2-2	300	200	1	0.4	70	3	20	13.21
3-1	300	200	3	3.2	20	1	20	62.13
3-2	300	200	3	3.2	20	1	20	60.76
4-1	10	200	3	3.2	70	3	5	52.12
4-2	10	200	3	3.2	70	3	5	33.93
5-1	300	320	1	3.2	70	1	5	79.04
5-2	300	320	1	3.2	70	1	5	79.81
6-1	10	320	1	3.2	20	3	20	69.00
6-2	10	320	1	3.2	20	3	20	77.13
7-1	10	320	3	0.4	70	1	20	75.02
7-2	10	320	3	0.4	70	1	20	72.93
8-1	300	320	3	0.4	20	3	5	77.35
8-2	300	320	3	0.4	20	3	5	79.32

*10 μm (D$_{90}$), ** 300-420 μm(for all grind sizes)

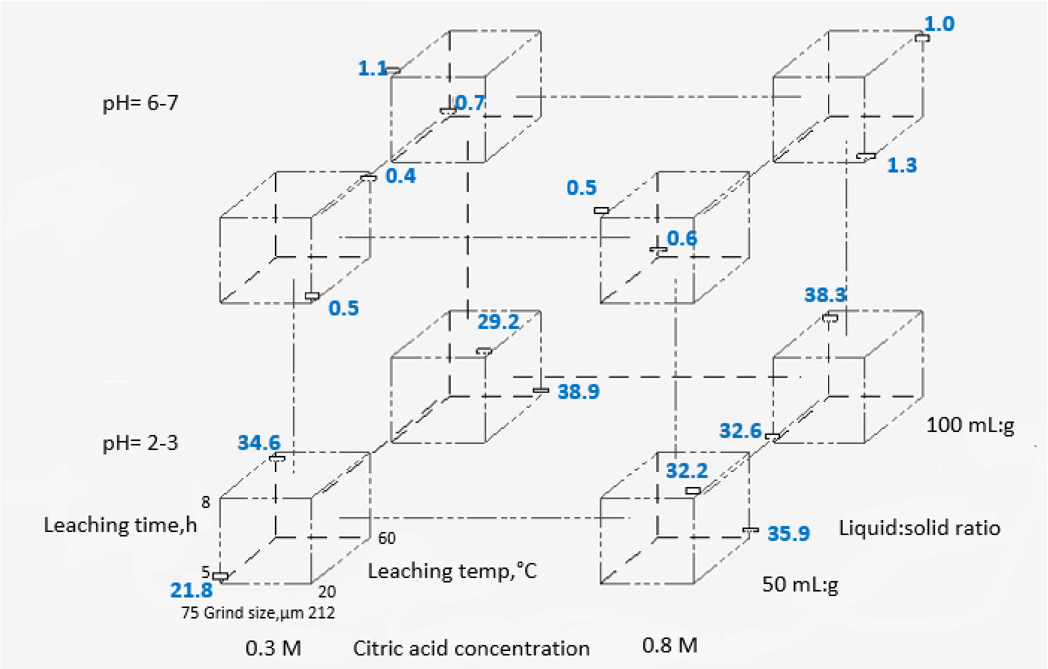


Figure N-2: Co-leaching recoveries of zirconium on citric acid leaching of REE from large-grained eudialyte minerals in SG concentrate

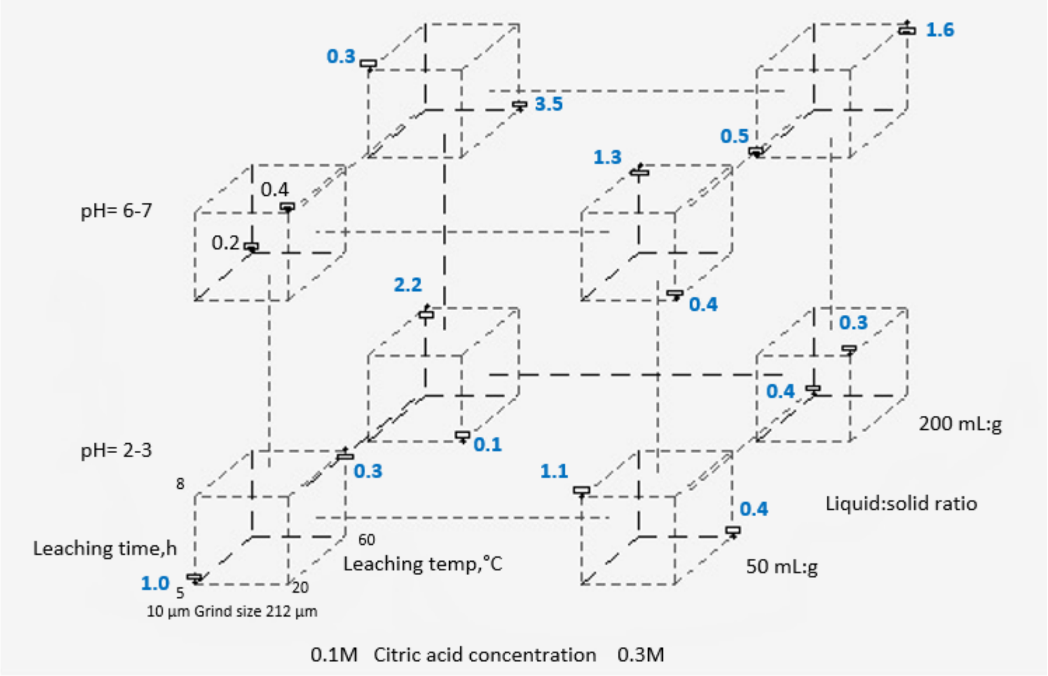


Figure N-3: Co-leaching recoveries of zirconium on citric acid leaching of REE from fine grained eudialyte in DT ore

Appendix O. Repeat Analysis of Leach Solutions from Sulfuric Acid Leaching of Eudialyte

Material	Sample Code	Elemental assay, mg/L				Assay difference, %			
		Ce	La	Y	Zr	Ce	La	Y	Zr
SG concentrate	Leach soln 1	159	100	53	651	3	2	4	5
	re-assay	154	98	51	621				
	Leach soln 2	142	101	130	2080	25	19	4	11
	re-assay	107	82	125	1850				
DT ore	Leach soln 1	115	90	6	40	26	27	10	159
	re-assay	91	66	2	3				

Appendix P. Analysis of Hydrolysis Products from Citric Acid Leaching of SG Concentrate & DT Ore

Procedure: Precipitates collected from solution containers of SG concentrate and DT ore which were leached prior using citric acid were dried, digested with 5% HCl and submitted for analysis by ICP-OES.

Outcome: The analysis of the precipitates from the citric acid leaching of SG concentrate and DT ore reflected comparable assays (Table P). This result indicated that the hydrolysis product formed from the citric acid leaching of SG concentrate and DT ore was the same compound. Due to limited sample weight, the chemical formula of the hydrolysis product was not determined.

Table P: Assay of hydrolysis products of SG concentrate and DT ore citric acid leaching

Sample description	Concentration (mg/L)				
	La	**Ce**	**Y**	**Zr**	**Si**
SG precipitate	38	53	30	848	2286
DT precipitate	37	53	30	853	2266

Appendix Q. Ambient Water Leaching of DT Ore

Procedure: Test samples comprising of 25 g of 850 µm and 53 µm DT ore were leached at room temperature (23 °C) for 8 h using 225 ml of deionized water. The objective was to determine water solubility of REE and silicon at ambient conditions.

Outcome There was nil dissolution of REE and silicon with water leaching of DT ore as shown in Figure Q.

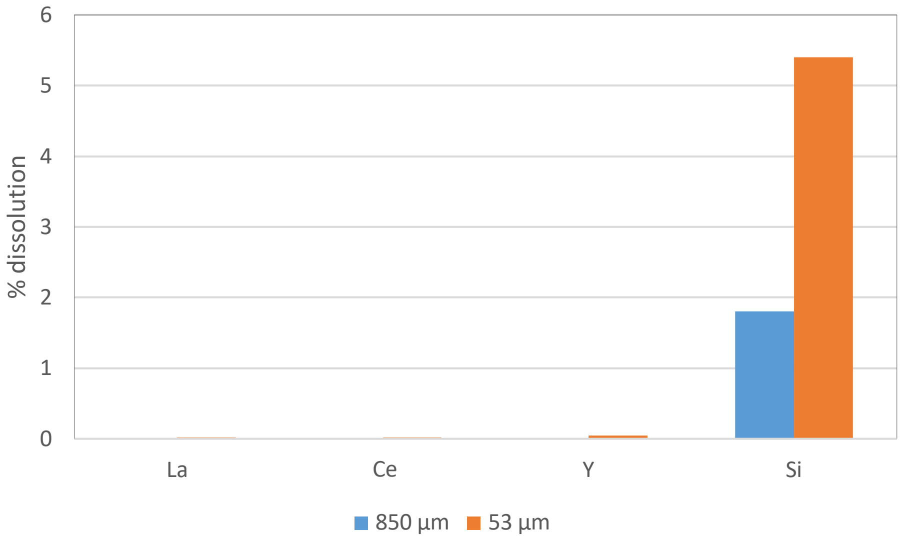


Figure Q: Results of ambient leaching of DT ore showing nil dissolution of REE and Si on water leaching

Appendix R. Author Attribution Declaration

I, Hazel Lim, contributed all laboratory work, data interpretation and writing to the following publication:

Lim, H., D. Ibana and J. Eksteen (2016). "Leaching of rare earths from fine-grained zirconosilicate ore." Journal of Rare Earths **34**(9): 908-916.

The co-authors provided technical support with laboratory testing and experimental design, proof reading and corrections.

Hazel Lim
Author

Signature of Candidate

I, as a Co-Author, endorse that this level of contribution by the candidate indicated above is appropriate.

Don Ibana
Co –Author 1

Signature of Co-Author 1

Jacques Eksteen
Co-Author 2

Signature of Co-Author 2

Appendix S. Copyright Permission by Correspondence

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