

The feasibility of extraction of thorium and rare earths from monazite through a thermal plasma and a chemical treatment process

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I. Abstract

Monazite is a chemically inert, rare earth phosphate mineral, which is difficult to process using conventional chemical digestive techniques. Monazite contains important commercial sources of thorium and lanthanides. The monetary value of monazite stems from the light rare earth metals (Ce, La, Pr, Nd and Y), thorium and uranium contained within its crystal structure. Conventional chemical processing of monazite requires the use of harsh chemicals in a highly complicated, corrosive, laborious and expensive process which can cause severe environmental damage as has been demonstrated in China. South Africa plans to beneficiate monazite as part of its mineral beneficiation strategy. Doing so competitively would require a cost effective and environmentally friendlier process. A new process that involves feeding monazite into a plasma reactor to alter the crystal structure is being investigated. If successful, this new process has the potential to make monazite chemically reactive and recovery of rare earth oxides susceptible to less harsh chemical methodologies.

To confirm the chemical decomposition of monazite in the presence of carbon, thermodynamic calculations were used. Monazite can be decomposed in the presence of carbon into the rare earth oxides at a temperature of between 1200 and 1400 °C with a monazite-carbon ratio of 2:5. Thorium- and uranium carbide can be formed in the same plasma process assuming the temperature is above 2170 °C. The rare earth oxides, thorium- and uranium carbides are desired products as they are more susceptible to leaching with aqueous mineral acids. Monazite, in the absence of carbon, theoretically decomposes into the oxides above the melting point of the rare earth phosphates. Using current thermodynamic data, the decomposition temperature of monazite in the absence of carbon remains unconfirmed. It was determined that the energy cost of decomposing monazite on its own would be higher than when monazite and carbon are heated together to decompose the monazite.

Theoretical calculations of the reaction between monazite and the selected rare earth oxides with ammonium bifluoride were conducted. It was determined that ammonium bifluoride can be used as a viable alternative for the fluorination of monazite and the

rare earth oxides. The fluorinated rare earth mixture can then be separated using various methods.

It is hypothesised that by placing monazite in a high temperature plasma, its chemical reactivity could be increased. To evaluate this theory, monazite was placed in a DC direct arc batch reactor. When the high temperature plasma heat was not applied directly for the correct length of time, the monazite has a minor increase in chemical reactivity. By increasing the reaction time (heating period) the monazite melts and the resulting molten monazite becomes more inert to chemical and physical attack. The high temperature plasma heat must be applied directly onto the monazite and a correct reaction time is a requirement to ensure the correct conversion of the crystal structure of the monazite.

The proper treatment of monazite in a plasma is evident using microscopic and chemical analysis. When treated correctly with a plasma, the original monazite structure is converted into a more chemically reactive phase that permits the removal of 30.49 % of the rare earth elements, which is 21 times more effective than from untreated monazite, 16.89 % of the thorium and 42.70 % of the uranium using 32 % HCl at 80 °C for 1 h. Visual analysis of the Plasma Treated Monazite (PTM) which was leached confirmed that not all of the monazite was decomposed during plasma treatment which results in not all of the REE, thorium and uranium being leached. The extraction of rare earths from treatment of monazite may be improved by optimizing the carbon to monazite ratio in an inflight plasma (temperature above 1400 °C).

In this study the effect of the plasma interaction on the monazite crystal structure to ensure increased extractability of rare earths from generated PTM with different mineral acids were evaluated. Theoretical calculations were initially conducted on the leaching of the rare earth phosphates and oxides along with thorium- and uranium carbide with the mineral acids. This indicated that PTM can be leached more easily at low temperatures as PTM is chemically more reactive than monazite. Using the conventional digestion processes on PTM, higher quantities of the REE were leached; however the same chemical and radioactive waste would still be present as what is found when monazite is treated. The direct digestion of PTM with 32 % HCl at 80 °C for 1 h extracted the highest quantities of the REE, thorium and uranium into the

aqueous mineral acids and the extraction is higher than the conventional digestion process when used on monazite.

The overall conclusion of the study is that the plasma treatment of monazite increases its chemical reactivity. This process can now be used to develop a more efficient and economical process than the comparable conventional chemical digestion methods currently employed to digest monazite. This new process will use an in-flight plasma with a monazite-carbon mixture followed by leaching of the plasma product with an aqueous mineral acid such as HCl.

Keywords: Monazite, plasma treatment, rare earth, thorium, rare earth oxide.

II. Declaration

I, Dian Kemp, hereby declare that this thesis entitled:

The feasibility of extraction of thorium and rare earths from monazite through a thermal plasma and a chemical treatment process

is my own work and has not been submitted to any other university before. Where publications involving co-authors were used, the necessary permission from these authors had been obtained in writing. Relative contributions by the different authors are acknowledged in the relevant chapters.

Signed at Potchefstroom on _____.

III. Acknowledgements

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I would like to thank God and my saviour Jesus for giving me the courage when I was down and forgiveness when everything went wrong.

IV. Statements from Co-Author

Statement of consent: A.C. Cilliers

To whom it may concern, I, Anthonie Christoffel Cilliers, give my consent to Dian Kemp, candidate for the degree Philosophiae Doctor in Nuclear Engineering at the North-West University, to include the following articles in his thesis entitled “The feasibility of thorium and rare earth extraction from monazite through a thermal plasma and a chemical treatment process”, of which I am a co-author:

Kemp, D., Cilliers, A.C., 2014. Fluorination of rare earth, thorium and uranium oxides and phosphates from monazite: a theoretical approach, *Advanced Materials Research*. doi:10.4028/www.scientific.net/AMR.1019.439

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The relative contributions to the paper by the different authors are given in Chapter 4, to Chapter 7. This statement serves to comply with academic rules 5.4.2.8 and 5.4.2.9 of the University.

Signed at Potchefstroom on _____.

A.C. Cilliers

V. Format of this thesis

The format of the thesis is in accordance with academic rule 5.4.2.7 states: “Where a candidate is permitted to submit a thesis in the form of a published research article or articles or as an unpublished manuscript or manuscripts in article format and more than one such article or manuscript is used, the thesis must still be presented as a unit, supplemented with an inclusive problem statement, a focused literature analysis and integration and with a synoptic conclusion, and the guidelines of the journal concerned must also be included.”

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VIII. List of Abbreviations

ABF	-	Ammonium BiFluoride
AMI	-	Advanced Metals Initiative
BWR	-	Boiling Water Reactor
CANDU	-	CANada Deuterium Uranium
CFD	-	Computational Fluid Dynamics
DC	-	Direct Current
EC	-	Equilibrium Composition
GFE	-	Gibbs Free Energy
HTM	-	Heat Treated Monazite
IMz	-	Inductive Monazite
LWR	-	Light Water Reactor
Mz	-	Monazite
Mzc	-	Monazite crushed
NORM	-	Naturally Occurring Radioactive Material
PDZ	-	Plasma Dissociated Zircon
PTM	-	Plasma Treated Monazite
PTM _H	-	Plasma Treated Monazite Heat
PTM _L	-	Plasma Treated Monazite Low
PTM _{LH}	-	Plasma Treated Monazite Low Heated
PWR	-	Pressurised Water Reactor
RE	-	Rare Earth
REE	-	Rare Earth Elements
RF	-	Radio Frequency
XRD	-	X-Ray Diffraction
XRF	-	X-Ray Fluorescence

1. Introduction

1.1 Problem Statement

South Africa has large monazite deposits and aims to develop a local process to recover rare earths from this mineral thus beneficiating this valuable monazite. The problem is that monazite is a highly inert phosphate mineral which is expensive and difficult to process using conventional chemical digestion processes with the added disadvantage of the generation of large quantities of secondary radioactive and chemical waste. The main interests in monazite is the possibility of extracting the large concentrations of Rare Earth Elements (REE) present in the crystal structure as well as significant concentrations of thorium and uranium.

The aim of this research was to determine whether by converting the crystal structure of monazite using a high temperature thermal plasma, into a more chemically reactive crystal structure from which the REE, thorium and uranium can be extracted more efficiently. This research is a first of a kind study on the plasma treatment of monazite with the express intent of producing a more chemically leachable monazite that could be investigated further alternative which will require further research to fully exploit the potential of treating monazite in a plasma.

It is not the aim of this project to fully develop the process with regard to kinetics, design and optimization as it is beyond the scope of this study.

1.2 Background

South Africa has a resource based economy with an estimated in-situ mineral wealth of US \$ 2.5 trillion, making it potentially one of the wealthiest mining jurisdictions in the world. In order for South Africa to benefit from these natural resources, the South African government has adopted a new economic developmental policy which has identified mineral beneficiation as a priority growth node as a considerable portion of South Africa's minerals are exported as raw or partially processed ore with very little benefit to the country. This led to the development of the mineral beneficiation strategy which provides the framework to translate the country's sheer inherent mineral

resources into a national competitive advantage by recommending a set of integrated solutions to develop the country's mineral value chains (South African Department of Mineral Resources, 2011).

One of the selected value chains focuses specifically on uranium and thorium (South African Department of Mineral Resources, 2011) as South Africa contains an estimated 18 % of the world's uranium resources (Dasnois, 2012) and between 1 and 2 % of the world's thorium reserves (IAEA, 2005). Thorium is commonly found in the mineral monazite as a black sand along the east and west coast of South Africa in locations like Steenkampskraal (Blench, 2010), Namakwa sands (Philander and Rozendaal, 2010) and Richards Bay (Selby, 2010). Monazite can also be found in the northern interior of South Africa in Naboomspruit (Selby, 2010) and Pilanesberg (Lurie, 2010).

Monazite contains, apart from thorium, the light Rare Earth Elements (REE = Ce, La, Pr, Nd, and Y) as the Rare Earth (RE) phosphate (REPO_4), and uranium (Kim et al., 2009). The REE are in high demand for a wide range of applications due to their unique chemical, catalytic, electrical, magnetic and optical properties (Xie et al., 2014). The problem with monazite processing is the highly inert nature of its phosphate crystal lattice (El-Nadi et al., 2005) which requires the use of aggressive chemical processes to crack and extract the REE (Ball, 1927; Xie et al., 2014). The exploitation of monazite is so dangerous and toxic that China, which controls 97 % of the world rare earth market through the exploitation of their Bantou ore (Hurst, 2010), has prohibited the exploitation of monazite within its borders due to the high quantity of thorium and toxic chemical waste produced (Zhu et al., 2015).

The problem of using highly corrosive and expensive chemical processes can be circumvented by increasing the chemical reactivity of monazite. One possibility of increasing the chemical reactivity of monazite is to pass it through a high temperature plasma which could thermally crack the monazite crystal lattice. The cracking of mineral ores through the use of a high temperature thermal plasma is not uncommon and has been achieved for various different minerals including zircon, serpentine, rhodonite and ilmenite. As an example, when zircon, which is highly inert, is utilized in a high temperature alkaline process, the mineral's crystal lattice is cracked which

makes it more reactive (Rendtorff et al., 2012; Toumanov, 2003). The cracking of the crystal lattice occurs through the dissociation of zircon (ZrSiO_4) into monoclinic zirconia (ZrO_2) and silica (SiO_2). Subsequent rapid quenching prevents the re-association of the ZrO_2 and SiO_2 species. This subsequently forms monoclinic zirconia which is embedded in an amorphous silica matrix (Havenga and Nel, 2012; Snyders, 2007). This makes the extraction of zirconium metal easier and profitable to produce (Simpson et al., 2015).

Monazite contains inter alia thorite (ThSiO_4), a thorium bearing mineral which contains a structure similar to zircon (ZrSiO_4). This is one reason why it has been hypothesised that through the use of plasma processing the monazite crystal lattice could be destroyed (Toumanov, 2003). Thus an opportunity to explore the possibility of producing a chemical reactive monazite species through the use of a high temperature thermal plasma is presented.

1.3 Research Methodology

The aim of this research is to investigate the possibility of improving the chemical reactivity and leachability of monazite by treatment of monazite in a high temperature thermal plasma to develop a new economically and environmentally friendlier route to beneficiate monazite. In order to achieve this aim, the following objectives of the research methodology must be met (Figure 1-1).

1. To model the thermal decomposition of monazite to determine whether there is any feasibility in placing monazite in a plasma.
2. To feed the monazite to a plasma, to compare the results with the first objective and to evaluate the chemical reactivity of the Plasma Treated Monazite (PTM).
3. To evaluate the PTM using various types of reagents (HCl , HNO_3 , H_2SO_4 , NaOH) to determine how well the REE, thorium and uranium can be extracted.

The outcomes of the objectives are summarised in the results which are discussed, compared and supported with information obtained from the literature. These results, positive or negative, will establish whether using current available plasma technology

could form a chemically reactive product of monazite or, alternatively, make it more inert. If the plasma treatment of monazite results in the formation of a chemically more reactive product of monazite from which the REE, thorium and uranium can be extracted more easily and effectively it would confirm the hypothesis and the objectives of this thesis.

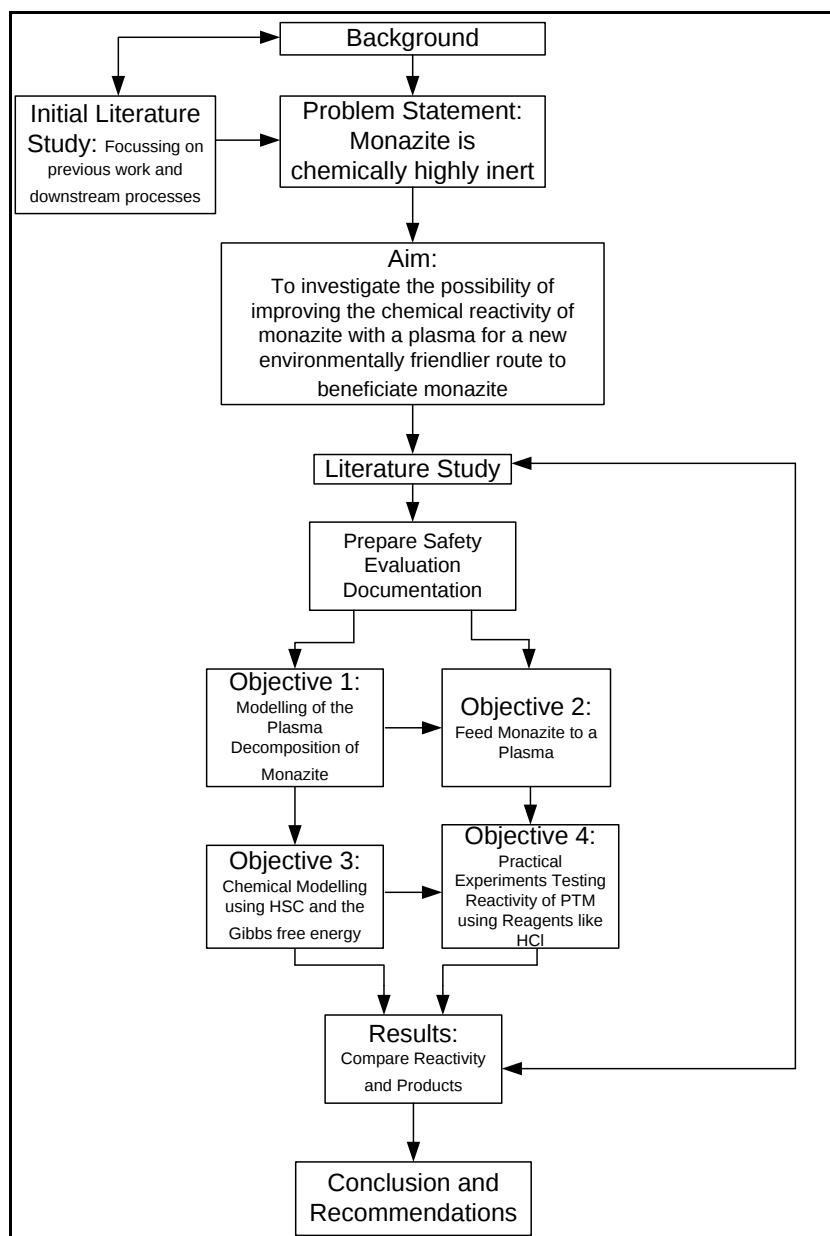


Figure 1-1: Flow diagram of the research methodology.

1.4 Original Contribution to Science

South Africa and the South African Nuclear Energy Corporation SOC Ltd (Necsa) have developed plasma technologies for various processes including the dissociation of zircon to produce PDZ for the continuous production of zirconium metal and the spheroidization of zirconium and titanium powders (Bisset et al., 2015; Simpson et al., 2015; van der Walt et al., 2015). Previously, Necsa had no interest in the development of a process for the beneficiation of monazite, the rare earths or thorium (Havenga and Nel, 2012).

A literature study conducted using Google, Google Scholar, Scopus and Science Direct using the keywords monazite, plasma, chemically reactive species, thermal plasma, RF plasma, DC plasma and thermal plasma in various combinations was conducted. The literature search for plasma and monazite produced articles on the chemical analysis of monazite for the determination of the aging of geological features (Godoy et al., 2007) or the spheroidization of rare earth phosphates (Ananthapadmanabhan et al., 2009). The only direct interest in the plasma treatment of monazite found in literature was by Toumanov (2003) which stated that the plasma processing of monazite could result in the total destruction of the monazite crystal lattice. By opening monazite, the quantity of reactants consumed and the level of corrosion of the chemical equipment would be reduced which would result in higher extraction of thorium, uranium and the REE. The only other relevant document was a patent where an RF/Microwave plasma was used to process monazite in the presence of carbon in an inert argon atmosphere to form metal oxy-carbides (Tanner-Jones, 2007). No further reference to the plasma treatment of monazite could be found. However the high temperature treatment of monazite in the presence of carbon has indicated that monazite decomposes to either the oxide or carbide above 1200 °C (Xing et al., 2010). No process has been developed using this information nor has it been implemented with a plasma.

The purpose of this research was to place monazite in the heat zone in a plasma reactor and to evaluate the newly formed product for downstream processing. The uniqueness of this process is that, as far as the literature study was able to determine, there are currently no known studies of monazite being treated in a high temperature

thermal plasma with the sole intent of making it chemically more reactive and to chemically evaluate the plasma product's extraction potential of the REE, thorium and uranium. The newly formed product, Plasma Treated Monazite (PTM), was treated with ammonium bifluoride (ABF), mineral acids (HCl, HNO₃ and H₂SO₄) and NaOH in various concentrations and at various temperatures. What is unique about this process is that this new form of monazite may be reactive at low temperatures (< 100 °C) and may permit the use of aqueous mineral acids to leach the REE, thorium and uranium. The results indicated a significant increase in the leachability of the REE, thorium and uranium. The use of a diluted mineral acid at low temperature for the leaching of the REE, thorium and uranium is unique as it has never been possible due to the highly inert nature and the low extraction potential of the rare earth minerals.

1.5 Challenges to the Process.

Monazite has not been treated in a plasma before with the intent of increasing the chemical reactivity. Zircon contains a silicone crystal lattice with physical properties different to that of monazite, which has a phosphate crystal lattice. As the bonds in the crystal differ to that of zircon and other minerals which have been treated in a plasma, no evidence currently exists to indicate that the monazite crystal would be affected by the thermal shock of the plasma and become susceptible to chemical attack as hypothesised. Additionally, monazite is known to be difficult to decompose at high temperatures. The monazite crystal structure is highly inert due to the strong phosphate bonds which could be too strong for the plasma to break resulting in no increase in chemical reactivity. Post plasma treatment of the monazite could indicate that PTM is more inert than its predecessor, resulting in no increase in chemical reactivity. The final challenge is that monazite is radioactive and must be managed accordingly.

1.6 Thesis Layout

The thesis is laid out in the form of four chapters of which the first is the introduction, followed by a brief literature study and then two chapters of a technical nature. This is followed by four stand-alone articles which collectively investigate the treatment of the monazite particle in a high temperature plasma. Two chapters each investigate a

theoretical component of the heat treatment of monazite. Each is precluded with a short literature study and a conclusion. Each article is preceded by an “Introduction to the article” to place the article in context with the thesis. After the article, where relevant, an appendix to the article is presented which provides raw or additional data which would be extraneous in an article but was used to guide the process. This is followed by the concluding remarks.

Chapter 1 is the introduction to this thesis followed by the literature study in Chapter 2. The literature study provides a broad discussion on REE, thorium and uranium, the challenges in extracting these elements from monazite and a brief description on the separation of the REE, thorium and uranium. The plasma process is based on the Advance Metals Initiative (AMI) Zirconium Metal process which is described to provide context followed by a brief description of the plasma and the dissociation characteristics of zircon. This literature study is a brief overview with more information provided in the articles and the extended literature study in the appendix.

As monazite has never been placed in a plasma before and the material itself is radioactive, an initial theoretical study had to be conducted to evaluate and confirm whether there is merit in placing monazite in a plasma, determine what the potential chemical composition of PTM could be, the temperature at which monazite would dissociate and whether the use of graphite would be more beneficial (Chapter 3). The anticipated chemical composition of PTM is subsequently compared to literature to establish whether PTM could be more reactive and can be leached using an aqueous mineral acid.

The originally objective of this research was to treat PTM with a fluoride. A theoretical study on the process was completed to evaluate the potential of fluorinating the PTM with ammonium bifluoride (Chapter 4). The practical experiments for the fluorination of PTM provided inconclusive results and no innovative process could be developed to separate the REE from thorium and uranium. For these reasons further research on PTM with the fluorides was deemed outside the scope of this research.

In Chapter 5 contains a discussion of the change of monazite in a DC direct arc plasma to produce PTM. PTM and monazite were evaluated under an optical microscope and

chemical leaching using HCl. After leaching of PTM with HCl, monazite and PTM were leached using other types of mineral acids, like H_2SO_4 , HNO_3 and NaOH (Chapter 6).

Chapter 7 is a summary of the thesis in article form which summarizes the results and provides a foundation for future work on the plasma treatment of monazite for the improved extraction of the REE, thorium and uranium. Chapter 8 is the conclusion of the thesis followed by Chapter 9 which contains all the references from all the articles contained in this thesis.

The first chapter of the Appendix, Chapter A is the extended literature study which includes information relevant to this research which can sometimes fall outside the scope. The final chapter of the Appendix, Chapter B, is a Computational Fluid Dynamic (CFD) model to determine the heating profile of the monazite particle, to determine whether the current plasma which is located at Necsa is sufficient to heat monazite, what the average mass feed would be and the maximum and minimum sizes of the monazite particles which can be fed to the plasma while still obtaining full dissociation.

2. Literature Study

This literature study provides a brief overview of the most pertinent literature to the thesis. A brief literature study is provided for each chapter and article along with an extended literature study in the appendix.

2.1 Monazite

Monazite is found as a black sand in the heavy mineral sands along with zircon and ilmenite. It is a highly inert, radioactive, phosphate mineral which contains mainly the light Rare Earth Elements (REE), thorium and uranium. Monazite's chemical composition consists of the rare earth phosphates (REPO_4 , RE = Ce, La, Nd, Pr, Y) of which 70 % are the rare earth metal oxides with the rare earths constituting 20 – 30 % Ce_2O_3 and 10 – 40 % La_2O_3 with significant amounts of Nd, Pr and Sm along with 27 % P_2O_5 and 1 - 10 % radioactive thorium with low concentrations of uranium. Monazite is found on beaches worldwide in countries like India, Brazil, Sri Lanka, South Africa, Russia, Australia and the Scandinavian countries (Amaral and Morais, 2010; Ashry et al., 1995; Cardarelli, 2008; Dilorio et al., 2012; Kaya and Bozkurt, 2003; Kim and Osseo-Asare, 2012; Kim et al., 2009; Stepanov et al., 2012).

The problem with monazite is that it is chemically very stable and highly inert (El-Nadi et al., 2005). The use of conventional chemical processes to extract the REE, thorium and uranium from monazite has developed into a highly complicated and costly exercise (Hurst, 2010). The two most common processes for monazite processing is the sulphuric acid process and the sodium hydroxide process (Abreu and Morais, 2010; Calkins, 1957; Gupta and Krishnamurthy, 2005; Kim et al., 2009). Both processes use reagents in high concentrations at high temperatures for several hours resulting in the production of excessive quantities of chemical and radioactive waste. This waste has to be disposed of properly otherwise these contaminants will pollute the surrounding area as inappropriate care of rare earth element waste has previously resulted in environmental contamination, loss of habitat and excess levels of corrosion (Hurst, 2010; Yemel'Yanov and Yevstyukhin, 2013).

2.2 Rare Earth Elements

The REE are a group of elements which include the lanthanides in the atomic number range from 57 (La) to 71 (Lu), yttrium (39) and scandium (21) (Abreu and Morais, 2010; Goyne et al., 2010; Hurst, 2010; Pratiwi et al., 2011). The REE are divided in two groups, light and heavy. The light REE are lanthanum (La), cerium (Ce), praseodymium (Pr) neodymium (Nd) and samarium (Sm) (atomic numbers 57 – 62) and are more abundant than the heavier REE. The heavier REE consist of the elements with atomic numbers 64 – 71 (Gd – Lu) along with scandium (Sc) and yttrium (Y) (Abreu and Morais, 2010). This research will mainly focus on the light REE.

The REE are unique in their spectroscopic and magnetic properties which are increasingly being used for important roles in the development of advanced materials for a variety of technical applications (Abreu and Morais, 2010) in society including wind turbines, hybrid and electric cars, cell phones, permanent magnets and numerous other applications (Kim et al., 2009; Lemont and Resin, 2008). In recent years rare earth prices have been on the decline (Carnac, 2015; Dickson, 2015) due to a sharp decrease in demand and prices outside of China (Bradsher, 2011). However, the decline might come to an end as China is planning on abolishing its decade-old export quota in favour of controlling domestic supply (Els, 2015).

There are approximately 250 different minerals which contain the REE (Jordens et al., 2013) of which 10 % are considered economically mineable using current mining techniques (Pratiwi et al., 2011; Tropper et al., 2011; Wenqi et al., 2010). The three most common minerals in use for rare earth production are bastnaesite ($\text{RE}(\text{CO}_3)\text{F}$), monazite (REPO_4) and xenotime (YPO_4) (Jordens et al., 2013; Xie et al., 2014; Zhu et al., 2015). Of the three mentioned minerals, monazite is the most abundant (Abreu and Morais, 2010).

2.3 Thorium

Thorium and uranium can be found with the REE in minerals like monazite and bastnaesite where it is extracted as a radioactive by-product in the rare earth extraction process (Dilorio et al., 2012). Thorium is an environmentally unfriendly metal

due to its daughter products, ^{222}Ra and thorium, and radioactive nature (Dilorio et al., 2012; Kamei and Hakami, 2011). For this reason the majority of the thorium which is currently being extracted is disposed of as radioactive waste as an unusable, economically unrecoverable waste (Zhu et al., 2015).

While the removal of thorium as radioactive material from monazite for future use as a nuclear fuel can be regarded as positive, there is a need to properly store this thorium due to the potential of harming the environment if released to the atmosphere. Fortunately thorium is regarded safe as long as the disposal and use of the material can be properly regulated (Dilorio et al., 2012). Alternatively, by feeding monazite to a plasma and subsequently leaching the thorium into a more usable product, the thorium can potentially be converted into thorium oxide which is chemically and thermally more stable for radioactive waste disposal (Kok, 2009) or alternatively thorium can be used downstream as nuclear fuel in a modern day nuclear reactor (du Toit, 2012). The development of a process of the leached thorium compound to thorium oxide is beyond the scope of this research.

The economic incentive to keep and store thorium in a usable form is that it can be used as fuel in a nuclear reactor (Kaya and Bozkurt, 2003) and can be easily stored (Kok, 2009). Currently there is almost zero economic value for thorium as a nuclear fuel source as all power supply nuclear reactors currently rely on uranium (Kaya and Bozkurt, 2003). However, interest in thorium has grown in numerous countries, including China and India (Dilorio et al., 2012). Interest in the thorium fuel cycle is mainly due to thorium's ability to produce electricity, to incinerate plutonium and the minor actinides due to thorium's inherent proliferation resistance (Chang et al., 2006; Trellue et al., 2011) but also for its favourable neutronics, thermal and chemical properties and as the only other naturally occurring nuclear fuel source (Dilorio et al., 2012).

2.4 Conventional Method of Monazite Processing

The conventional extraction of the REE, thorium and uranium from monazite is known to be a costly and complicated exercise due to monazite's highly inert matrix (El-Nadi et al., 2005; Hurst, 2010). To process monazite effectively requires the use of harsh

chemical treatment like sulphuric acid, sodium hydroxide, nitric acid and hydrofluoric acid at high temperatures for extended periods of time. This can result in high levels of corrosion and the production of toxic by-products (Ball, 1927; Xie et al., 2014).

The two most common processes to digest monazite is either the acidic, using concentrated sulphuric acid (H_2SO_4) at 200 – 230 °C for 4 h , or the alkaline route, with sodium hydroxide (NaOH) at 140 °C for 3 h (Abdel-Rehim, 2002; Abreu and Morais, 2010; Amaral and Morais, 2010; Barghusen and Smutz, 1958; Calkins, 1957; Cardarelli, 2008; Kim and Osseo-Asare, 2012; Kim et al., 2009) although some publications like Gupta and Krishnamurthy (2005) indicate a reaction period of 4 h. The complete process from mining until production of the rare earth oxides, takes approximately ten days. The rare earth oxides are the end products and the natural starting material for final conversion to the metal (Gupta and Krishnamurthy, 2005). A basic block diagram illustrates both routes (Figure 2-1) (Kim and Osseo-Asare, 2012) with more detailed illustrations found in the appendix (Figure A-5 and Figure A-6).

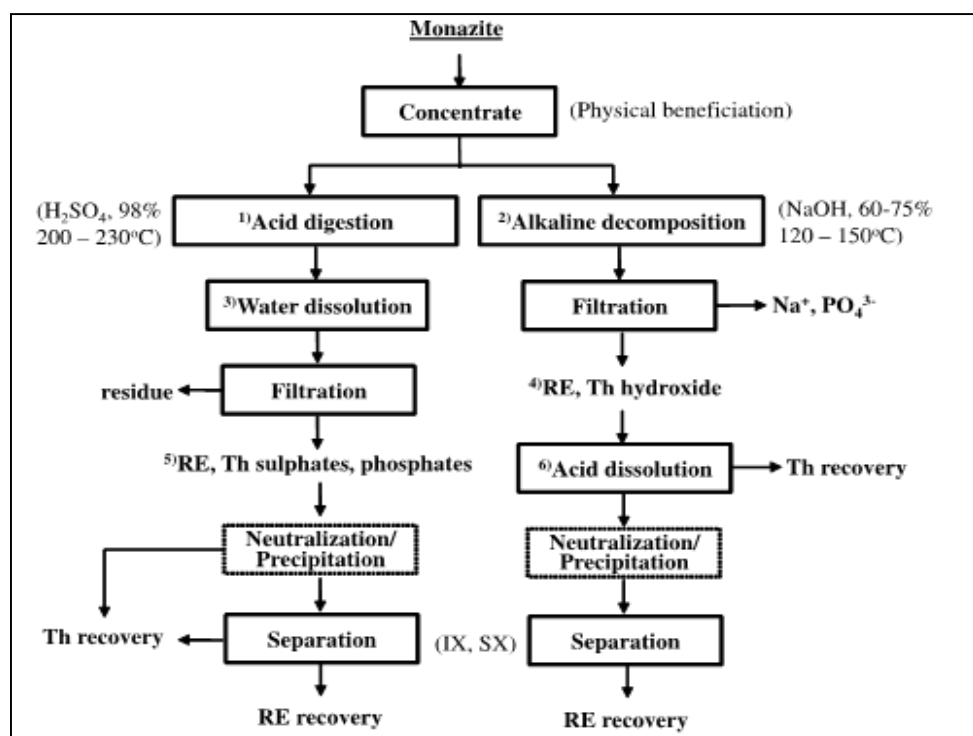


Figure 2-1: Flow Chart of the different chemical methods to process monazite

The sulphuric acid process commences by roasting monazite in a concentrated (98 %) sulphuric acid solution at a temperature of 230 °C to “crack” the monazite and form the rare earth sulphates. The rare earth sulphates are leached using

demineralised water after which it proceeds to solvent extraction to separate the individual REE. Sulphur dioxide is found in the off gas from the roasting process and requires the use of large volumes of water or alkaline solutions to remove safely. This results in the generation of large volumes of acidic effluent which is neutralized downstream (Xie et al., 2014). Radioactive thorium is precipitated in the process as thorium pyrophosphate (ThP_2O_7). This thorium compound cannot be recovered economically as it is inert to mineral acid digestion (Zhu et al., 2015).

The sodium hydroxide process involves cracking the monazite concentrate by heating the sample to between 120 and 150 °C in a 60 - 70 % NaOH solution (Taylor, n.d.). During decomposition, the strong alkali transforms the monazite into the rare earth hydroxides ($\text{RE}(\text{OH})_3$). After cooling, water is used to remove the soluble Na_3PO_4 while leaving the REE behind as insoluble rare earth hydroxides. The rare earth hydroxides are subsequently dissolved in a mineral acid to form soluble mixed rare earth compounds. The thorium remains behind as insoluble thorium hydroxide, $\text{Th}(\text{OH})_4$ (Abdel-Rehim, 2002; Cardarelli, 2008; Kaya and Bozkurt, 2003; Taylor, n.d.).

The alkaline process is the preferred route over the acidic route as it removes the phosphor during leaching, regenerates the alkaline and produces sodium phosphate as a by-product. However, the two-step solid-liquid reaction of the alkaline process, the precise control of the pressure, temperature, pH (Kim et al., 2009) and the side processes of calcium removal by acid pickling (Xu et al., 2012) makes this process intermittent and unfavourable for mass production (Gupta and Krishnamurthy, 2005).

2.5 Separation of the Rare Earth Elements

The REE are highly depended on the purity and quality of the final product (Desouky, 2006). The most common method of separating the REE is solvent extraction (Desouky, 2006; Maharana and Nair, 2005; Y. Zhang et al., 2012) which is generally accepted as the most appropriate commercial technology (Xie et al., 2014). Separation of the REE is achieved using soluble rare earth compounds in an acidic medium such as the chlorides (Banda et al., 2012; Eskandari Nasab et al., 2011; Fontana and Pietrelli, 2009; Gupta and Krishnamurthy, 2005; Maharana and Nair, 2005; Tong et al., 2009; Urbanski et al., 1996; Wang et al., 2011), nitrates (Helaly et al., 2012; Jin et

al., 2011; Jorjani and Shahbazi, 2012; Xu et al., 2012), sulphates (Abreu and Morais, 2010; Y. Zhang et al., 2012), carbonates (da Silva Queiroz et al., 2011), carboxylic acid (Singh et al., 2006), thiocyanate (Reddy et al., 1998), acetic acid (Chang et al., 2010) or lactic acid solutions (Yin et al., 2010). Solvent extraction techniques for the heavier REE have been developed for various mediums (Hála, 1998; Kim et al., 2012; Nagaphani Kumar et al., 2010; Radhika et al., 2011). The thorium and uranium can be separated from the rare earths using solvent extraction (Ali et al., 2007) in nitric acid or chloride solution (Zhu et al., 2015).

2.6 The Plasma

Plasmas are used in industry for numerous applications including thermonuclear synthesis, electronics, lasers and fluorescent lamps. Plasma technology was originally developed around 100 years ago for the production of light. More recently it is utilized for various applications due to its high energy efficiency, specific productivity and selectivity over a wide range of chemical processes. A plasma, for the purpose of this research, is an ionized gas where at least one electron is no longer bound to an atom or a molecule, while operating at extreme temperatures ($> 2000\text{ }^{\circ}\text{C}$). Plasma chemical processing has at least three major chemical features: temperatures in excess of conventional chemical technologies, production of high concentrations of energetic chemically active species, and systems which are far from thermodynamic equilibrium (Fridman, 2008).

Plasmas are ideally suited for processing refractory materials like zircon and monazite due to its high operating temperatures ($10\,000\text{ }^{\circ}\text{C}$), good thermal conductivity and high heat content (Rendtorff et al., 2012). The high temperatures attained by the plasma “crack” and alter the mineral’s crystal structure to make them chemically reactive. The increased chemical reactivity allows for less harsh chemicals to be used to process the mineral (Eletskii and Smirnov, 1985; Fridman, 2008).

Zircon (ZrSiO_4) is a mineral with a chemically inert crystal structure which requires the use of harsh alkaline treatment to crack and extract the zirconium metal (Biswas et al., 2010). The conventional zirconium process is expensive and produces large quantities of chemical and radioactive waste (Yugeswaran et al., 2015). When feeding zircon to

a DC non-transferred are plasma, the zircon crystal structure can be cracked to produce Plasma Dissociated Zircon (PDZ) ($\text{ZrO}_2 \cdot \text{SiO}_2$). PDZ is chemically reactive and can be processed more efficiently and economically than zircon (Havenga and Nel, 2012; Rendtorff et al., 2012) and can be processed using alternative methods (Simpson et al., 2015).

The concept of using a plasma to make a mineral more reactive was achieved with the AMI zirconium metal plasma process (Havenga and Nel, 2012; Simpson et al., 2015; van der Walt et al., 2015) with the conversion of zircon into Plasma Dissociated Zircon (PDZ). Zircon's chemical bonds (Figure 2-2) are broken by the plasma between Zr-O and Si-O (Figure 2-3), with new bonds being formed (Figure 2-4). If the same procedure can be applied to monazite then it can be hypothesised that the plasma treatment of monazite would make monazite more susceptible to chemical attack due to the destruction of the crystal lattice (Toumanov, 2003).

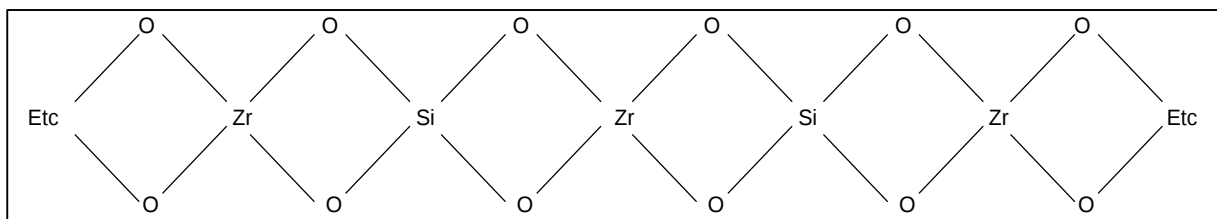


Figure 2-2: Crystal structure of zircon

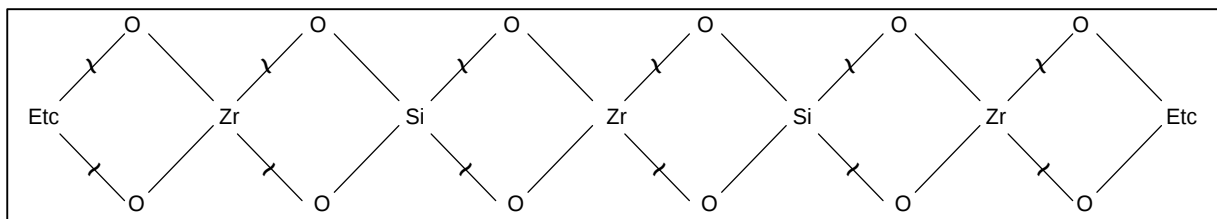


Figure 2-3: Crystal structure of PDZ upon plasma treatment.

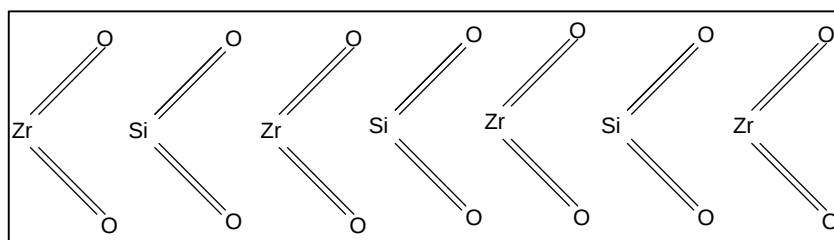


Figure 2-4: Crystal structure of PDZ post plasma treatment.

Zircon dissociates into PDZ at a temperature of 1727 °C (2000 K) with complete dissociation at 1977 °C (2250 K). When the dissociation is repeated in the presence of carbon, the dissociation temperature is reduced by 250 °C to 1477 °C (1750 K) with complete dissociation at 1727 °C (2000 K). The basic mechanism which decreases the dissociation temperature in zircon was found to be independent of the crystal as the carbon does not interact directly with zircon but rather releases thermal energy which lowers the dissociation temperature. The carbon contributes to the enhanced dissociation of zircon through the release of energy when the carbon combusts in air to form carbon dioxide. The energy released varies between -393.51 kJ/mol at 298 K to -398.96 kJ/mol at 3000 K. The added benefit of using carbon is that the silica is removed as silicon oxide (SiO) gas (Yugeswaran et al., 2015).

The mechanism involved in the dissociation of zircon involves the combustion of carbon to oxygen at 1500 K (1227 °C) along with CO₂ which dissociates into CO and O between 1500 and 2500 K (1227 to 2227 °C) (Yugeswaran et al., 2015). For this reason it is possible that a similar mechanism would operate on monazite when it is decomposed in the presence of carbon. This has already been proven by Xing *et al.* (2010) when monazite decomposes into the rare earth oxides when heated in the presence of carbon at a temperature of between 1200 and 1400 °C.

2.7 Radioactive Concerns of Monazite

Monazite is classified as a Naturally Occurring Radioactive Material (NORM) because it contains a radionuclide of natural origin with the potential to significantly increase the public or a worker's exposure to radiation (El Afifi et al., 2006). The main elements responsible for the radioactivity found in monazite are the long lived isotopes ²³⁸U, ²³⁵U, ²³²Th, ⁴⁰K and ⁸⁷Rb (El Afifi et al., 2006; Malain et al., 2010; Malanca et al., 1998). The activity concentration of ²³⁸U and ²³²Th in monazite or thorium ore is the highest in monazite and second highest in zirconium ore. Monazite's effective dose is generally above 4.3 x 10⁻² Sv/y (Iwaoka et al., 2009). When monazite is processed, the radioactivity could increase to 1800 µG/h due to the build-up of ²²⁸Ra activity in the processing chemicals. The processing of monazite thus requires the use of standard radiation practices to be followed (Pillai, 2005; Sroor, 2003).

2.8 Waste Generated from the Monazite Process

The mining and processing of the REE and monazite, when not carefully controlled, can create vast environmental disasters (Hurst, 2010; D. Zhang et al., 2012). For the processing of a Bantou ore, whose treatment is similar to monazite, it is estimated that for every ton of REE produced, 8.5 kg of fluorine along with 13 kg of dust is generated. High temperature calcinations techniques indicates a generation of between 9,600 to 12,000 cubic meters of waste gas. These gases contain dust concentrate, hydrofluoric acid, sulphur dioxide and sulphuric acid. Approximately 75 cubic meters of acidic waste water, a ton of radioactive waste residue and more than ten types of waste water is generated throughout the various processes. The disposal of the tailings and the ground up materials contributes to the problem with an estimated 2,000 tons of mine tailings produced for every ton of REE. These tailings contains radioactive thorium which is classified as radioactive waste. This level of thorium release is allowable in China as it has very low environmental guidelines from the authority (Hurst, 2010) but China have commenced to the treating of generated liquid waste using various waste water techniques including stripping, chlorination and ion exchange (D. Zhang et al., 2012).

3. Evaluation of monazite dissociation in a thermal plasma: Basis and Hypothesis

3.1 Introduction

The high temperatures (10 000 °C), good thermal conductivity and high heat content of thermal plasmas make them ideally suited for the processing of highly inert minerals. The thermal cracking of highly inert minerals using a high temperature thermal plasma have been used to increase their chemical reactivity which results in the development of faster, cleaner and more economical processes (Fridman, 2008; Havenga and Nel, 2012; Simpson et al., 2015; Toumanov, 2003). High temperature thermal cracking with a plasma have been used to dissociate various mineral ores, such as serpentine, rhodonite (MnSiO_3), ilmenite (FeTiO_3), molybdenite (MoS_2) and zircon (ZrSiO_4) (Rendtorff et al., 2012; Toumanov, 2003). The plasma product is more susceptible to chemical attack than the original material. Plasmas are thermally more efficient at heating materials to very high temperatures than other operations like conventional gasification, pyrolysis and mass burn and can do it at a very high rate (Young, 2010). The most widely used electrical methods for producing thermal plasmas are high-intensity arc, inductively coupled high frequency plasma and microwave discharges (Boulos et al., 1994).

Monazite has a highly inert monazite crystal structure which is very stable at high temperatures (Xing et al., 2010). It has been hypothesised that by treating monazite in a plasma it would increase its chemical reactivity (Toumanov, 2003) which would increase the extraction of the rare earths, thorium and uranium and reduce the quantities of corrosive reagents used which will lower the corrosion levels of the process. In order to decompose monazite, a conventional oven or a high temperature thermal plasma would be required. However, strict rules and regulatory processes associated with radioactive substance experimentation are in place. The problem is that monazite is radioactive, stable up to its melting point (Ananthapadmanabhan et al., 2009) and can contaminate expensive equipment which would render it useless for any non-radioactive work. Afterwards the equipment would have to be either

decontaminated, used for other radioactive experiments, or be disposed of as radioactive waste (Khoathane and Sekano, 2010).

Literature has indicated that when monazite is heated gently in the presence of carbon, it can be decomposed to the rare earth oxides at a temperature between 1200 and 1400 °C (Xing et al., 2010). Thorium and uranium oxide present in the monazite can be treated using the same system to form thorium and uranium carbide (Lundgren, 2014; Prescott and Hincke, 1927). An added benefit of the decomposition of monazite in the presence of carbon is the removal of phosphorus which is a contaminant which can pulverize the rare earth alloys (Yugeswaran et al., 2015). Before a plasma system can be sacrificed, theoretical evaluation of the decomposition of monazite in a high temperature plasma must be conducted to confirm whether the monazite crystal lattice can be destroyed and to confirm the temperature at which monazite potentially decomposes in the presence of carbon.

3.2 Method of Evaluation

The Gibbs free energy (GFE) and equilibrium composition calculations were done using HSC version 6.1. The HSC library contains approximately 28 000 compounds (“HSC Chemistry software | Outotec,” 2016) and their relevant thermodynamic information. Other software with similar functions like ThermoCalc, Chemsage and Fact could not be used due to time constraints. Plasmas operate with a flame temperature of up to 10 000 °C but cools down as the sample is passed through. The plasma calculations have been completed up to 4000 °C as above this temperature most materials would decompose into its elemental constituents (Boulos et al., 1994).

3.3 Theoretical Evaluation and Discussion

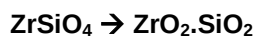
In order to determine whether a plasma could destroy the monazite crystal lattice, it needs to be compared with a known mineral, such as zircon (ZrSiO_4), which decomposes in a plasma. Using values obtained in literature, it was found that monazite has a weaker crystal lattice strength than zircon due to its lower ionic strength (Russian Foundation of Basic Research, 2008), chemical bond strength (Cottrell, 1966), and melting point (Hikichi and Nomura, 1987; Pirkle and Podmeyer,

1988) (Table 3-1). For these reasons a plasma which is capable of destroying the zircon crystal lattice should be capable of destroying the monazite crystal lattice.

Table 3-1: Physical properties of monazite and zircon

	Zircon	Monazite
Melting Point	2100 – 2300 °C	1975 - 2072
Ionic Strength	24	9
Chemical Bond	Si – O: 798 kJ/mol	P – O: 596 kJ/mol
Strength	Zr – O: 760 kJ/mol	RE – O: (ave) 753 kJ/mol

According to literature, zircon dissociates into Plasma Dissociated Zircon ($\text{ZrO}_2\cdot\text{SiO}_2$) at 1727 ± 10 °C (Equation 3-1) (Kaiser et al., 2008; Telle, n.d.; Yugeswaran et al., 2015). The GFE for the dissociation of zircon was plotted in HSC and found to be between 1600 - 1700 °C (Figure 3-1) which is accurate for the purpose of this investigation. The kink at 2700 °C is due to the phase change the zirconium oxide undergoes from tetragonal to cubic (Havenga and Nel, 2012; Kaiser et al., 2008).



Equation 3-1

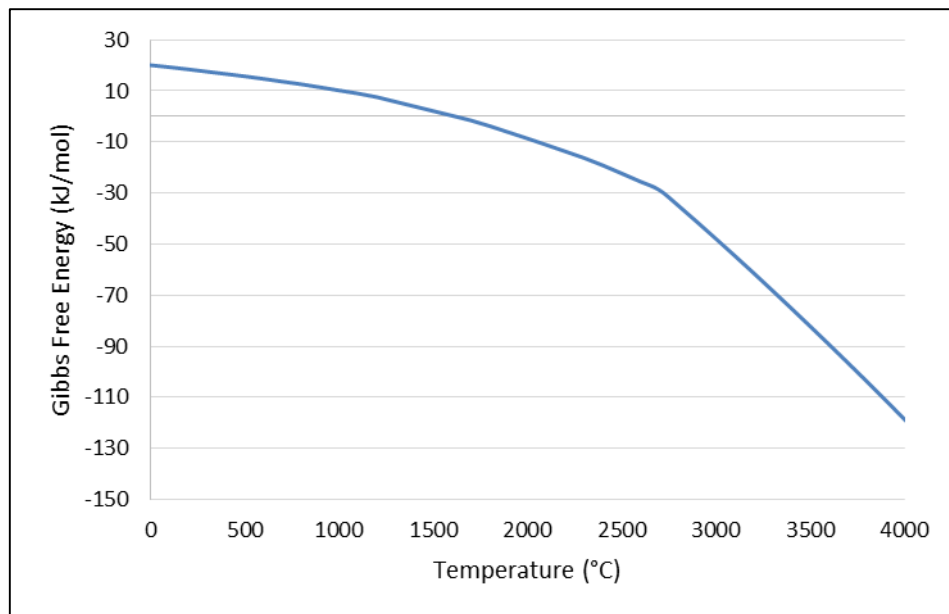


Figure 3-1: Gibbs free energy diagram of the decomposition reaction of zircon (ZrSiO_4) into zirconium oxide and silicone oxide

The dissociation of zircon can be lowered by 250 °C when carbon is added in the presence of oxygen (Yugeswaran et al., 2015). The reaction of carbon with oxygen

release additional energy which is absorbed by the reaction which lowers the dissociation temperature.

Monazite in the presence of carbon decomposes into the rare earth oxide, phosphor, and carbon monoxide with a monazite to carbon ratio of 2:5 at a temperature between 1200 and 1400 °C (Equation 3-2) (Xing et al., 2010). The formation of CO indicates that it can be assumed that a similar reaction mechanism, as proposed for zircon, is in effect for this reaction. The GFE of the decomposition of monazite in the presence of a 2:5 molar ratio with carbon indicated a decomposition temperature of between 1100 and 1400 °C (Figure 3-2). The results indicate that CePO₄ will decompose first at 1100 °C followed by NdPO₄ at 1200 °C, LaPO₄ at 1400 °C and YPO₄ at 1300 °C. This establishes the decomposition temperature of monazite in the presence of carbon to a more reactive compound, the rare earth oxide, which can be leached using a diluted mineral acid (Adachi et al., 2004; Peelman et al., 2014). For this reason the plasma treatment of monazite can theoretically produce a more reactive compound.



Equation 3-2

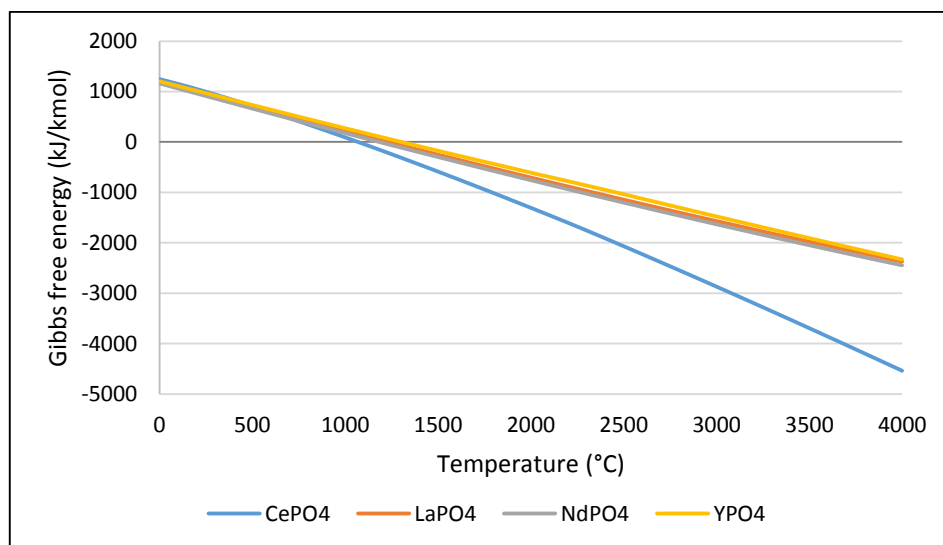


Figure 3-2: Gibbs free energy of the reaction between the rare earth phosphates and carbon

A feature of HSC is that it can determine the most stable compounds of a given set of elements at a constant pressure at various temperatures, henceforth referred to as the equilibrium composition diagram. When the individual rare earth phosphates of monazite are heated in the presence of carbon, with compositionally correct monazite

((Ce:La:Nd:Y) molar ratio was 10:5:3:1), and a monazite to carbon molar ratio of 2:5, then the results indicate that CePO_4 (Figure 3-3) is more stable as the oxide up to 700 °C where after it decomposes into cerium oxide. The formation of a number of different cerium oxide compounds indicate that a certain amount of finesse would be required as not all of the cerium oxide compounds, like CeO_2 , can be dissolved in a mineral acid like HCl (Weast and Astle, 1974).

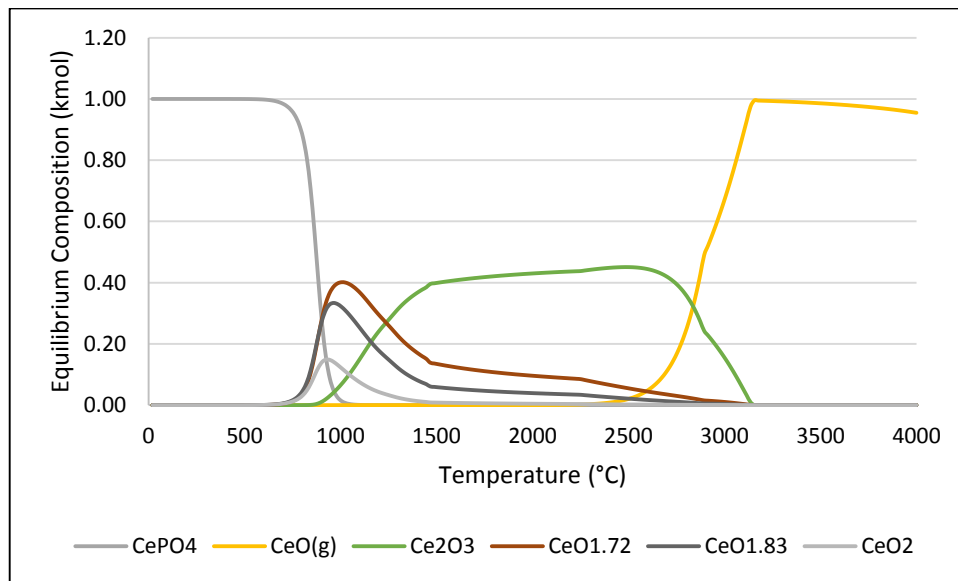


Figure 3-3: Equilibrium composition of reaction products formed during interaction CePO_4 in the presence of carbon at a molar ratio of 2:5

The remaining rare earth phosphates are stable up to a range of between 1000 and 1400 °C (Figure 3-4). At 1400 °C, the remaining rare earth phosphates is decreased by at least 60 %. This does not indicate that monazite dissociates at these temperatures, unlike the GFE, but rather that above a certain temperature which rare earth compound is more stable and has the lowest GFE. The results indicated that in the specified temperature range only the oxides are formed, even at higher temperatures, while none of the oxy-carbides or carbides are formed. For this reason, the plasma can safely operate at very high temperatures without forming the rare earth carbides.

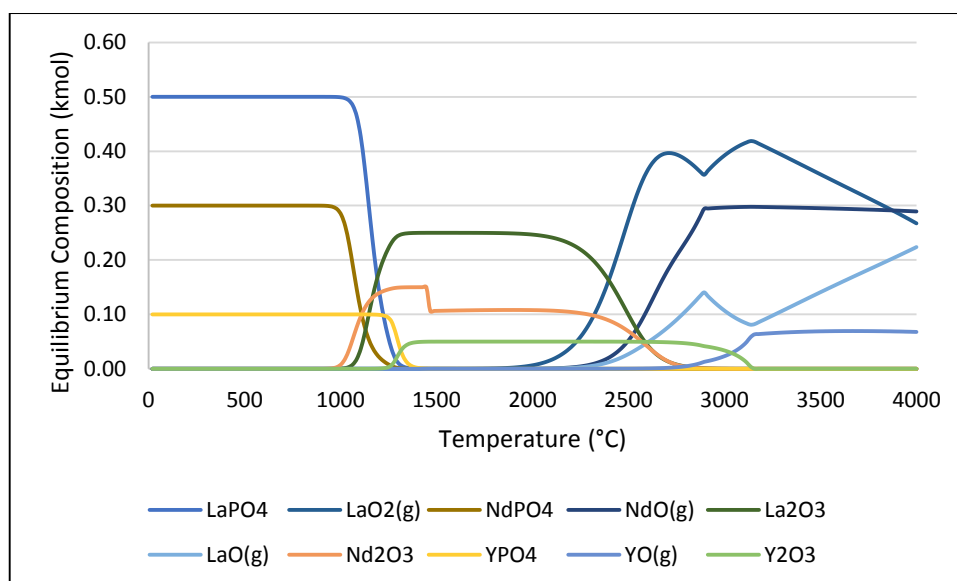


Figure 3-4: Equilibrium composition reaction products formed during interaction of selected rare earth phosphates in the presence of carbon at a molar ratio of 2:5

When the ratio of monazite to carbon was increased to a ratio of 1:10, which is in excess of the required amount, then the rare earth carbides are the more stable compounds above 2000 °C (Figure 3-5 and Figure 3-6). This confirms theoretically that the formation of the rare earth oxides are dependent on the quantity of carbon present in the mixture. In order to produce a more reactive compound either the oxide or the carbide would suffice as both can be treated with aqueous mineral acids. The problem with producing the carbide is that more than four times more carbon would be required to produce the carbide and, when submerged in water, forms the rare earth hydroxide and hydro-carbon gas (Griess, 1974).

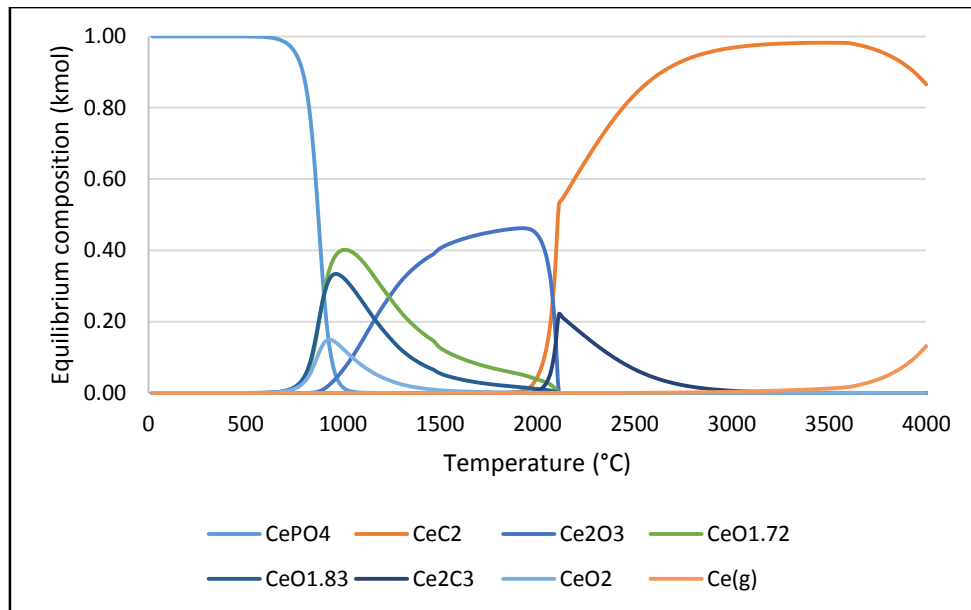


Figure 3-5: Equilibrium composition of reaction products formed during interaction of CePO₄ in the presence of excess carbon

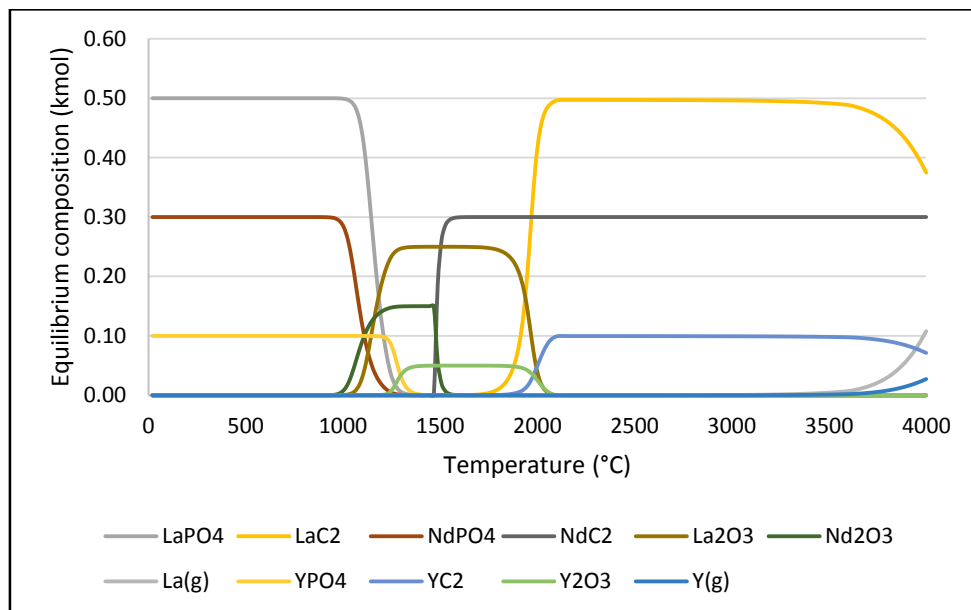


Figure 3-6: Equilibrium composition of reaction products of selected rare earths during processing with excess carbon

It has been established that HSC can model the dissociation of monazite in the presence of carbon accurately. For this reason, HSC can be used, within reason, to model the decomposition of monazite in the absence of carbon into the rare earth oxides and a phosphor compound. In order to establish where the rare earth oxides would be more stable and which phosphor compound is formed at which temperature,

the equilibrium composition of a compositionally correct monazite sample was calculated to a temperature of 4000 °C.

The equilibrium composition of CePO_4 (Figure 3-7), La-, Nd- and YPO_4 (Figure 3-8) and phosphor are presented separately. The results indicate that CePO_4 , similar to what was observed when carbon is present, is more stable at a lower temperature as the oxide than the other REE from 1200 °C. The remaining rare earth phosphates are more stable as the oxides between 2200 and 2700 °C. This concurs with Ananthapadmanabhan *et al.* (2009) which showed that LaPO_4 is stable up to its melting point of $2345 \pm 20 \text{ K}$ (2108 °C) and confirms the statement by Xing *et al.* (2010) that monazite is very stable at high temperatures.

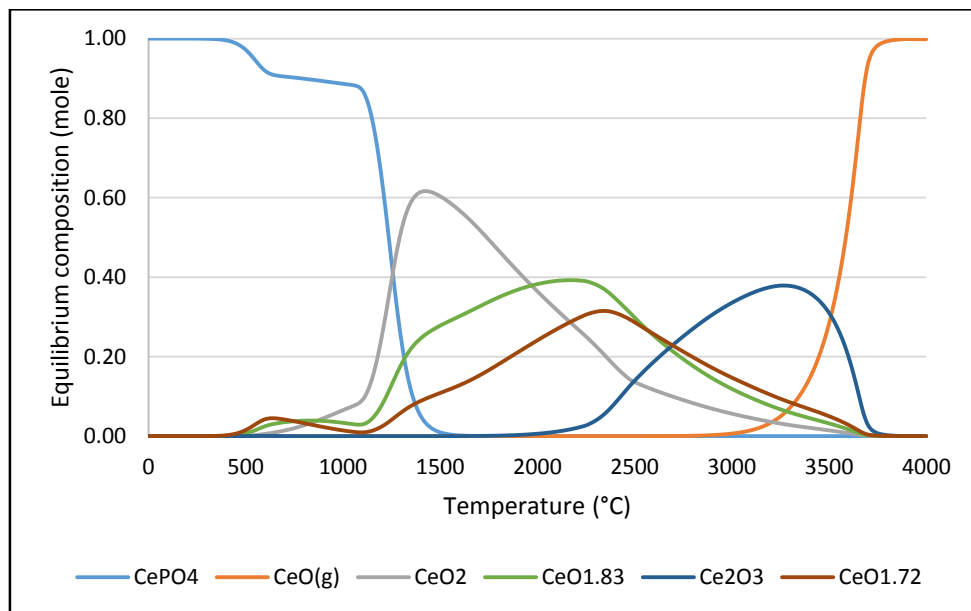


Figure 3-7: Equilibrium composition of the anticipated dissociation of CePO_4

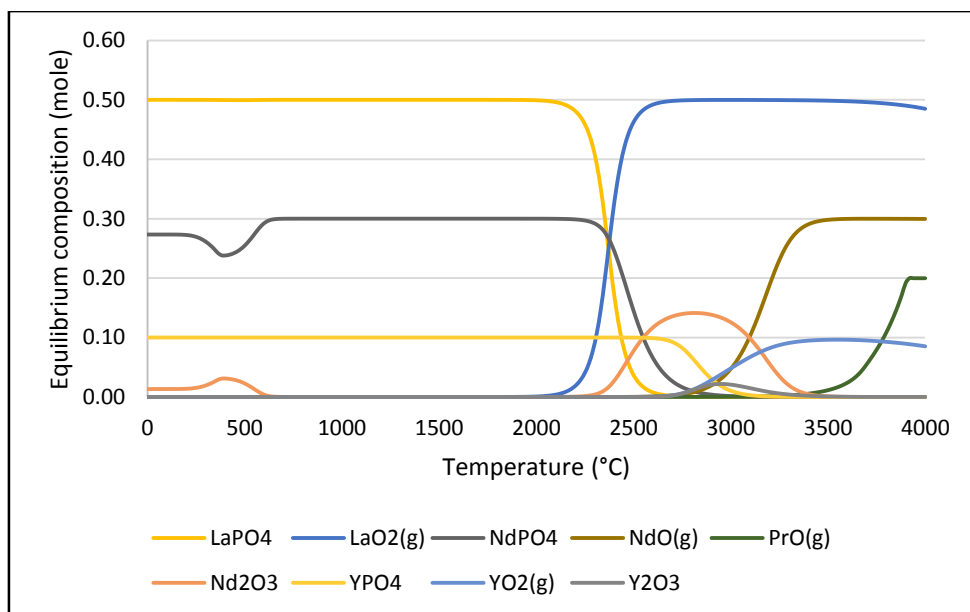


Figure 3-8: Equilibrium composition of the dissociation of LaPO_4 , NdPO_4 and YPO_4

In order to calculate the correct GFE of the decomposition of the rare earth phosphates, the correct phosphor compound needs to be determined. The potential phosphor compounds formed during the decomposition of the rare earth phosphates are P_2O_5 , PO , PO_2 , P_4O_6 and P (Figure 3-9). The first significant increase is with the formation of P_2O_5 , along with the decomposition of CePO_4 . The biggest increase in production is with PO_2 (g) between 2000 and 2600 °C as the remaining rare earth phosphates decompose into the oxide.

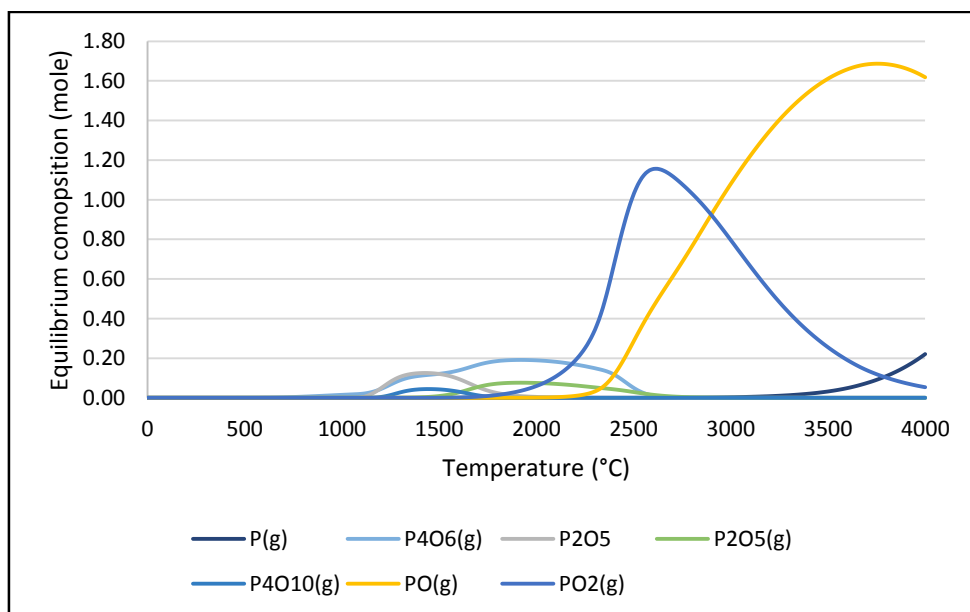


Figure 3-9: Equilibrium composition of the phosphor products formed during the dissociation of monazite

The GFE of the dissociation of the rare earth phosphates with each of the phosphate products was calculated for the following chemical reaction. This reaction covers all of the REE and all the potential phosphor compounds (Equation 3-3).



Equation 3-3

(RE = Ce, La, Nd, Y; X = P_2O_5 , $\text{P}_2\text{O}_5(\text{g})$, $\text{PO}(\text{g})$, $\text{PO}_2(\text{g})$, $\text{P}_4\text{O}_6(\text{g})$, $\text{P}(\text{g})$; y & z stoichiometry)

The GFE of the dissociation of CePO_4 (Figure 3-10) indicates that it commences between 1500 and 1600 °C when either P_2O_5 or P_4O_6 is formed, which concurs with the equilibrium composition (Figure 3-7). The dissociation temperatures obtained from HSC for CePO_4 was found to be within a reasonable approximation due to the similar melting points of monazite and zircon and the chemical and physical bonds in monazite being weaker than zircon. When the other phosphate products are formed for the dissociation of CePO_4 , then the dissociation temperature increases to a maximum value of 2300 °C with the formation of phosphor.

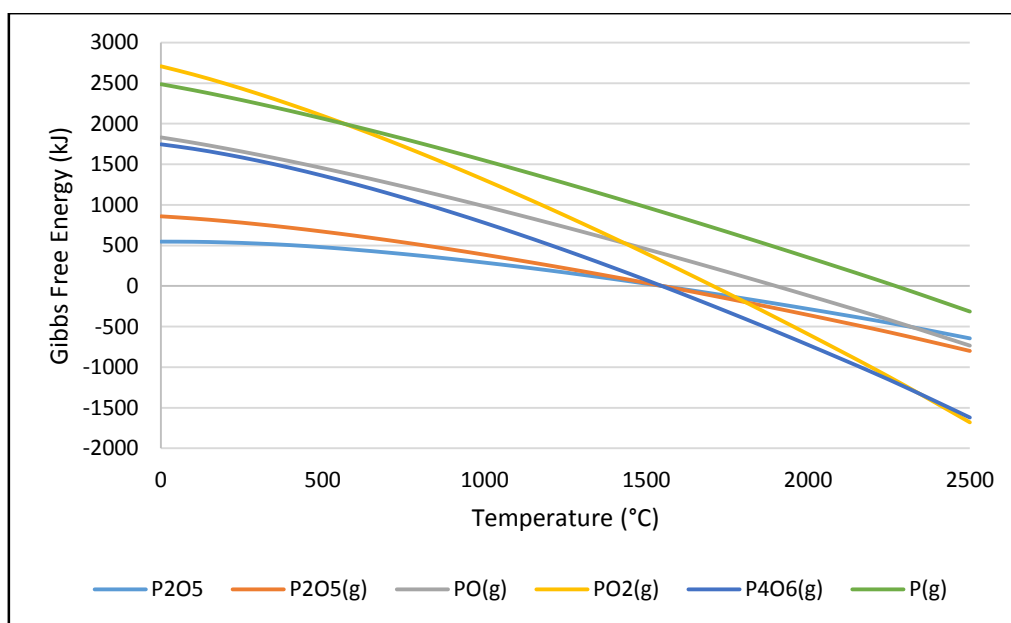


Figure 3-10: The dissociation of CePO_4 into cerium oxide and X (X = P_2O_5 , $\text{P}_2\text{O}_5(\text{g})$, $\text{PO}(\text{g})$, $\text{PO}_2(\text{g})$, $\text{P}_4\text{O}_6(\text{g})$ and $\text{P}(\text{g})$)

Thermal behavior studies have indicated that LaPO_4 is stable up to its melting point indicating that the GFE of the decomposition of LaPO_4 (Figure 3-11), NdPO_4 (Figure 3-12) and YPO_4 (Figure 3-13) will be incorrect as HSC does not have data available for these compound in their molten state and indicates a decomposition

temperature above 2700 °C. While it is anticipated that La will be higher than Ce similar to when it was decomposed in the presence of carbon, the increase in temperature is significantly higher than anticipated. The high decomposition temperature of monazite and the uncertainty of the decomposition temperature ensures that the treatment of monazite in a plasma in the absence of carbon is beyond the scope of this research as a detailed thermodynamic study will be required. For the purpose of this research, monazite will be dissociated in the presence of carbon as the energy requirements are known.

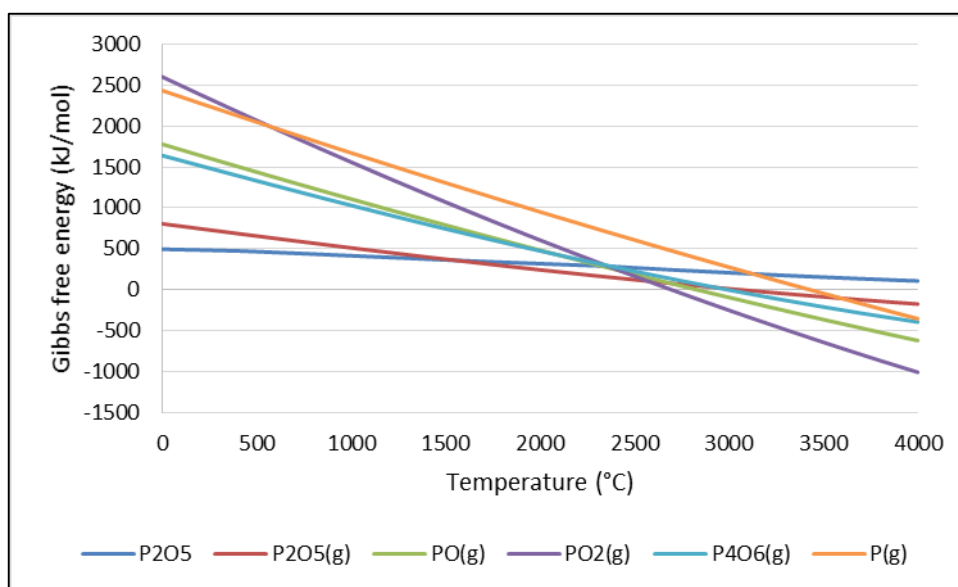


Figure 3-11: The dissociation of LaPO_4 into lanthanum oxide and X ($\text{X} = \text{P}_2\text{O}_5$, $\text{P}_2\text{O}_5(\text{g})$, $\text{PO}(\text{g})$, $\text{PO}_2(\text{g})$, $\text{P}_4\text{O}_6(\text{g})$ and $\text{P}(\text{g})$)

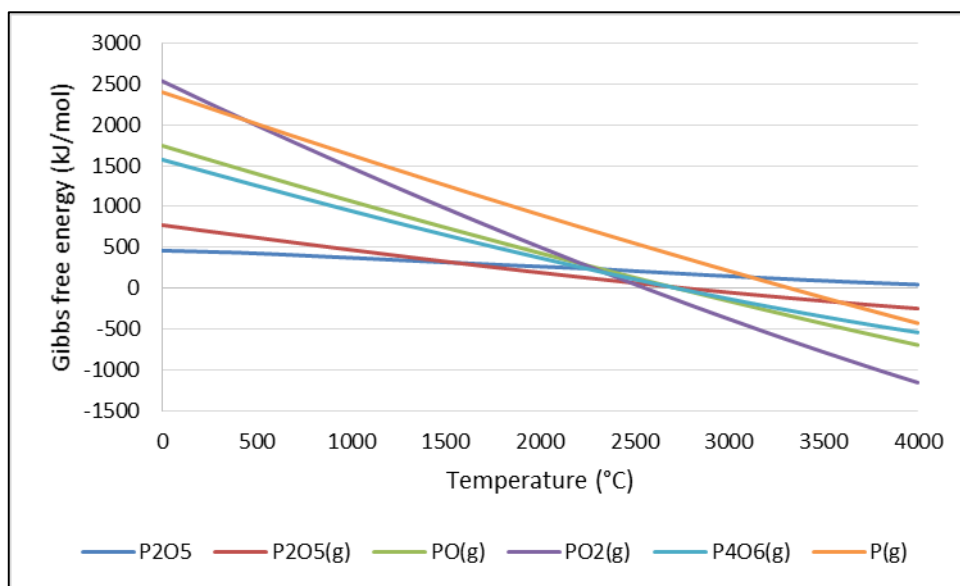


Figure 3-12: The dissociation of NdPO_4 into neodymium oxide and X ($\text{X} = \text{P}_2\text{O}_5$, $\text{P}_2\text{O}_5(\text{g})$, $\text{PO}(\text{g})$, $\text{PO}_2(\text{g})$, $\text{P}_4\text{O}_6(\text{g})$ and $\text{P}(\text{g})$)

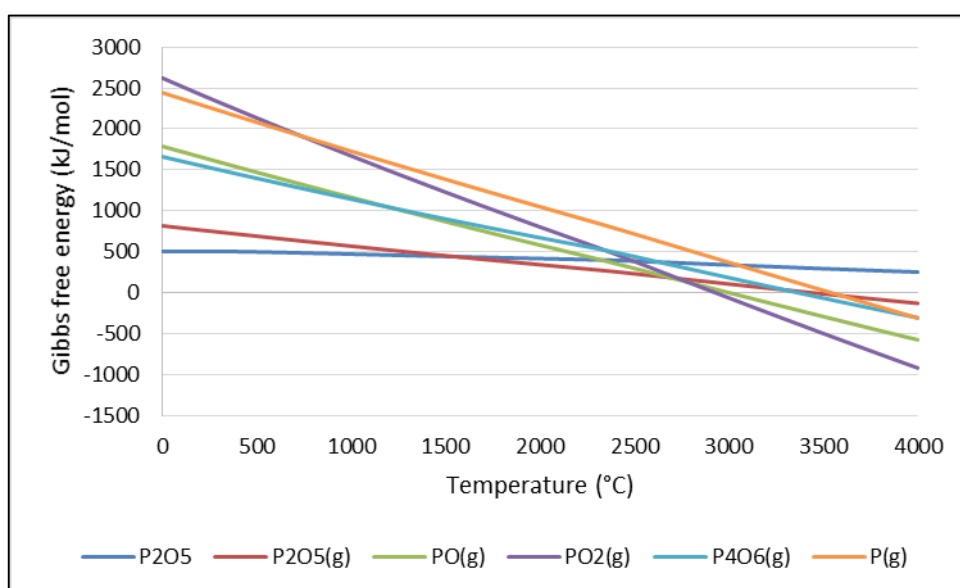


Figure 3-13: The dissociation of YPO_4 into yttrium oxide and X ($\text{X} = \text{P}_2\text{O}_5$, $\text{P}_2\text{O}_5(\text{g})$, $\text{PO}(\text{g})$, $\text{PO}_2(\text{g})$, $\text{P}_4\text{O}_6(\text{g})$ and $\text{P}(\text{g})$)

The rare earth elements also consist of all the lanthanides, La – Lu. It was determined that the decomposition temperature of the majority of these phosphates is below that of CePO_4 , starting at 1400 °C (Figure 3-14). Only SmPO_4 and EuPO_4 decompose at a higher temperatures. For this reason minerals which contain the heavier rare earth elements as phosphates, like xenotime, has the potential to be successfully treated in

a plasma. Other common rare earth minerals, like bastnaesite, which are found as a fluorocarbon, RECO_3F (Peishan et al., 1995) are not present in HSC and the decomposition temperature could not be determined.

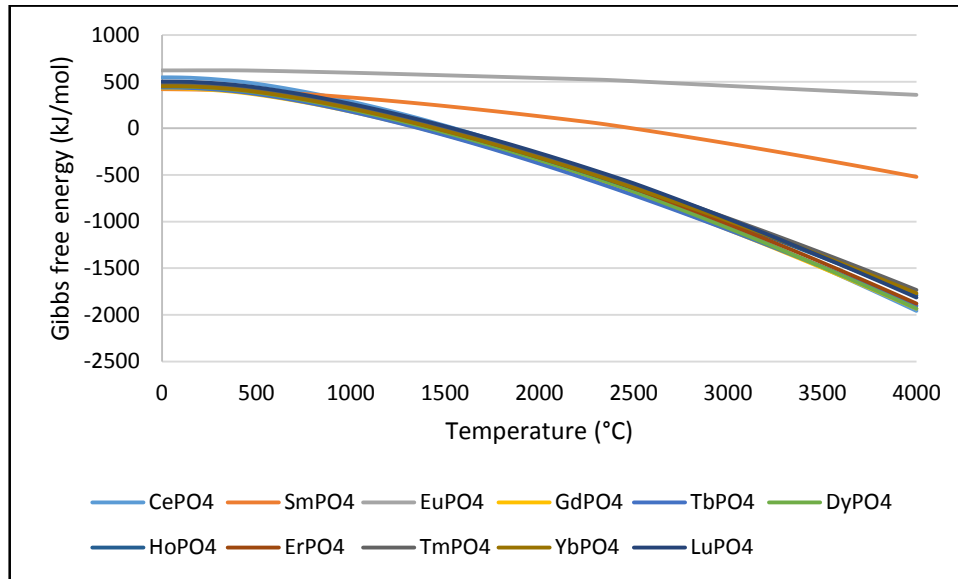


Figure 3-14: Gibbs free energy of the dissociation of the other rare earth phosphates forming P_2O_5

Thorium is present in monazite as either thorium phosphate or thorium oxide (Gupta and Krishnamurthy, 2005; Zhu et al., 2015). HSC does not have thorium phosphate present in its database and for this reason cannot be evaluated. When thorium oxide is heated in the presence of carbon, it reacts rapidly at high temperature to form thorium carbide with the free energy becoming zero at 2395 K (2122 °C) (Prescott and Hincke, 1927; Yemel'Yanov and Yevstyukhin, 2013). The GFE of the reaction (Equation 3-4), as calculated by HSC, between thorium oxide and carbon indicates the conversion at 2200 °C (Figure 3-15).



Equation 3-4

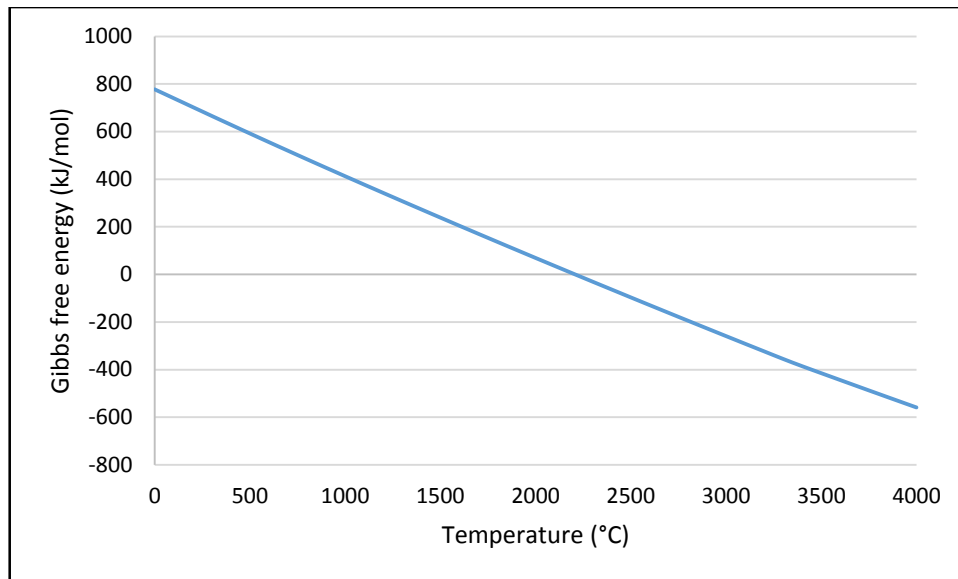


Figure 3-15: Gibbs free energy of the reaction between thorium oxide and carbon

Uranium in monazite can be found as an oxide as either uranium dioxide (UO_2) or as natural uranium (U_3O_8) (Gupta and Krishnamurthy, 2005). Literature indicates that the conversion can commence at as low as 1400 K (Lundgren, 2014). The GFE of the reaction between either UO_2 or U_3O_8 and carbon (Figure 3-16) indicates the conversion occurs at 1900 °C and 1500 °C, respectively. The data from HSC contradicts literature but does indicate that the conversion temperature below that of thorium. This permits, as shown later, more of the uranium to be extracted from plasma treated monazite than thorium.

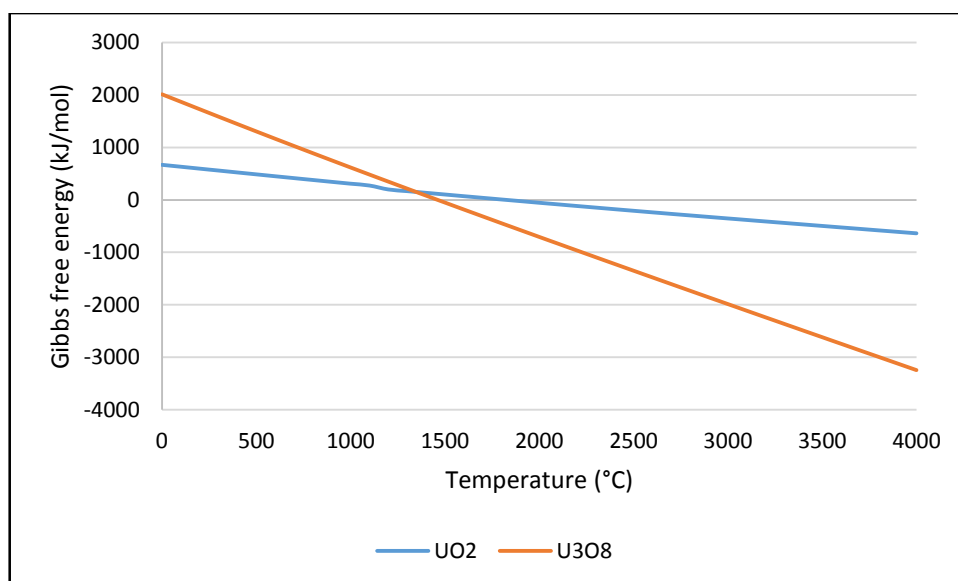


Figure 3-16: Gibbs free energy of the reaction between UO_2 and U_3O_8 and carbon

3.4 Conclusion and Recommendations

This research project requires a theoretical basis to confirm whether monazite can be thermally decomposed into a more reactive compound. Physical properties of monazite was compared to zircon, which has been dissociated in a plasma, using values found in literature. It was determined that monazite contains a physically weaker ionic strength, chemical bonds and a lower melting point. Monazite is reduced into its oxides or oxy-carbides when treated in the presence of carbon at a temperature of between 1200 and 1400 °C. The GFE, calculated by HSC, of the dissociation of zircon and the reaction with monazite and carbon have been shown to have good accuracy.

The assumption of the equilibrium composition is that the decomposition of monazite as the rare earth phosphates (CePO_4 , LaPO_4 , NdPO_4 and YPO_4) is that CePO_4 decomposes into the oxide at 1600 °C with the remaining selected rare earth phosphates decomposing also into oxides at temperatures above 2000 °C. Due to this high temperature conversion, the study will consider the decomposition of monazite in the presence of carbon in order to enhance the formation of oxides at a lower temperature in order to create a more chemically reactivity monazite. The decomposition of the remaining lanthanides as rare earth phosphates, with the exception of EuPO_4 and SmPO_4 , all decompose at a similar temperature to CePO_4 .

Analysis of the GFE of ThO_2 , UO_2 and U_3O_8 with carbon has indicated that at a sufficiently high temperature, which the plasma can attain, it is assumed that they are converted to the carbide. This research recommends that more accurate thermodynamic data be presented for the rare earth phosphates to more accurately determine monazite's decomposition temperature in the absence of carbon.

4. Fluorination of rare earth-, thorium- and uranium oxides and phosphates: A theoretical approach

4.1 Introduction to the article

When monazite interacts with a high temperature plasma in the presence of carbon, then it is assumed that the monazite crystal structure will be altered forming chemically reactive Plasma Treated Monazite (PTM). Based on calculations it is assumed that the PTM material consists of oxides. The plasma treatment of monazite originates from the plasma dissociation of zircon (ZrSiO_4) into PDZ ($\text{ZrO}_2 \cdot \text{SiO}_2$) where the silicate crystal is dissociated and forms an oxide. Processing of the generated PDZ is accomplished by fluorinating the PDZ material into zirconium fluoride with Ammonium BiFluoride (ABF). Zirconium fluoride can then be processed into zirconium metal. In this chapter a theoretical study was conducted to evaluate the fluorination of monazite (consisting of phosphates) and PTM (assumed to be oxides) with ABF by determining the Gibbs free energy for the fluorinating reaction at different temperatures.

This purpose of this article was to theoretically determine whether monazite and PTM can be digested using ABF as an alternative to HF. This article was published in the proceedings of the 2014 Advanced Metals Initiative Light Metals Development Network conference. The format and referencing style has been adapted to the style used for the International Journal of Mineral Processing which is in line with the format and referencing style for this thesis. This article is presented identically in this research to what was presented in the conference proceedings. Only spacing and referencing changes have been made.

4.2 Article: Fluorination of rare earth-, thorium- and uranium oxides and phosphates: A theoretical approach

By

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Keywords: Thorium, Plasma, rare earth, fluoride, zirconium

Abstract

Monazite is a light rare earth phosphate which is difficult to process when using conventional chemical processes. It is considered to be one of the most important commercial sources of thorium and lanthanides. Using conventional chemicals to process monazite have caused severe environmental damage as has been demonstrated in the Baotou region, China. Monazite is found in combination with other minerals in nature such as bastnaesite and xenotime.

The conventional techniques and chemicals used for the processing of monazite are expensive. In order to address this issue, South Africa would like to beneficiate monazite as part of its mineral beneficiation strategy. Doing so competitively would require a new cheaper and more environmentally friendlier process.

A new method for the processing of monazite is currently being investigated. The monazite is fed into a plasma reactor to crack the crystal structure. The cracking of the crystal allows the monazite to be more reactive and susceptible to react with less harsh chemicals. The plasma treated monazite is reacted with a fluorinating compound such as ammonium bifluoride. Ammonium bifluoride is used rather than fluorine or hydrogen

fluoride as it is less dangerous to handle. The fluorinated rare earth mixture can now be separated using various methods.

1. Introduction and Background Information

South Africa has embarked on a mineral beneficiation program to add value to locally procured minerals. The local Department of Mineral Resources has developed a mineral beneficiation strategy which includes the production of uranium, thorium and rare earths (South African Department of Mineral Resources, 2011). Monazite is a mineral which contains these elements (Gupta and Krishnamurthy, 2005).

Monazite is a rare earth phosphate which usually occurs naturally as a crystal. This crystal is chemically highly inert, difficult to process (Clavier et al., 2011) and is considered to be one of the most important commercial sources of thorium and the lanthanides (Abdel-Rehim, 2002). Monazite is found in South Africa, India, Australia, China, United States and Brazil (Gupta and Krishnamurthy, 2005). It can be found amongst various other minerals such as bastnaesite and xenotime (Abreu and Morais, 2010).

Traditional processing of monazite follows one of two processes namely the acid or alkaline digestion process. The acid processing of monazite involves the digestion of monazite in sulphuric acid at 200 – 220 °C with 98 % sulphuric acid (H_2SO_4) for 4 hours (Abreu and Morais, 2010). The alkaline method involves the digestion of monazite with molten sodium hydroxide (NaOH) for 4 hours at 140°C (Gupta and Krishnamurthy, 2005). This process was suggested for the Steenkampskraal mine in the Western Cape (Blench, 2010).

The processing of monazite is considered to be “wet” processes and environmentally very unfriendly as demonstrated in the Baotou region in China. Both methods of monazite digestion have their advantages and disadvantages. The biggest disadvantages are the generation of large quantities of highly toxic chemical and radioactive waste (Hurst, 2010).

The economic interest in the beneficiation of monazite is driven by the rare earth content. Monazite typically contains 70 % rare earth metal oxides. The rare earths

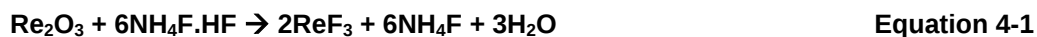
constitute 20 – 30 % cerium oxide (Ce_2O_3), 10 – 40 % lanthanum oxide (La_2O_3) along with significant amounts of neodymium (Nd), praseodymium (Pr) and samarium (Sm). Monazite also contains the radioactive element thorium at concentrations between 1 – 10 % and a small quantity of uranium. Therefore, monazite is classified as a Naturally Occurring Radioactive Mineral (NORM). Various other trace elements are also present and can be produced as by-products through various chemical processes (Gupta and Krishnamurthy, 2005; Kim and Osseo-Asare, 2012; Kim et al., 2009).

Necsa has developed and patented a new process for the beneficiation of zircon to produce nuclear grade zirconium metal. This process is known as the AMI zirconium metal process (Nel et al., 2014). This process involves the production of Plasma Dissociated Zircon (PDZ) and the fluorination thereof by a fluorinating agent such as ammonium bifluoride (ABF) (Nel et al., 2011; Pretorius et al., 2012; Retief et al., 2012). The resulting zirconium tetrafluoride is heat treated by a process such as sublimation to remove any impurities (Augustyn et al., 2010).

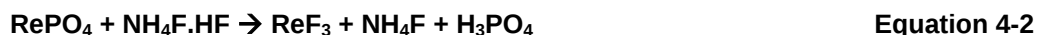
Hafnium occurs naturally in zircon deposits but unfortunately it has a relatively high thermal neutron absorption cross section (Benedict et al., 1981). Therefore nuclear grade zirconium metal must be hafnium “free” (< 100 ppm) (Ux Consulting Services, 2013). Processes like solvent extraction, sublimation, and selective precipitation are traditionally used to remove the hafnium (Li et al., 2011). The pure zirconium salt, which can be zirconium tetrafluoride or zirconium tetrachloride, is treated in a continuous plasma process with magnesium as reductant to produce zirconium metal powder (Augustyn et al., 2010). It is anticipated that a plasma process similar to the AMI zirconium metal process can be adapted to process monazite.

The highly chemically inert crystal structure of monazite makes it very difficult to crack and to recover the elements within the crystal structure. Plasma reactors have the benefit over chemical processing as they employ highly concentrated amounts of energy to a very small area. This concentrated energy source may “crack” the monazite crystal structure, to produce Plasma Treated Monazite (PTM), making it more amendable for further processing (Havenga and Nel, 2012).

The PTM process is expected to “destroy” the original monazite crystal structure. The chemical reaction between the rare earth content of the PTM and ABF is presented in the following reaction equation (using rare earth oxides as an example):



The anticipated reaction between the rare earth phosphates and ABF is presented in the following reaction equation:



The exact crystal structure which will be obtained from the PTM is unclear but the two reactions, as presented above, will give a good indication on the chemistry. This article will focus on a thermodynamic study of the rare earth, thorium, uranium and zirconium oxides and phosphates as anticipated being present in the PTM.

2. Methodology

Computer software such as HSC Chemistry (“HSC Chemistry software | Outotec,” 2016) is used to calculate the Gibbs free energy of the proposed chemical reactions. HSC has a vast database which further allows the user to compare chemicals, the ability to effectively separate the chemicals and their physical properties. HSC makes the assumption that all reactions are under equilibrium and in a closed system.

The Gibbs free energy is a good indicator to determine whether or not a particular chemical reaction is thermodynamically viable. The Gibbs free energy by definition states that an irreversible process at constant temperature and pressure has to proceed in a direction which would cause the Gibbs energy of the system to decrease (Smith et al., 2005). The Gibbs free energy which is thus calculated at a particular temperature and pressure needs to be negative such that the reaction can take place thermodynamically. However, a negative Gibbs free energy does not mean that the process is viable from a kinetic point of view.

3. Results and Discussion

For the discussion below, it is assumed that the rare earths, thorium uranium and zirconium are present as oxides in the PTM. The reactions of these elements as phosphates will be discussed in Section 3.2.

3.1 Thorium, Uranium, Zirconium and Rare Earths Oxides

The processing of the rare earth oxides with HF and fluorine has been well described in literature (Gupta and Krishnamurthy, 2005). Fluorine and HF are extremely dangerous and corrosive (Kotz et al., 2012). The fluorination of the oxides with fluorine and HF is possible. However, the highly corrosive nature, cost of construction materials, high cost of fluorine and HF and the difficulty with handling these chemicals justify an investigation into rather using ABF, which is less dangerous. The Gibbs free energy of the reaction of ZrO_2 with HF and ABF as a point of reference to the AMI zirconium process is also indicated.

Figure 4-1 presents the Gibbs free energy for anhydrous HF reacting with metal oxides in PTM using HSC.

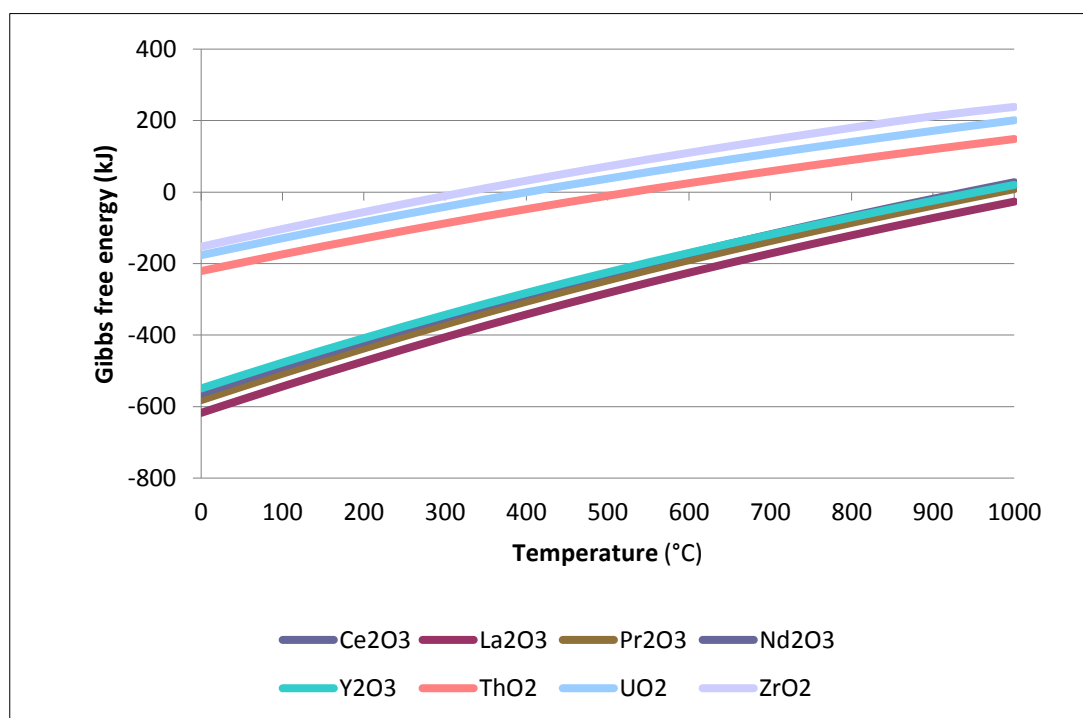


Figure 4-1: Gibbs free energy of anhydrous HF with the metal oxides in PTM

Figure 4-2 presents the Gibbs free energy for the metal oxides reacting with aqueous HF. In contrast to anhydrous HF, the higher the temperature the more negative the Gibbs free energy becomes.

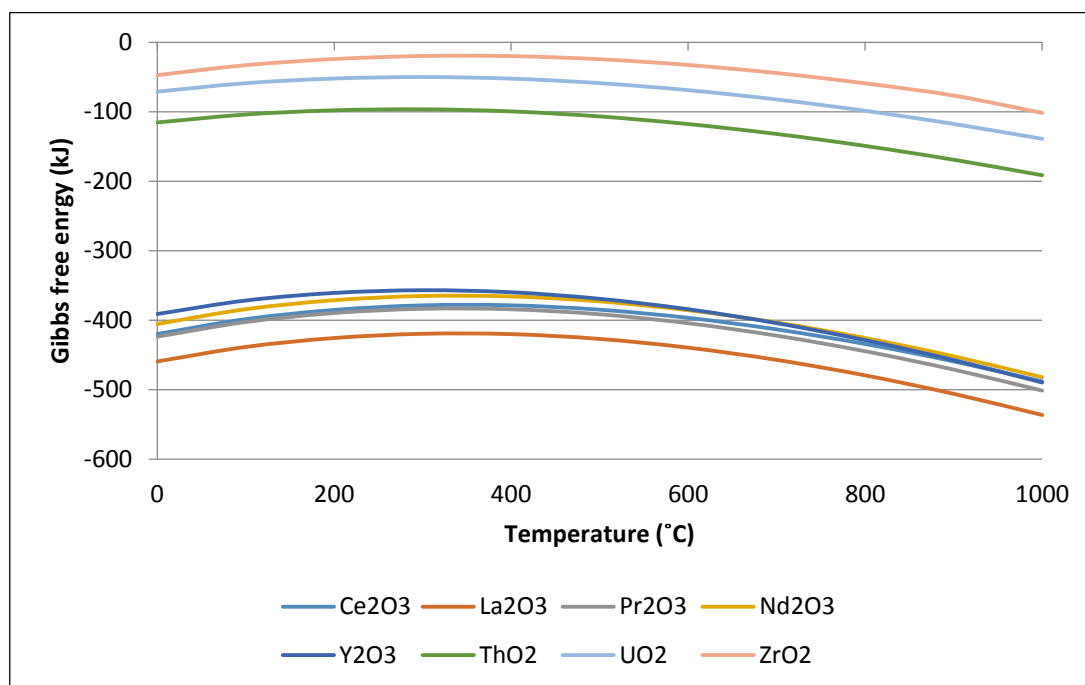


Figure 4-2: Gibbs free energy of aqueous HF with the metal oxides in PTM

Figure 4-3 shows the Gibbs free energy for the rare earth oxides reacting with ABF.

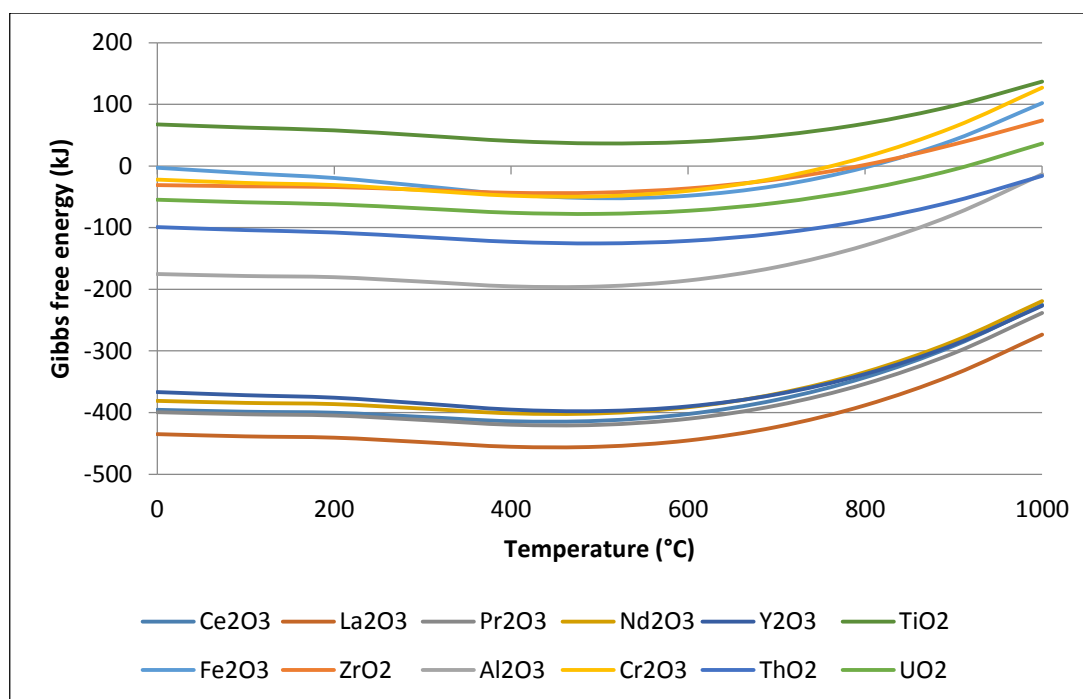


Figure 4-3: Gibbs free energy for the reaction between the metal oxides from monazite and ammonium bifluoride.

The ABF and HF reaction with the rare earth oxides have both been previously documented and studied. According to literature from Gupta & Krishnamurthy (2005), the reaction between the rare earth oxides and anhydrous HF takes place over 8 hours at 700 °C with 99.9 – 99.98 % efficiency. The ABF reaction on the contrary uses 30 % excess ABF heated to 300 °C (Gupta and Krishnamurthy, 2005). Comparing the conflicting data from Figure 4-1 and Figure 4-3, it must be pointed out that although the Gibbs free energy for aqueous HF is more negative and thermodynamically more spontaneous than the reaction with ABF, the kinetics of both reactions are the opposite, thus showing that a highly negative Gibbs free energy does not necessarily mean that good kinetics will also be achieved (Gupta and Krishnamurthy, 2005).

The reaction between thorium/uranium oxide and ABF has also been mentioned in literature with the reaction between ABF and uranium completed in 8 hours to form the compound $(\text{NH}_4)_4\text{UF}_8$ (Yeaman, 2008). The reaction between ABF and thorium oxide takes place over two hours at room temperature and forms $(\text{NH}_4)_4\text{ThF}_8$ (Wani et al., 1989; Yeaman, 2008).

The Gibbs free energy for the reaction of the rare earth oxides with anhydrous HF, as shown in Figure 4-1, is more negative than both the aqueous HF and the ABF up till 200 °C and then becomes positive at about 900 °C. The Gibbs free energy of the reactions between thorium, uranium and zirconium oxide become positive at about 300 °C.

The reaction with aqueous HF, Figure 4-2, initially has the same trend as anhydrous HF but evens out at 300 °C and then becomes more negative above 1000 °C. The Gibbs free energy for the ABF reaction, Figure 4-3, become more negative until 500 °C and remains negative until past 1000 °C. When the anhydrous HF and ABF reactions are compared, the ABF's Gibbs free energy remains stable whereas HF becomes less negative very sharply. It is speculated that the reason for this phenomenon is that ABF dissociates at high temperatures, thus allowing for more fluoride ions are available for reaction. Comparing the reaction of HF with ABF, the Gibbs free energy between the two is nearly the same as illustrated in Figure 4-4.

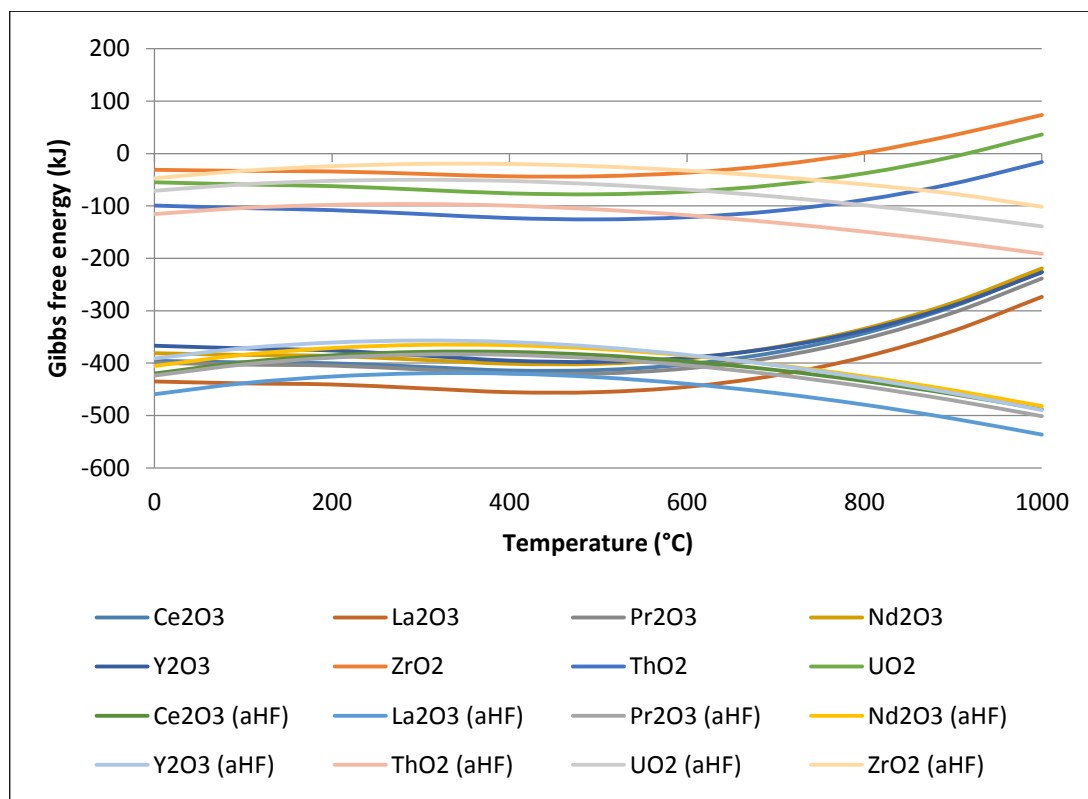


Figure 4-4: Gibbs free energy of the metal oxides reacting with aqueous HF and ABF

Figure 4-4 indicates that whether aqueous HF or ABF is used, from a thermodynamics point of view, will react the same way. As indicated earlier, lower quantities of ABF at a lower temperature produces the same fluorination reaction. ABF is less dangerous to handle than aqueous HF, which makes the use of ABF a better alternative from a practical and safety point of view.

3.2 Direct reaction with the Phosphates

Monazite has never been cracked in a plasma before, hence it is unknown at present whether or not the phosphate will crack and if a new chemical structure would be formed. Assuming that the phosphate structure remains then the reaction between the phosphate, RePO_4 , and ABF takes place. This chemical reaction shown in Figure 4-5 and presented below:



Equation 4-3

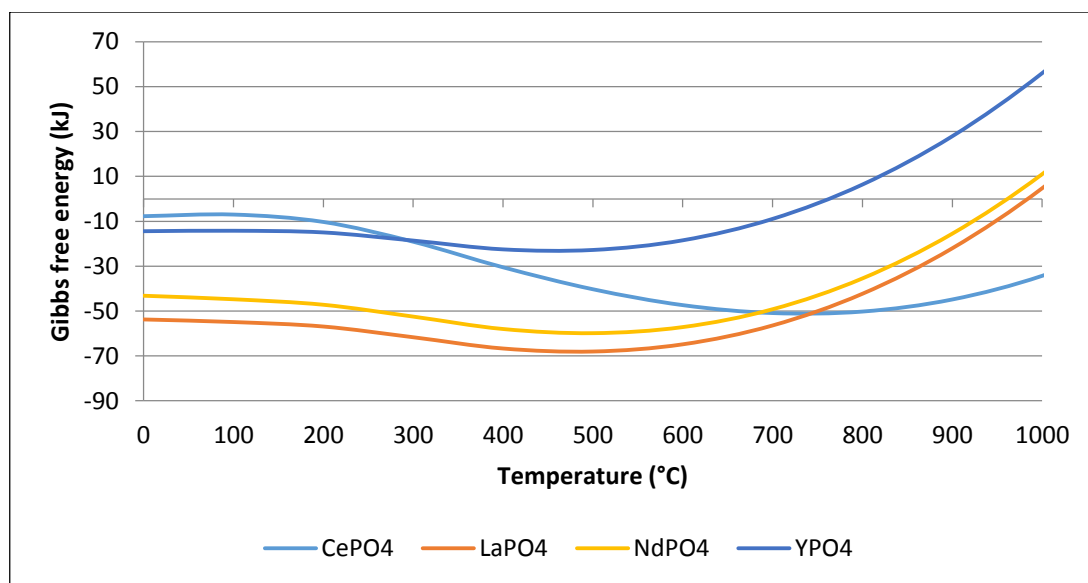


Figure 4-5: Gibbs free energy of the rare earth phosphate with ABF.

PrPO_4 is the only rare earth not included in the HSC database as a solid but is present as an aqueous solution. These results are presented in Figure 4-6.

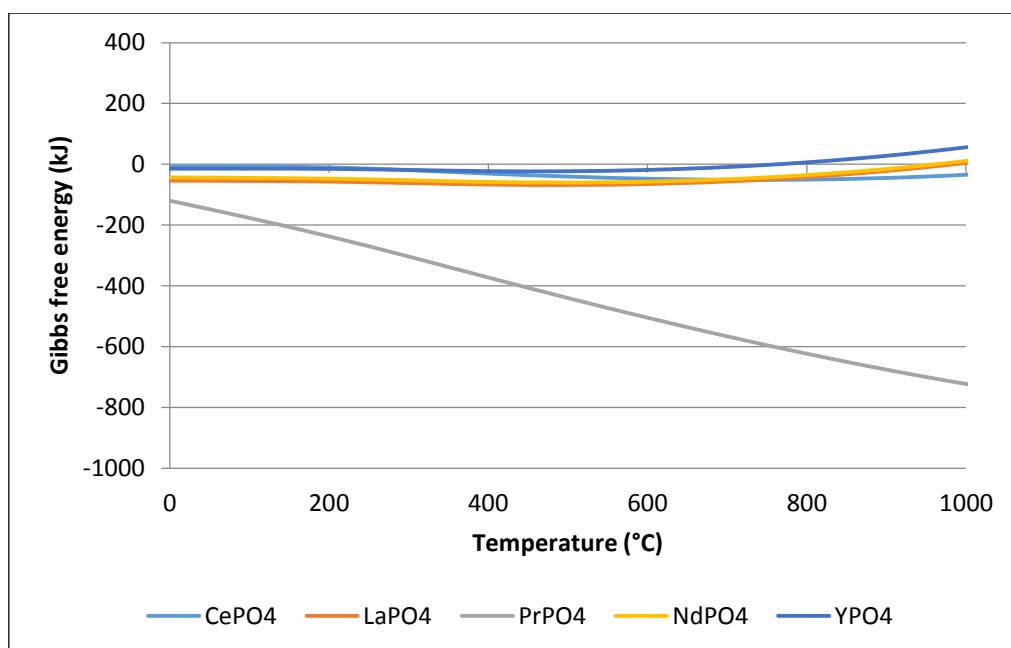


Figure 4-6: Gibbs free energy of the rare earth phosphate with ABF and PrPO_4 in the aqueous state.

The aqueous product of praseodymium is more thermodynamically possible in the reaction with the ABF than the non-aqueous reaction as presented in Figure 4-5.

4. Conclusion

The study of monazite of which the crystal structure is destroyed with a plasma process to produce the corresponding metal oxides and phosphates has been theoretically studied with the thermodynamic simulation program HSC in order to calculate the Gibbs free energy of these oxides and phosphates with anhydrous and aqueous HF and ABF. This study demonstrates that ABF could be used as a viable alternative for aqueous HF for the purpose of fluorination. This will be experimentally determined as part of future work.

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4.3 Concluding Remarks

The article concluded that ABF can be used as an effective fluorinating agent for the rare earth phosphates and oxides and will convert the thorium and uranium alongside. However, it was not able to shed any information on the potential reactivity between monazite and PTM except that it is easier and less complicated to digest the oxides rather than the phosphates. When practical experiments were conducted, using the information obtained in this article, no conclusion could be made on the potential improved chemical reactivity in the conversion of monazite to PTM. This is due to the formation of an insoluble solid from which the conversion and reactivity of the PTM and monazite could not accurately be determined. The digestion of PTM with ABF was abandoned in favour of digestion with the mineral acids.

As the use of ABF to evaluate the extraction potential of PTM versus monazite for the extraction of the REE, thorium and uranium was unsuccessful, an alternative extraction method were investigated in the following chapter. The theoretical determination of these reactions are discussed in Chapter 6 as part of the digestion of monazite and PTM with the mineral acids and alkaline solution.

5. High temperature plasma treatment of monazite

5.1 Introduction to the article

The current hypothesis is that monazite decompose into the rare earth oxides, thorium- and uranium carbide after being treated in a high temperature thermal plasma in the presence of carbon. The rare earth oxides are potentially more reactive due to the oxygen bonds which are weaker than the phosphate bonds and can be dissolved using a diluted mineral acid (Adachi et al., 2004; Peelman et al., 2014). Thorium and uranium carbide can similarly be leached using mineral acids (Sears and Ferris, 1969). This chapter describes the process whereby monazite is fed to a plasma to produce Plasma Treated Monazite (PTM) using a sustainable process. PTM was evaluated under an optical microscope and chemically to compare the chemical reactivity to that of monazite and other forms of heat treated monazite to confirm that the plasma treatment of the monazite is the sole reason for the increase in reactivity.

This article's abstract is currently under review for presentation at the 2017 European Rare Earth resources conference to be held in Santorini, Greece on the 28 - 31 May 2017 and may be published in the Journal of Sustainable Metallurgy.

5.2 Article: High temperature plasma treatment of monazite

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Keywords: Monazite, plasma, rare earth, thorium, thermal decomposition

Abstract

It has been hypothesised that by placing monazite in a high temperature plasma, its chemical reactivity would be increased. To evaluate this theory, monazite was placed in a DC direct arc batch reactor. When the high temperature plasma heat is not applied directly for the correct length of time, the monazite has a minor increase in chemical reactivity. If the monazite is treated for an extended period of time and becomes melted, then the resulting molten monazite becomes more inert to chemical and physical attack. The high temperature plasma heat must be applied directly to the monazite for the correct length of time in order to properly treat the monazite. The proper treatment of monazite in a plasma is evident using optical microscopic and chemical analysis. When properly treated with a plasma, the original monazite becomes chemically more reactive which permits the removal of 30.49 % of the rare earth elements, is 21 times more than from the original monazite, 16.89 % of the thorium and 42.70 % of the uranium using 32 % HCl at 80 °C for 1 h. The treatment of monazite can be improved by optimizing the carbon to monazite ratio and by treating monazite in an inflight plasma. This would heat and treat the monazite more efficiently to allow more of the rare earth elements, thorium and uranium to be extracted using a mineral acid. Future work will include optimizing the plasma and leaching of the plasma treated monazite using different chemicals for better extraction of the rare earth elements and to optimize downstream separation.

1. Introduction

The problem with monazite processing is that as a highly inert mineral it requires the use of a difficult and costly process to extract the valuable REE. These complications have led to the production of vast quantities of chemical and radioactive waste (Hurst, 2010). Monazite is a rare earth phosphate (REPO_4 with RE = Rare Earth) mineral which contains the light Rare Earth Elements (REE) Ce, La, Nd, Y, and Pr (Ashry et al., 1995; Cardarelli, 2008; Hassan et al., 1997). Monazite is comprised of varying concentrations of ilmenite, magnetite, zircon, rutile, garnet and monazite (Ashry et al., 1995; Sroor, 2003) as a black sand found on beaches worldwide (Dilorio et al., 2012). Monazite also contains 1 to 10 % radioactive thorium and a small quantity of uranium (Amaral and Morais, 2010; Cardarelli, 2008).

Zircon, another highly inert mineral, is processed in a high temperature thermal plasma where it is dissociated into a chemically reactive product (Havenga and Nel, 2012; Simpson et al., 2015). It is hypothesised that a similar process on monazite could increase its chemical reactivity to improve downstream processing. This would increase the output of the REE, thorium and uranium while simultaneously permitting the use of less aggressive chemical processes (Toumanov, 2003).

Monazite decompose into the rare earth oxides when heated above 1400 °C in the presence of carbon with a 2:5 molar ratio (Yugeswaran et al., 2015). The rare earth oxides are desired products as they can be leached using diluted mineral acids, particularly aqueous HCl (Adachi et al., 2004; Sears and Ferris, 1969), unlike monazite, which is more difficult to leach due to the stronger, more inert, phosphate bonds (Peelman et al., 2014). For this reason, the decomposition of the rare earth phosphates (monazite) into the rare earth oxides, can potentially break the monazite crystal bonds similar to zircon. Thorium and uranium carbide can also be formed from monazite when reacted with carbon above temperatures of 2100 °C (Lundgren, 2014; Prescott and Hincke, 1927) and can be leached using HCl or other mineral acids (Sears and Ferris, 1969).

The plasma treatment of monazite has the potential to make the processing of monazite more favourable as it would increase the chemical reactivity, reduce the

quantities of reactive reagents and increase the extraction of the rare earth elements, thorium and uranium (Toumanov, 2003). To that end, the objective of this study is to place monazite in a high temperature thermal plasma, to analyse the various plasma products, determine the process conditions to treat monazite in the plasma and whether Plasma Treated Monazite (PTM) is chemically more reactive and easier to process than monazite. In addition, alternative heating and physical processes, like heating the monazite to 1800 °C or crushing, has been done to do a comparative chemical reactivity analysis in parallel with monazite and PTM. These samples along with PTM and monazite have been treated with aqueous HCl.

2. Materials and Methods

Monazite sand was obtained from an external source. The sand consists of 69.55 % monazite, 17.67 % zircon and 4.85 % ilmenite with various other minerals occupying the remaining mass. The 32 % HCl used in all chemical experiments was obtained from Merck.

Crushed monazite was produced by pummelling 10 g of monazite using a hand crusher for 10 min. Heat treated monazite is produced by placing 20 g of monazite in an alumina crucible at 1000 °C for 3 h and subsequently rapidly quenching the product with water. Inductive monazite is produced by placing 20 g of monazite into a graphite vessel which is heated to 1800 °C in an induction oven, cooled naturally and removed. Plasma Treated Monazite Low (PTM_L) are PTM whose crystal structure was not altered during plasma treatment. Plasma Treated Monazite Heated (PTM_H) and Plasma Treated Monazite Low Heated (PTM_{LH}) are PTM and PTM_L respectively which are heated to 650 °C for 24 h to remove excess graphite which was present during plasma treatment.

The plasma experiments were conducted using a DC direct arc plasma batch reactor. The plasma reactor is a circular reactor with a stainless steel lid. It has a 21 mm hole drilled at the top and bottom of the reactor to allow a copper rod to be fed through and complete the circuit. The top copper tube is the cathode and the bottom is the anode. The reactor and the electrodes are all water cooled using demineralised (demin) water. The cathode is fixed to a mechanism which allows the tip of the cathode to travel up

and down inside the reactor. A basic process flow diagram of the plasma reactor (Figure 5-1) and the internal components, including the graphite crucible which contains the monazite, is provided (Figure 5-2 and Figure 5-3).

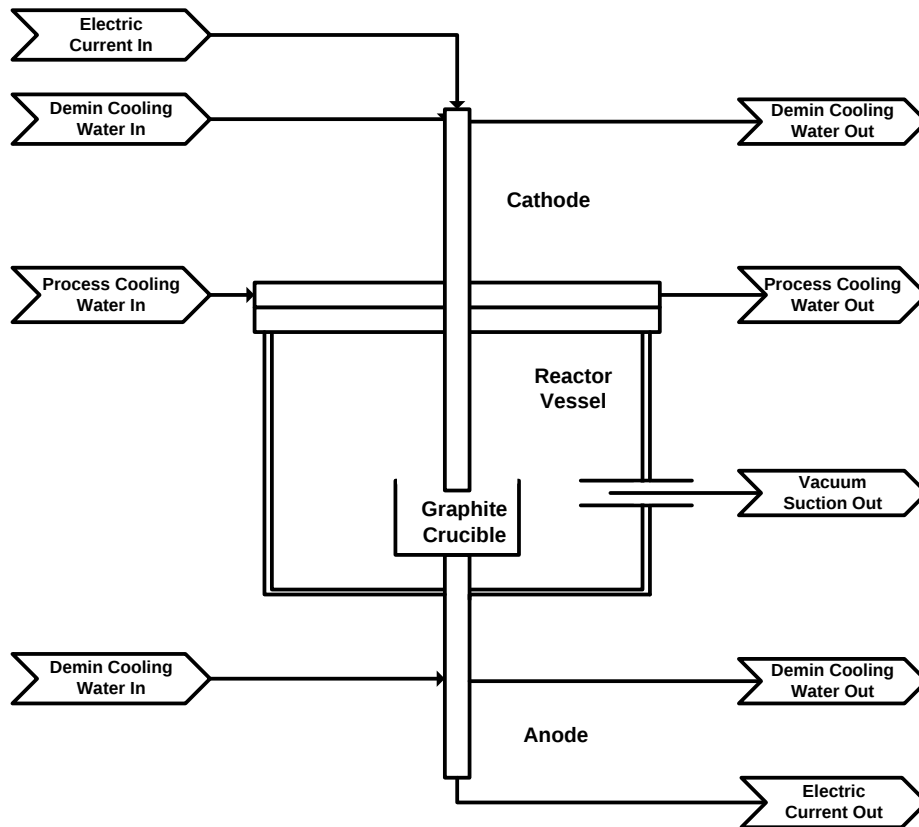


Figure 5-1: A basic process flow diagram of the DC direct arc plasma using a graphite crucible

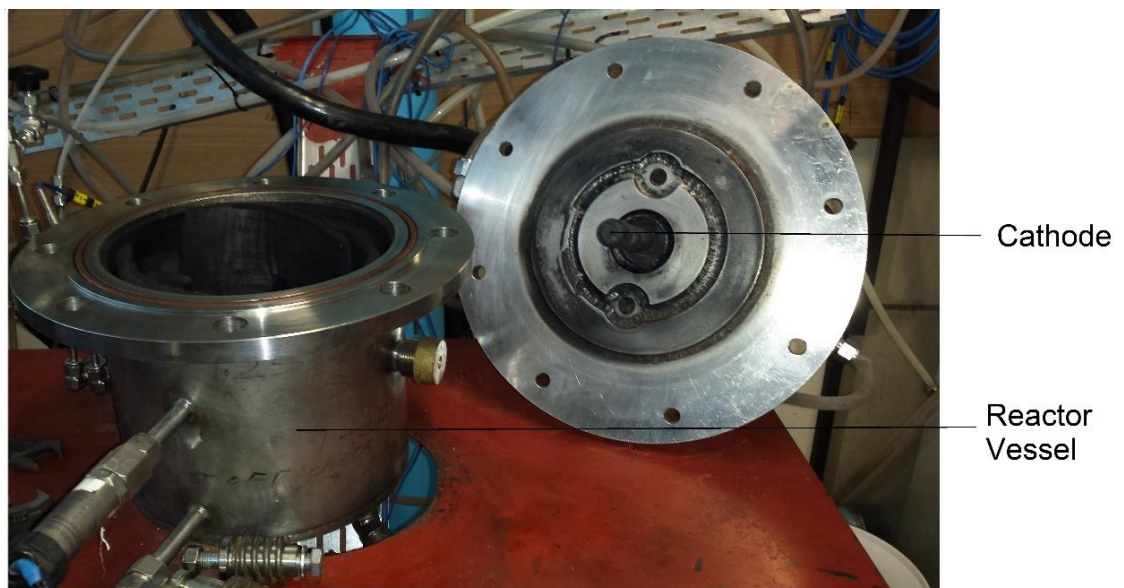


Figure 5-2: The bottom portion of the plasma reactor lid presenting the cathode electrode



Figure 5-3: The internal structure of the bottom of the plasma reactor

Approximately 20 to 30 g of monazite is placed in the graphite crucible for each experiment. A clear area is maintained using a piece of filter paper and a small elevated node, made of graphite which is consumed during the process. This is to provide a contact area between the cathode and the graphite for an electric current to pass through (Figure 5-4). The graphite crucible has a housing and a lid which contains the heat and any monazite which may sputter (Figure 5-5). The plasma reactor vessel is closed with an airtight seal (Figure 5-6).

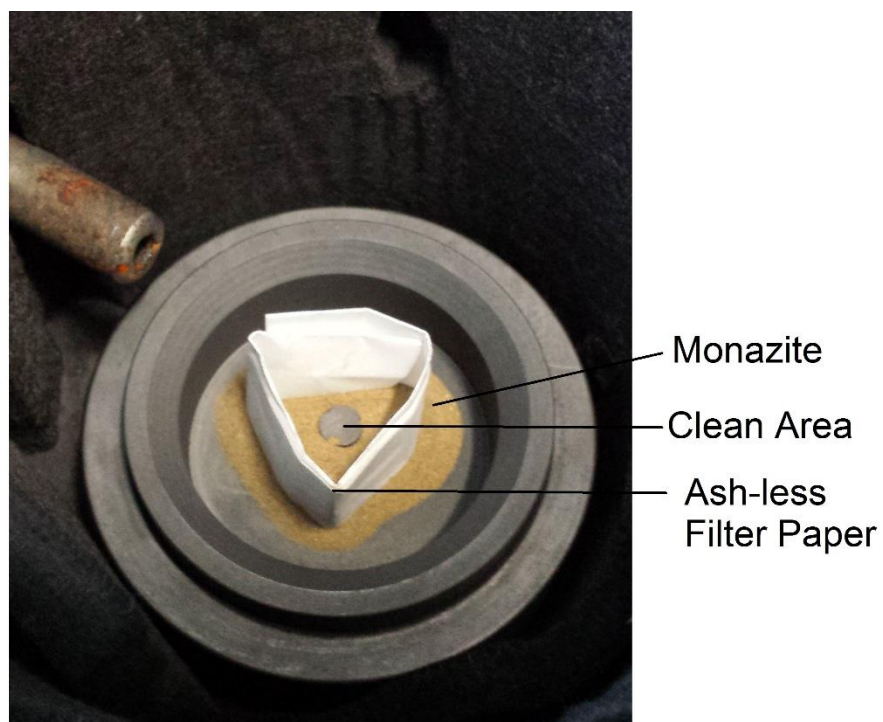


Figure 5-4: Monazite loaded into the plasma for a plasma run

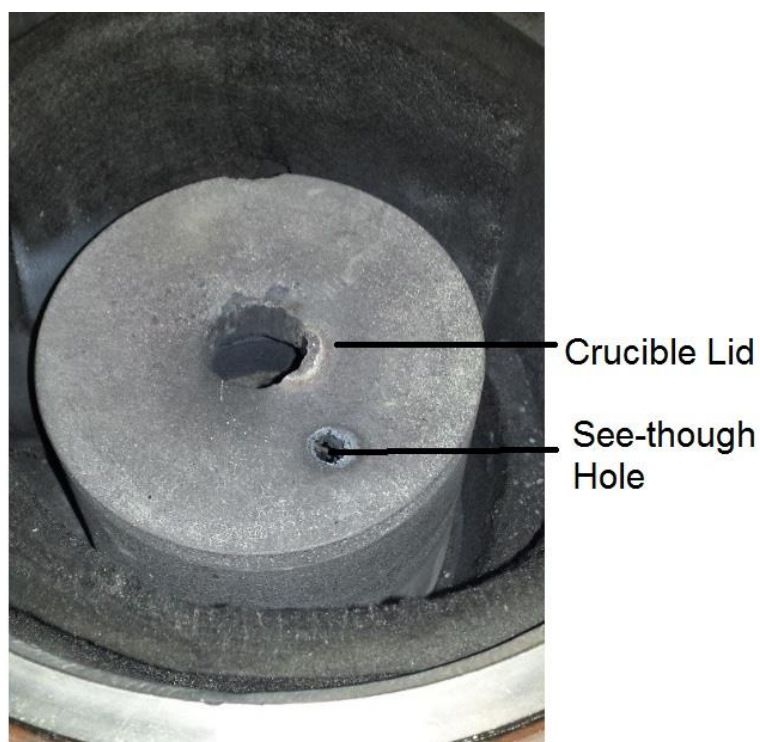


Figure 5-5: Closed graphite crucible with the monazite

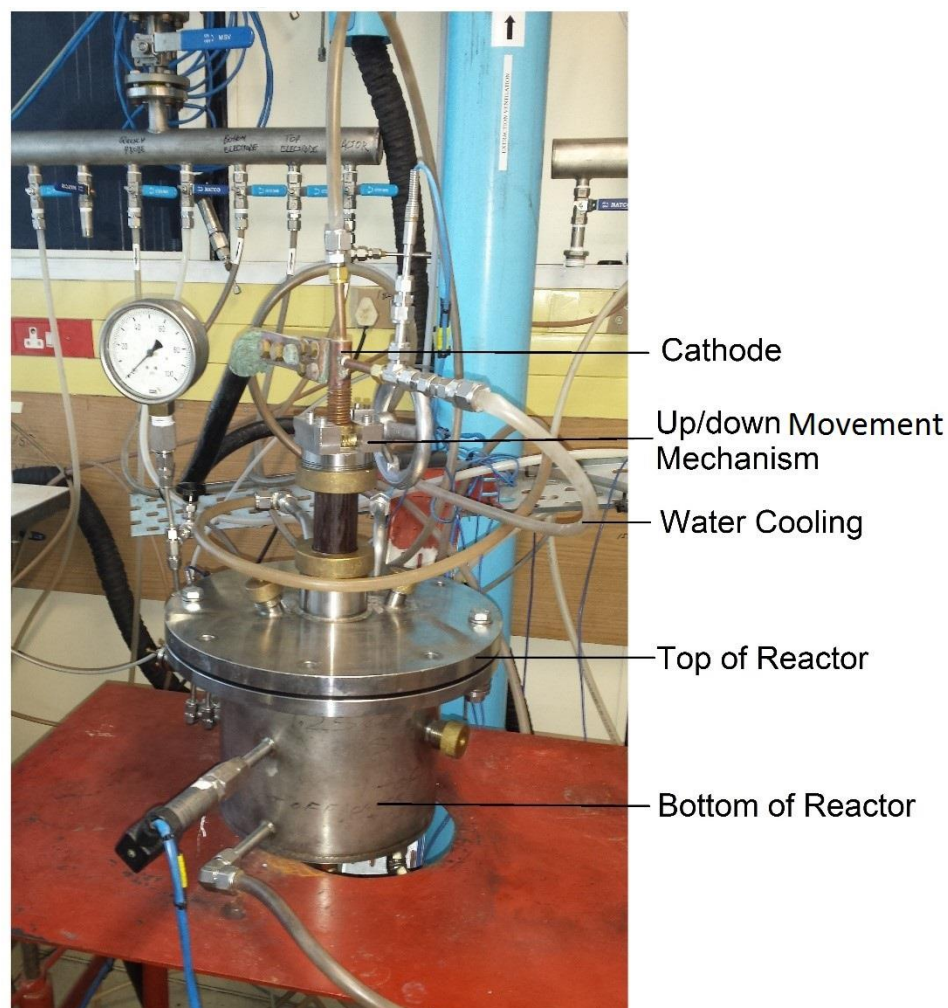


Figure 5-6: DC direct arc plasma (External)

During the experiment a vacuum is generated within the vessel using a vacuum pump. The plasma reactor is initiated by placing the cathode in contact with the graphite crucible to let a current pass through. The cathode is subsequently pulled apart from the graphite anode until a spark is generated, similar to an electric arc weld. This spark forms the plasma which treats the monazite. The operating voltage is roughly 200 V and 15 A which is maintained for a period of 1 to 3 min. After the experiment the current is turned off and the reactor and its products are left to cool naturally with the cooling water still in operation. After 30 min the reaction vessel is opened to remove the PTM. All of the auxiliary water cooling lines are switched off. After the PTM is removed, the product is placed in an alumina crucible. This crucible is placed in an oven at 650 °C for 24 h to remove excess carbon which is mixed with the PTM during the plasma process. The product removed from the heating is Plasma Treated Monazite Heated (PTM_H).

All samples are analysed using an optical microscope and X-ray fluorescence (XRF). The analysis were completed to evaluate the composition and particle structure of the plasma product to establish whether they have been altered. The optical microscope is used to evaluate the visual appearance of the plasma product and to determine if the particles were affected. The XRF was used to determine the elemental composition of the plasma products. X-ray diffraction analysis was attempted on the plasma products but due to unreliable preparation methods employed during preparation of the samples the results were generally inconclusive.

The final test to evaluate the plasma treated product was to test the chemical reactivity using chemicals. The chemical experiments were conducted and compared to various heat and plasma treated products of monazite using various processes, like heating the monazite to 1800 °C or crushing the particles. Emphasis was placed on keeping the reactions as simple as possible in order to ensure that the plasma treatment of monazite is the only reasonable explanation for the increase in reactivity rather than other factors like chemical reagents, environmental conditions, agitation or catalysts. For comparison reasons and to ensure that plasma treatment was the only reason for any increased chemical reactivity, a number of other monazite products were generated using various other heat and physical treatment processes as described. The chemical treatment of all these products are completed by placing 0.1 g of the required sample in a reaction vessel with 10 ml 32 % HCl which is then heated to 80 °C in a temperature controlled oven with no agitation. After 1 h the aqueous solution is cooled, decanted and sent for ICP wet chemical analysis using an external laboratory.

3. Results and Discussion

3.1 Plasma Process

Before the monazite was treated in a plasma it was analysed using an optical microscope. The analysis revealed a number of brown, red, white and black smooth cylindrical shaped particles, reminiscent of this specific monazite sample (Figure 5-7).



Figure 5-7: Microscopic Image of Monazite

Post-plasma treatment of the monazite produces Plasma Treated Monazite (PTM) as a black mass. PTM is either a black sand, a hard solid mass or a brittle mass (Figure 5-8). The black colouring of PTM is due to contamination from the graphite node, which is destroyed during the experiment. The PTM was scraped off the crucible and used directly or heat treated to remove the excess carbon before chemical leaching. X-ray fluorescence analysis was conducted on all PTM samples to determine the elemental compositional changes produced due to the plasma treatment. No statistical elemental compositional changes were observed between monazite and 11 different samples of PTM.



Figure 5-8: Plasma Treated Monazite (PTM) within the graphite crucible after a successful plasma run

The formation of Plasma Treated Monazite Low (PTM_L) occurs by having too little plasma heat applied to the monazite or the application of the plasma heat for an extended period of time. When too little heat is applied to the monazite only a small percentage of the monazite is treated and the chemical reactivity of the PTM increase partially. When PTM_L is analysed using an optical microscope, a large number of cylindrical shaped particles, similar to what was found with monazite, were still present. The presence and shape of these particles indicate that the monazite did not receive adequate treatment from the plasma to properly decompose and destroy the monazite crystal structure (Figure 5-9).

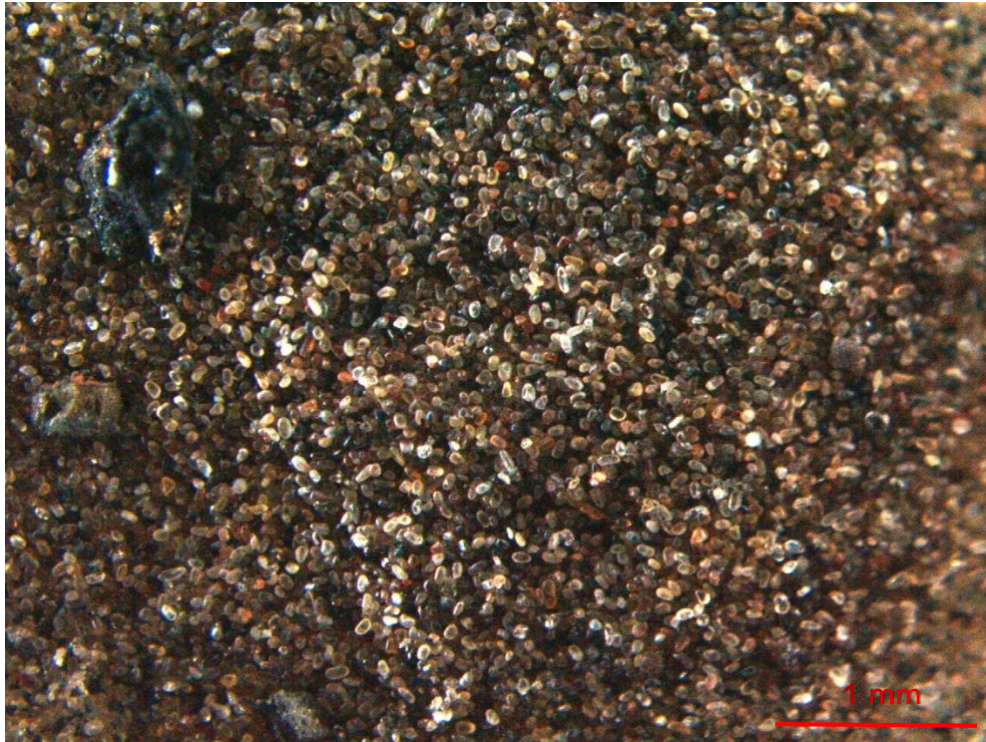


Figure 5-9: Microscopic image of Plasma Treated Monazite Low (PTM_L) in the presence of graphite.

When the plasma treatment is applied for an extended period of time, the monazite will melt and form a hard solid mass. This mass protects the remaining monazite which has been placed further away from the plasma. This monazite will remain untreated, despite its close proximity to the plasma. When it was analysed under an optical microscope, it appeared identical to the original monazite in colour and shape.

The solid mass of molten monazite was determined to be chemically more inert than the original monazite, difficult to crush and impervious to high temperature heat treatment. When the solid mass was analysed using an optical microscope (Figure 5-10), a number of crater like structures, melting formations and loss of the oval shaped monazite particles were observed. These structural changes, loss of surface area and the increase in hardness are the main reason for an increase in the level of inertness of PTM when it has melted.



Figure 5-10: Microscopic image of PTM which has been treated in the plasma for too long and melted

A removable lid was placed on the graphite crucible to keep the sputtering and heat of the plasma treatment process contained within the crucible. When the lid is removed for an experiment, a white powder is deposited around the inside of the plasma reactor (Figure 5-11 and Figure 5-12). This is similar to what Tanner-Jones (2007) described after his experiments and which was identified as phosphorous.

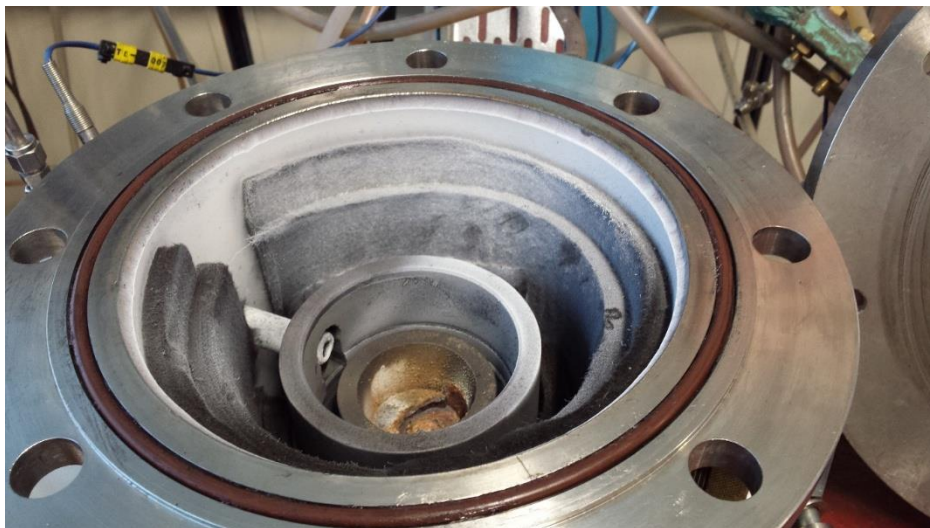


Figure 5-11: The plasma reactor when the incorrect crucible and no lid is used



Figure 5-12: Plasma reactor lid with the dispersed white powder

As all of the plasma experiments were conducted using a consumable graphite crucible which is partially destroyed in the process, all of the PTM is contaminated with graphite which provides PTM's grey-black colour. To remove the excess graphite, the PTM_L and PTM were placed in a temperature controlled laboratory oven at 650 °C for 24 h to drive off the excess carbon, forming two new products, Plasma Treated Monazite Low Heated (PTM_{LH}) and Plasma Treated Monazite Heated (PTM_H). When PTM_{LH} is removed from the oven a general colour change is observed, however using an optical microscope it appeared similar to monazite due to the cylindrical oval shaped particles (Figure 5-13).

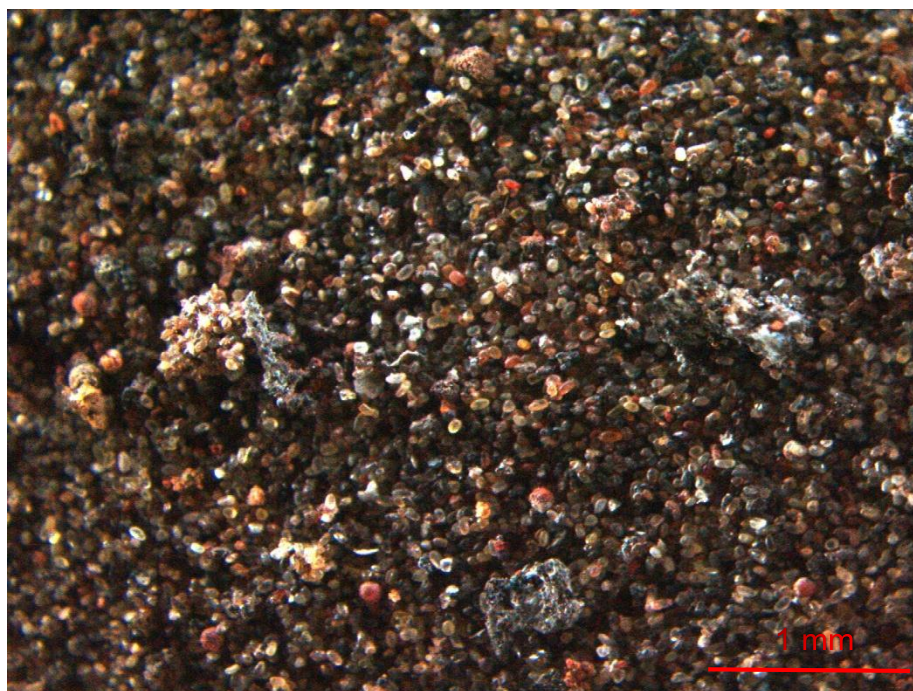


Figure 5-13: Microscopic view of PTM_{LH}

When monazite was properly treated in the plasma and analysed under an optical microscope, a clear difference between PTM and PTM_L is observed as all of the cylindrical oval shaped monazite particles are destroyed, a general colour change is observed along with the formation of a crumble like structure (Figure 5-14). Microscopic analysis of PTM_H indicates a similar difference (Figure 5-15) as no cylindrical oval shaped particles are detected and the particles appear crumble like.



Figure 5-14: Microscopic image of PTM

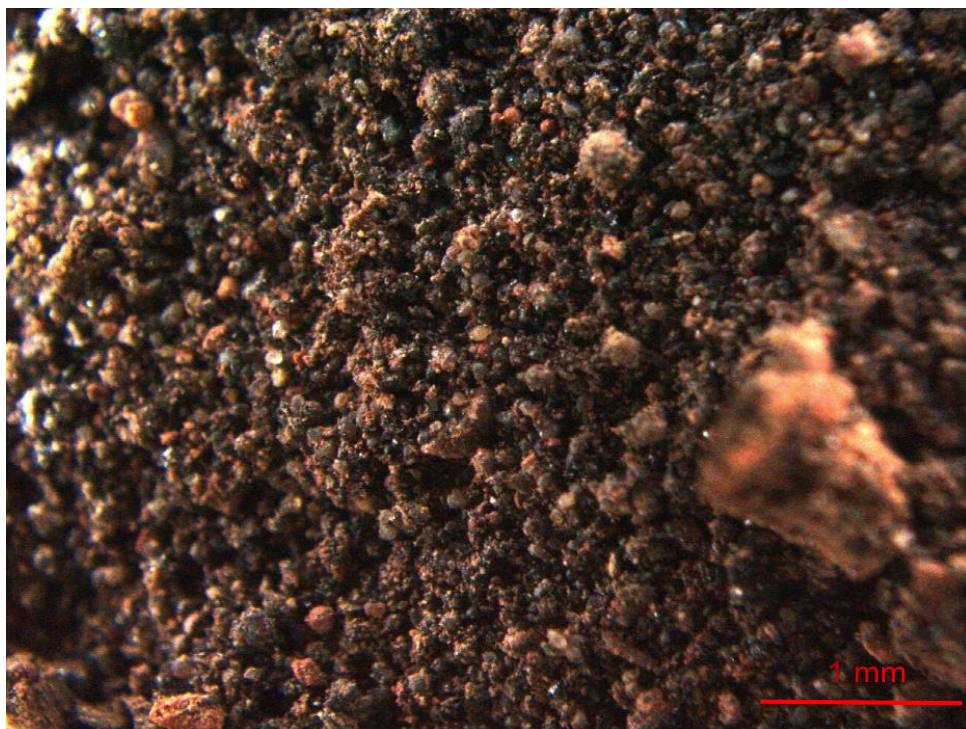


Figure 5-15: Microscopic image of PTM_H before it is leached

An XRD analysis of the crumble like structure of PTM_H revealed it to be completely amorphous. The advantage of the amorphous nature of PTM_H is that the crystal

structure within the monazite matrix is completely destroyed. This makes the REE, thorium and uranium more vulnerable to chemical attack and would improve their respective extraction efficiencies. The downside is that due to the amorphous nature of PTM_H, the crystal structure and its composition cannot be evaluated using XRD and must be re-examined using other analytical techniques. A more refined analysis of monazite and PTM_H is beyond the scope of this study.

3.2 Chemical Reactivity

In order to determine whether there is an increase in the chemical reactivity of PTM and to confirm the hypothesis that the plasma treatment of monazite produces a chemically more reactive product, a series of simple chemical experiments were conducted using 32 % HCl. The results present the quantity of the specific element extracted as a percentage of the original amount of the specific element in the starting material. These percentage extraction efficiencies were subsequently compared between the various starting materials and processes.

The experimental results confirmed that only the proper treatment of monazite in a plasma increase the chemical reactivity of ordinary monazite as all other forms of alternative monazite heating or alteration, including heating to 1800 °C, crushing the monazite to increase the surface area, did not provide a significant increase in the REE, thorium and uranium extraction (Figure 5-16). In contrast PTM and PTM_H extracted 21 times more REE, 7 times more thorium and 11 times more uranium from PTM than the original monazite using the same conditions with no agitation, temperature variations or catalysis. The standard deviation is shown as error bars for PTM and PTM_H.

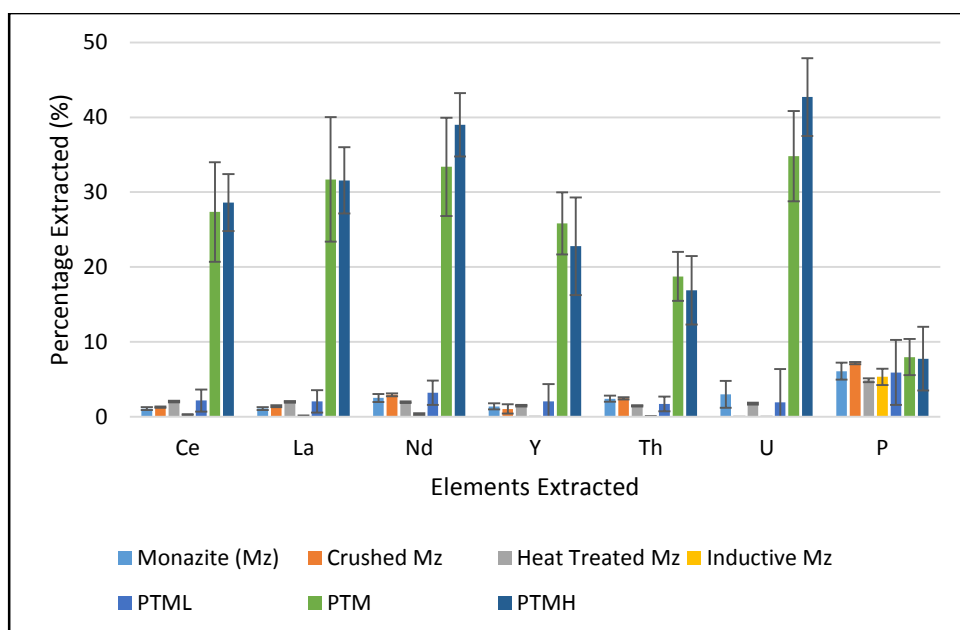


Figure 5-16: Extraction efficiency of various forms of monazite formed with 32 % HCl at 80 °C for 1 h

Thorium and uranium were extracted successfully from PTM and PTM_H using HCl. Based on literature it is suggested that thorium and uranium carbide is formed during the plasma process. The higher percentage of uranium which is extracted compared to thorium is suggested to be due to the lower conversion temperature of uranium oxide to the carbide than thorium, thus allowing more uranium to be converted.

The experiments did indicate a small but significant influence on the extraction efficiency due to the contamination of graphite as the sample which had its graphite removed had an overall increase in extraction of 3 %. The phosphorous content which was extracted remained relatively constant and cannot be used as an accurate indicator to evaluate the conversion nor the extraction efficiency of the process.

Based on literature, if the rare earth oxides were formed then all of the REE should have been leached, while only 30.49 % of the REE were. When analysing the monazite residue after being leached by HCl (Figure 5-17) it is suggested that the monazite did not fully decompose during the plasma treatment with a significant portion of the monazite left untreated. This could be due to an insufficient quantity of carbon which reacts with the monazite, insufficient heating of the monazite or the configuration of the batch reaction during the plasma treatment process. For this

reason it is recommended that in order to increase the decomposition of monazite, a continuous flow plasma reactor with a known monazite-carbon mixture be used rather than the DC direct arc batch reactor, whereby the monazite can be overheated but will not form larger particles and the monazite-carbon mixture can be controlled more effectively.



Figure 5-17: Microscopic image of PTM_H residue post leaching with 32 % HCl at 80 °C for 1 h

The results validate the need to properly treat monazite in a high temperature plasma to increase the chemical reactivity. Monazite must be treated in the plasma directly with the appropriate amount of heat and length of time in order to gain this advantage. The plasma treatment of monazite is found to be the predominant reason for improved REE's, thorium and uranium extraction as the plasma treatment destroys the monazite crystal matrix producing a more reactive form of monazite.

4. Conclusion

Monazite's highly inert nature makes it a difficult and complex mineral to process in a clean and efficient manner. It is hypothesised that by feeding monazite to a plasma,

that its chemical reactivity could be improved. This theory was evaluated by placing monazite in a DC direct arc batch reactor to produce PTM.

When monazite is treated using a high temperature plasma and the heat of the plasma is not applied directly to the monazite for the correct length of time, then the monazite will only have with a minor increase in chemical reactivity. The study has revealed that the lack of transformation of PTM_L and PTM_{LH} compared to monazite is evident under an optical microscope and upon chemical treatment. Microscopic analysis of the material has showed no discernible difference in the structure of monazite and the plasma product PTM_L. When monazite is treated for too long and has melted, it is more inert and difficult to process. For these reasons, the high temperature plasma heat must be applied correctly to the monazite for the correct length of time in order to properly treat the monazite and produce a chemically reactive form of monazite.

Microscopic analysis of PTM and PTM_H reveal alterations to the particles from the original monazite particle structure. The particles appear crumble like and the XRD presents an amorphous substance. This permits digestion using a diluted mineral acid at low temperature for the effective extraction of the REE, thorium and uranium.

Chemical reactivity tests were conducted using 32 % HCl which revealed that crushing and heating the monazite to high temperatures, even 1800 °C in the presence of a graphite crucible, has a small effect on the extraction efficiency of the monazite and that it is not the main cause for the increase in reactivity. The increased chemical reactivity is obtained from the plasma treatment of monazite which increases the extraction of the REE by 21 times, 7 times more for thorium and 11 times for uranium than the original monazite using the same conditions. Post visual analysis of the residue of the PTM which has been leached indicates that not all of the monazite has been decomposed in the plasma, resulting in low extraction efficiencies.

5. Acknowledgements

The authors thank the South African Nuclear Energy Corporation SOC Ltd (Necsa) and the Nuclear Materials Development Network of the Advanced Metals Initiative of the Department of Science and Technology of South Africa for financial support.

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5.3 Appendix

The results of the leaching of monazite, PTM and the various monazite compounds are presented in Table 5-1 and Table 5-2. Presented along with these results are the leaching efficiency for zirconium and titanium as their starting materials, zircon and ilmenite, were present in the original monazite sample. The results indicated a similar trend with an increase in extraction efficiency when comparing monazite to PTM and PTM_H.

Table 5-1: Raw data of the leaching efficiency of monazite, PTM and its substituents with 32 % HCl at 80 °C for 1 h with no agitation as percentage

	Ce	La	Nd	Y	Th	U	Ti	Zr	P
Monazite (Mz)	1.09	1.10	2.51	1.39	2.42	3.00	0.68	0.04	6.09
Crushed Mz	1.29	1.42	2.94	1.04	2.47	0.00	1.06	0.00	7.17
Heat Treated Mz	2.05	2.00	1.96	1.47	1.46	1.78	0.15	0.04	4.87
Inductive Mz	0.28	0.07	0.35	0.00	0.04	0.00	0.37	0.00	5.33
PTM_L	6.54	6.98	9.25	4.84	4.10	4.48	8.01	0.90	11.24
PTM	27.36	31.70	33.38	21.54	18.75	34.81	12.15	2.18	7.97
PTM_H	28.60	31.57	38.99	22.78	16.89	29.02	15.40	4.05	7.76

Table 5-2: Standard deviation of the raw data of the leaching efficiency of monazite, PTM and its substituents with 32 % HCl at 80 °C for 1 h with no agitation as percentage

	Ce	La	Nd	Y	Th	U	Ti	Zr	P
Mz	0.19	0.19	0.53	0.41	0.39	1.81	0.12	0.00	1.14
Crushed Mz	0.10	0.11	0.19	0.62	0.15	0.00	0.39	0.00	0.16
Heat Treated Mz	0.10	0.11	0.10	0.11	0.07	0.13	0.06	0.00	0.25
Inductive Mz	0.09	0.10	0.12	0.00	0.05	0.00	0.10	0.00	1.09
PTM_L	1.48	1.49	1.62	2.32	0.99	4.46	2.83	0.59	4.34
PTM	6.65	8.30	6.55	4.15	3.29	6.04	1.49	1.07	2.42
PTM_H	3.81	4.44	4.22	6.53	4.56	5.18	2.46	1.24	4.26

X-ray fluorescence analysis was completed on all PTM samples to determine the elemental compositional changes produced due to the plasma treatment. No statistical

elemental compositional changes were observed between monazite and 11 different samples of PTM (Table 5-3).

Table 5-3: X-Ray Fluorescence chemical analysis of the major elements of Monazite (Mz), PTM and PTM_H

%m/m	Ce	La	Nd	Y	Th	U	Ti	Zr	P
Mz	24.93	10.91	4.70	0.00	6.81	0.38	9.31	17.54	2.94
PTM	21.48	9.57	6.04	1.36	7.22	0.37	7.19	16.99	3.68
Std Dev	4.07	1.65	1.36	0.97	2.69	0.12	0.08	2.65	0.93

5.4 Concluding Remarks

This chapter determined that when monazite was properly treated in a plasma it produces a chemically reactive product of monazite called PTM which can be digested using a diluted mineral acid such as 32 % HCl at a low temperature. The results did not indicate what the crystal structure or chemical composition of PTM was but XRF analysis indicated that the elemental composition did not alter significantly.

6. Experimental evaluation of the leaching of monazite and plasma treated monazite

6.1 Introduction to the article

Monazite decomposes into a chemically reactive compound when treated with a plasma. It was established that ABF is ineffective in determining the chemical reactivity of PTM relative to monazite. For this reason an alternative method of leaching monazite and PTM was used to compare the reactivity of PTM compared to the original monazite. This article investigated the leachability of monazite and PTM using various mineral acids at various temperatures for various reaction times.

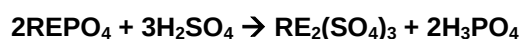
Before the chemical processing of monazite and PTM, the Gibbs free energy of the reaction between either the phosphates or oxides with the mineral acids or an alkali and thorium and uranium carbide with the mineral acids was studied. The hypothesis is that when monazite is decomposed in the presence of carbon, the rare earth oxides are formed. The aim of the theoretical analysis was to determine the merits of working with the rare earth oxides (Gupta and Krishnamurthy, 2005) and what the theoretical conversion of the leaching of these compounds could be as literature has indicated that the rare earth oxides and thorium- and uranium carbide can be dissolved in the mineral acids (Adachi et al., 2004; Peelman et al., 2014; Sears and Ferris, 1969). Using this information new potential processes for the extraction of the REE, thorium and uranium can be investigated and developed.

The article which follows is currently under review at the International Journal of Mineral processing, reports on the experimental results which have been obtained when monazite and PTM was leached with various mineral acids and an alkali.

6.2 Theoretical Study of Monazite and PTM

The following is a discussion on the theoretical digestion of monazite and PTM, with PTM presumed to be the rare earth oxide, with the various mineral acids and an alkali. Monazite is normally digested with 98 % H₂SO₄ at 230 °C or 60 % NaOH at 140 °C to produce the rare earth hydroxides. The rare earth hydroxides are subsequently leached with either aqueous HCl or HNO₃ at 80 °C.

The Gibbs Free Energy (GFE) of the reaction between the Rare Earth (RE) phosphates and H₂SO₄ (Equation 6-1) is presented for the temperature range 0 to 250 °C (Figure 6-1). The GFE of the reaction for Ce, La and Nd is negative, indicating that the phosphates readily convert to the sulphate, as anticipated and based on literature. The increase in the GFE as a function of temperature for Y does not coincide with literature as the GFE is positive above 130 °C where the digestion of monazite occurs. This suggest that a more complex reaction occurs which enables Y to be leached.



Equation 6-1

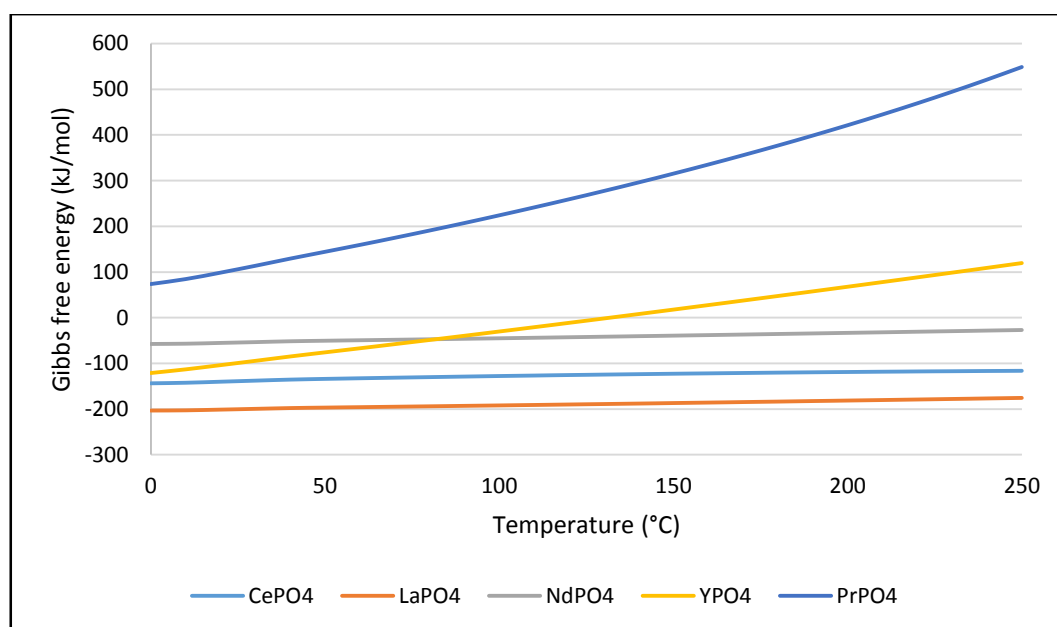
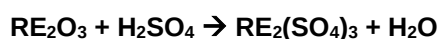


Figure 6-1: Gibbs free energy of the reaction between the rare earth phosphates and H₂SO₄ in the temperature range 0 to 250 °C

The GFE of the reaction between the rare earth oxides and H₂SO₄ (Equation 6-2) is more negative for all of the Rare Earth Element (REE) oxides including Pr and Y (Figure 6-2). This indicates that the conversion for all the rare earth oxides to the sulphate is possible when the rare earth phosphates are first converted to the rare earth oxides, as anticipated, in a plasma. The more negative Gibbs free energy indicates that the rare earth oxides are more stable at converting to the sulphates than the rare earth phosphates and are more likely to react. This theory is plausible, as the rare earth oxides can be leached using diluted mineral acids (Peelman et al., 2014).



Equation 6-2

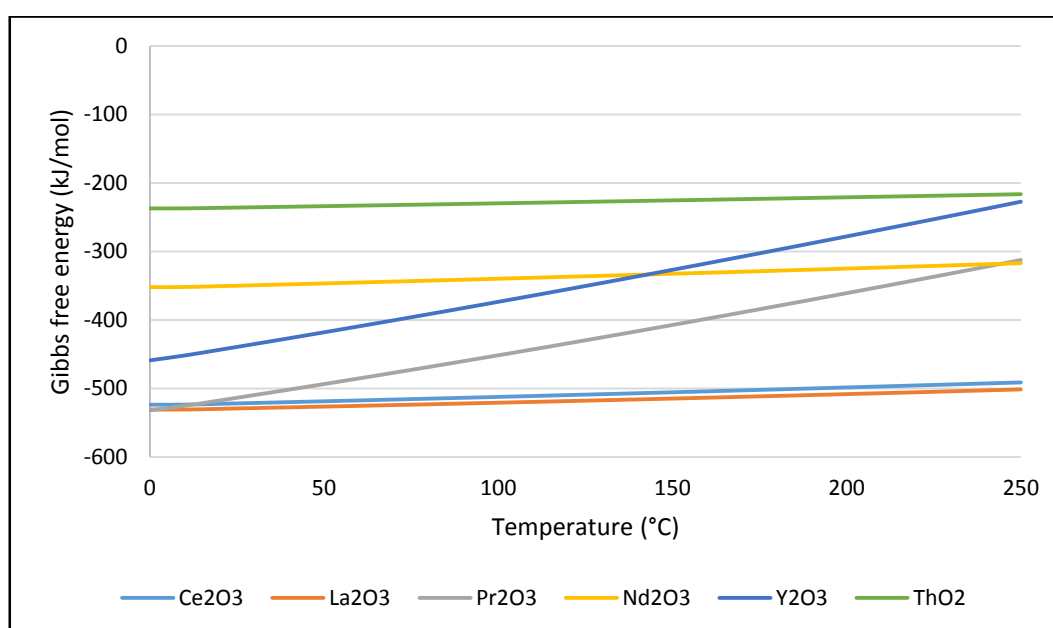


Figure 6-2: Gibbs free energy of the reaction between the rare earth oxides and H₂SO₄ in the temperature range 0 to 250 °C

The negative GFE of the digestion of ThO₂ with H₂SO₄ indicates that it may be possible to leach Th at a lower temperature. This is unlike the physical experiments at higher temperatures which convert thorium into thorium pyrophosphate, which cannot be treated with a mineral acid and is often disregarded as an economically unrecoverable radioactive and chemical waste. By leaching thorium oxide more readily with an aqueous mineral acid, an alternative process to leach thorium from monazite for downstream applications is presented.

Investigating this increase in reactivity, the GFE of the reaction (Equation 6-3) between aqueous sodium hydroxide and the Rare Earth (RE) phosphates (Figure 6-3) indicates

that CePO_4 , PrPO_4 and YPO_4 for the given reaction are unreactive, as the GFE is positive throughout the specified temperature range. LaPO_4 and NdPO_4 are the only Rare Earth Elements (REE) which convert to the hydroxide in the specified temperature range due to their negative GFE. This is in contrast to what is described in literature and indicates that a side reaction occurs. When the equilibrium composition was calculated no clear distinction could be made.



Equation 6-3

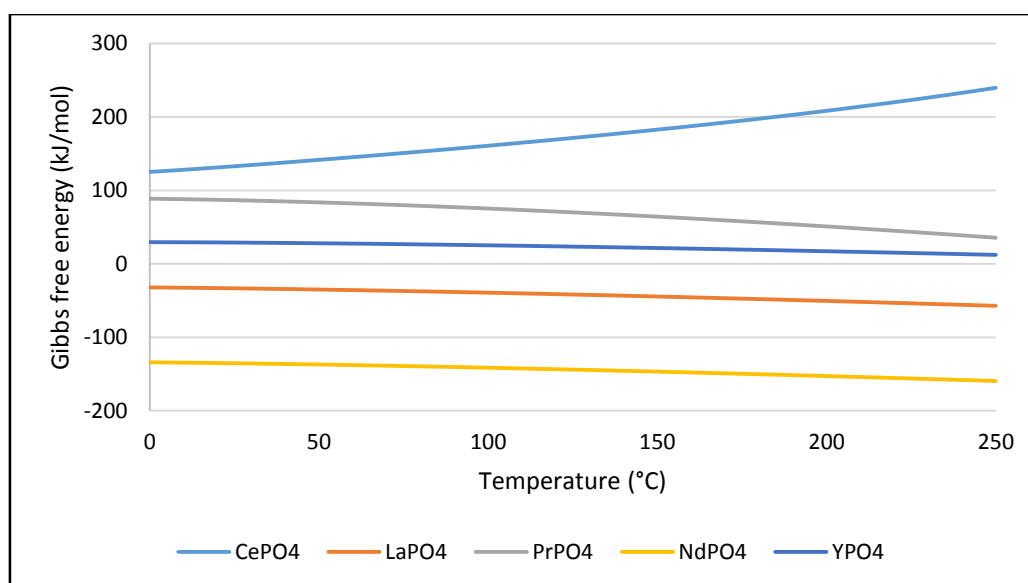
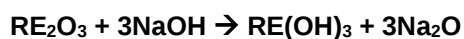


Figure 6-3: Gibbs free energy of the reaction between the rare earth phosphates and aqueous NaOH in the temperature range 0 to 150 °C

The alkaline digestion of the rare earth oxides, including ThO_2 , indicates that the specified reaction (Equation 6-4) is unlikely, as the GFE for each of the reactions over the specified temperature range are positive (Figure 6-4). These results indicate that if all of the monazite is converted to the oxide in the plasma then there would be no significant improvement in the extraction efficiency of PTM after it has been treated with NaOH.



Equation 6-4

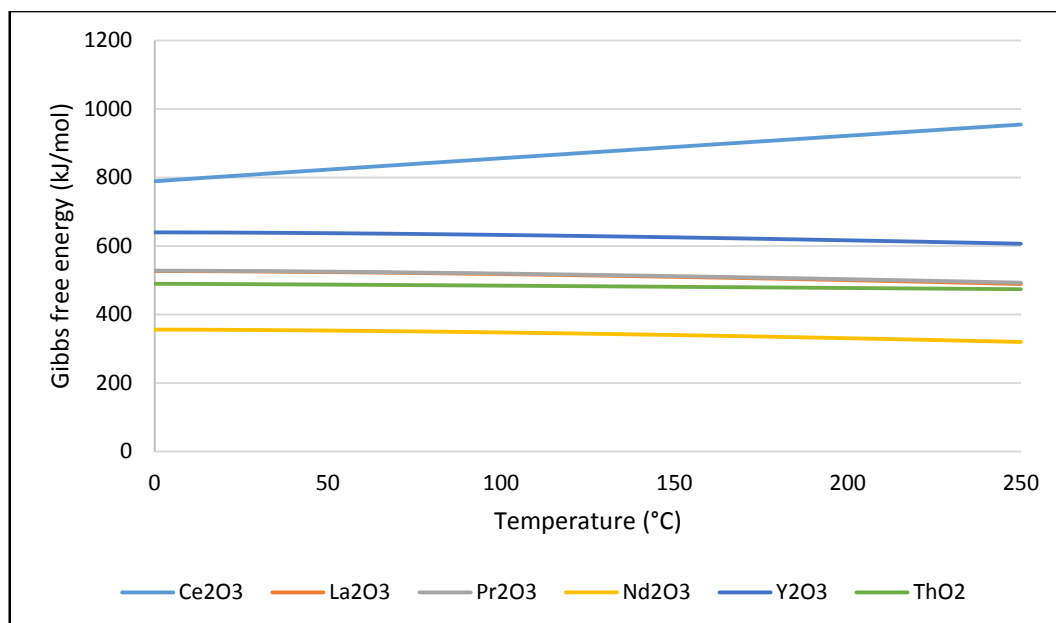
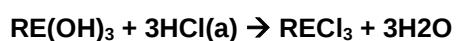


Figure 6-4: Gibbs free energy of the reaction between the rare earth oxides and aqueous NaOH in the temperature range 0 to 150 °C

The products produced when monazite is digested with NaOH are the insoluble rare earth hydroxides and thorium hydroxide. These compounds are digested with mineral acids, like 32 % HCl and 65 % HNO₃, which converts them into the water soluble chloride or nitrate compounds. This is required to facilitate downstream separation of the REE using solvent extraction (Calkins, 1957; Gupta and Krishnamurthy, 2005). Leaching of the rare earth hydroxides are accomplished by digesting the hydroxides with mineral acids at 80 °C for 1 h (Zhu et al., 2015) although the original patent has stated at 90 to 110 °C for 1½ h (Calkins, 1957). Thorium is separated from the rare earths in this process through precipitation of insoluble thorium hydroxide (Calkins, 1957; Hurst, 2010; Zhu et al., 2015).

The thermodynamic evaluation of this reaction commences with the GFE of the conversion of the rare earth hydroxides using aqueous HCl (Equation 6-5). HNO₃ is not available in HSC and had to be excluded for this portion of the study. The GFE of the reaction between aqueous HCl and the rare earth hydroxides confirms that Ce, La and Pr are converted to the chloride, however both Nd and Y require higher temperatures. Thorium remains behind as Th(OH)₃ (Figure 6-5). These results concur with literature.



Equation 6-5

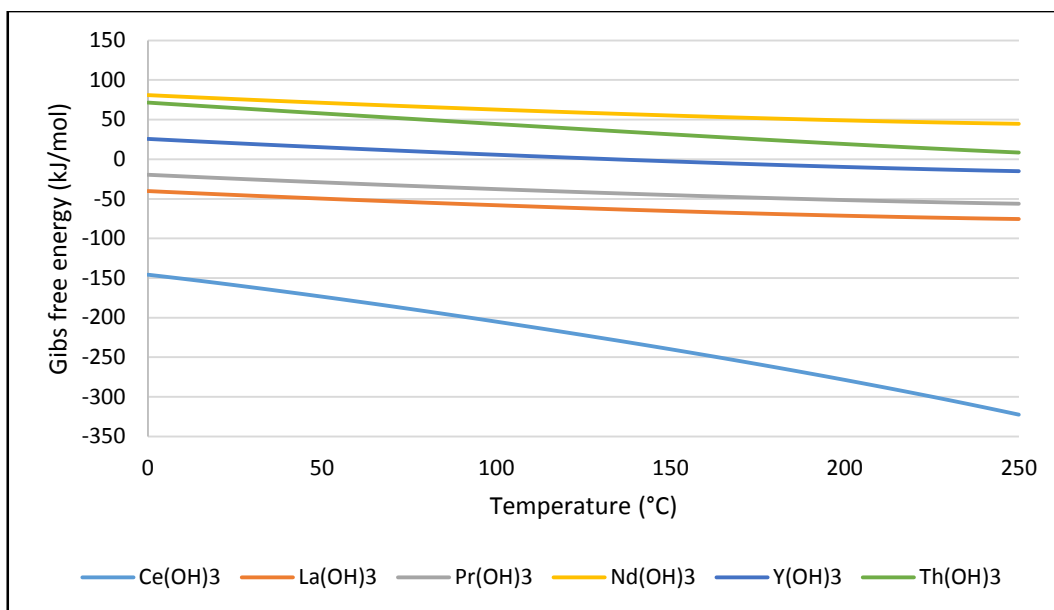
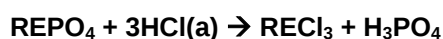


Figure 6-5: Gibbs free energy of the reaction between the rare earth hydroxides and aqueous HCl in the temperature range 0 to 100 °C

According to the Gibbs Free Energy (GFE), the direct digestion of the rare earth phosphates and aqueous HCl (Equation 6-6) is not possible as the GFE is positive over the entire temperature range (Figure 6-6) and indicates why no literature could be found on the direct digestion of monazite with HCl.



Equation 6-6

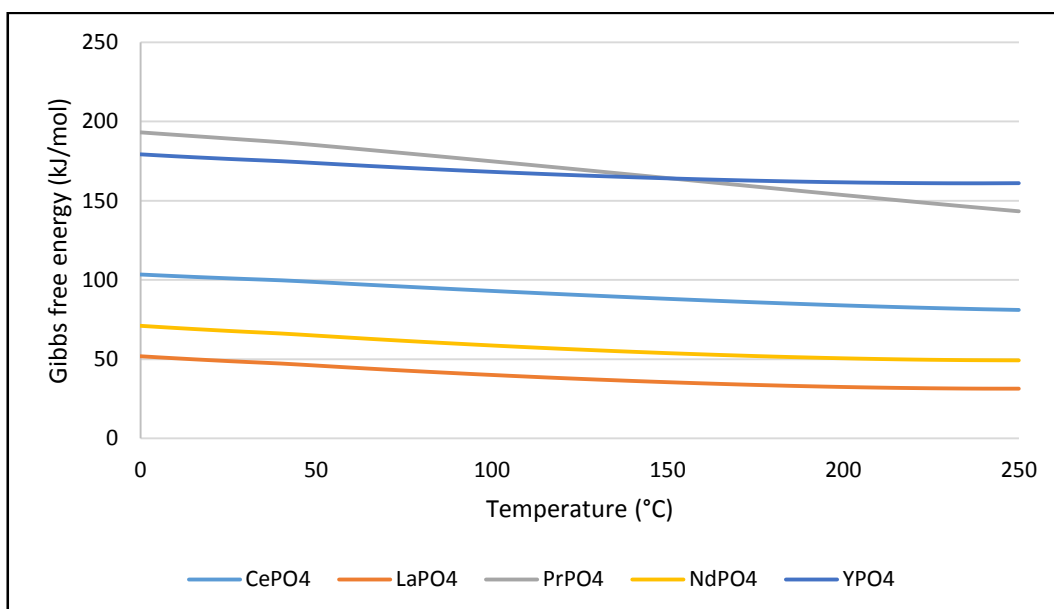
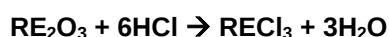


Figure 6-6: Gibbs free energy of the reaction between the rare earth phosphates and aqueous HCl in the temperature range 0 to 110 °C

The advantage of producing PTM as a rare earth oxide is that it can be leached with HCl (Equation 6-7) as the GFE of the reaction between the rare earth oxides and aqueous HCl show (Figure 6-7). This confirms, at least theoretically that the rare earth oxides, except for yttrium, convert fully to the rare earth chlorides at a low temperature. ThO₂, similar to the hydroxide reactions, remains behind as an insoluble compound. For the purpose of separating thorium from the REE, the use of HCl can accomplish this as the thorium will remain behind as an insoluble compound which can be processed downstream. If the plasma treatment of monazite, as theoretically predicted, produces the rare earth oxides, then from a theoretical observation the plasma product, PTM, would be chemically more reactive.



Equation 6-7

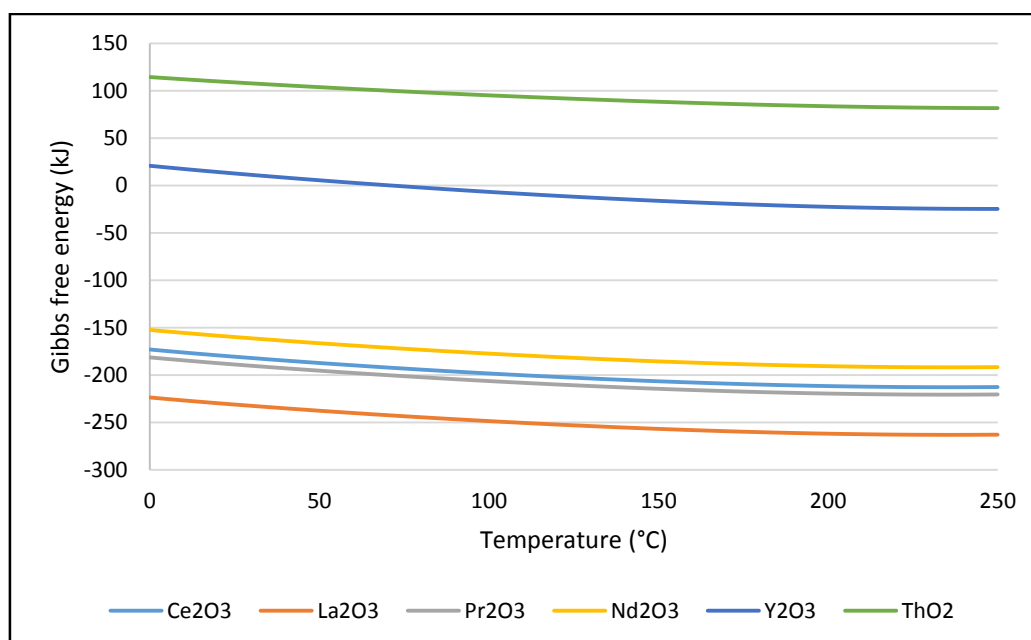


Figure 6-7: Gibbs free energy of the reaction between the rare earth oxides and aqueous HCl in the temperature range 0 to 110 °C

In order to leach thorium and uranium, it needs to be converted into a compound which can be leached at low temperature with a mineral acid. Thorium and uranium carbide can be leached with a diluted mineral acid including HCl and H₂SO₄ (Sears and Ferris, 1969) as confirmed by the Gibbs free energy of ThC and UC with HCl (Figure 6-8) and ThC and UC with H₂SO₄ (Figure 6-9) at low temperature. The digestion of monazite in the presence of carbon at high temperatures is also more effective for uranium and

thorium (Lundgren, 2014; Prescott and Hincke, 1927). From a nuclear vendor perspective, an opportunity to extract thorium, which can be used as an alternative fuel, or uranium as a by-product can now be exploited further.

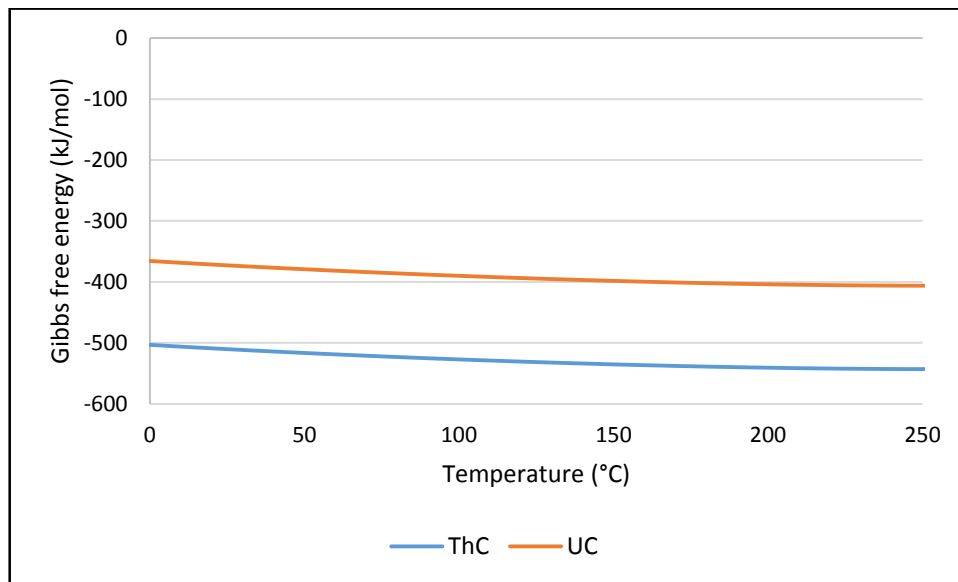


Figure 6-8: Gibbs free energy of the reaction between thorium carbide and uranium carbide with HCl

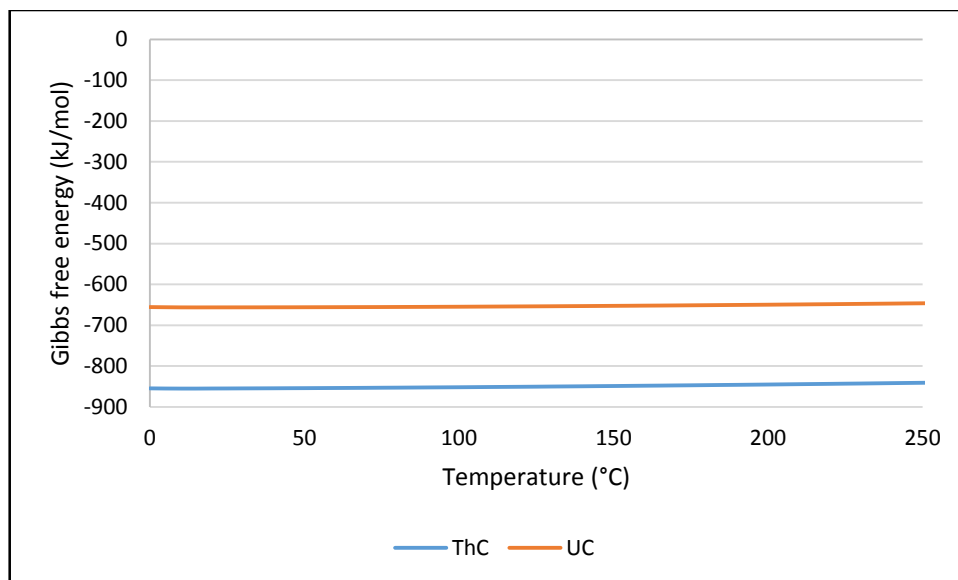


Figure 6-9: Gibbs free energy of the reaction between thorium carbide and uranium carbide with H₂SO₄

6.3 Article: Experimental evaluation of the leaching of monazite and plasma treated monazite

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Keywords: Monazite, plasma, rare earth oxide, thorium, diluted, H₂SO₄ digestion

Abstract

Chemical experiments on monazite and PTM were conducted using different mineral acids at various temperatures and reaction times. Literature on the leaching of the rare earth phosphates and oxides with the mineral acids indicated that the rare earth oxides are more easily leached with diluted mineral acids and can attain higher equilibrium conversions. Leaching of monazite and PTM established that PTM is chemically more reactive than monazite. Using the conventional digestion processes on PTM leached higher quantities of the REE, however the same chemical and radioactive waste would still be present. The direct digestion of PTM with 32 % HCl at 80 °C for 1 h extracted the highest quantities of the REE, thorium and uranium compared to the other aqueous mineral acids and also higher quantities than the conventional digestion process for monazite.

1. Introduction

Monazite contains the light rare earth elements (REE) Ce, La, Pr, Nd and Y and the radioactive element thorium and uranium (Hassan et al., 1997; Kim et al., 2009). The problem is the highly inert nature of the monazite crystal matrix (El-Nadi, 2007) which requires aggressive chemicals and techniques to process (Ball, 1927; Xie et al., 2014). The by-products of these reactions leave large quantities of chemical and radioactive waste behind, like thorium, in an economically unrecoverable form (Zhu et al., 2015). The two most common processes in use for monazite digestion is the sulphuric acid process, which operates at 230 °C for 4 h, and the sodium hydroxide process, which operates at 140 °C for 3 h (Calkins, 1957; Gupta and Krishnamurthy, 2005; Kim and Osseo-Asare, 2012; Welt and Smutz, 1958).

In the H₂SO₄ process, monazite is digested in 98 % H₂SO₄ for 3 to 4 h to transform the rare earth compounds into the rare earth sulphates. The resulting liquid is sent to a solvent extraction plant which separates the individual rare earth compounds (Gupta and Krishnamurthy, 2005). The disadvantage of the H₂SO₄ digestion of monazite are the high cost of the process, the quantities of chemical and radioactive waste produced and the formation of sulphur dioxide. An additional problem is the formation of thorium pyrophosphate (ThP₂O₇) which is insoluble even in a strong mineral acid solution. It is considered economically unrecoverable and is potentially an economic loss as thorium can be used as nuclear fuel in a nuclear reactor (Xie et al., 2014; Zhu et al., 2015).

The alkaline process is currently the preferred process as it removes the phosphorus during leaching and regenerates the alkaline to produce the by-product sodium phosphate (Kim et al., 2009). Alkaline processing is when monazite is heated to 140 - 150 °C with a 60 - 70 % NaOH solution (Cardarelli, 2008; Taylor, n.d.). During decomposition, the strong alkali is transformed into rare earth hydroxides (REOH), which can be dissolved in a mineral acid after removal from a supernatant solution of alkaline phosphates while leaving behind thorium as a Th(OH)₄ precipitate (Taylor, n.d.). The mineral acid digestion utilizes either HCl or HNO₃, for 1 h between 80 and 110 °C (Gupta and Krishnamurthy, 2005). A major advantage of the alkaline process is the removal of the phosphates as Na₃PO₄, as the Rare Earth Metals (REM)

are highly sensitive to the concentration of phosphor downstream in the alloying phase and must be maintained at a minimum. If the phosphor concentration is deemed to be too high, a reaction between the phosphor and REE pulverises the rare earth alloy (Xing et al., 2010). The alkali method is considered to be cleaner than the acid route but intermittent. The two-step solid-liquid reaction, followed by washing, makes the process unfavourable for mass production as it requires precise control of the pressure, temperature and pH (Kim et al., 2009).

A new process presented in this study attempts to find a cleaner, more economical process to beneficiate monazite. The new process first utilizes a high temperature thermal plasma to treat monazite to produce Plasma Treated Monazite (PTM), which is potentially a more reactive form of monazite. The production of the rare earth oxides, thorium and uranium carbide are desired as it can be leached using diluted mineral acids (Adachi et al., 2004; Peelman et al., 2014; Sears and Ferris, 1969). The problem is that PTM has not been produced before nor has its chemical reactivity been evaluated. The purpose of this article is to evaluate the leaching capability of PTM relative to monazite, using various mineral acids and an alkali including a comparison of the conventional digestion methods using H_2SO_4 and NaOH .

The extraction of thorium is viewed as a product rather than a waste as the majority of rare earth producers regard thorium as radioactive waste whereas most advanced nuclear reactor vendors view it as a potential nuclear fuel. The problem with simply viewing thorium as a waste is that, similar to the H_2SO_4 and NaOH processes, it can be produced in an economically unrecoverable form which is difficult to work with downstream (Zhu et al., 2015). This study promotes the conversion of thorium into a water soluble product which can be converted downstream into thorium oxide. Thorium oxide, unlike the other radioactive waste streams can be disposed of as either a radioactive waste or shipped to a nuclear vendor as nuclear fuel which could potentially lead to a future income stream (Kok, 2009).

2. Materials and Methods

Monazite was obtained from an external source. The PTM is produced using a DC direct arc plasma in a crucible which was subsequently placed in an alumina crucible

for 24 h at 650 °C to drive off the excess carbon due to contamination of the destruction of the graphite crucible during plasma treatment. The 98 % H₂SO₄, 99 % NaOH pellets, 32 % HCl and 65 % HNO₃ were obtained from Merck. Monazite (Mz) and PTM are the starting materials of all the experiments.. Additional experiments using mineral acids are completed in addition to these experiments to evaluate the increased chemical reactivity. All samples were not agitated during the reaction. After all experiments, the samples were transferred to individual falcon tubes and sent for ICP analysis. The unreacted residue was cleaned with demineralised water and dried.

The conventional digestion of the starting materials using 98 % H₂SO₄ and NaOH is based on the procedures obtained in literature (Calkins, 1957; Welt and Smutz, 1958). For the H₂SO₄ digestion, 0.2 g of the starting material was placed in a round bottom flask on a heating mantle with 20 ml of 98 % H₂SO₄. The sample was heated to boiling point (230 °C) for 2 - 4 h. The flask was attached to a water cooled condenser.

Concentrated (60 %) and diluted (10 %) NaOH solutions were produced. For the conventional NaOH digestion, 0.1 g of the starting material was placed in a PFA vessel with 10 ml of 60 % (concentrated) NaOH solution. The vessel was placed in a preheated temperature controlled oven at 140 °C for 3 h with no agitation. Upon completion of the first stage the sample was cooled at room temperature and decanted. The solid residue was washed at least three times with demineralised water. Subsequent to the washing, 10 ml 65 % HNO₃ or 32 % HCl was added. The vessel was placed in a preheated temperature controlled oven at 80 °C for 1 h with no agitation.

For the diluted (10 %) NaOH digestion, 0.1 g of the starting material was placed in a borosilicate polytop with 10 ml of a 10 % NaOH solution. The polytop was placed in a preheated oven at 80 °C for 1 h with no agitation. The alkaline solution was decanted and the solid residue was washed at least three times using demineralised water. Subsequent to the washing, 10 ml of 32 % HCl was added and placed in a preheated oven at 80 °C for 1 h with no agitation.

For all other remaining experiments with the mineral acids, 0.1 g of the selected starting material was placed in a borosilicate polytop. A 10 ml sample of the mineral acid (98 % or 10 % H₂SO₄, 32 % HCl or 65 % HNO₃) was placed in the polytop. The

polytop was placed in a preheated temperature controlled oven at 80 °C for 1 h with no agitation of the reaction mixture.

3. Results and Discussion

The objectives of the chemical evaluation of Plasma Treated Monazite (PTM) is to determine whether PTM is more reactive than monazite, determining a possible reason for the improvement, propose methods in optimizing the reactivity and establish whether an easier, more economical process to process monazite can be developed. To achieve these objectives monazite (Mz) and PTM were treated using various chemical processes including the standard procedures for treating monazite.

Monazite and PTM were the starting materials for all the experiments. The results were compiled from more than 500 chemical tests, which included numerous replications. The results present the quantity of the specific element extracted, as a percentage of the original amount of the specific element in the starting material. These percentage extraction efficiencies were subsequently compared between the various starting materials and processes. The rare earth element Pr is excluded as it was below the detection limits and could not be verified with confidence. The standard deviation in all graphs are presented as error bars.

Monazite is usually processed using 98 % H_2SO_4 at 230 °C for 3 to 4 h or, alternatively, using a 60 to 70 % NaOH solution for 3 to 4 h at 140 °C, followed by digestion with HCl or HNO_3 at 80 °C for 1 h (Gupta and Krishnamurthy, 2005). The leaching of both monazite and PTM were conducted using concentrated (98%) H_2SO_4 at 230 °C for 2 – 4 h per the standard digestion of monazite. The extraction efficiency of phosphor is excluded as the H_2SO_4 was contaminated with excess phosphor. The starting materials were digested for 4 h at 230 °C using the method described for H_2SO_4 digestion of monazite as described in literature (Calkins, 1957). PTM was treated in the same solution for 2 and 4 h to determine if the digestion time of PTM can be reduced.

The results from the experiment indicated that the digestion of PTM reached equilibrium, with only 5 % more material extracted, faster than monazite. A higher extraction for Ce and La was obtained from PTM. However, higher quantities of Nd, Y

and U were extracted from monazite (36.85 %) as the highest quantity of material extracted from PTM was 33.97 % (Figure 6-10). A definitive conclusion could not be made on whether PTM is more reactive as the results do not support this notion. For this reason additional experiments were required before it could be determined whether PTM is more reactive than monazite.

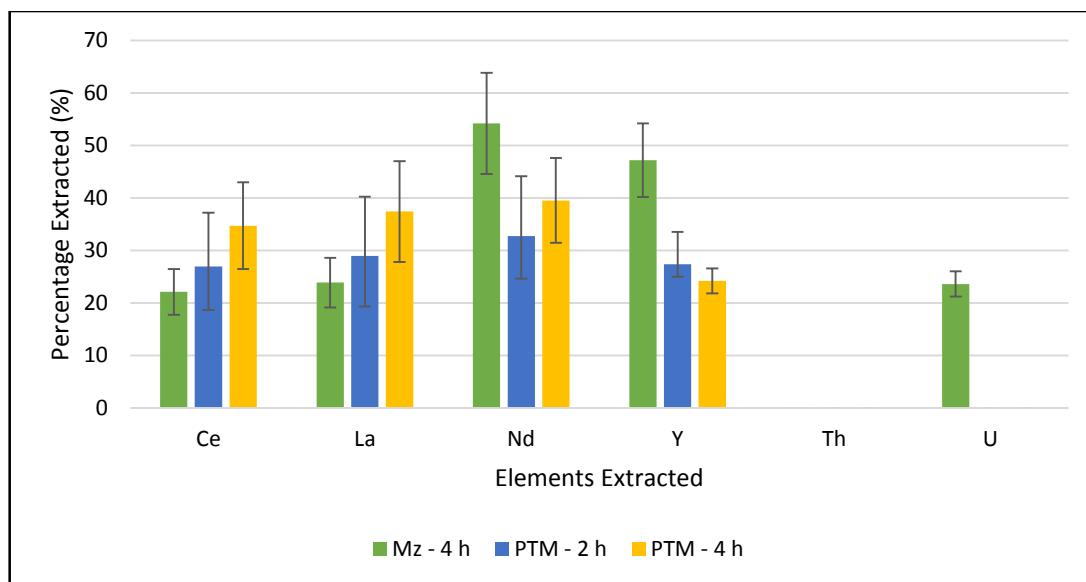


Figure 6-10: Elements extracted from monazite and PTM with 98 % H₂SO₄ at 230 °C for 4 h and PTM for 2 h

The extraction of thorium was consistently below detection limits for all high temperature experiments. The loss of thorium could be due to the formation of thorium pyrophosphate, an economically unrecoverable form of thorium which is insoluble in water or the formation of some other insoluble thorium compound (Zhu et al., 2015). For this reason, the high temperature process with H₂SO₄ should be avoided to extract thorium to be processed downstream for later conversion to thorium oxide. The higher than anticipated Nd and Y extraction from monazite is consistent for all high temperature H₂SO₄ reactions. This is presumed to either be an inherent advantage to the monazite, which the PTM loses during the plasma treatment, or due to an experimental error. This phenomenon will be investigated in future research and is beyond the scope of this study.

The alternative digestion process of treating monazite is to use a 60 to 70 % NaOH solution at 140 °C for 3 h, whereby the REE are converted to the water insoluble rare

earth hydroxides. Subsequently the rare earth hydroxides are leached with HCl or HNO₃ at 80 °C for 1 h to produce a water soluble compound which can be separated using solvent extraction (Gupta and Krishnamurthy, 2005). Phosphor is not present in the results as it is removed when the monazite or PTM is digested with NaOH. Monazite and PTM are digested in a 60 % NaOH solution at 140 °C for 3 h. PTM is also digested for 1½ h to evaluate whether the digestion time of PTM can be reduced. The samples are subsequently treated with 32 % HCl or 65 % HNO₃ at 80 °C for 1 h.

The results indicate that the REE are leached more effectively from PTM than monazite (16.99 %) with double the quantity of REE extracted (33.60 %). The extraction efficiency between digesting the sample for 1½ h or 3 h delivered only a 1.7 % increase in the extraction efficiency (Figure 6-11). Thorium and uranium were extracted more efficiently when PTM was digested for 3 h at 140 °C with 31.13 % more thorium and 66.91 % more uranium extracted.

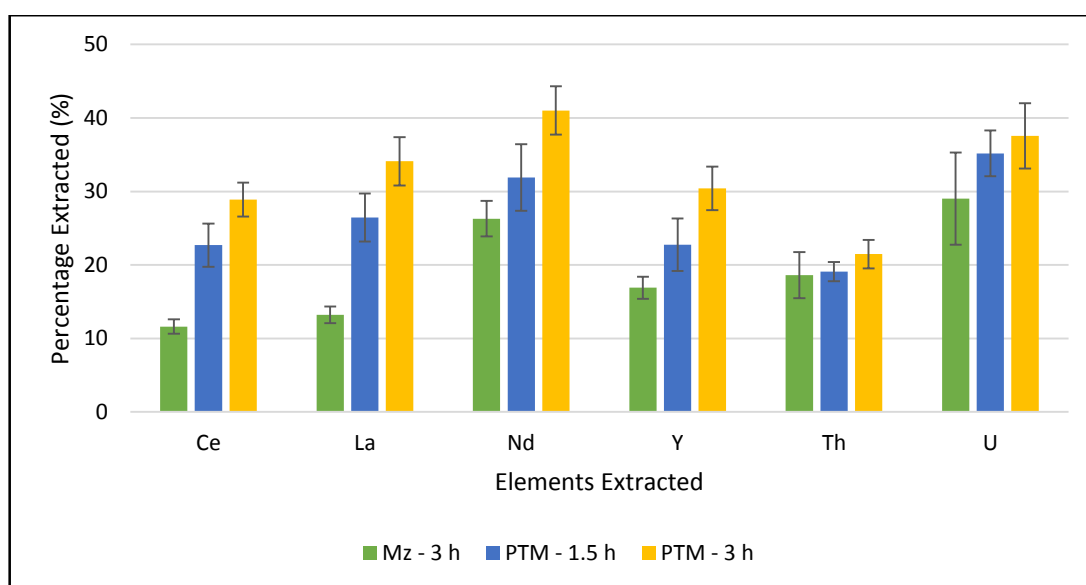


Figure 6-11: Elements extracted from monazite and PTM using 60 % NaOH digestion of monazite and PTM for 1½ and 3 hours at 140 °C followed by 32 % HCl digestion for 1 h at 80 °C

The conventional digestion of monazite using the alkaline digestion process alternatively use HNO₃ to digest the hydroxides. Samples of the monazite and PTM which were digested using the conventional process were treated with 65 % HNO₃

rather than HCl at 80 °C for 1 h. The results indicates that, similar to HCl, equilibrium is reached after 1½ h. The HNO₃ had an increase in REE extraction of 51 % over monazite using the same reaction process. The biggest difference is that 55.71 % of the total Nd is extracted. Lower thorium and uranium levels were obtained with thorium increasing by 18.36 % and uranium by 11.87 % (Figure 6-12). The extraction results obtained by the alkaline digestion of monazite followed by HCl or HNO₃ digestion showed a significant increase in chemical reactivity.

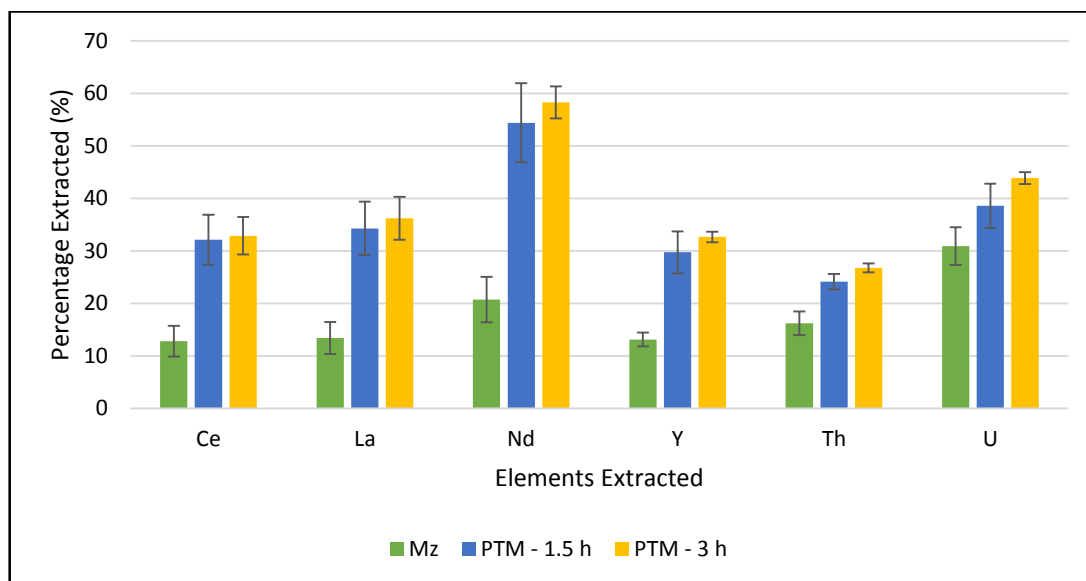


Figure 6-12: Elements extracted from monazite and PTM using 60 % NaOH digestion of monazite and PTM for 1½ and 3 h at 140 °C followed by 32 % HNO₃ digestion for 1 h at 80 °C

The increased reactivity of PTM was investigated further by digesting it directly with 32 % HCl or 65 % HNO₃. The experimental digestion of the starting materials with 32 % HCl at 80 °C for 1 h with no agitation indicates an increase in chemical reactivity with an average REE extraction of 1.57 % for monazite while an average REE extraction of 33.06 % was attained for PTM (Figure 6-13). This represents a 21 fold increase in REE extraction using low temperatures with a shorter reaction time than the conventional monazite process. The thorium and uranium extraction efficiencies also improve as for thorium, 2.42 % was extracted from monazite compared to 16.89 % for PTM while uranium had an extraction efficiency of 2.99 % from monazite and 29.02 % from PTM. The phosphor content remained relatively constant throughout.

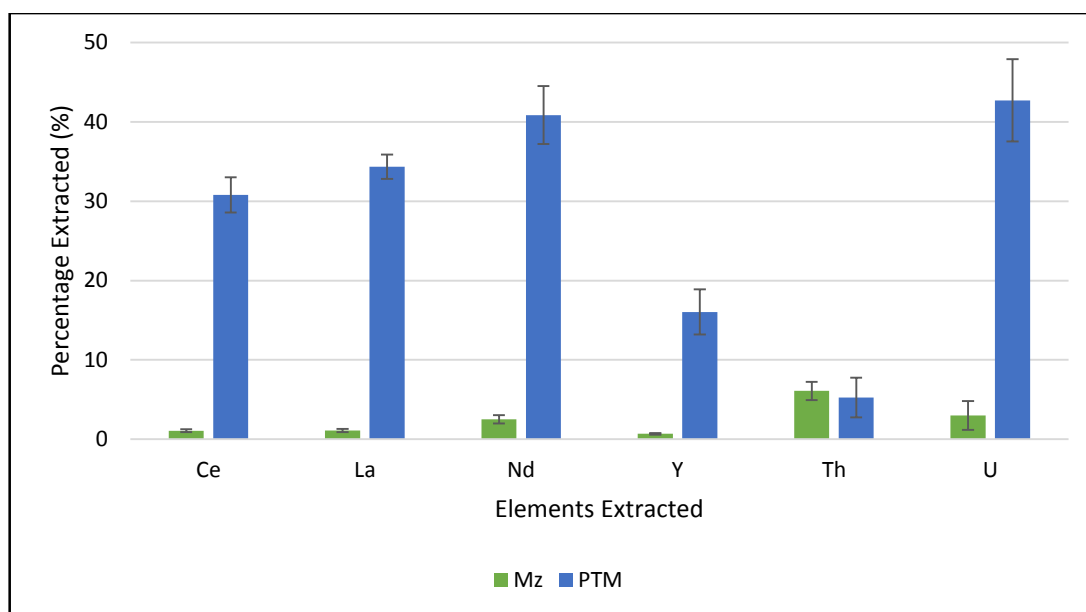


Figure 6-13: Elements extracted from monazite and PTM using HCl at 80 °C for 1 h

The results indicated that incomplete extraction of the REE was achieved. When the rare earth oxides are leached using a mineral acid all of the material are dissolved readily (Adachi et al., 2004). When PTM is treated using the same process only a portion of the PTM is dissolved as not all of the monazite was fully decomposed into PTM during the plasma process.

When the starting materials were digested with 65 % HNO_3 for 1 h at 80 °C (Figure 6-14), the analysis indicated that the digestion of PTM with HNO_3 is not as effective in extracting the REE, Th and U compared to HCl. An increase in the quantities of the REE extracted was obtained when comparing monazite (2.25 %) to PTM (26.02 %). The low increment is similar to when HNO_3 was used after monazite and PTM was digested using NaOH. The phosphor content, similarly to HCl, remains relatively constant. The uranium extraction efficiencies improve with the treatment of monazite as uranium has an extraction efficiency of 2.99 % from monazite and 16.50 % from PTM. Thorium, however, shows no major advantage in the extraction efficiency between monazite and PTM.

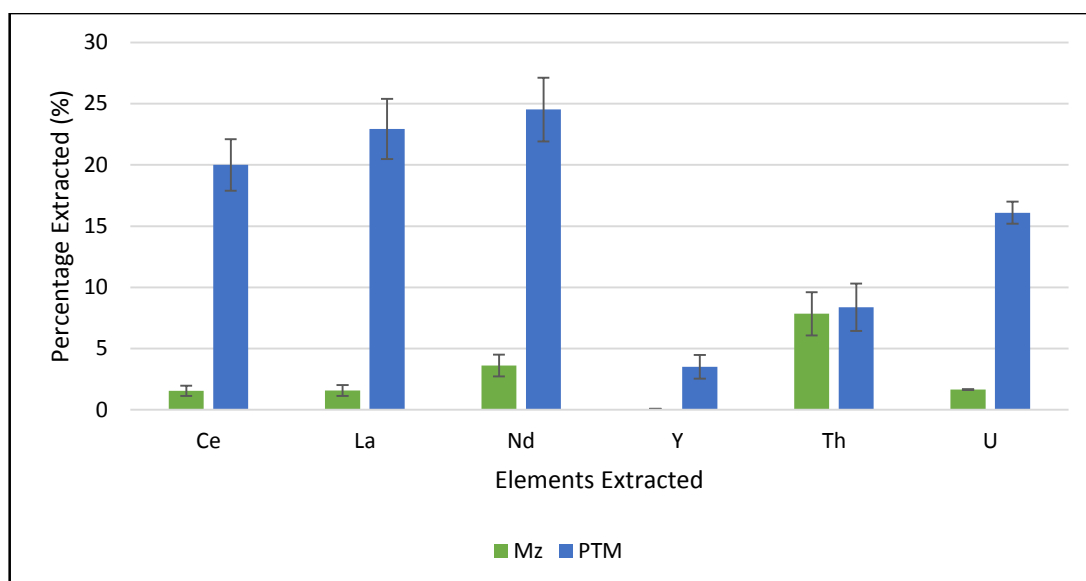


Figure 6-14: Elements extracted from monazite and PTM using 65 % HNO₃ at 80 °C for 1 h

The difference between a concentrated versus a dilute acid on the leaching and extraction of the REE from monazite and PTM was evaluated. The leaching of the starting materials with 98 % H₂SO₄ at 80 °C for 1 h was conducted initially. The analysis indicated a very low extraction efficiency of 0.44 % from monazite and 1.35 % from PTM with thorium below the detection limit (Figure 6-15). Uranium, in contrast, has a higher extraction efficiency than the REE. For this reason it is recommended that all mineral acid leaching of PTM be conducted in the diluted aqueous phase.

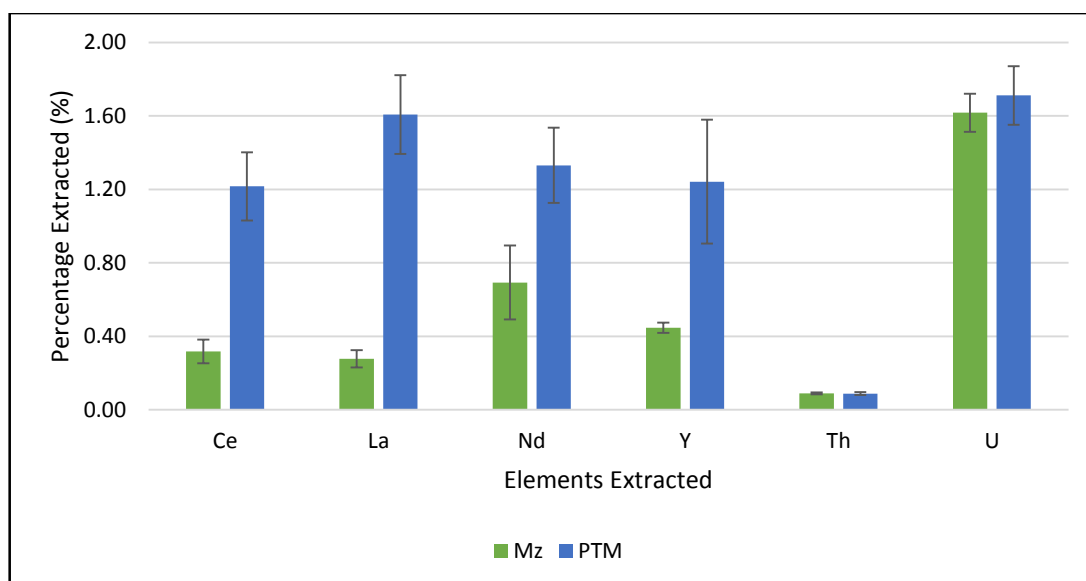


Figure 6-15: Elements extracted from monazite and PTM using 98 % H₂SO₄ at 80 °C for 1 h

When the concentrated acid was diluted to 10 % H₂SO₄ and reacted with the starting materials at 80 °C for 1 h, the results indicate that the use of a dilute mineral acid is superior to the use of a more concentrated acid at low temperature. The average extraction efficiency using dilute H₂SO₄ was below detection limits for monazite whereas for PTM 24.75 % of the REE, 10.76 % for thorium and 3.31 % for uranium were extracted (Figure 6-16). Thorium is extracted more effectively with dilute H₂SO₄ rather than concentrated H₂SO₄. The diluted H₂SO₄ does not have a significant increase in the uranium extracted as both values were below the detection limits. This increased reactivity from the diluted mineral acid is not uncommon, as diluted mineral acids are known to be more corrosive than their concentrated counterparts (Craig and Anderson, 1994).

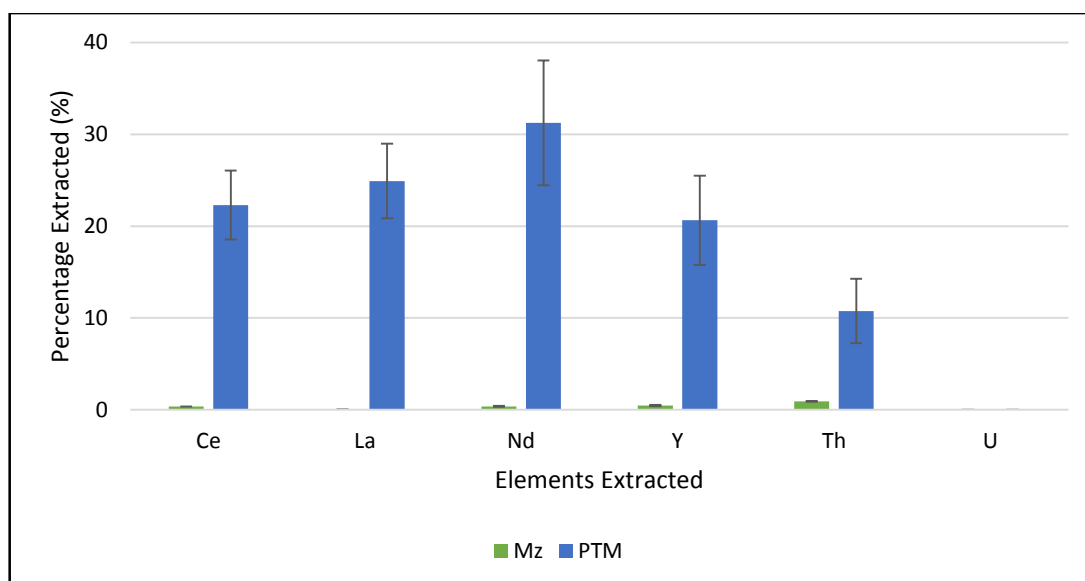


Figure 6-16: Elements extracted from monazite and PTM using 10 % H₂SO₄ at 80 °C for 1 h

The use of a diluted acid at low temperature rather than concentrated acid at a high temperature is both an advantage and a disadvantage. The advantage lies in the use of cheaper materials of construction, like glass or plastic which operates at low temperatures and the process parameters which are easier to manage. However a dilute acid can be more corrosive than a concentrated solution, would require a larger volume of material for the same number of moles to be reacted, would increase the size of the equipment, construction costs and the plants physical footprint.

When PTM was digested an improvement in the extraction efficiencies were obtained when 98 % H₂SO₄ (concentrated) was substituted for 10 % (diluted) H₂SO₄ at 80 °C for 1 h. Digestion of monazite and PTM with 10 % NaOH at 80 °C for 1 h to establish whether, as with H₂SO₄, the process is more efficient at extracting the REE and thorium at low temperature using a more diluted reagent. The digestion of monazite and PTM with 10 % NaOH is compared with the results of the conventional digestion of monazite with 60 % NaOH at 140 °C for 3 h. Both samples were subsequently digested with 32 % HCl at 80 °C for 1 h.

The results indicated that the diluted NaOH digestion of PTM is better than when monazite is digested using the conventional process (Figure 6-17) but not as efficient as when the conventional digestion process is used on PTM. This indicates that a

more diluted sample of NaOH does not deliver improved extraction of the REE, thorium and uranium unlike what was presented with H₂SO₄.

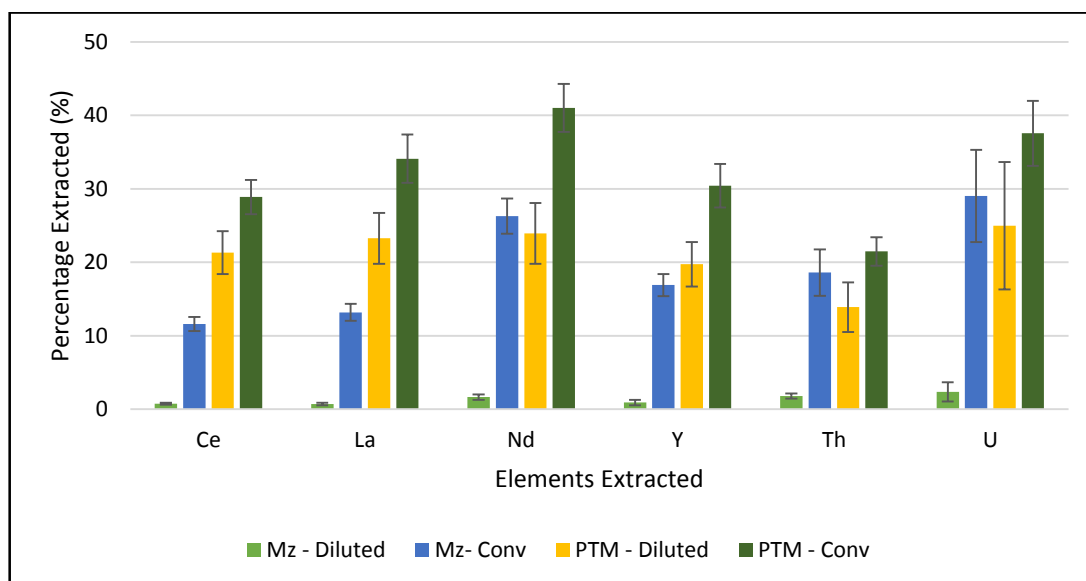


Figure 6-17: Elements extracted from monazite and PTM using 10 % NaOH digestion of monazite and PTM for 1 h at 80 °C followed by HCl digestion for 1 h at 80 °C

In order to determine which process has the best extraction potential, all of the digestion processes evaluated in this study were compared (Figure 6-18 and Figure 6-19). Comparing the extraction efficiencies of the rare earths, thorium and uranium between the various concentrations and reaction temperatures, it was determined that the conventional digestion process is the optimum for maximum rare earth and uranium extraction for both monazite and PTM. This higher level of extraction is not surprising as the reaction occurs over a longer reaction period and at higher temperatures. In contrast the diluted mineral acids, specifically HCl, extract a significant quantity of the REE which compares well with the conventional NaOH digestion process on monazite.

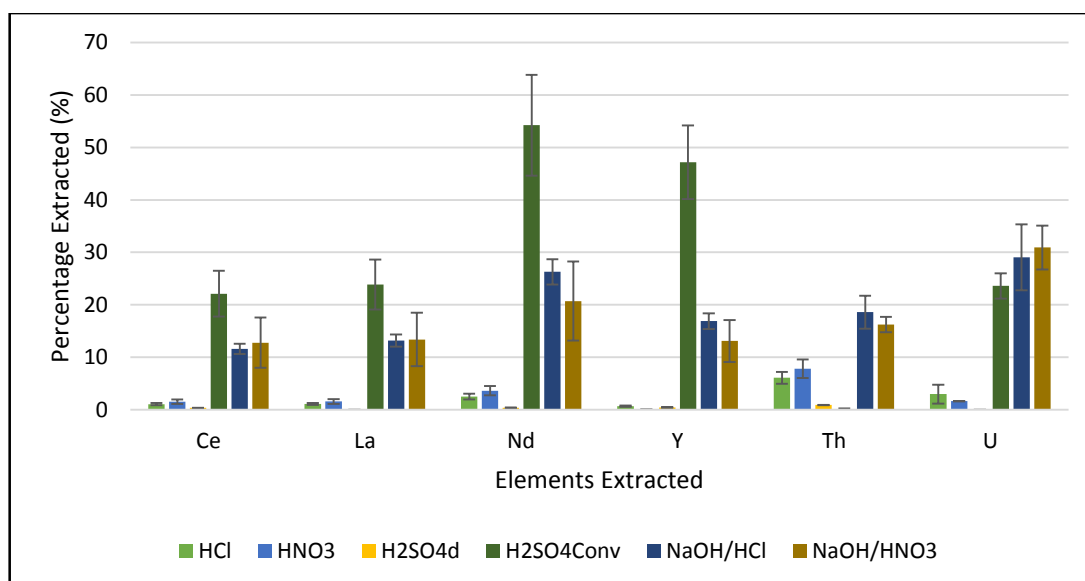


Figure 6-18: Digestion of monazite with various reagents

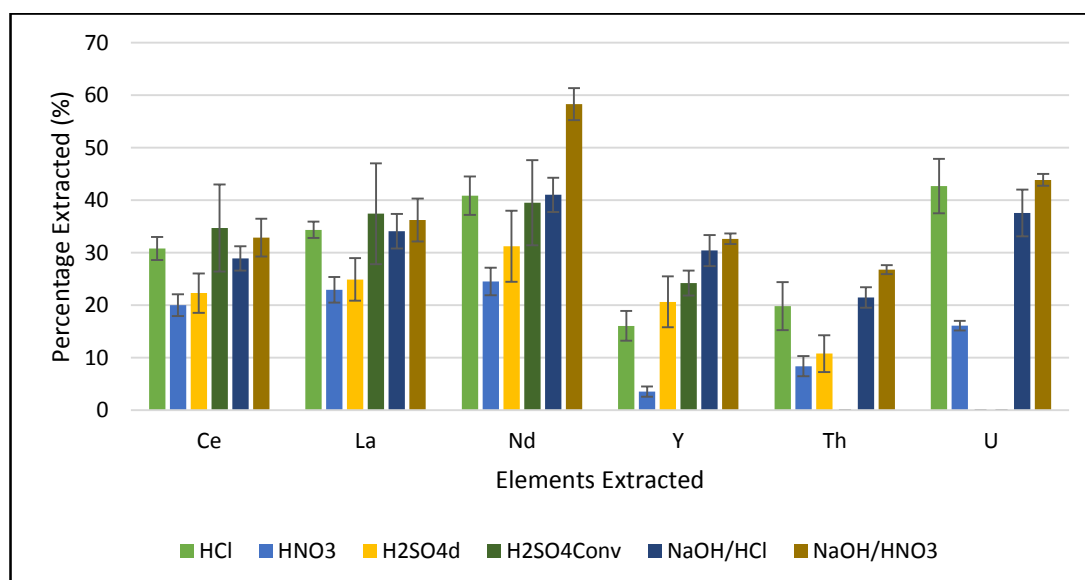


Figure 6-19: Digestion of PTM with various reagents

The digestion of PTM using dilute acids at low temperatures would have a significant impact on the methodology of separating the REE and thorium as various other combinations of diluted or alternative mineral acids can be evaluated in order to optimize the downstream separation of the REE. The simpler diluted mineral digestion indicated, on average, with the exception of Nd and Y, higher extraction efficiencies of the REE, thorium and uranium than the conventional monazite processes. It is suggested that using a different type of plasma in order to convert more of the

phosphates in the monazite structure to oxides, higher extraction efficiencies could be obtained.

4. Conclusion

This research focussed on the digestion of monazite and PTM using a variety of mineral acids and alkaline solutions at various temperatures and reaction times in order to establish whether PTM is a more reactive form of monazite. Monazite and PTM were initially digested with 98 % H_2SO_4 at 230 °C for 2 to 4 h. The results indicated that while certain portions of PTM was more reactive, particularly for Ce and La, monazite was more reactive for the extraction of Nd, Y and U. Thorium extract could not be detected as it was below detection limits.

The digestion of monazite and PTM using the conventional NaOH digestion process followed by HCl or HNO_3 digestion clearly indicated the increased reactivity of PTM over monazite as, for HCl, double the quantity of the REE were extracted along with 31.13 % more thorium and 66.91 % more uranium. When HNO_3 was used rather than HCl a 51 % increase in REE extraction was observed, with 54.42 % of the total Nd extracted, as well as 18.36 % more Th and 11.87 % U.

The development of a simpler process using aqueous mineral acids at 80 °C for 1 h indicated a significant increase in the reactivity between monazite and PTM as a 21 fold increase in REE extraction was obtained when PTM was extracted using 32 % HCl. The quantity of material extracted using this process at present is on par to the conventional digestion of monazite and can be considered as a viable extraction method using current rudimentary chemical methods. Using more sophisticated methods have the potential to increase the dissociation percentage of the PTM and remove any impurities which impede full extraction of the REE, thorium and uranium.

The use of HNO_3 for the extraction of the REE, thorium and uranium is lower than for HCl. Comparing concentrated 98 % H_2SO_4 with diluted 10 % H_2SO_4 when extracting the REE, the concentrated solution obtained minimal extraction of the REE of 1.10 % whereas the diluted solution obtained an extraction efficiency of 23.93 % along with a significant quantity of thorium. When the concentration of NaOH was similarly reduced

to 10 %, the increase in REE, thorium and uranium was higher than the conventional digestion process of monazite but less than if PTM was used.

5. Acknowledgements

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6.4 Appendix

The following additional notes present the raw collective data of all the physical experiments conducted on monazite and PTM for this study. These result offer additional information for the reader. The following tables present the extraction efficiency and standard deviation (Table 6-1 to Table 6-18) for each process.

Table 6-1: Elements extracted from the reaction between monazite and PTM with 98 % H₂SO₄ at 230 °C for 4 h and PTM for 2 h as percentage

	Ce	La	Nd	Y	Th	U	Ti	Zr	P
Mz - 4 h	22.11	23.87	54.22	47.18	0.11	23.61	4.40	1.08	351.95
PTM - 2 h	26.94	28.93	32.75	27.40	0.00	0.00	10.72	4.03	199.98
PTM - 4 h	34.72	37.41	39.53	24.21	0.00	0.00	9.87	3.86	206.92

Table 6-2: Standard deviation of the reaction between monazite and PTM with 98 % H₂SO₄ at 230 °C for 4 h and PTM for 2 h as percentage

	Ce	La	Nd	Y	Th	U	Ti	Zr	P
Mz - 4 h	4.37	4.73	9.62	7.00	0.40	2.42	2.39	0.40	29.10
PTM - 2 h	10.23	11.29	11.38	6.15	0.00	0.00	4.75	1.47	14.47
PTM - 4 h	8.28	9.60	8.10	2.39	0.00	0.00	3.22	0.87	8.41

Table 6-3: Elements extracted from the reaction between monazite and PTM using 60 % NaOH digestion of monazite and PTM for 1½ and 3 h at 140 °C followed by 32 % HCl digestion for 1 h at 80 °C as percentage

	Ce	La	Nd	Y	Th	U	Ti	Zr	P
Mz - 3 h	11.61	13.19	26.29	16.90	18.60	29.04	3.09	0.48	8.18
PTM - 1.5 h	22.69	26.45	31.90	22.75	19.10	35.18	17.16	5.17	6.99
PTM - 3 h	28.89	34.10	41.01	30.41	21.47	37.55	19.90	5.14	5.21

Table 6-4: Standard deviation of the reaction between monazite and PTM using 60 % NaOH digestion of monazite and PTM for 1½ and 3 h at 140 °C followed by 32 % HCl digestion for 1 h at 80 °C as percentage

	Ce	La	Nd	Y	Th	U	Ti	Zr	P
Mz	0.96	1.14	2.40	1.50	3.14	6.27	1.25	0.30	0.69
PTM - 1.5 h	2.95	3.26	4.51	3.58	1.31	3.12	1.29	0.64	0.42
PTM - 3 h	2.33	3.29	3.28	2.96	1.94	4.44	1.30	0.42	1.09

Table 6-5: Elements extracted from the reaction between monazite and PTM using 60 % NaOH digestion of monazite and PTM for 1½ and 3 h at 140 °C followed by 65 % HNO₃ digestion for 1 h at 80 °C as percentage

	Ce	La	Nd	Y	Th	U	Ti	Zr	P
Mz	12.80	13.41	20.72	13.12	16.22	30.92	1.58	0.40	2.04
PTM - 1.5 h	32.13	34.29	54.42	29.73	24.13	38.58	6.54	3.35	1.25
PTM - 3 h	32.89	36.22	58.28	32.66	26.77	43.88	12.71	4.91	0.28

Table 6-6: Standard deviation of the reaction between monazite and PTM using 60 % NaOH digestion of monazite and PTM for 1½ and 3 h at 140 °C followed by 65 % HNO₃ digestion for 1 h at 80 °C as percentage

	Ce	La	Nd	Y	Th	U	Ti	Zr	P
Mz	2.94	3.03	4.32	1.30	2.24	3.60	0.46	0.01	1.37
PTM - 1.5 h	4.79	5.10	7.53	3.99	1.46	4.19	1.21	0.26	1.21
PTM - 3 h	3.59	4.08	3.05	1.00	0.84	1.12	1.99	0.25	0.48

Table 6-7: Elements extracted from the reaction between monazite and PTM using 32 % HCl at 80 °C for 1 h as percentage

	Ce	La	Nd	Y	Th	U	Ti	Zr	P
Mz	1.09	1.10	2.51	0.68	6.09	3.00	2.42	0.04	1.39
PTM	30.79	34.35	40.84	16.04	5.25	42.70	19.82	3.72	27.05

Table 6-8: Standard deviation of the reaction between monazite and PTM using 32 % HCl at 80 °C for 1 h as percentage

	Ce	La	Nd	Y	Th	U	Ti	Zr	P
Mz	0.19	0.19	0.53	0.12	1.14	1.81	0.39	0.00	0.41
PTM	2.22	1.54	3.65	2.84	2.50	5.18	1.50	1.39	1.40

Table 6-9: Elements extracted from the reaction between monazite and PTM using 65 % HNO₃ at 80 °C for 1 h as percentage

	Ce	La	Nd	Y	Th	U	Ti	Zr	P
Mz	1.55	1.58	3.62	0.07	7.84	1.64	2.87	0.04	1.91
PTM	20.00	22.94	24.52	3.52	8.37	16.09	11.77	3.34	18.53

Table 6-10: Standard deviation of the reaction between monazite and PTM using 65 % HNO₃ at 80 °C for 1 h as percentage

	Ce	La	Nd	Y	Th	U	Ti	Zr	P
Mz	0.42	0.45	0.88	0.01	1.76	0.02	0.54	0.00	0.50
PTM	2.10	2.46	2.60	0.96	1.93	0.90	1.42	0.89	1.10

Table 6-11: Elements extracted from the reaction between monazite and PTM using 98 % H₂SO₄ at 80 °C for 1 h as percentage

	Ce	La	Nd	Y	Th	U	Ti	Zr	P
Mz	0.32	0.28	0.69	0.45	0.09	1.62	0.07	0.03	4.21
PTM	1.22	1.61	1.33	1.24	0.09	1.71	0.16	0.09	5.43

Table 6-12: Standard deviation of the reaction between monazite and PTM using 98 % H₂SO₄ at 80 °C for 1 h as percentage

	Ce	La	Nd	Y	Th	U	Ti	Zr	P
Mz	0.07	0.05	0.20	0.03	0.01	0.10	0.00	0.00	0.96
PTM	0.19	0.21	0.21	0.34	0.01	0.16	0.09	0.06	0.80

Table 6-13: Elements extracted from the reaction between monazite and PTM using 10 % H₂SO₄ at 80 °C for 1 h as percentage

	Ce	La	Nd	Y	Th	U	Ti	Zr	P
Mz	0.36	0.01	0.37	0.47	0.92	0.00	0.06	0.00	1.89
PTM	22.30	24.91	31.23	20.63	10.76	0.00	4.93	2.64	15.00

Table 6-14: Standard deviation of the reaction between monazite and PTM using 10 % H₂SO₄ at 80 °C for 1 h as percentage

	Ce	La	Nd	Y	Th	U	Ti	Zr	P
Mz	0.01	0.02	0.06	0.06	0.03	0.00	0.00	0.00	0.03
PTM	3.73	4.07	6.79	4.87	3.49	0.00	2.12	0.93	4.21

Table 6-15: Elements extracted from the reaction between monazite and PTM using 10 % NaOH digestion of monazite and PTM for 1 h at 80 °C followed by HCl digestion for 1 h at 80 °C as percentage

	Ce	La	Nd	Y	Th	U	Ti	Zr	P
Mz - Diluted	0.74	0.72	1.66	0.91	1.80	2.36	0.27	0.02	4.16
Mz- Conv	11.61	13.19	26.29	16.90	18.60	29.04	3.09	0.48	8.18
PTM - Diluted	21.32	23.27	23.94	19.73	13.89	24.97	12.65	3.60	3.98
PTM - Conv	28.89	34.10	41.01	30.41	21.47	37.55	19.90	5.14	5.21

Table 6-16: Standard deviation of the reaction between monazite and PTM using 10 % NaOH digestion of monazite and PTM for 1 h at 80 °C followed by HCl digestion for 1 h at 80 °C as percentage

	Ce	La	Nd	Y	Th	U	Ti	Zr	P
Mz - Diluted	0.13	0.19	0.38	0.36	0.36	1.32	0.15	0.02	0.81
Mz- Conv	0.96	1.14	2.40	1.50	3.14	6.27	1.25	0.30	0.69
PTM - Diluted	2.92	3.46	4.13	3.04	3.37	8.68	3.18	0.78	1.10
PTM - Conv	2.33	3.29	3.28	2.96	1.94	4.44	1.30	0.42	1.09

Table 6-17: Comparing the elements extracted from monazite using various reagents and process conditions as percentage

	Ce	La	Nd	Y	Th	U	Ti	Zr	P
HCl	1.09	1.10	2.51	0.68	6.09	3.00	2.42	0.04	1.39
HNO₃	1.55	1.58	3.62	0.07	7.84	1.64	2.87	0.04	1.91
H₂SO₄d	0.36	0.01	0.37	0.47	0.92	0.00	0.06	0.00	1.89
H₂SO₄Conv	22.11	23.87	54.22	47.18	0.11	23.61	4.40	1.08	351.95
NaOH/HCl	11.61	13.19	26.29	16.90	18.60	29.04	3.09	0.48	8.18
NaOH/HNO₃	12.80	13.41	20.72	13.12	16.22	30.92	1.58	0.40	2.04

Table 6-18: Comparing the elements extracted from PTM using various reagents and process conditions as percentage

	Ce	La	Nd	Y	Th	U	Ti	Zr	P
HCl	30.79	34.35	40.84	16.04	5.25	42.70	19.82	3.72	27.05
HNO₃	20.00	22.94	24.52	3.52	8.37	16.09	11.77	3.34	18.53
H₂SO₄d	22.30	24.91	31.23	20.63	10.76	0.00	4.93	2.64	15.00
H₂SO₄Conv	34.72	37.41	39.53	24.21	0.00	0.00	9.87	3.86	206.92
NaOH/HCl	28.89	34.10	41.01	30.41	21.47	37.55	19.90	5.14	5.21
NaOH/HNO₃	32.89	36.22	58.28	32.66	26.77	43.88	12.71	4.91	0.28

The Gibbs free energies of the reaction with the remaining rare earth phosphates and oxides were conducted out of interest with HCl. Predictably the rare earth phosphates are inert to leaching with HCl in the designated temperature range. The remaining oxides indicated that above 170 °C, all of the rare earth oxides are converted to the oxides. While this reaction did occur with aqueous HCl, the results indicate that the downstream processing of HCl on the rare earth oxides will facilitate leaching of all the rare earth oxides into the chloride. This analysis requires further study but does indicate that for the heavier REE, that the same process of decomposing the material into the oxide has the potential of being leached with HCl.

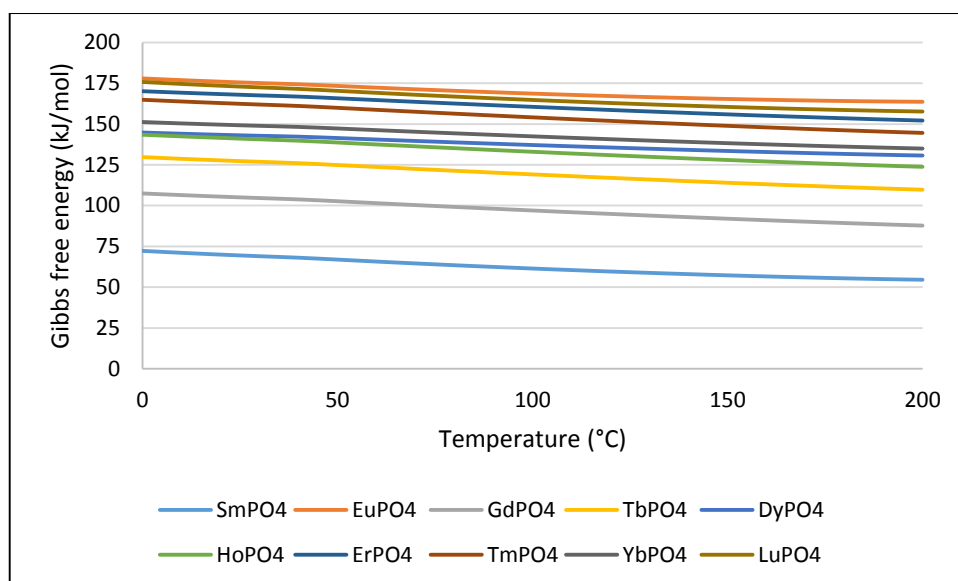


Figure 6-20: Gibbs free energy of the reaction of the other rare earth phosphates with aqueous HCl

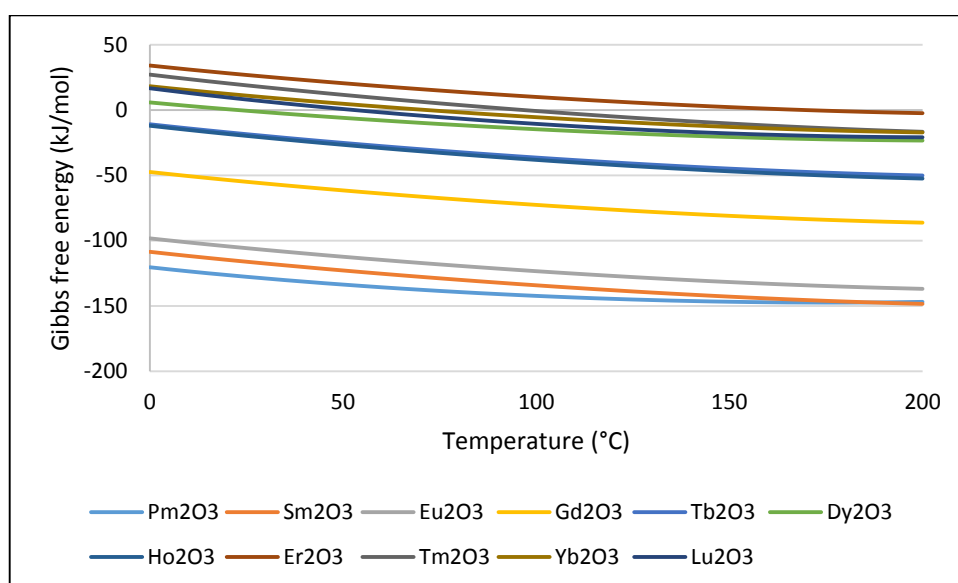


Figure 6-21: Gibbs free energy of the reaction of the other rare earth oxides with aqueous HCl

6.5 Concluding Remarks

The objective of this research indicated that using simple mineral acids can provide as efficient an extraction process as the use of more extreme and highly concentrated chemical processes on monazite which can cause large scale environmental damage and generate large quantities of chemical and radioactive waste. The digestion of PTM with HCl and HNO₃ confirmed that a simpler process can be developed to digest

monazite after it has been treated in a plasma. The possibility that when the monazite was decomposed in a thermal plasma and forming the rare earth oxide was verified when the Gibbs free energy and the experimental results of the digestion of PTM with NaOH followed by HCl digestion was compared to only HCl digestion and no difference could be determined.

7. High temperature thermal plasma treatment of monazite followed by the aqueous digestion

7.1 Introduction to article

This article summarizes the complete process of treating monazite in a plasma followed by digestion using a mineral acid and using the conventional digestion procedures of monazite. The objectives of this article is to combine all the information into one review article to provide an overall picture of the process and to indicate future work to advance this process. This article has been reviewed, accepted and published in the Journal of the Southern African Institute of Mining and Metallurgy, Volume 116, pages 901 to 906. This article is presented identically in this research to what was presented in the journal. Only minor spacing and referencing changes have been made.

7.2 Article 7: High temperature thermal plasma treatment of monazite followed by aqueous digestion

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Monazite is a chemically inert, radioactive phosphate mineral that contains the light rare earth metals (Ce, La, Nd, Pr and Y), thorium and uranium. A new process, which improves the extraction efficiency of monazite, is under development. The equilibrium mole composition, in conjunction with the Gibbs free energy, indicates that as monazite is heated in the presence of carbon to a temperature above 1400 °C, it decomposes into the rare earth oxides. These temperatures are within the operational limits of a thermal plasma. When monazite is fed to a DC plasma it forms amorphous plasma-treated monazite (PTM), which is more susceptible to chemical attack. This increased chemical reactivity permits dilute mineral acids to digest the PTM, which leads to higher extraction efficiencies of the rare earth elements than when monazite is digested using the conventional processes. When the conventional process for digestion of monazite is adapted to PTM, the extraction of rare earth elements, thorium and uranium is increased significantly.

1. Introduction

South Africa is a resource-based economy with an estimated *in-situ* mineral wealth of US\$ 2.5 trillion. This makes South Africa one of the wealthiest mining jurisdictions in the world. However, considerable amounts of South Africa's minerals are exported as raw or partially processed ore. South Africa has embraced a mineral beneficiation strategy to develop the value chain for various minerals. One such mineral is monazite (South African Department of Mineral Resources, 2011) which, until now, underwent minimal industrial beneficiation in South Africa (Kemp and Cilliers, 2014).

Monazite is a chemically inert, radioactive phosphate mineral and is considered to be one of the most important rare earth minerals in the world (Amaral and Morais, 2010; Dill et al., 2012; Hassan et al., 1997). Monazite is a component of 'black sand' found in various beach deposits worldwide (Dilorio et al., 2012) in combination with varying concentrations of ilmenite, magnetite, zircon, rutile and garnet (Ashry et al., 1995; Sroor, 2003). Monazite contains the light rare earth elements (LREE) Ce, La, Pr, Nd and Y, which are in high demand, and the radioactive elements thorium and uranium (Kim et al., 2009). Conventional monazite processing is a complicated, laborious and expensive process (Hurst, 2010) that utilizes highly corrosive media like concentrated sulphuric acid or sodium hydroxide, at elevated temperatures for extended periods of time (Zhu et al., 2015). This process produces large volumes of radioactive and acidic effluents (Xie et al., 2014). For these reasons, China, which produces 97% of the world's rare earth elements (Hurst, 2010), has prohibited the exploitation of monazite deposits (Zhu et al., 2015). This opens the market for new and innovative technologies for the processing of monazite.

Zircon (ZrSiO_4) is a mineral with a chemically inert crystal structure, which requires harsh alkaline treatment to extract the zirconium metal (Biswas et al., 2010). To overcome the chemical inertness of zircon sand, the South African Nuclear Energy Corporation SOC Ltd (Necsa) has developed a process using a DC non-transferred plasma to convert zircon into plasma-dissociated zircon (PDZ – $\text{ZrO}_2\cdot\text{SiO}_2$). PDZ is chemically more reactive than zircon and can be processed more efficiently (Havenga and Nel, 2012; Rendtorff et al., 2012). The high temperatures (10 000°C), good thermal conductivities and high heat contents of thermal plasmas make them ideal for

the processing of materials like zircon (Rendtorff et al., 2012; Toumanov, 2003). It is hypothesised that a similar process could increase the chemical reactivity of monazite in order to improve downstream processing efficiency. This would increase the output of the REE, thorium and uranium while simultaneously permitting the use of less aggressive chemical processes (Toumanov, 2003).

If plasma-treated monazite (PTM) can be processed using less harsh chemicals, as hypothesised, it would create a unique competitive advantage for future rare earth and thorium developers. The new process reduces the environmental and radioactive hazards of monazite processing by treating monazite in a high-temperature thermal plasma followed by low-temperature mineral acid leaching. This paper provides a summary of the current development of this process.

2. Experimental Procedure

Thermodynamic data from HSC version 6.1, developed by Outotec, was used to evaluate the Gibbs free energy, the equilibrium composition of the dissociation of monazite and to present alternative chemical processes that could require further investigation, or need to be avoided. Monazite is represented as the rare earth (RE) phosphate (REPO_4 , with RE = Ce, La, Pr, Nd and Y).

We treated monazite in a DC direct arc plasma batch reactor with the monazite housed in a graphite crucible. The reactor produces a high-temperature electric arc which is used to treat the monazite and produce PTM. The PTM product was heated in a high-temperature oven at 650°C for 24 hours to drive off excess graphite formed during the plasma processing.

Crushed monazite (Mzc) was produced by hand-crushing 10 g of monazite for 10 minutes. Heat-treated monazite (HTM) was produced by heating 20 g of monazite in an alumina crucible at 1000 °C for 3 hours, then rapidly cooling the product with water. Inductive monazite (IMz) was produced by heating 20 g of monazite in a graphite vessel to 1800°C in an induction oven. The product was cooled naturally and removed.

Monazite and PTM were leached with various commercially available mineral acids (32 % HCl, 65 % HNO₃ and 10 % H₂SO₄) at 80 °C for 1 hour; concentrated H₂SO₄ at 230 °C for 4 hours, or by alkaline leaching (60 % NaOH) at 140 °C for 3 hours followed by mineral acid digestion (HCl or HNO₃) at 80 °C for 1 hour. The concentrations of the individual REE in the leachate samples were determined by ICP analysis at an external laboratory. These values were used to calculate the extraction efficiency of the process.

3. Results and Discussion

3.1 Theoretical Decomposition of Monazite

In order to evaluate whether monazite (rare earth phosphates) would dissociate in a plasma, its physical properties were compared to values from the literature and theoretical simulations for a known mineral, zircon (ZrSiO₄). Monazite has a physically weaker crystal lattice than zircon due to its lower chemical bond strength (Cottrell, 1966) and melting point (Table 7-1) (Hikichi and Nomura, 1987; Pirkle and Podmeyer, 1988). From a physical strength perspective, the monazite crystal is weaker and could be destroyed more easily using less energy than required for zircon. As the plasma can destroy the zircon crystal lattice (Havenga and Nel, 2012; Kock et al., 2011) it is probable that the monazite crystal could be destroyed in a similar manner.

Table 7-1. Physical properties of monazite and zircon in relation to crystal strength.

	Zircon		Monazite	
Melting point (°C)	2100 – 2300		2057	
Chemical bond strength (kJ/mol)	Si – O:	798	P – O:	596
	Zr – O:	760	RE – O: (av.)	753

The temperature, at which monazite dissociates without the use of a reagent is unknown at present. Monazite in the presence of excess carbon dissociates into the rare earth oxide, phosphor and carbon monoxide at a temperature between 1200 and

1400°C (Equation 7-1) (Xing et al., 2010). According to the literature, zircon dissociates into PDZ at $1673 \pm 10^\circ\text{C}$. The dissociation temperature can be lowered by 250°C when excess carbon is added in the presence of oxygen (Kaiser et al., 2008; Telle, n.d.; Yugeswaran et al., 2015).



It is anticipated that the presence of carbon in the plasma could have a similar effect on monazite, which would lower its dissociation temperature by a few hundred degrees Celsius. To determine the potential dissociation temperature of monazite, the Gibbs free energy was used to estimate the temperature at which the individual rare earth (RE = Ce, La, Nd, Pr and Y) phosphates dissociate into the rare earth oxides and a phosphor-oxygen complex.

The dissociation temperature of zircon without excess carbon was accurately plotted using the Gibbs free energy at 1600–1700 °C. Similarly, the Gibbs free energy of the dissociation of monazite in the presence of excess carbon was plotted for a dissociation temperature between 1100 and 1300 °C. The Gibbs free energy of the dissociation of the rare earth phosphates (Equation 7-2) indicates that CePO_4 dissociates at 1700°C, as predicted. However the remaining rare earth phosphates dissociate between 2500 and 3000 °C (Figure 7-1), which is beyond the anticipated temperature range compared to zircon and CePO_4 . This dissociation will be investigated further.



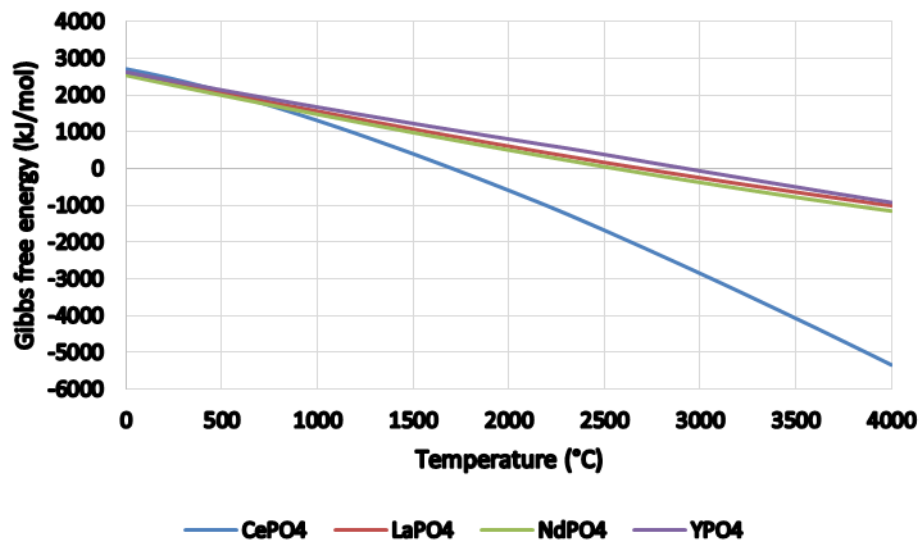


Figure 7-1. Gibbs free energy of the dissociation of monazite (rare earth phosphate) into the rare earth oxides and phosphor dioxide

The formation of the rare earth oxides from monazite would improve the leachability of the plasma-treated monazite (PTM). This is because the highly inert monazite crystal would have been destroyed enabling the rare earth oxides to be leached using a diluted mineral acid, unlike the rare earth phosphates (Peelman et al., 2014).

3.2 Plasma Treatment of Monazite

The starting material for all plasma cycles was monazite sand obtained from an external source. The sand consisted of 69.55% monazite, 17.67% zircon and 4.85% ilmenite with the remaining 7.93% consisting of other materials. Examination of the monazite sand by optical microscopy revealed a number of oval-shaped brown, red, white and black particles (Figure 7-2). These oval-shaped particles are reminiscent of this monazite sample and may differ from other monazite samples.

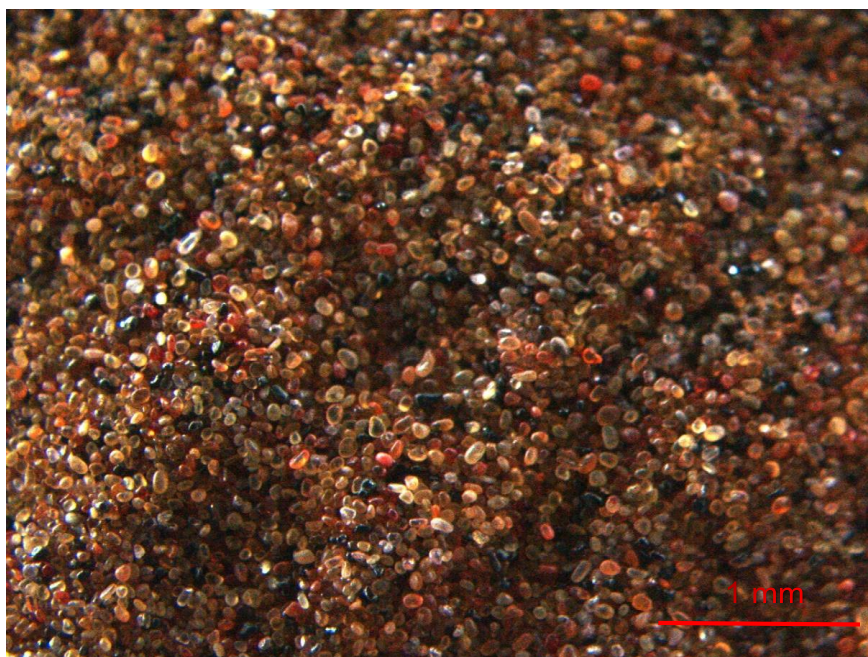


Figure 7-2. Optical micrograph of monazite

X-ray diffraction (XRD) analysis of monazite sand (Figure 7-3) and PTM was used to determine whether plasma treatment induces any structural or compositional changes in monazite. The XRD pattern of this monazite shows peaks at $2\theta = 26.5^\circ$, 28° , 35° and 47° , along with a number of smaller peaks. The peak at $2\theta = 26.5^\circ$ was positively identified as that of the rare earth phosphates, which are components of monazite. No further analysis for this study was completed.

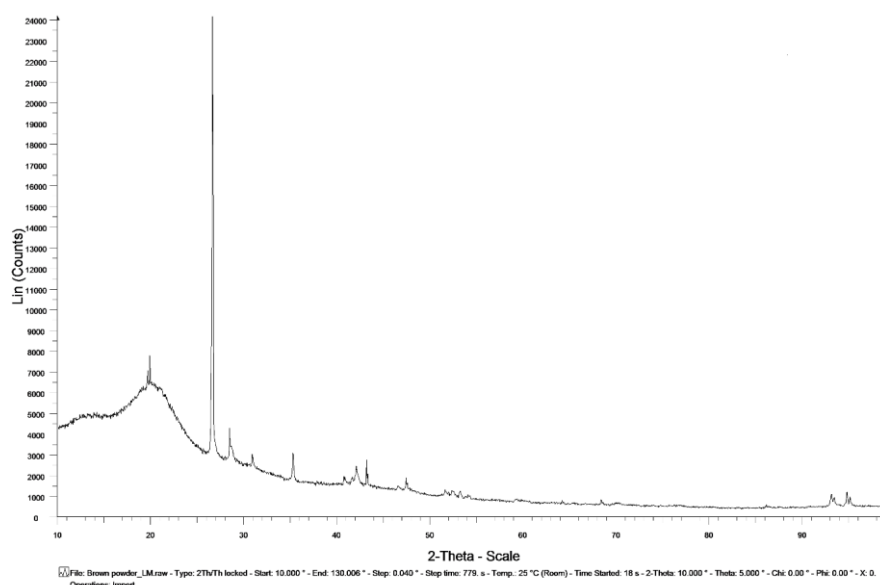


Figure 7-3. XRD analysis of monazite sand

We produced PTM by placing monazite sand in a graphite crucible and treating it in a DC direct arc plasma. We removed the PTM graphite layer after plasma treatment by heating the PTM in a conventional oven at 650°C for 24 hours, producing plasma-treated monazite heated (PTM_H). We found that when monazite is treated incorrectly it behaves and looks like monazite when viewed under an optical microscope and analysed using XRD. If monazite is heated in the plasma for too long it melts and forms larger, more inert monazite particles. When monazite is treated correctly in the plasma then the changes to the physical structure of the particles are visible under an optical microscope, as all of the oval-shaped particles are destroyed (Figure 7-4). For this reason, it can be concluded that the proper treatment of monazite can be verified partially through the use of an optical microscope. Elemental X-ray fluorescence analysis on all PTM samples indicated no statistical difference in the elemental composition compared with the original monazite.

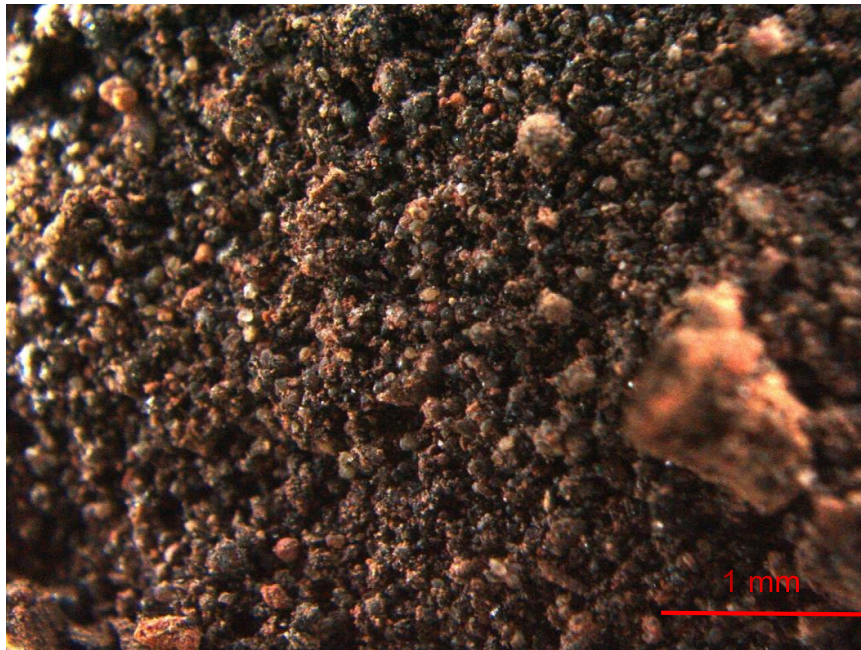


Figure 7-4. Optical micrograph of plasma-treated monazite.

XRD analysis of PTM_H confirmed the destruction of the monazite crystal structure. The absence of the monazite peaks (Figure 7-5) indicates that a completely amorphous powder has been produced. This indicates that the inert phosphate crystal matrix, which is responsible for the inert nature of monazite (El-Nadi et al., 2005), has been destroyed. The disadvantage of the formation of the amorphous substance is that the presence of the more reactive rare earth oxides cannot be confirmed. Other minerals, like zircon, have also been destroyed.

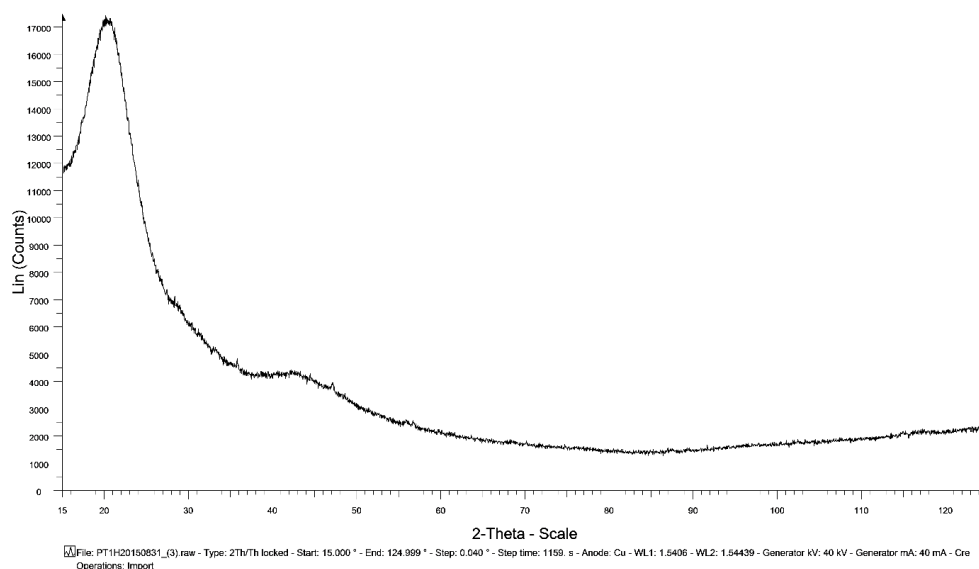


Figure 7-5: XRD pattern of amorphous plasma-treated monazite

3.3 Chemical Reactivity of Plasma-treated Monazite

In order to confirm the hypothesis that the plasma treatment of monazite delivers a more reactive product, PTM and PTM_H were digested using a variety of different lixivants multiple times. The results indicate the quantity of the specific element extracted, as a percentage of the original amount of that element in the starting material. The standard deviation is shown as error bars. In order to obtain a proper comparison of the reactivity, additional samples were tested, like monazite (Mz), crushed monazite (Mzc), heat-treated monazite (HTM) and inductive monazite (IMz).

Digestion of PTM extracted on average 21 times more of the REE, 7 times more thorium and up to 11 times more uranium compared with untreated samples. Comparison of the extraction efficiency from Mz, Mzc, HTM, IMz, PTM and PTM_H with 32 % HCl (Figure 7-6) shows that simply heating the monazite (HTM and IMz) in a graphite crucible, even to a temperature above 1800 °C, does not result in a more reactive product. The phosphor content remained reasonably constant throughout and cannot be used as an accurate indicator of the efficiency of the extraction process.

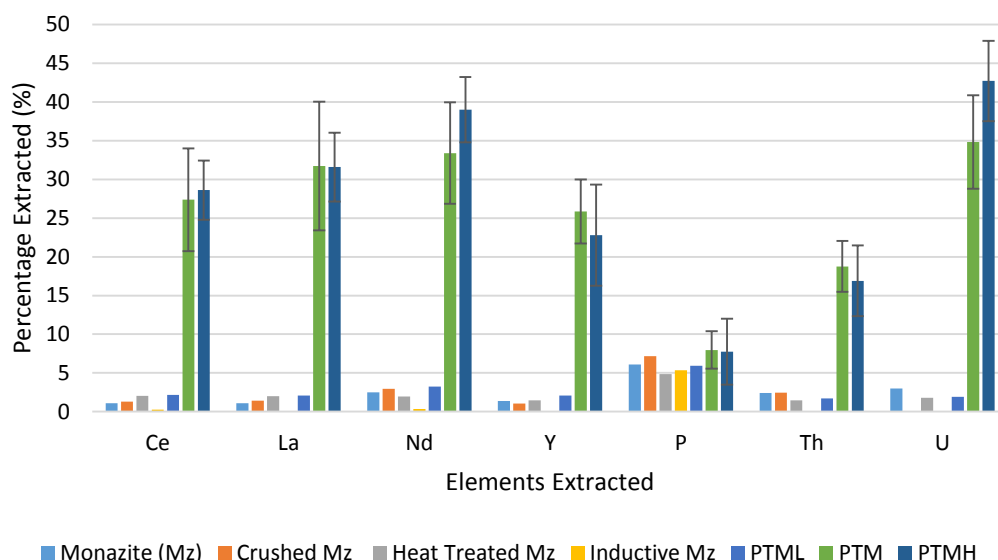


Figure 7-6. Extraction efficiency from various forms of monazite using 32% HCl at 80°C for 1 hour.

The results demonstrate the importance of using an appropriate temperature and treatment time period in order to increase the chemical reactivity of monazite. The plasma treatment of monazite is the predominant reason for improved REE and thorium extraction, as the plasma treatment destroys the monazite crystal matrix and produces amorphous PTM. Comparing the REE extraction efficiencies between heat-treated (PTM_H) and non-heat-treated PTM reveals a small but significant increase in the extraction efficiency. The multiple experiments conducted for this study were not optimized and the potential advantage gained by removing graphite from PTM requires further investigation.

In order to develop the process, the digestion of monazite and PTM_H with various reagents were compared. Each experiment was repeated several times until a satisfactory standard deviation was achieved. These reagents included 65 % HNO₃ (HNO₃) and 10 % H₂SO₄ (H₂SO_{4d}) at 80 °C for 1 hour, 98 % H₂SO₄ at 230 °C for 4 hours (H₂SO_{4c}) and 60 % NaOH at 140 °C for 3 hours followed by either 32 % HCl (NaOH/HCl) or 65 % HNO₃ (NaOH/HNO₃) at 80°C. The average extraction efficiencies of the various digestion processes over multiple experiments for monazite (Figure 7-7) and PTM_H (Figure 7-8) show clearly that PTM_H is more reactive than monazite. The optimum REE extraction using aqueous digestion from PTM_H was obtained using

32 % HCl, which resulted in an average extraction efficiency of 38.44 %. Alkaline digestion followed by HNO₃ yielded the highest possible extraction efficiency of 38.56 % for the REE. Digestion using concentrated H₂SO₄ did not result in any vast improvement on the process, but did indicate that thorium was not extracted. Phosphor, which is still present in the PTM_H, is a contaminant that reduces the percentage of material extracted from the process (Kemp and Cilliers, 2016).

The simpler diluted mineral acid digestion delivered higher extraction efficiency values for the REE, thorium and uranium from PTM_H – within 30 % of those obtained using the conventional process – and has the distinct advantage of being simpler, easier to work with and potentially more economical. The conventional monazite digestion processes is more efficient at extracting the REE from PTM_H than the diluted mineral acids, with varying degrees of success for thorium and uranium. The extraction values obtained for Nd and Y by the conventional H₂SO₄ process were consistently high. No explanation can be given at this time, and this phenomenon will be investigated further.

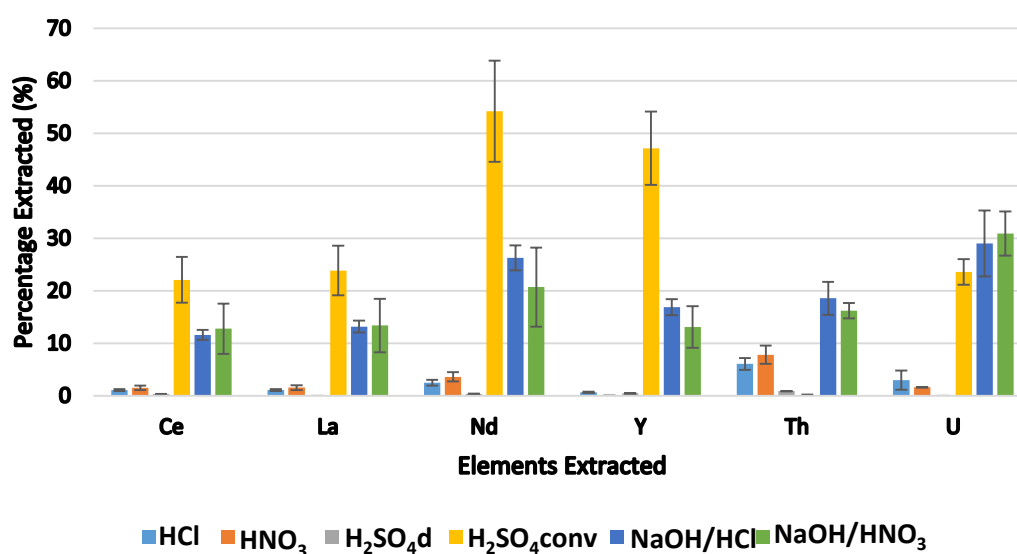


Figure 7-7. Extraction efficiencies of the rare earths, thorium and uranium from monazite for each reagent

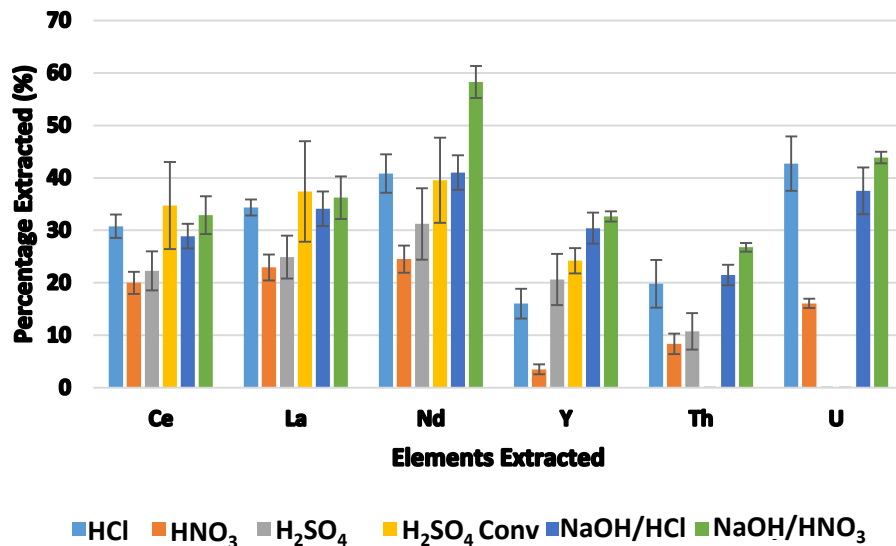


Figure 7-8. Extraction efficiencies of the rare earths, thorium and uranium from PTM_H for each reagent

Thorium is found in monazite worldwide and can be used as fuel in a nuclear reactor (Greneche et al., 2007). 32% HCl extracted 16.89 % of the available thorium from monazite, PTM and PTM_H. The digestion of PTM_H with 60% NaOH followed by HNO₃ obtained the highest extraction efficiency for thorium along with the REE. This is surprising, as the thorium should have been at a minimum due to it precipitating out as Th(OH)₄. This phenomenon will be investigated further.

To produce PTM the monazite sample must be rapidly heated to allow it to properly dissociate, and cooled rapidly to prevent the monazite particles from fusing together to form larger, more inert particles. This can be accomplished with the use of an in-flight RF induction plasma or a DC non-transferred arc plasma, whereby the monazite would be subjected to the required rapid heating rate. After the rapid heating of the monazite particles, the design of the in-flight plasma would allow the particles to cool fast enough to prevent the formation of excessively large particles or recombination as a rare earth phosphate (Boulos, 1985).

4. Conclusion

The objective of this study was to treat monazite in a plasma in order to extract the rare earths, thorium and uranium more efficiently. Theoretically, when monazite, as a rare earth phosphate, is treated in a thermal plasma at 1600 °C, it decomposes into chemically more reactive rare earth oxides. XRD analysis of plasma-treated monazite (PTM) indicated that the monazite crystal matrix was destroyed to produce an amorphous substance. It was determined that in order for the monazite to become more reactive the temperature and duration of the plasma treatment are crucial, otherwise, there would only be a minimal increase in chemical reactivity. PTM can be leached using a dilute mineral acid at a lower temperature, and in less time, than in the conventional monazite processes, while obtaining similar extraction values. The overall conclusion of the study is that the plasma treatment of monazite increases its chemical reactivity. This knowledge can now be used to develop a more efficient and economical process than the comparable conventional chemical digestion methods currently employed to process monazite.

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7.3 Concluding Remarks

This final article summarizes the whole process from the initial development of theoretically decomposing monazite in HSC, feeding it to the DC plasma to produce PTM and reacting it with various reagents to evaluate the extraction potential of PTM_H with monazite. The final conclusion is that PTM and PTM_H are more reactive than the original monazite and that a simpler process for the extraction of the REE, thorium and uranium can be developed.

8. Conclusion

Monazite is a chemically inert radioactive phosphate mineral which contains the light rare earth elements, thorium and uranium. Conventional chemical processing of monazite requires the use of harsh chemicals in a complicated, highly corrosive, laborious and expensive process. A new process, which feeds monazite to a plasma, produces chemically reactive amorphous plasma treated monazite which can be digested with a mineral acid.

The research project requires a theoretical basis to confirm whether monazite can be thermally decomposed into a more reactive compound. Monazite was compared to zircon, which has been dissociated in a plasma, using values found in literature. It was determined that monazite contains a physically weaker crystal structure, chemical bonds and a lower melting point. Monazite is reduced into its oxides or oxy-carbides when treated in the presence of carbon at a temperature of between 1200 and 1400 °C. The Gibbs free energy calculations by HSC, of the dissociation of zircon and the reaction with monazite and carbon have been shown to be fairly accurate.

The equilibrium composition of the decomposition of monazite as the rare earth phosphates (CePO_4 , LaPO_4 , NdPO_4 and YPO_4) indicated that CePO_4 decomposes into the oxide at 1600 °C with the remaining rare earth phosphates decomposing above their melting point. For this reason, this study will decompose monazite in the presence of carbon to evaluate whether the chemical reactivity of monazite can be increased. The decomposition of the remaining lanthanides as rare earth phosphates, with the exception of EuPO_4 and SmPO_4 , all decompose at a similar temperature to CePO_4 . This research recommends that more accurate thermodynamic data be presented for the rare earth phosphates to more accurately determine monazite's decomposition temperature in the absence of carbon.

The study of monazite of which the crystal structure is destroyed with a plasma process to produce the corresponding metal oxides and phosphates has been theoretically studied using the thermodynamic simulation program HSC in order to calculate the Gibbs free energy of these oxides and phosphates with anhydrous and

aqueous HF and ABF. This study demonstrates that ABF could be used as a viable alternative for aqueous HF for the purpose of fluorination.

It has been hypothesised that by feeding monazite to a plasma that its chemical reactivity could be improved. This theory was evaluated by placing monazite in a DC direct arc batch reactor to produce PTM. When monazite is treated using a high temperature plasma and the heat of the plasma is not applied directly to the monazite for the correct length of time, the monazite will only have with a minor increase in chemical reactivity. This study has revealed that the lack of transformation of PTM_L and PTM_{LH} compared to monazite is evident under an optical microscope and chemical treatment. Microscopic analysis of the material has showed no discernible difference in the structure of monazite and the plasma product PTM_L. When monazite is treated for too long and has melted then it is more inert and difficult to process. For these reasons, the high temperature plasma heat must be applied correctly to the monazite for the correct length of time in order to properly treat the monazite and produce a chemically reactive form of monazite.

Microscopic analysis of PTM and PTM_H reveal the alterations to the particles, from the original monazite particle structure, has been altered with the particles appearing crumble like and the XRD presenting an amorphous substance. This permits digestion using a diluted mineral acid at low temperature for the effective extraction of the REE, thorium and uranium.

Chemical reactivity tests were conducted using 32 % HCl which revealed that crushing and heating the monazite to high temperatures, even 1800 °C in the presence of a graphite crucible, has a small effect on the extraction efficiency of the monazite and that it is not the main cause for the increase in reactivity. The increased chemical reactivity is obtained from the plasma treatment of monazite which increases the extraction of the REE by 21 times, 7 times more for thorium and 11 times more for uranium from PTM than the original monazite using the same conditions. Post visual analysis of the residue of the PTM which has been leached indicates that not all of the monazite has been decomposed in the plasma, resulting in low extraction efficiencies.

Monazite and PTM were digested using a variety of mineral acids and an alkali at various temperatures and reaction times in order to establish whether PTM is a more

reactive form of monazite. Monazite and PTM were initially digested with 98 % H_2SO_4 at 230 °C for 2 to 4 h. The results indicated that while certain elements in PTM was better extracted, particularly Ce and La, better extraction of Nd, Y and U was obtained from monazite. Thorium extracted in was quantities which fell below the detection limits of the equipment used.

The digestion of monazite and PTM using the conventional NaOH digestion process followed by HCl or HNO_3 digestion clearly indicated the increased reactivity of PTM over monazite as, for HCl, double the quantity of the REE were extracted along with 31.13 % more thorium and 66.91 % more uranium. When HNO_3 was used rather than HCl a 51 % increase in REE extraction was observed, with 54.42 % of the total Nd extracted, as well as 18.36 % more Th and 11.87 % more U.

The development of a simpler process using aqueous mineral acids at 80 °C for 1 h indicated a significant increase in the reactivity between monazite and PTM as a 21 fold increase in REE extraction was pronounced when PTM was extracted using 32 % HCl. The quantity of material extracted using this process is on par to the conventional digestion of monazite and can be considered as a viable extraction method using current rudimentary chemical methods. Using more sophisticated methods could potentially increase the dissociation percentage of the PTM and remove any impurities which impede full extraction of the REE, thorium and uranium.

The use of HNO_3 for the extraction of the REE, thorium and uranium is lower than for HCl. Comparing concentrated 98 % H_2SO_4 with diluted 10 % H_2SO_4 when extracting the REE, the concentrated solution obtained minimal extraction of the REE of 1.10 % whereas the diluted solution obtained an extraction efficiency of 23.93 % along with a significant quantity of thorium. When the concentration of NaOH was similarly reduced to 10 %, the increase in REE, thorium and uranium was higher than the conventional digestion process of monazite but less than if PTM was used.

Overall PTM is more reactive than monazite whereby the REE, thorium and uranium can be extracted more efficiently and effectively from the PTM. The future design of this process will become a balancing act between the use of simple chemical reactions, which can deliver similar REE extraction values, against the use of conventional monazite extraction processes which are already established but can

attain higher REE extraction values while leaving thorium and uranium behind as radioactive waste.

The overall conclusion of the study is that the plasma treatment of monazite increases its chemical reactivity. This process can now be used to develop a more efficient and economical process than the comparable conventional chemical digestion methods currently employed to digest monazite.

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A. Appendix 1: Extended Literature Study of Rare Earths and Thorium

Monazite is a rare earth phosphate mineral which contains the REE along with the radioactive elements thorium and uranium. Monazite is a highly inert phosphate mineral which is expensive and difficult to process. The high difficulty in obtaining these elements is offset by their high commercial value (Hurst, 2010; Massari and Ruberti, 2013; Pratiwi et al., 2011; Weber, 2012). The aim of this thesis is to thermally treat the monazite crystal structure to be able to more easily process the monazite.

A.1 Monazite and the Rare Earth Minerals

There are approximately 200 different minerals which contain REE of which 10 % are considered to be economically mineable using current mining techniques. The more commonly mined rare earth minerals are monazite, bastnaesite, ceriotes, xenotime, gadolinite, fergusonite, allanite, phosphorite and samarskite (Pratiwi et al., 2011; Tropper et al., 2011; Wang et al., 2010) and the rare earths occur as an accessory in metapelites, granulites, peraluminous granites, carbonatites and limberlites (Hassan et al., 1997; Ni et al., 1995; Stepanov et al., 2012). The majority of the extractable REE resources are associated with monazite, bastnaesite and xenotime. Monazite is the most abundant of the three (Abreu and Morais, 2010) and the second most important source for the REE (Amaral and Morais, 2010; Dill et al., 2012; Hassan et al., 1997).

The mining methods to retrieve the rare earth minerals can vary between surface mining, collection of beach washings and dredge mining (Cardarelli, 2008; Pillai, 2005). The rare earth minerals contain sizeable quantities of thorium and uranium which account for the high natural background radioactivity (Abreu and Morais, 2010; Cardarelli, 2008; Pratiwi et al., 2011) and are often found together in their respective mineral deposits (Kaya and Bozkurt, 2005).

Monazite, a rare earth phosphate mineral, is predominantly found in the black sand deposits in various countries like India, Brazil, Sri Lanka, South Africa, Russia,

Australia and the Scandinavian countries (Ashry et al., 1995; Cardarelli, 2008). Monazite consists of roughly 70 % rare earth metal oxides which constitutes 20 - 30 % Ce_2O_3 , 10 - 40 % La_2O_3 with significant quantities of Nd, Pr and Sm and between 1 - 10 % thorium along with uranium and various other phosphates (Amaral and Morais, 2010; Ashry et al., 1995; Cardarelli, 2008; Kim and Osseo-Asare, 2012; Kim et al., 2009; Malanca et al., 1998; Stepanov et al., 2012).

Various processes have been developed in industry to process and extract the REE from monazite sand. Industrial chemical processing of monazite utilizes one of two processes namely the acid and the alkaline digestion processes. The current disadvantage of these processes are that high quantities of excess radioactive and chemical waste are produced along with the excessively high levels of corrosion (Dilorio et al., 2012; Hurst, 2010). Other REE minerals, due to the presence of monazite within the crystal structure like bastnaesite, are difficult to decompose due to the inert nature of monazite (Wu et al., 2007).

Monazite preferentially incorporates the lighter REE (La – Gd) whereas xenotime, a similar mineral to monazite, incorporates the heavier REE (Tb – Lu and V) (Ni et al., 1995). Xenotime is less abundant than monazite but is commonly associated with monazite, found worldwide and accounts for the yttrium commonly found in monazite (Pratiwi et al., 2011). Xenotime is rich with the other heavier rare earths and is processed using similar methods to monazite (Alex et al., 1998).

A.1.1 Rare Earth Elements

REE are a group of elements which include the lanthanides in the atomic number range from 57 (La) to 71 (Lu), yttrium (39) and scandium (21) (Abreu and Morais, 2010; Goyne et al., 2010; Hurst, 2010; Pratiwi et al., 2011). The REE are in demand globally for their use in various high tech applications and in a variety of fields including chemical engineering, metallurgy, optical, magnetic, luminescence and laser materials, high-temperature superconductors, secondary batteries, catalysis, the alloying of iron and steel in the machinery, automotive and in the military industry (Alex et al., 1998; El-Nadi, 2012; Kim and Osseo-Asare, 2012; Kim et al., 2009; Kovács et al., 2009; Wu et al., 2013; Xiao et al., 2013a; Xing et al., 2010). The increase in

consumption and interest in REE has increased the level of exploration and exploitation for new sources of REE which drives the development of new processes to extract the REE (Pratiwi et al., 2011).

The REE are unique in their spectroscopic and magnetic properties and plays an important role in the development of modern advanced materials (Abreu and Morais, 2010; Pratiwi et al., 2011; Sroor, 2003). The REE are characterized into two groups, light and heavy. The light REE are lanthanum (La), cerium (Ce), praseodymium (Pr) neodymium (Nd) and samarium (Sm), atomic numbers 57 – 62, and are more abundant than the heavier rare earth metals. The heavy rare earth metals are not as abundant as the lighter elements but are still used in various high tech operations. These elements are the elements with atomic numbers 64 – 71 (Gd – Lu) along with scandium (Sc) and yttrium (Y) (Abreu and Morais, 2010).

A number of REE have been deemed critical (Figure A-1) for the short term and medium term. Amongst the light REE, neodymium is deemed to be critical and for the heavier REE, four are critical. These are dysprosium, europium, terbium and yttrium (“Rare Earths Exploration & Development Company | Frontier,” n.d.)

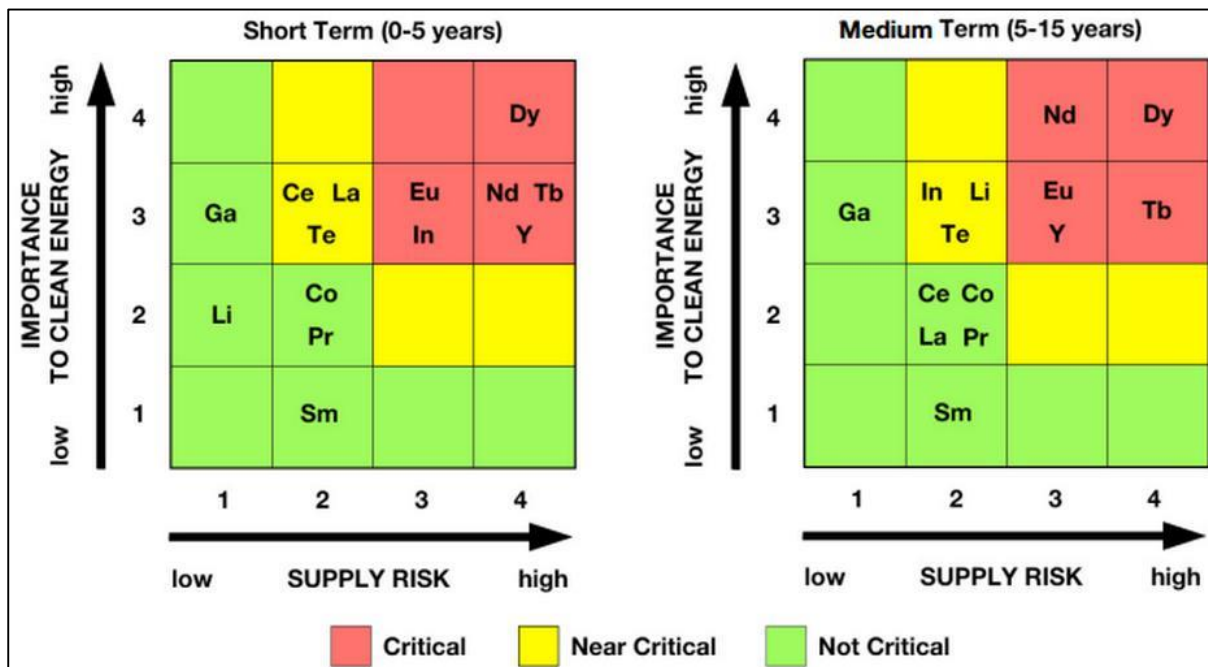


Figure A-1: The short and medium term forecast for the critical REE

A.1.2 Radioactive Elements in Monazite

Monazite contains sizable quantities of the radioactive elements thorium and uranium, both of which can be used as fuel in a nuclear reactor. Thorium is found with the REE and uranium, hence its production as by-product of rare earth extraction from minerals such as monazite (Dilorio et al., 2012). Monazite is considered to be the most common and commercially important thorium bearing mineral containing between 3 and 9 % thorium oxide (Abdel-Rehim, 2002; Dilorio et al., 2012; Kaya and Bozkurt, 2005). The other radioactive element present in monazite, uranium is the primary source of fuel for nuclear reactors since the beginning of the nuclear age (Kaya and Bozkurt, 2005).

A.1.3 Monazite Thermal and Physical Properties

Monazite consists of various phosphates, LaPO_4 , CePO_4 , NdPO_4 , YPO_4 , and PrPO_4 . While each of these compounds have their individual heat capacities, due to the nature of the REE their physical properties are very similar (Popa et al., 2006). The C_p values for LaPO_4 is 101.28 J/mol.K and for CePO_4 106.43 J/mol K. These values compare very well to the heavier rare earth phosphate's heat capacity with GdPO_4 measured at 102.21 J/mol.K (Popa et al., 2006) and ErPO_4 at 101.08 J/mol.K (Gavrichev et al., 2012). Hikichi & Nomura (1987) obtained an average melting point for monazite of 2057 °C along with the individual melting points for the various phosphates.

Table A-1: Melting point of the individual rare earth phosphates

Material	Melting Point (°C)
LaPO_4	2072 °C
CePO_4	2045 °C
PrPO_4	1938 °C
NdPO_4	1975 °C

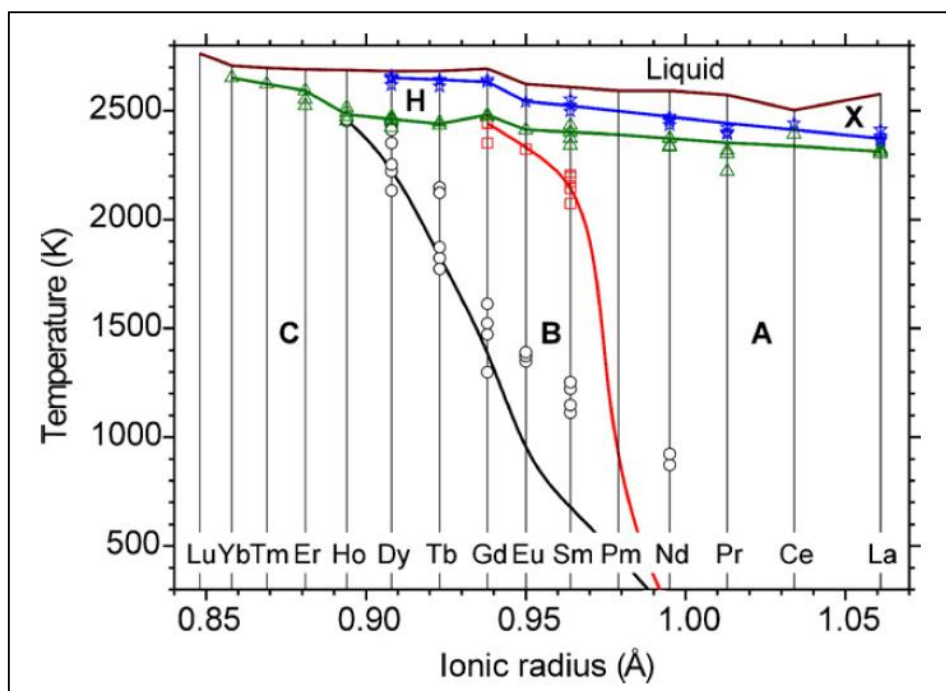


Figure A-2: The scheme of polymorphic transformations in lanthanide sesqui-oxides

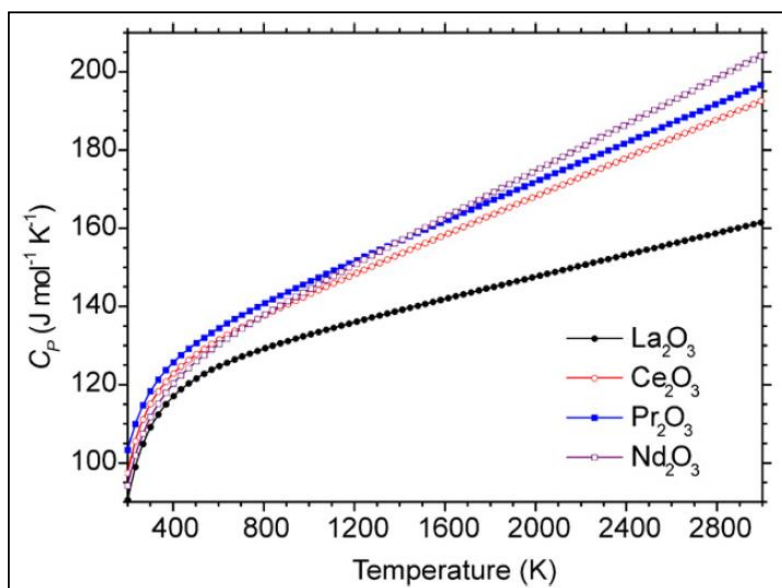


Figure A-3: Assessed heat capacities La_2O_3 , Ce_2O_3 , Pr_2O_3 , and Nd_2O_3

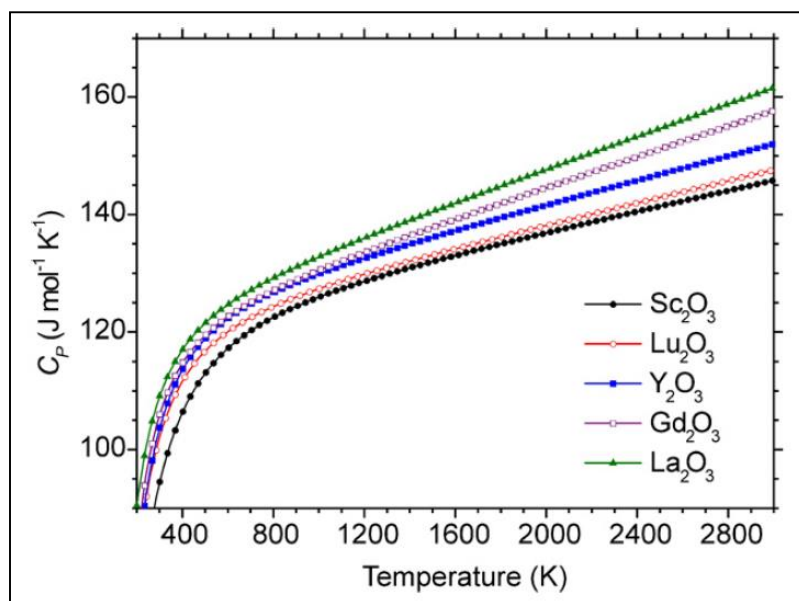


Figure A-4: Assessed heat capacities of Sc_2O_3 , Lu_2O_3 , Y_2O_3 , Gd_2O_3 , and La_2O_3 as functions of temperature

A.1.4 Conventional Monazite Process

The extraction of the REE from monazite is a complicated and costly exercise (Hurst, 2010). Monazite is a chemically stable crystalline phosphate which is difficult to dissolve in an acid or an alkaline solution (Cardarelli, 2008). Several processing methods have been developed in the past on industrial sized operations to extract the REE, thorium and uranium. The high stability of the REE minerals, specifically monazite, has discouraged various other attempts to treat monazite using various other chemical or electrolytic reduction techniques (Gupta and Krishnamurthy, 2005) including sintering with sodium carbonate at 900 °C (Abdel-Rehim, 2002; Goyne et al., 2010), sintering with sodium hydroxide at 400 – 500 °C, chlorination of a mixture with coal at 700 – 800 °C, decomposition using perchloric acid (Willard and Gordon, n.d.) and smelting with coke, lime and flux (calcium fluoride) in an electric furnace at 1750 °C (Abdel-Rehim, 2002).

Among all of these processes the two most favourable are sulphuric acid leaching at 230 °C for up to 4 h (Abdel-Rehim, 2002; Barghusen and Smutz, 1958; Cardarelli, 2008; Groot, 2010; Willard and Gordon, 1948) and alkaline leaching with sodium hydroxide solutions at 140 °C for 3 h (Amaral and Morais, 2010; Calkins, 1957; Cardarelli, 2008; Kim and Osseo-Asare, 2012). Other reagents such as ammonium

hydroxide, sodium sulphate, oxalic acid and hydrofluoric acid are used after NaOH digestion to precipitate and neutralize the REE products. Separation of the REE are done using solvent extraction or ion exchange (Kim and Osseo-Asare, 2012).

The sulphuric acid process (Figure A-5) (Taylor, 2011) starts with the roasting of monazite with concentrated sulphuric acid at 300 °C to “crack the monazite”. The rare earth sulphates formed during this process are leached with water and the excess acid is neutralized and filtered (Gupta and Krishnamurthy, 2005). The leach solution proceeds for further treatment and separation of the REE using solvent extraction. The radioactive element thorium is precipitated from the leach residue as ThP_2O_7 , where it cannot be recovered economically. This results in the loss of thorium and increases the number of potential environmental hazards generated. Sulphur dioxide is found in the off gas after roasting and requires large volumes of water or alkaline solutions to remove safely which can often results in large volumes of acidic effluents being generated (Xie et al., 2014).

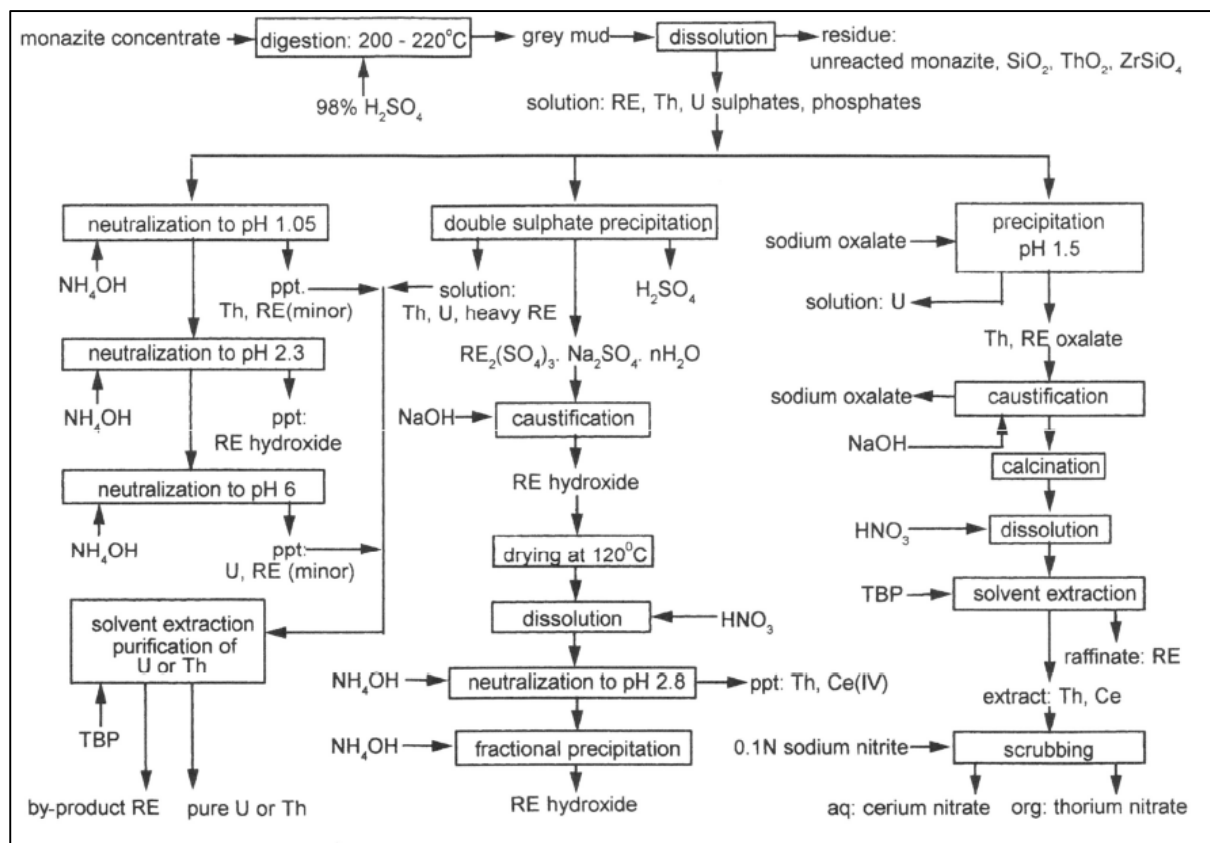


Figure A-5: Detailed image of the sulphuric acid digestion of monazite

The alkaline processing of monazite is the more common process in use at present. Monazite is cracked by heating the concentrate up to 140 - 150 °C with a 60 - 70 % NaOH solution (Cardarelli, 2008; Taylor, 2011). During decomposition, the strong alkali is transformed into rare earth hydroxides (REOH), which is dissolved in a mineral acid after removal from a supernatant solution of alkaline phosphates (Figure A-6) (Taylor, 2011). This is the major advantage of the alkaline process as the phosphates are removed as Na_3PO_4 . This process step benefits the Rare Earth Metals (REM) recovery downstream which are highly sensitive to the concentration of phosphor present in the alloying phase and must be at a minimum. If the phosphor concentration is too high, a reaction between the phosphor and rare earths pulverises the rare earth alloy (Xing et al., 2010).

While the alkali method is considered to be cleaner than the acidic route, it is an intermittent rather than a continuous process making this process unfavourable for mass production. Other downsides of the alkaline decomposition is the precise control of the pressure, temperature, pH (Kim et al., 2009) and the side processes of calcium removal by acid pickling (Xu et al., 2012).

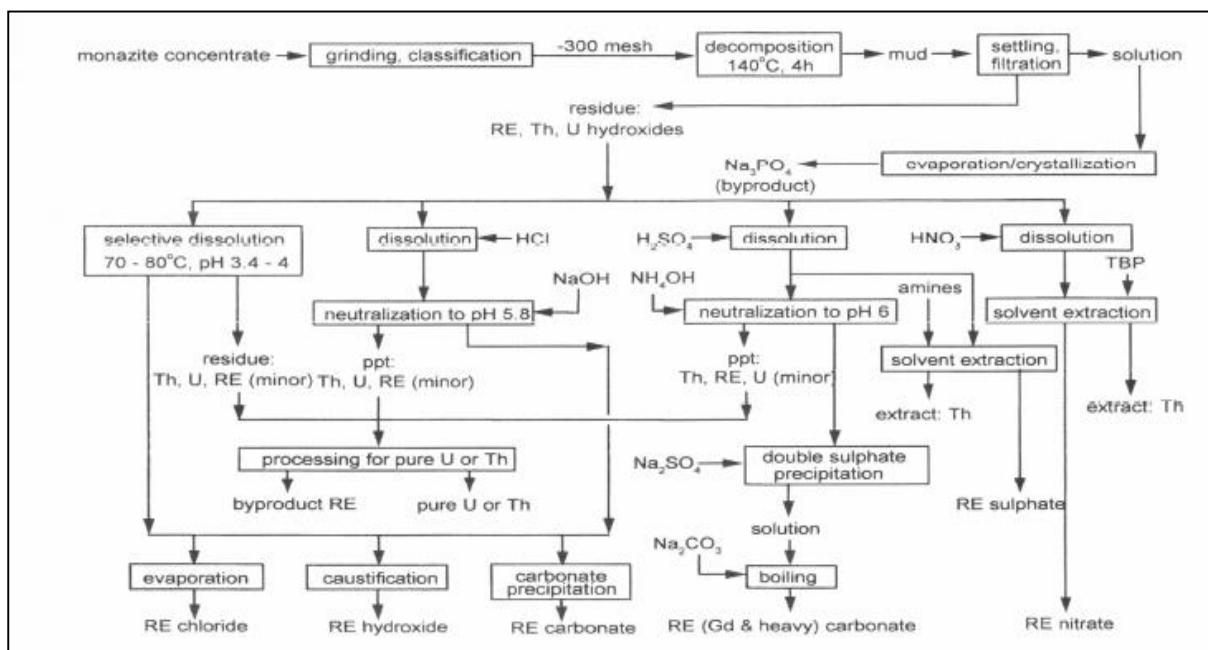


Figure A-6: A more detailed image of the alkaline processing of monazite

The complete process, from mining until production of the rare earth oxides takes approximately 10 days (Gupta and Krishnamurthy, 2005). The rare earth oxides are the end products and the natural starting material for final conversion to a metal.

A.1.5 Rare Earth Waste Processing

When the mining and processing of the REE are not carefully controlled, it has the potential to create vast environmental disasters (Hurst, 2010; Zhang et al., 2010). It is estimated that for every ton REE produced, 8.5 kg of fluorine along with 13 kg of dust is generated. By using concentrated sulphuric acid, high temperature calcinations techniques generates 9 600 to 12 000 cubic meters of waste gas which contains dust concentrate, hydrofluoric acid, sulphur dioxide and sulphuric acid. Approximately 75 cubic meters of acidic waste water and a ton of radioactive waste residue is generated with more than ten types of wastewater using the various processes (Hurst, 2010).

China currently treats their water using various waste water techniques including stripping, chlorination and ion exchange (Zhang et al., 2010). China's environmental concerns are alleviated due to all the rare earth enterprises in the Bantou region which discharge approximately 10 million tons of waste water every year without an effective water treatment plan. The wastewater contaminates the potable water, the surrounding water and farmlands which are essential for daily living. The disposal of the tailings and the ground up materials contributes to the problem by containing radioactive thorium with as much as 2,000 tons of mine tailings produced for every ton of REE (Hurst, 2010).

This level of pollution is only possible in China as it has very lax environmental laws. Other countries like the United States, Australia and European countries have strict controls which are in place to control the disposal of the rare earth waste. This increase the cost of production, which does not affect China as severely and is the reason why China can operate and sell their REEs at such a reduced rate (Hurst, 2010).

Uranium and thorium mining are nearly identical and produce the same quantity of waste. After mining, thorium comes out as a usable nuclear fuel isotope which does not require enrichment, unlike uranium. The enrichment process produces large quantities of waste. This makes the thorium fuel cycle waste overall less dangerous

than that of uranium (Dilorio et al., 2012). The radioactive waste produced from the mining and conversion of thorium for a nuclear reactor is two orders of magnitude lower.

Uranium mining leaches significant pollutants such as manganese and ^{226}Ra into the effluents. Thorium processing, while cleaner, does produce ^{226}Ra and ^{228}Ra along with chemicals such as lead, fluorides and phosphates which needs to remain under constant surveillance (Sundararajan et al., 1998).

A.1.6 Separation of the Rare Earths

The main reasons for separating these metals are the high commercial and economic values of the REE. However, high purity and quality is required for the final product. The separation of the individual REE has traditionally been a difficult and costly exercise. The most common method for rare earth separation is solvent extraction. The high cost of solvent extraction is because it requires hundreds of stages of mixers and settlers to obtain the desired purity level (Abreu and Morais, 2010; Cheng et al., 2013; Feng et al., 2012; Maharana and Nair, 2005; Xiao et al., 2013b; Xie et al., 2014).

Solvent extraction is where an organic and an aqueous solution are mixed together and flow into a settler. The mixed phases are laced with an extractant which removes the desired element from the aqueous stream and transfers it to the organic phase. The two phases are separated using gravity (Wu et al., 2013). One extractant, Tributyl phosphate (TBP) is at present the most selective solvent for commercial use and is satisfactory for the cerium (IV) extraction from a nitrate aqueous solution media (Helaly et al., 2012). Other solvent extraction processes use a sulphuric acid solution for the separation of yttrium, cerium and lanthanum (Desouky et al., 2009) or various other media including phosphoric (Li et al., 2004; Nagaphani Kumar et al., 2010; Preston et al., 1996; Radhika et al., 2011, 2010; Yang et al., 2013) or sulphuric solutions (Abreu and Morais, 2010; Ghada et al., 2008; Zhang et al., 2012, 2013), carbonates (da Silva Queiroz et al., 2011), carboxylic acid (Singh et al., 2006), thiocyanate (Reddy et al., 1998), acetic acid (Chang et al., 2010), chloride (Banda et al., 2012; Gupta and Krishnamurthy, 2005; Maharana and Nair, 2005; Tong et al., 2009; Urbanski et al., 1996) and lactic acid solutions (Yin et al., 2010).

Solvent extraction has also been used to separate the heavier REE like thulium, ytterbium and lutetium using Cyanex272-P507 (Liao et al., 2010). Nuclear grade dysprosium oxide can be separated to a purity of > 98 % purity in a continuous cycle with the extractant 2-ethylhexylphosphonic acid or mono-2-ethylhexylester (EHEHPA). The same overall process also produces yttrium at 93 % purity and terbium at 54 % purity (Singh et al., 2008). The thorium and uranium are separated from the rare earths using solvent extraction by stripping the thorium hydrous oxide after alkaline dissolution followed by an alkaline carbonate solution (Ali et al., 2007).

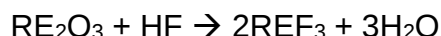
Solvent extraction processes requires hundreds of stages of mixers and settlers which have been set up in a train to obtain the desired separations. The process for separating the REE has improved over time as new techniques and processes like hollow fibre membrane technology becomes available. This technology is currently being developed at the North-West University and is commonly known as Membrane Based Solvent Extraction (MBSX) or Pertraction (van der Westhuizen et al., 2011). It has the potential to reduce the number of stages along with the size and the cost of the process. This has successfully been proven for the zirconium/hafnium solvent extraction process (van der Westhuizen et al., 2011), for platinum group metals (van der Westhuizen et al., 2013) and uranium and thorium separation (Ura et al., 2006). Hollow fibre technology has also been used successfully on lanthanides (Gaikwad and Rajput, 2010; Pabby and Sastre, 2013; Ramakul et al., 2009).

Other than solvent extraction, an electrochemical process (Castrillejo et al., 2002; Vasudevan et al., 2005), a dry process using chemical vapour transportation (Jiang et al., 1997; Murase et al., 1996), a combination of selective reduction and vacuum distillation (Uda, 2000), electrostatic pseudo liquid membrane (Yang et al., 1995), rapid radiochemical separation (Rengan and Meinke, 1964) and electrochemical reduction (Gibilaro et al., 2008) are available.

A.1.7 Fluorination of Rare Earths and Thorium

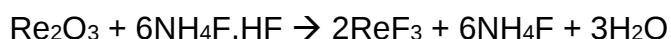
A number of methods have been used to prepare the rare earth fluorides in the past (Li et al., 2007). The most common fluorination process is a dry process where the oxide is converted directly using anhydrous hydrogen fluoride at elevated

temperatures. Most of the rare earths are converted at 700 °C within 8 hours (Gupta and Krishnamurthy, 2005):

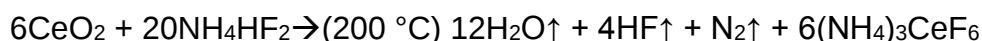


The REE have all been prepared with this method while reaching a conversion efficiency of 99.9 – 99.98%. The large scale production of rare earth fluorides is carried out using a rotary batch reactor, fluidized beds and the vibrating tray method (Gupta and Krishnamurthy, 2005). This reaction using high temperatures with highly corrosive chemicals which emphasizes the need to rather use a less dangerous chemical like ABF.

An alternative fluorinating route uses ammonium bifluoride (ABF) at 300 °C. An excess of 30% ABF is used when the mixture is heated with the conversion occurring quantitatively (Gupta and Krishnamurthy, 2005).



In certain instances the reaction can form an ammonia complex, $(\text{NH}_4)_3\text{ReF}_6$, with ABF at 200 °C, however it was completed with cerium (IV) oxide and not cerium (III) oxide which is more prevalent in monazite (MacPerson, 1959).



$(\text{NH}_4)_3\text{CeF}_6$ decomposes to CeF_3 at 600 °C (MacPerson, 1959) but literature does show it can start at 150 °C (Watanabe and Nishimura, 1988). If PTM does form the oxide then the digestion of PTM with ABF could provide an easier route to remove the REE, thorium and uranium.

The fluorination of thorium has been documented using a variety of chemicals including HF and ABF (Cardarelli, 2008). The reaction between thorium oxide and ABF produces the soluble compound ammonium thorium octafluoride $((\text{NH}_4)_4\text{ThF}_8)$ or ammonium thorium heptafluoride $((\text{NH}_4)_3\text{ThF}_7)$ (Silva et al., 2009; Wani et al., 1989). The kinetics (Figure A-7) determined that $(\text{NH}_4)_3\text{ThF}_7$ was formed in 2 days and $(\text{NH}_4)_4\text{ThF}_8$ was formed after 20 days (Silva et al., 2009). If this reaction can be perfected with PTM it could facilitate immediate removal of thorium and uranium.

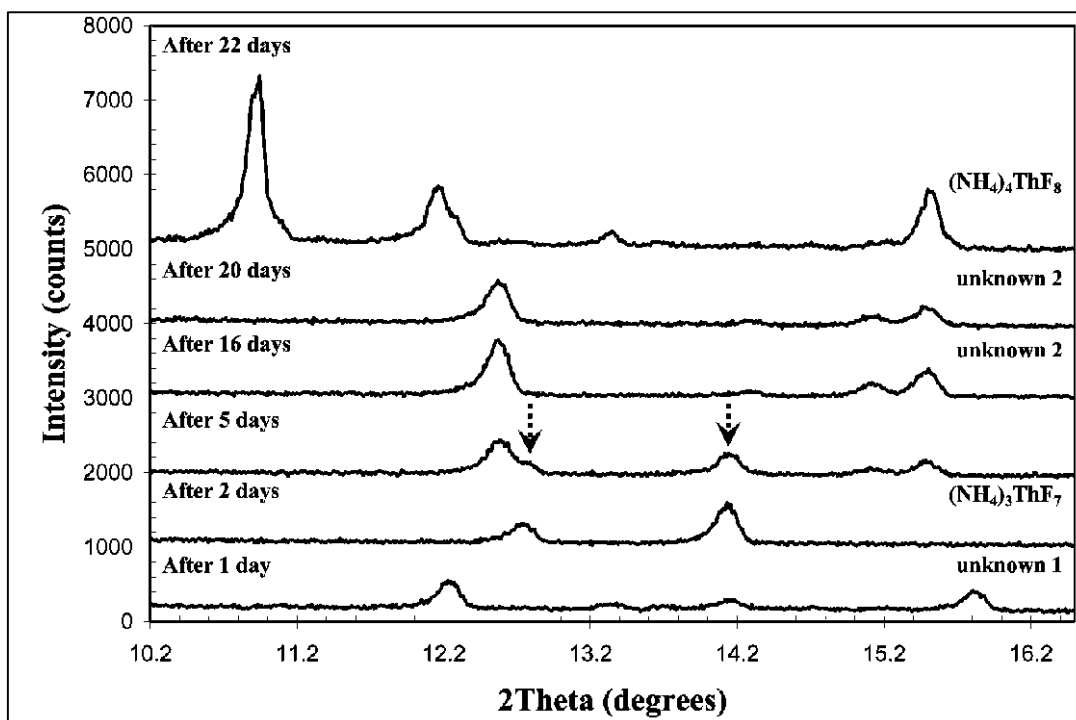


Figure A-7: XRD patterns indicating the reaction progress of ThO_2 mixed with excess NH_4HF_2

A.1.8 Radioactive Concerns with Monazite

Monazite is classified as a Naturally Occurring Radioactive Material (NORM). This definition describes a mineral which contains radionuclide of a natural origin and has the potential to significantly increase a worker or the public's exposure to radiation (El-Afifi et al., 2006). NORMs are present in the environment such as food, soil, water, building materials, and the human body (Malain et al., 2010). The activity concentration of ^{238}U and ^{232}Th in monazite or thorium ore is often the highest with monazite and second highest with zirconium ore. Monazite contains between 0.2 - 0.4 % U_3O_8 and 4.5 – 9.5 % ThO_2 (Pillai, 2005; Sroor, 2003). The main cause for the radio-activities found within these NORMs is the long lived isotopes such as ^{238}U , ^{235}U , ^{232}Th , ^{40}K , and ^{87}Rb (El-Afifi et al., 2006; Malain et al., 2010; Malanca et al., 1998). This gives monazite an effective dose above $4.3 \times 10^{-2} \text{ Sv/y}$ (Iwaoka et al., 2009). When monazite is processed, the radioactive equilibrium is disturbed. Radiation fields of about 1800 $\mu\text{G/h}$ have been observed due to the build-up of ^{228}Ra activity. For this reason standard radiation practices have to be used to control occupancy of these areas (Pillai, 2005; Sroor, 2003).

NORM's are generally found congregated together in large quantities, causing certain areas to have higher than normal background radiation levels. Such areas with high external radiation levels have been found in Austria, Brazil, China, India, France, Thailand, Italy and a number of other countries. The highest concentrations and areas are where monazite and other similar minerals are found, for example in Brazil in the state of Espirito Santo, Iran and India (Malain et al., 2010; Malanca et al., 1998; Termizi Ramli et al., 2005). A major concern with regards to NORMS is its safe disposal, either as a solid, gas or liquid medium with each medium requiring its own special considerations for disposal. A number of countries has looked at various disposal methods including burial in land, sea, incineration and smelting using similar techniques to what is currently being proposed for high level nuclear waste (Bhattacharyya, 1998).

A.1.9 International Interest in Monazite

South Africa contains an estimated 1 million metric tons or more rare earth oxides (du Preez, 2010). Rare earth mines in South Africa are found in areas like Steenkampskraal (Blench, 2010), Richard Bay sands (Ashry et al., 1995; Blench, 2010; Selby, 2010), Namakwa sands (Philander and Rozendaal, 2010), Piketberg (Western Cape) (Rozendaal and Boshoff, 2010) and the Pilansberg area (Lurie, 2010). The black sand found at these mines are composed mainly of ilmenite, magnetite, zircon, rutile, garnet and monazite (Ashry et al., 1995). China dominates the rare earths market, accounting for roughly 97 % of world trade in rare earth metals (Hurst, 2010). China's main resources of REM are concentrated in the iron-niobium rare earth deposits in Inner Mongolia in the north and in the mining of ion absorption ores in the south (Naumov, 2008). China obtains its rare earths from its Bantao ore which consists of 60 % monazite and 40 % bastnaesite (Xing et al., 2010).

Rare earth mining is expensive and environmentally unfriendly. China with its lax environmental laws continues to produce and control 97 % of the world rare earth market (Hurst, 2010; Massari and Ruberti, 2013; Pratiwi et al., 2011; Weber, 2012). China commenced the mining of REM in 1981 with an output of less than 3000 t with a world production of 40 000 t/y. By 2006 China has grown to 120 000 t which equates to 95 % of all REM produced worldwide.

India contains large quantities of monazite on its beaches on both the east and west coast (Alex et al., 1998) along with rich heavy mineral deposits in the south-west and south-east coastal regions. The major minerals found in India are ilmenite, zircon, rutile, garnet, monazite and silliminite. The Bihar region, including the Sirtiver basin of Madhya Pradesh further contains large volumes of placer deposits of rare earths contained within both monazite and xenotime (Pillai, 2005).

India does not have vast resources of uranium (Anantharaman et al., 2008; Dilorio et al., 2012; Urak, 2000) but vast thorium resources due to its natural monazite deposits which will soon assume a greater significance (Dilorio et al., 2012). For this reason it has become a strong proponent for thorium which can achieve high burn-ups (Kaya and Bozkurt, 2005). Thorium is becoming a major part of the Indian nuclear fuel cycle, due to its high abundance (Dilorio et al., 2012) and being the second largest producer of rare earth metals in world, mainly producing yttrium from monazite (Naumov, 2008).

Turkey is in a similar situation to India as it contains large quantities of thorium in the bastenite ore, second only to India, and very little uranium. Turkey's thorium reserves are estimated at 380 000 tons, roughly a third of the world's thorium reserves, at a grade of roughly 0.21 %. Turkey is currently evaluating the strategic importance of thorium for their nuclear future with the aim of one day becoming energy independent and provide cheap energy for its developing industry (Kaya and Bozkurt, 2005).

Other countries, such as the United States possess large resources and until 2002 still has one of the richest deposits of the cerium group. The main reason why the US is not exploiting these resources is the environmental consequences associated with the disposal of the thorium containing waste (Naumov, 2008).

Egypt's beach sands contain in the region of about 15 % heavy economic minerals such as ilmenite, rutile, magnetite, zircon and monazite. These beach deposits are the main thorium ore for Egypt as well as the Rosetta region (El-Afifi et al., 2006; El-Nadi et al., 2005).

Australia has an embargo on radiation related activities (Australian Radiation Protection, 1999) but does mine monazite. Over the last 10 years Australia's rare earth mine's output has decreased by a factor of 3.5 due to decreasing ore quality. Currently

Australia contains some of the richest bastnaesite deposits within Mount Weld with a 16 – 23 % concentration of REM oxides per 1 million tons of resources. This deposit is currently not being mined (Naumov, 2008).

A.1.10 The Rare Earth Market

In 2010 it was predicted that by 2014 the global demand for REE will exceed 200 000 tons per year (Hurst, 2010). The main reason why monazite is not exploited more is due to the high quantity of thorium present in the mineral and the strict control most countries have over its use (Naumov, 2008).

The use of Rare Earth Metals (REM) has increased due to their utilization in modern technology. For this reason, the REM market rises and falls violently. Between 1964 and 1997 the REM market has increased by a factor of 17, between 1997 and 2007 by a factor of 20.5. At present the prevalent source of REM's is bastnaesite which constitutes 80 – 90 % of the REM materials produced worldwide. To an insignificant degree, xenotime and monazite are used as well (Naumov, 2008). The balance between the demand and supply of REM have always been unstable, hence the volatility in the market. The current world consumption of REM is 70 – 75 % of total production. Officials at the Balyunebo Iron mine have stated that since 1958, about 12.5 million tons of REM ores have been mined, yet only 1.2 million tonnes (10 %) have been used. The long term prospect for the rare earths may indicate that it will eventually become impossible to satisfy the demand for an individual REM by increasing the mining of current ores (Naumov, 2008). Prices for rare earths in 2014 (Table A-2) ("Rare Earths Exploration & Development Company | Frontier," n.d.) and the import and export demand in the European Union from 2007 to 2012 (Figure A-8 and Figure A-9) indicate the rare earth market is very volatile and difficult to predict (Brown et al., 2014).

Table A-2: Rare earth oxide prices as of April 2014

RE Element	3 YrAvg \$/KG	2 YrAvg \$/KG	1 YrAvg \$/KG	China FOB \$/KG	China Dom \$/KG
Lanthanum	46	18	8	6	3
Cerium	45	17	8	5	3
Praseodymium	134	108	91	124	89
Neodymium	141	100	71	68	48
Samarium	60	41	15	9	3
Europium	2139	1907	1188	925	607
Gadolinium	95	72	47	47	22
Terbium	1745	1536	985	825	478
Dysprosium	998	828	552	465	247
Yttrium	86	60	27	19	8

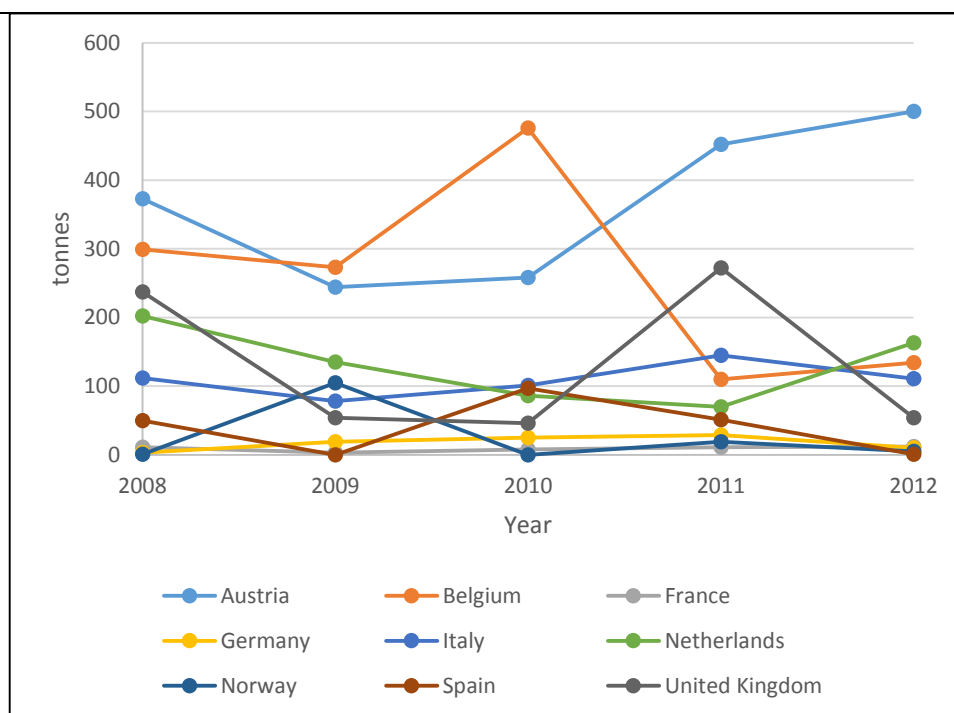


Figure A-8: The Rare Earth Metal Export per country for the years 2008 to 2012

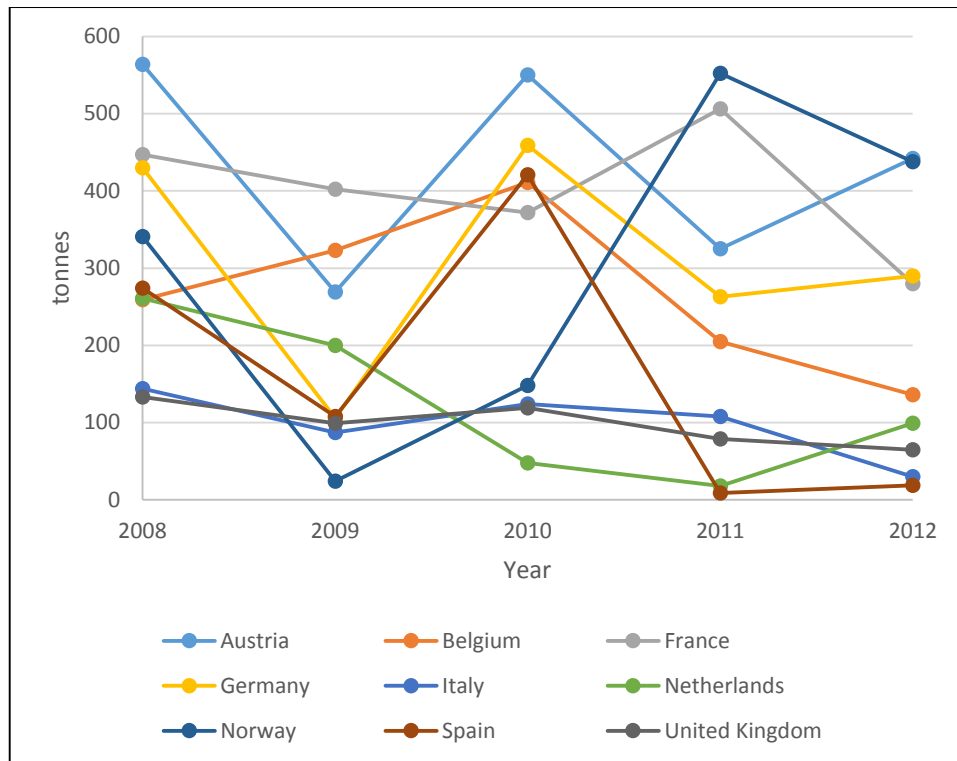


Figure A-9: Graph on the Rare Earth Metal Import per country for the years 2008 to 2012

A.2 Nuclear Power

Nuclear energy, according to numerous experts, presents a clearer and more sustainable option than fossil fuels (Dilorio et al., 2012). Nuclear energy's main concerns are in the form of high capital costs, radioactive waste management and links to possible uses as weapons of mass destruction (Herring et al., 2001). This brings nuclear energy to the centre of numerous political debates; mainly for the waste it produces (Nuttin et al., 2005). Other concerns about nuclear energy include nuclear proliferation and the safety of the facilities to both accidents and terrorist attacks. Despite the concerns listed above nuclear power is still recognized as an effective countermeasure against global warming (Kamei and Hakami, 2011).

Nuclear power is currently attracting the attention of a number of developed countries around the world to meet their future energy needs (Permana et al., 2011). The main reactor type used in the nuclear industry is the Light Water Reactor (LWR), such as the Pressurised Water Reactor (PWR) and Boiling Water Reactor (BWR), which have been used in operation for the last 40 – 60 years, followed by the Canada Deuterium

Uranium (CANDU) reactor (Sahin et al., 2001). However, since the incidences in Three Mile Island and Chernobyl, the global profile for nuclear energy has been nearly dormant, except in the fast growing economies of China, India and South Korea (Sinha, 2011). China has embraced its need for more energy by expanding their use of nuclear energy with 11 plants in current operation, 12 under construction and are in the process of planning another 147 (Kamei and Hakami, 2011). The latest information of China's expansion into nuclear energy is its plan to build 200 nuclear plants in the next 15 years (Wang, n.d.).

If the share in nuclear energy for primary energy demand increases by more than 30 % by 2050, then a number of essential requirements need to be implemented. This is to ensure the sustainable development and preservation of the earth's natural resources for future generations which would require fissile regeneration requirements to be imposed (Nuttin et al., 2005). The breeding of new nuclear fuel and the need to become more economical, clean and as safe as possible would mitigate the restrictions on nuclear energy and advance future nuclear development needs (Permana et al., 2011; Nuttin et al., 2005).

All reactors require a certain amount of reactivity in the fuel to operate. This is accomplished through the use of low enriched uranium (Sahin et al., 2001). The main workhorse of the nuclear industry is the PWR which represents a third of all the nuclear reactors in use today. The PWR utilizes uranium enriched to 5 % to sustain the nuclear fission chain reaction. The remaining 95 % consists of the un-fissionable isotope ^{238}U which is transmuted in plutonium (^{239}Pu) during normal operation of a nuclear reactors operation (Lamarsh and Baratta, 2011; Nuttin et al., 2005; Urak, 2000)

A.2.1 Thorium

Thorium is found in the ground in over 40 stable minerals and is easier, gentler and safer on the environment to mine than comparative uranium mining. The retrievable resources of thorium are estimated to be between 3 to 4 times more than the known reserves for uranium worldwide (Dilorio et al., 2012; Herring et al., 2001; Insulander Björk et al., 2011; Kamei and Hakami, 2011; Kaya and Bozkurt, 2005; Sahin et al., 2001). The current concentration of thorium within the crust is estimated between 6

and 10 ppm (Dilorio et al., 2012) or roughly 1.5 million tonnes of reasonably assured resources with an additional 3 million tonnes of estimated additional resources (Herring et al., 2001). For this reason the utilization of thorium as nuclear fuel presents the opportunity to increase the sustainability of nuclear power (Insulander Björk et al., 2011) and increase the mining activity of monazite (Herring et al., 2001).

Thorium is a naturally fertile metal which can be transmuted into fissionable ^{233}U through the absorption of a neutron and used as fuel in the nuclear reactor (Dilorio et al., 2012; Kamei and Hakami, 2011). Pure thorium metal is a soft, highly ductile metal which is silvery-white and retains its lustre for several months. The physical properties of thorium are greatly influenced by the degree of contamination with the oxide. Thorium dioxide is used in a nuclear reactor as a dust material, manufactured into small pellets using simple metallurgical methods. The powdered, pelletized and wafer thorium dioxide produces ^{233}U while it is in the reactor. The pellets are loaded into the fuel claddings and lowered into the reactor core (Kaya and Bozkurt, 2005).

The melting point of thorium dioxide (3300 °C) is higher than uranium dioxide (2865 °C), a key advantage for it to remain below the critical temperature of a reactor for operational and safety reasons (Cozzo et al., 2011; Lung and Gremm, 1998). Thorium is found in the quadrivalent form and its compounds are very stable with some of the highest known refractories. The chemical stability is the reason that these compounds are very difficult to separate and process (Herring et al., 2001; Lung and Gremm, 1998). Some of the physical properties of thorium oxide are presented (Table A-3) (Kaya and Bozkurt, 2005).

Table A-3: Physical properties of thorium oxide (ThO_2)

Molecular weight	264.037 g/mole
Melting point (Oxide)	3300 °C
Boiling Point (ThO_2)	4400 °C
Colour	White
Appearance	Crystalline

Thorium's advantage as a nuclear fuel lies in its higher potential for breeding than the uranium based, ^{238}U , fuel (Kaya and Bozkurt, 2005; Lafuente and Piera, 2010).

Thorium is a better material than the alternative ^{238}U or ^{239}Pu in high temperature environments (Kaya and Bozkurt, 2005) with its excellent negative temperature coefficient, smaller reactivity (Chang et al., 2006; Lung and Gremm, 1998; Núñez-Carrera et al., 2008) usefulness in existing PWR reactors (Breza and Technology, n.d.; Elkhadrawi, 2008; Galperin et al., 1997) and contains approximately forty times more energy per unit mass than uranium. The long lived minor actinides resulting from the fissioning of ^{233}U is up to 10 times lower in quantity than the uranium and plutonium cycle due to its position in the periodic table of elements (Kaya and Bozkurt, 2005). Thorium oxide fuel's favourable neutronic, thermal and chemical properties enables it to obtain higher than normal fuel utilization or burn-up. This allows the reactor to operate for longer periods of time before it has to be refuelled (Tsige-Tamirat, 2011; Weaver and Herring, 2003).

Thorium can be used for non-nuclear purposes as it has excellent corrosion resistance, thermal conductivity and stable waste (Cozzo et al., 2011; Herring et al., 2001; Weaver and Herring, 2003). Due to its high melting point, the principle non-nuclear use for thorium is in the preparation of Welsbach mantle for portable gas lights. These mantles consisted of thorium oxide, cerium oxide and some other ingredients which glow with a dazzling light when heated in a gas flame. Thorium can also be used as an alloying element with magnesium to impart high strength and creep resistance at high temperatures (Kaya and Bozkurt, 2005).

When an economic analysis was performed on the new fuel cycle, it indicated that the fuel cycle costs is competitive with a standard uranium core design. The reasons for this are that the thorium fuel cost is anticipated to be lower as no level of enrichment is required. The cost to the thorium fuel cycle is improved further by the optimization of the reload cycles by reducing the blanket-seed assembly enrichment and reducing the number of fuel assemblies. A sensitivity analysis has indicated that the cost to refuel a reactor with thorium is competitive compared to uranium with the additional benefit of reducing the actinides and plutonium in the fuel (Núñez-Carrera et al., 2008).

Currently there is no economic value for thorium as a nuclear fuel but the feasibility of using thorium in a reactor in the near future is becoming more feasible thanks largely to China and India (Kaya and Bozkurt, 2005). Presently the majority of nations have

little or no use for it resulting in the majority of the thorium being produced, disposed of as radioactive waste and creating an oversupply. Environmental and regulatory concerns over radioactive waste has always been a concern for the public's health and safety, fortunately both uranium and thorium is regarded as very safe as long as it is very well regulated (Dilorio et al., 2012).

A.2.2 Thorium in the Nuclear Industry

Nuclear energy is considered both safe and environmentally friendly by experts and will play a significant role in the development of countries with an ever growing demand for more electricity (Hurst, 2010; Sundararajan et al., 1998). The only problem of this ever expanding energy solution of nuclear energy is the opposition groups (Herring et al., 2001) and the finite reserves of uranium (Dilorio et al., 2012).

The drawbacks to using uranium are the large quantities of plutonium which are produced, the cost of mining, processing of the raw material, cost of enrichment, the environmental impact and the potential risk of it being used as a nuclear weapon. Despite these drawbacks it is estimated that uranium will remain the preferred fuel for the foreseeable future as its performance is well known in industry and has an existing supporting infrastructure system already in place (Amaral and Morais, 2010).

Over time and with the rapid expansion of nuclear energy in China (Dilorio et al., 2012), it became clear that only using uranium is not the ideal long term solution (Dilorio et al., 2012) as it is a finite resource and the production of significant quantities of plutonium (^{239}Pu). To make nuclear energy more sustainable in the long term, nuclear fuel, like ^{239}Pu and ^{233}U , need to be bred to form new forms of nuclear fuel from natural uranium (^{238}U) and thorium (^{232}Th) (Permana et al., 2011). However, civilian nuclear facilities are accumulating large quantities of plutonium in their reactors with the estimated total accumulated plutonium in 2006 estimated at 1700 tonnes (Şahin et al., 2006a).

The consumption of plutonium worldwide is not happening fast enough to stabilize the large stockpiles of plutonium growing worldwide (Haas et al., n.d.; Schram and Klaassen, 2007). Various methods for treating and handling plutonium include incineration of the plutonium in a nuclear reactor for the production of electricity,

however when plutonium is used in conjunction with uranium, second generation plutonium is created (Şahin et al., 2006a). Alternatively by substituting thorium for uranium, the generation of plutonium is avoided (Chang et al., 2006; Haas et al., n.d.) and, as thorium fuels do not contain ^{238}U , the production of second generation plutonium is prevented (Schram and Klaassen, 2007).

Thorium based fuel is superior for plutonium incineration and needs to be considered as an alternative to traditional MOX-type fuels for current future reactor designs (Weaver and Herring, 2003). Thorium in a nuclear reactor consumes plutonium far more effectively than uranium. Plutonium can be effectively burned in existing light water reactors with some design changes being required for a full Th/Pu fuel core to operate safely (Kaya and Bozkurt, 2005).

Thorium is currently being investigated for its inherent proliferation resistance (Trellue et al., 2011), potential as a nuclear fuel (Kaya and Bozkurt, 2005) and as the only other naturally occurring nuclear fuel source. Thorium is found as a 100 % pure usable isotope which does not require any form of enrichment. Uranium in contrast needs to be enriched with ^{235}U from 0.7 to 5 % in order to obtain reactivity in the fuel to operate the reactor (Dilorio et al., 2012; Kaya and Bozkurt, 2005). Thorium and uranium are both capable of being used as fuel in a nuclear reactor or alternatively for the production of medical isotopes (Amaral and Morais, 2010; Dill et al., 2012; Hassan et al., 1997). Using thorium to incinerate plutonium is possible because ^{233}U is the only fissionable isotope formed in the nuclear reactor. The fission of the ^{233}U produces electricity while denaturing the plutonium with ^{232}U (Şahin et al., 2006b). This approach destroys plutonium more efficiently than conventional Pu-U MOX fuel (Chang et al., 2006; Haas et al., n.d.; Insulander Björk et al., 2011; Weaver and Herring, 2003) with some studies showing that when thorium is used, all the plutonium has been reduced (Kaya and Bozkurt, 2005).

By replacing uranium with thorium the consumption of plutonium increases along with an increase in the use of thorium. The downside of thorium is that the quantity of minor actinides produced, mainly neptunium, actinium and curium, as well. it cannot be used directly in the core of a nuclear reactor and needs a kick-starter material in the core (Kamei and Hakami, 2011; Kaya and Bozkurt, 2005). The overall actinide production

and associated radiotoxicity of the spent fuel is significantly lower than a conventional all UO₂ or MOX core (Schram and Klaassen, 2007). The use of Th/Pu fuel in a PWR require minimal design changes to enable it to consume more than a third of the core while still maintaining satisfactory reactor safety limits (Elkhadrawi, 2008; Trellue et al., 2011).

While the U.S. have slowed down their research, the study of using thorium-based fuels in nuclear reactors is ongoing in China and India (Dilorio et al., 2012). China is embracing thorium research by having a group of 140 PhD scientists working full time on China with an estimated budget of \$ 350 million (Jamasmie., 2013) and have recently moved up their time table by planning to build and commission a new thorium reactor in the next 10 years (Duggan., 2014). Modern day PWR reactors can also use this mixed oxide fuel with minimal changes to the reactor system (Cozzo et al., 2011; Kasten, 1998).

A.2.3 Cost of MOX type fuels

The three nuclear fuels, thorium oxide, uranium oxide and plutonium oxide, all have similar chemical characteristics and crystallizes in centred cubic form. This is an important property for the manufacture and stability of hybrid oxide fuels which permits very high burn-ups (Lung and Gremm, 1998).

There is, at present, a need for an alternative solution to uranium to reduce the plutonium, americium and curium quantities within the spent fuel (Trellue et al., 2011). Uranium has monetary value in each phase of the fuel cycle, including mining, enrichment, fabrication, energy production and waste disposal. A large scale, open-pit uranium mine currently being planned in Namibia with mining to commence in 2014 is estimated to produce 15 million pounds of uranium ore. The initial development cost of the project is estimated at \$ 1.6 billion. If transport, royalties and marketing costs are excluded, then the uranium ore can be produced at approximately \$ 28.50 /lb (Dilorio et al., 2012). Overall for a 45 000 MWd/t burn-up provides 360 000 kWh of electrical energy per kg, giving a fuel cost of 0.77 c/kWh (Dilorio et al., 2012). Thorium is currently produced alongside the lanthanide metals and sells for approximately \$ 88.5 /kg (Herring et al., 2001).

Calculations have shown the fuel costs for a mixed Th- UO_2 core are comparable to an all uranium core with a burn-up to 75 MWd/kg, the same and will be roughly 10 % higher for a burn-up of 45 MWd/kg. The calculations do not include the economic advantages associated with increased plant capacity factors and reduced outage cost due to longer fuel cycle lengths. By going to even longer cycle lengths, at 87 MWd/kg, the ThO_2 - UO_2 core will cost a few percent less. Overall if ThO_2 becomes the predominant nuclear fuel, it is estimated; that of the 105 plants currently operating in the US, it would save the federal government more than \$ 100 million per year as fewer spent fuel bundles will require temporary storage, handling, transportation and permanent disposal (Herring et al., 2001).

Mixed ThO_2 - UO_2 fuel is expected to be relatively insensitive to the price of thorium. No enrichment of thorium is required, therefore between 0.75 – 0.65 kg thorium is required per kg fuel (Herring et al., 2001; Urak, 2000). When mixed ThO_2 - UO_2 is compared to UO_2 at a similar burn-up of 45 MWd/kg the cost per unit of energy is roughly 10% higher and the same as high burn-up cores. If projected future prices are used, the cost will be about the same as conventional UO_2 and 9 % lower for high burn-up cores (Herring et al., 2001). With the development of MOX-fuel and the re-use of spent fuel, between 70 and 75 tonnes/year of reactor grade plutonium is produced. The amount of plutonium present in the civilian market in 2003 is estimated in the region of 1600 tonnes and can be re-used as mixed-oxide fuel. At present 10 % of all the reactors are licensed to use MOX-fuel for a third being loaded (Chang et al., 2006; Schram and Klaassen, 2007).

When thorium is used for MOX fuel the production of plutonium is reduced by a factor of 3 – 5. The thorium waste is more stable than uranium, however, the highly enriched fuel required with the thorium can have a negative impact on the fuel economy. Regardless, a properly designed micro-heterogeneous core can exhibit higher reactivity than an all-uranium core (Breza et al., 2010). MOX fuel consists of depleted or natural uranium with 7 % plutonium. The overall mixture itself contains roughly 65 % fissile material. The natural uranium which is still present in the MOX fuel also converted to fissionable plutonium. Using the MOX cycle a 100 MW plant can consume roughly 500 kg/year plutonium (Kamei and Hakami, 2011).

The fabrication of the MOX-fuel assembly is estimated to be twice as expensive when compared to a conventional Pu-U MOX-fuel assembly due to the presence of ^{232}U . ^{232}Th - ^{233}U fuel is estimated to cost more as ^{233}U as additional gamma shielding protection is required for the ^{232}U . This hindrance normally offsets any incentive to use thorium as a fuel. The development of a more streamlined fuel fabrication method for thorium, such as sol-gel palletisation, is being developed to ease the process of reprocessing thorium spent fuel (Lung and Gremm, 1998). PWR reactors typically operate at 3400 MWt with 90 tons of fuel typically within the reactor. Using thorium will produce similar concerns to using U-Pu MOX fuel in a reactor. Weapons grade plutonium attractiveness significantly decreases when the burn-up is increased from 47 to 94 MWd/kg HM (Trellue et al., 2011).

The amount of plutonium in the spent fuel for Pu-ThOX fuel is approximately four times higher than for UOX fuel as required by the high initial Pu content. U-Pu-ThOX fuel exhibits a higher Pu transmutation potential than Pu-ThOX fuel. Regardless in both types of fuels the MA content is higher than UOX fuel however the U-Pu-ThOX fuel has shown a lower MA production due to the initial content of ^{233}U and a lower content of Pu than Pu-ThOX fuel (Breza et al., 2010). The production of thorium mixed oxide fuel is estimated to be twice as expensive as UO_2 fuel but the absence of enrichment offset the additional cost of fabrication (Dilorio et al., 2012).

A.3 Plasma Treatment of Zircon to Produce Zirconium

Zircon is one of the most stable chemical compounds due to the strong bond between zirconia and silica. Therefore any extraction for zirconium metal or other useful zirconium compounds must start with the breakdown of these bonds (Abdelkader et al., 2008). The concept to treat monazite in a plasma and the process which inspired the project is the AMI zirconium metal process and is currently being further developed by Necsa and the Advanced Metals Initiative (AMI) (Figure A-10) (Simpson et al., 2015).

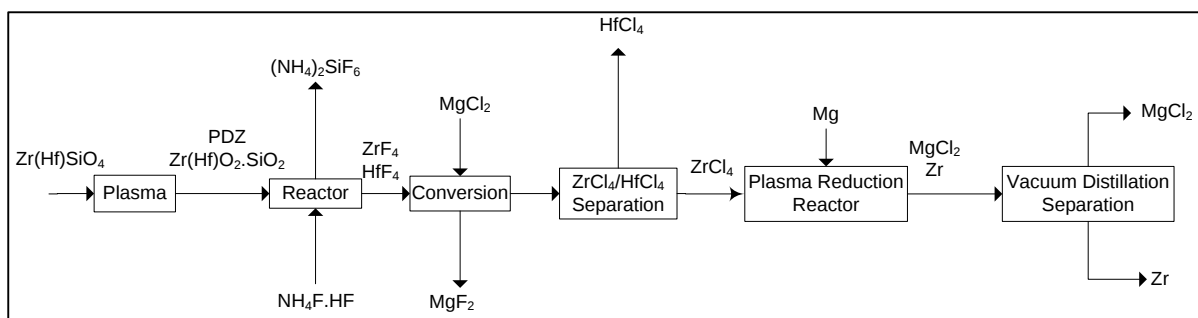


Figure A-10: Block flow diagram of the zircon plasma process

The zirconium process operates as follows: Zircon sand is fed to a plasma reactor where it is dissociated into Plasma Dissociated Zircon (PDZ) (Havenga and Nel, 2012; Kock et al., 2011). The PDZ is fed to a fluorinating reactor where the PDZ is reacted with ammonium bifluoride (ABF) to produce zirconium fluoride (ZrF_4) (Makhofane et al., 2013; Nel et al., 2011; Pretorius et al., 2012). The zirconium is subsequently converted into the chloride with subsequent downstream processing into nuclear grade zirconium metal (Perry and Green, 1997; Makhofane et al., 2013).

The treatment of the mineral in a plasma is better known with the conversion of zircon into PDZ as illustrated (Figure A-11 and Figure A-12). Zircon's chemical bonds are broken, between zirconium and oxygen and silicone and oxygen, and new bonds are being formed. It is hypothesised that a similar action will occur with monazite (Toumanov, 2003) whereby the plasma dissociation of monazite is anticipated to be treated in a similar manner to zircon and to be more reactive due to the destruction of the crystal structure.

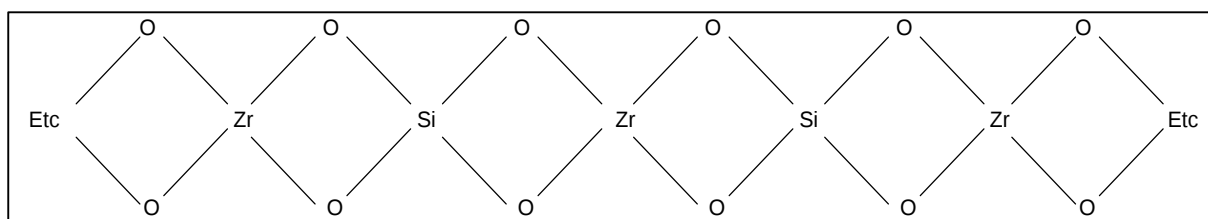


Figure A-11: Crystal structure of zircon

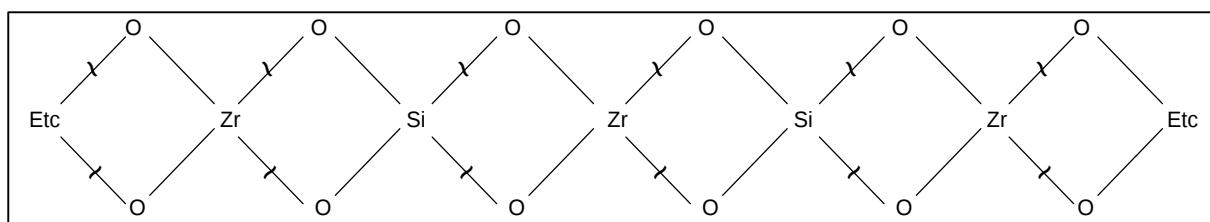


Figure A-12: Crystal structure of plasma dissociated zircon

Plasmas are ideally suitable for processing refractory materials like zircon or monazite due to its high operating temperatures (10 000 °C), good thermal conductivity and high heat content (Rendtorff et al., 2012) which can be used to treat the monazite crystal structure to make it chemically more reactive. The heating and cooling rates of a plasma are extreme in comparison to traditional processing ($\approx 10^6$ °C/s) and the achievable rates are higher than other advanced processing routes. This increases the reaction kinetics by several orders. These high temperatures alter the mineral's crystal structure, thereby, making it chemically more reactive which should allow less harsh chemical processing techniques to be used on monazite (Eletskii and Smirnov, 1985; Fridman, 2008).

Monazite is a rare earth phosphate crystal (Clavier et al., 2011) with a monoclinic structure consisting of a number of rare earth phosphates (Heuser et al., 2014; Li et al., 2007) and is anticipated to follow a similar path. With regards to the crystalline phase during plasma treatment, the high temperature anhydrous monoclinic phase is irreversibly up to about 750 °C after the total dehydration of the hexagonal hydrated structure. A poly-trioxo-phosphate secondary minor phase $\text{Re}(\text{PO}_3)_3$, which results from absorption of H_3PO_4 is formed at 950 °C and decomposes at 1350 °C (Bregiroux et al., 2006; Lucas et al., 2004) as presented in a high temperature XRD (Figure A-13) (Lucas et al., 2004):

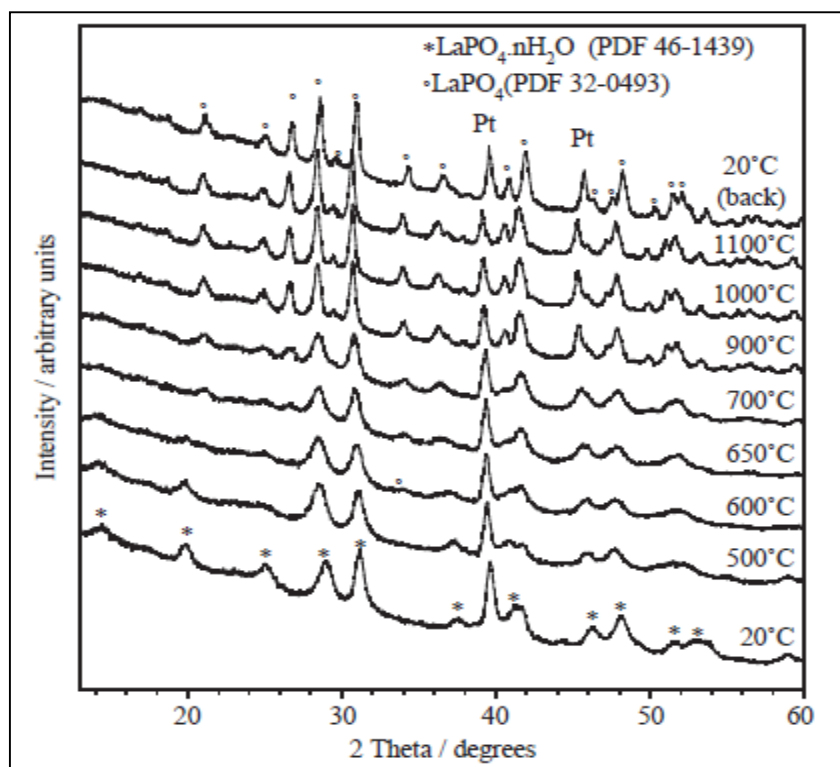
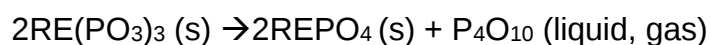


Figure A-13: High temperature XRD of lanthanum phosphate

Lucas et al (2004) detected a phase transformation between the rhabdophane-type structure (hexagonal) and the monazite structure (monoclinic). This phenomenon was observed at about 600 °C for LaPO₄ and at 650 °C for CePO₄. These results agree with literature data obtained by Jonasson & Vance (1986). The monoclinic phase remains stable at high temperature after it has cooled to room temperature. The decomposition of the poly-tri-oxo-phosphate into a rare earth phosphate occurs between 1050 °C and 1350 °C as per the following reaction (Lucas et al., 2004).



Further XPS and X-ray analysis have been completed on monazite by Glorieux *et al* (2004), Bradbury & Williams (2009) and Montel, Devidal & Avignant (2002) with similar results.

A.4 References for the Extended Literature Study

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B. Appendix 2: Modelling of a monazite particle as it travels through an in-flight RF plasma

B.1 Introduction

Plasmas are ideally suited for processing refractory materials like zircon and monazite due to their high operating temperatures (10 000 °C), good thermal conductivity and the high heat content (Feinman,1987; Rendtorff et al., 2012). The high operating temperatures in a plasma “crack” and alter the mineral’s crystal structure to produce a chemically reactive compound which are initially highly inert and require harsh chemical treatment. The increased chemical reactivity permits the use of less harsh chemicals to chemically process the minerals (Eletskii and Smirnov, 1985; Fridman, 2008).

The plasma treatment of monazite is hypothesised to allow monazite to be more susceptible to chemical attack due to the destruction of the crystal structure (Toumanov, 2003). The decomposition temperature of monazite in the presence of a monazite to carbon ratio of 2:5 is 1200 to 1400 °C to form the rare earth sequioxides (RE_2O_3) (Xing et al., 2010). These sequioxides, henceforth referred to as the oxides, dissolve readily in a diluted mineral acid, with the exception of CeO_2 , unlike their phosphate counterparts (Adachi et al., 2004; Peelman et al., 2014; Weast and Astle, 1974).

The high temperatures required to decompose monazite can only be obtained in an efficient, economical and effective manner through the use of an in-flight Radio Frequency (RF) induction plasma (Boulos, 1985) or a DC non-transferred arc plasma (Havenga and Nel, 2012; Feinman, 1987). RF plasmas are known to operate with a thermal efficiency of 40 to 60 % while DC non-transfer arc plasmas operate with thermal efficiencies of between 60 and 80 % (Boulos, 1985). For the purpose of this study the RF plasma will be used as modelling of this plasma since it is simpler than the DC non-transfer arc which is beyond the scope of this research, however the temperatures within the plasma will be lower (Boulos, 1985; Feinman 1987).

The need for a theoretical model using Computational Fluid Dynamics (CFD) analysis stems from a need to understand the heating of the monazite particles as it passes through the plasma. CFD analysis is a tool with the distinct advantage of determining the gas temperature and velocity at individual points within a system. From this, the location at which monazite decomposes and the individual particle temperatures can be determined. This information can then be used to optimize the plasma design which can be altered and re-analysed multiple times until an optimum solution presents itself to permit more efficient heating of the particles. Additional parameters such as particle size and plasma power can be optimized for the final design of the plasma. Doing such an exercise without the use of CFD would require multiple plasma reactors, lengthy periods between testing and costly changes to the system. CFD allows the same upgrades to be completed in the span of a day at a fraction of the cost and, as seen with this research, will allow new insight into the plasma and how it heats the particles within.

This appendix chapter is still a work in progress with the results deviating from published values for similar systems.

B.2 Experimental Procedure

Comsol is a multi-physics modelling program which utilizes Computational Fluid Dynamic (CFD) principals to evaluate arbitrary shapes and components. Comsol can evaluate various physical phenomenon including magnetic, electric and stress fields, heat and fluid flow, plasma flow, induction plasma, etc. Using a current RF reactor design, a generic RF induction plasma model was developed to perform the CFD calculations and to evaluate the heating cycle of a monazite particle as it passes through the plasma. CFD is used rather than conventional first principal calculations as CFD can calculate individual sections of the plasma more efficiently and accurately.

The CFD model is based on a RF plasma which develops a high temperature thermal plasma. The RF plasma currently resides at Necsa (Figure B-1). A basic generic model of the RF plasma, using argon as the carrier gas, was developed as per the specifications provided (Table B-1).

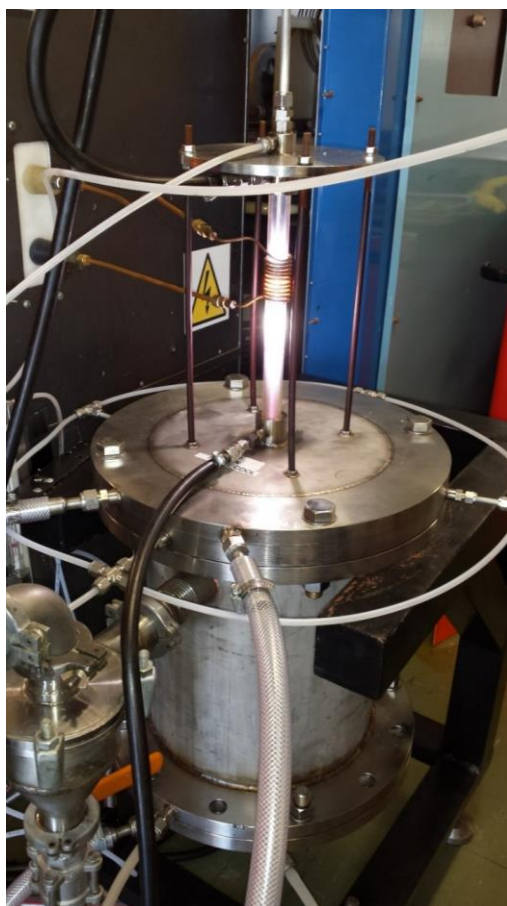


Figure B-1: Photo of the RF plasma currently in use at Necsa

Table B-1: Plasma Gas and Power Specifications

Property	Value	Units
Plasma Power Source	10	kW
Inlet Mass Flow (External)	0.42	g/s
Inlet Mass Flow (Internal)	0.06	g/s
Internal Pressure	40	kPa
Plasma Tube Diameter	15	mm
Inlet Diameter	6	mm
Reactor Vessel Width	80	mm
Reactor Vessel Length	500	mm
Inlet Length	50	mm
Plasma Length	40	mm
Plasma Width	11	mm
Distance to Exit	100	mm

The plasma gas enters the top of the plasma at a height of 600 mm using both the side gas inlets and the main central gas inlet. This central gas inlet will be used as the main feed tube for the monazite particles. The gas enters the plasma zone at a height of 545 mm and exits it at height of 505 mm. A plasma flame is formed below the plasma zone. The gas enters the “Distance to Exit” section whereby the entrance is fixed at the 500 mm marker. The length of the “Distance to Exit” section is varied between 0 and 150 mm. For this reason the gas may exit this section at any point between 500 and 350 mm marker. The inner diameter remains constant at 15 mm wide. The length of the Distance to Exit is initially set at 100 mm. After passing through the Distance to Exit section, the gas enters the Reactor Vessel. This vessel is modelled with a width of 80 mm but the boundaries can be larger as the walls of the model were set to permit flow of the gas across the boundary wall. The length of this vessel is varied in order for the height of the reactor to always be 600 mm (Figure B-2).

The RF plasma power supply is rated at 10 kW, however the thermal efficiency of an RF plasma is between 40 and 60 %. This will lower the amount of power which can be supplied to the plasma to between 4.0 and 6.0 kW which will be the available power to decompose the monazite. This is the applied plasma power to the system and is referred to as the plasma power in the text.

The aim of using Comsol is not to simulate the plasma but rather to study the heating profile of the monazite particles. While Comsol does have a feature to simulate the RF induction plasma, its use and development is beyond the scope for this study. For this reason, an alternative method of generating the plasma’s conditions was developed by designating a segment of the plasma as a heat source with the desired power requirements. Using the desired software packages available in Comsol, the monazite particles within Comsol were subjected to the same physical, energy and heat requirements as if it were a proper RF plasma. The advantage of using this approach is that pertinent information like the residence time and the heat cycle of the monazite along with the feasibility of feeding monazite to an actual RF plasma can be evaluated. The disadvantage of this approach is that the magnetic interference of monazite with the plasma and the exact shape of the plasma could cause the monazite to completely miss the heat zone.

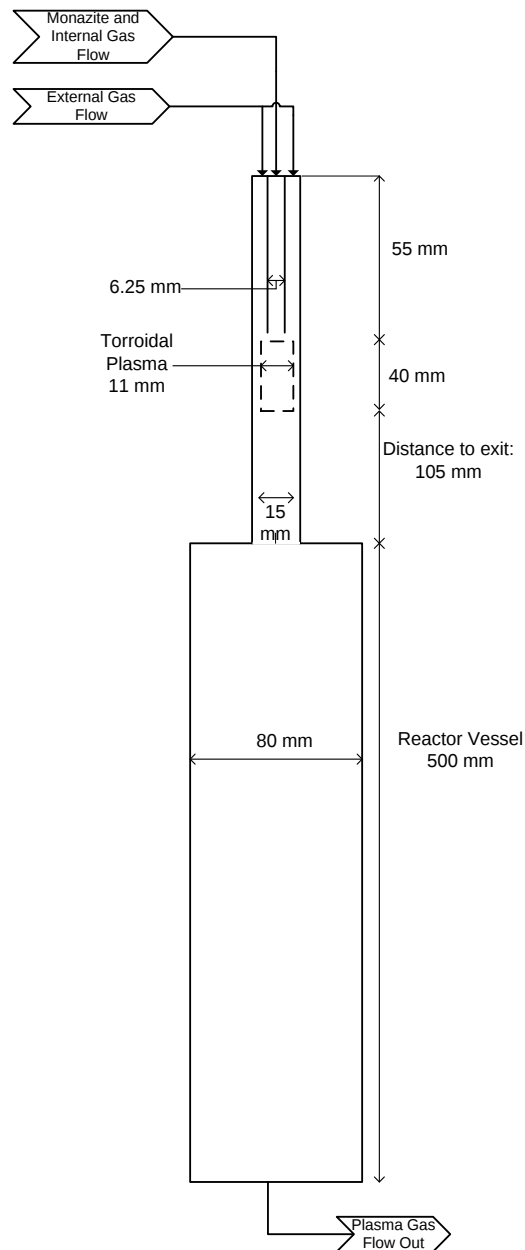


Figure B-2: Generic model of the RF Plasma

The model was evaluated using an extremely fine mesh to determine the particle temperature more accurately. For demonstration purposes, the top portion (Figure B-3) and the full model (Figure B-4) of the plasma are represented with a course mesh.

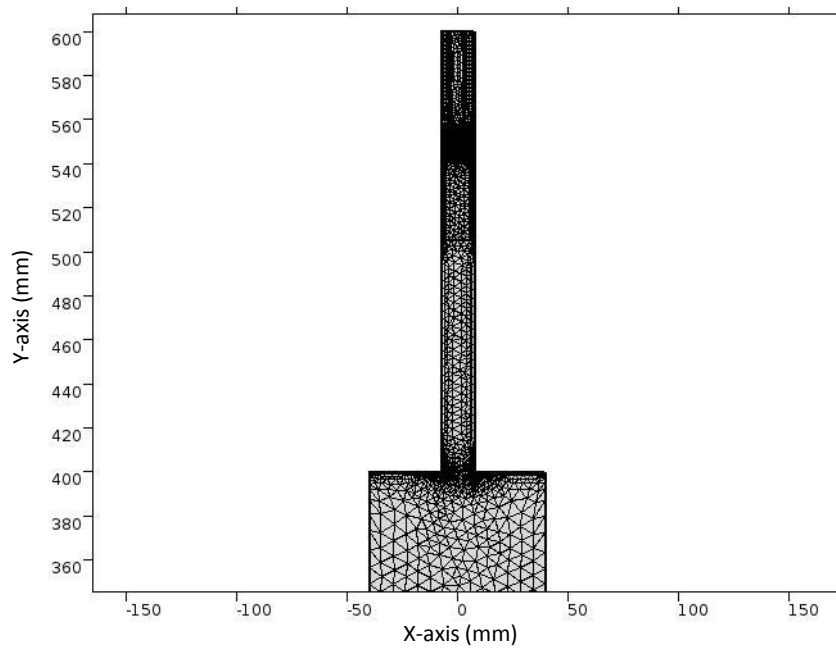


Figure B-3: Top portion of the generic RF plasma model with a coarse mesh with a distance to exit of 100 mm

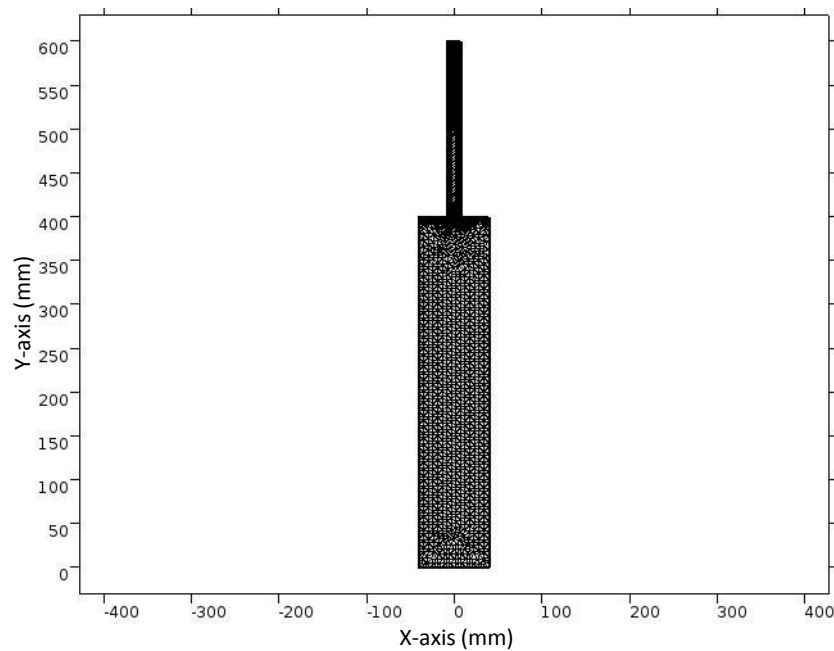


Figure B-4: Full view of the RF plasma with a coarse mesh

In order to determine the minimum requirements of the plasma, the monazite particles need to be heated up to the decomposition temperature of 1400 °C (Chapter 3) from which it can be assumed, for the purpose of this study, that all of the monazite particles have decomposed into the rare earth oxides. Comsol has a separate module for the purpose of tracing a particle as it traverses a fluid medium. This module requires that

the physical properties of the particles, such as the specific heat capacity and particle size, be entered manually. Comsol will determine the particle temperature of each individual particle as it travels through the plasma. The monazite particles are released into the plasma with the particle concentration as a function of the internal gas flow, thus the majority of the particles would be concentrated in the centre of the plasma.

A problem with modelling the heating of the particles is that the energy absorbed by the particles would cool the plasma gas. A factor which the Comsol models does not take into account. For this reason the energy required to heat the particles to their desired temperatures must be added separately. The energy absorbed by heating the particles can be negated for the initial models as only a small quantity of monazite is fed to the plasma for all simulations. The plasma power, as specified, is the power required to heat up the plasma flame to the minimum temperature required at which all of the particles will be heated to a minimum temperature of 1400 °C. When a significant quantity of monazite is fed to the plasma then the plasma flame would cool down. Additional calculations will be completed to determine how much additional energy is required per unit of mass in order to keep the plasma flame at the correct temperature. From this, using the maximum available power in the plasma of 6 kW, the mass flow can be determined.

The problem is that monazite will decompose into the rare earth oxides and graphite will dissociate into CO and CO₂ which would either absorb or release energy. Fortunately, the energy required to decompose monazite at 1400 °C and the energy released by the graphite when it decomposes is already accounted for. For this reason, the energy required to heat the small quantity of monazite to the average particle temperature where the maximum temperature obtained by the particle on the side is 1400 °C, and the average temperature of the graphite will be to determine how much additional energy is available in the 6 kW plasma. This quantity of energy will be used to determine what mass of monazite and carbon can be fed to the plasma to ensure that the plasma flame does not cool too significantly, resulting in un-decomposed monazite.

The density of monazite used for this model is 5150 kg/m³ (Hikichi et al., 1990) and for graphite, 2000 kg/m³ (Perry and Green, 1997). The specific heat capacity for

cerium orthophosphate was used as a substitute to monazite as it has the highest valid temperature range of all the phosphates (Equation B-1) and is within 1 – 3 % of the other rare earth phosphates (Thiriet et al., 2004). This equation, for the purpose of this study, substitutes as a reasonable approximation for monazite for the purpose of this study.

$$C_p(\text{CePO}_4) = 106.49 + 7.23 \times 10^{-2} \cdot T - 1.88 \times 10^{-5} \cdot T^2 - 1.77 \times 10^{-6} \cdot T^3 \quad \text{J/mol.K} \quad \text{Equation B-1}$$

The specific heat capacity of zircon (Equation B-2) was obtained from Brown et al. (2013).

$$C_p(\text{ZrSiO}_4) = -352.55 + 82.55 \cdot \ln T + 105087 \cdot T^{-2} - 0.0697 \cdot T \quad \text{J/mol.K} \quad \text{Equation B-2}$$

The specific heat capacity of graphite (Perry and Green, 1997), CO and CO₂ (Himmelblau and Riggs, 2004) is provided in Equation B-3 to Equation B-5:

$$C_p(\text{Graphite}) = 11.19 + 0.01095 \cdot T - 40742/T^2 \quad \text{J/mol.K} \quad \text{Equation B-3}$$

$$C_p(\text{CO}) = 28.96 + 0.411 \times 10^{-2} \cdot T + 0.3548 \times 10^{-5} \cdot T^2 - 2.22 \times 10^{-9} \cdot T^3 \quad \text{J/mol.K} \quad \text{Equation B-4}$$

$$C_p(\text{CO}_2) = 36.11 + 4.233 \times 10^{-2} \cdot T - 2.88 \times 10^{-5} \cdot T^2 + 7.464 \times 10^{-9} \cdot T^3 \quad \text{J/mol.K} \quad \text{Equation B-5}$$

B.3 The CFD Plasma Model

B.3.1 Basic Plasma

The RF model is developed in Comsol and simulated using the linear gas flow and heat transfer in fluids modules in steady state. The particle tracing is completed using a time dependent simulation with the steady state temperature and velocity values set as the basis for the simulation. The 6 kW plasma's gas velocity profile (Figure B-5) indicates that the gas enters at a higher speed, along the side of the plasma (1.37 m/s) than in the centre (0.01 m/s). When the gas reaches the plasma zone it concentrates in the centre of the plasma with a maximum central velocity of 0.75 m/s (Figure B-6). The gas obtains a new linear gas flow profile which it maintains until the gas exits the plasma. As the gas enters the reactor chamber, the gas expands and slow down to 0.41 m/s along the centreline before it exits the plasma model. The reason for the increase in speed at 540 mm is suspected to be due to the gas nearing a vortex which is at the start of the plasma zone where the gas circulates.

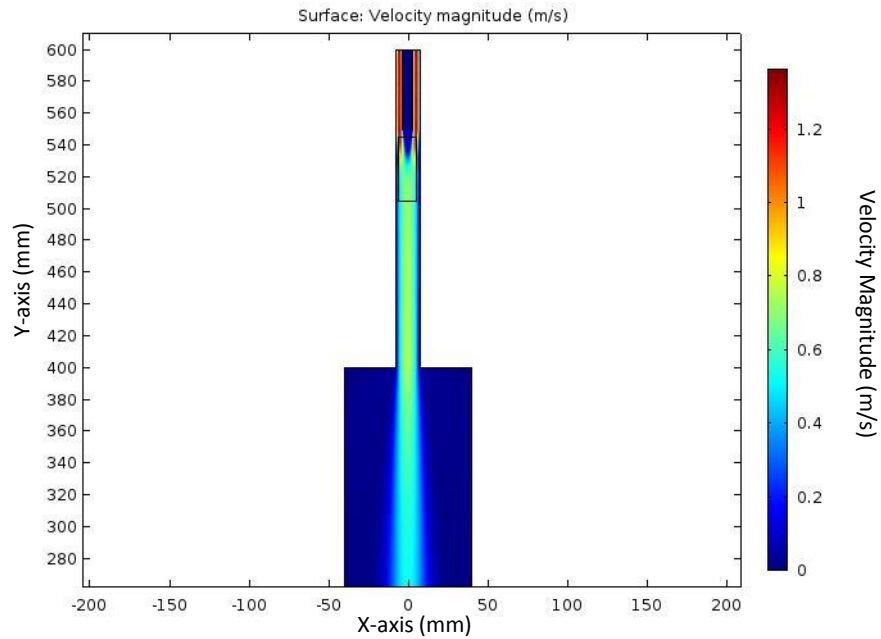


Figure B-5: Velocity profile of the plasma gas of a 6 kW plasma as specified

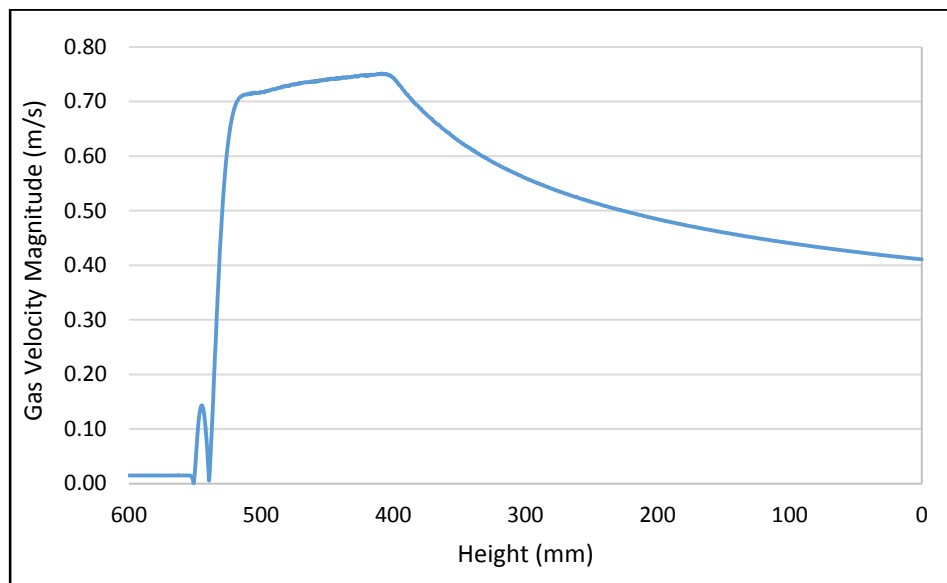


Figure B-6: Gas velocity magnitude, in m/s, of the 6 kW plasma along the centreline

The gas temperature profile (Figure B-7) indicates that a maximum temperature of 4136 °C is attained at the bottom of the plasma zone near the centre. The gas subsequently cools down to 500 °C very rapidly and finally down to 356 °C before exiting the model (Figure B-8). Rapid cooling of the gas occurs due to mixing of the cooler gas in the reactor chamber and the proximity of the water cooled plasma wall which helps cool down the particles. This would stop the rare earth oxide and

phosphor-oxide particles to recombine and reform the rare earth phosphates (Boulos et al., 1994).

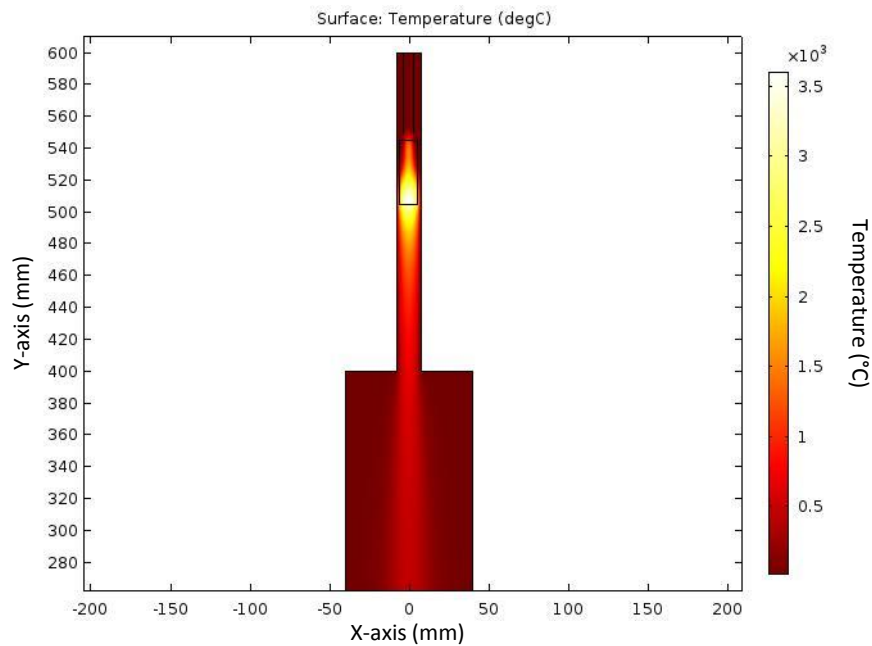


Figure B-7: Temperature profile of the plasma gas of a 6 kW plasma as specified.

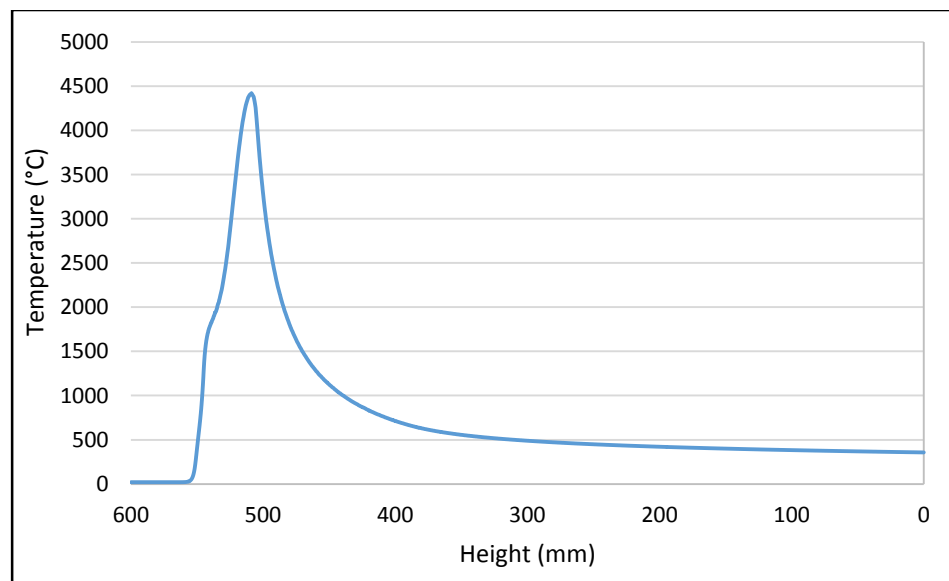


Figure B-8: Gas temperature along the centreline of the 6 kW plasma

The particle size distribution of the monazite sand used in the research (Figure B-9) indicated that 58.41 % of the particles are between the sizes of 90 and 150 μm . The remaining 41.59 % are mainly compromised of smaller particles with the exception of 0.14 % of the particles which are bigger than 150 μm . For the purpose of this study an

average particle size of 120 μm is used in the model as it is the average of the largest portion.

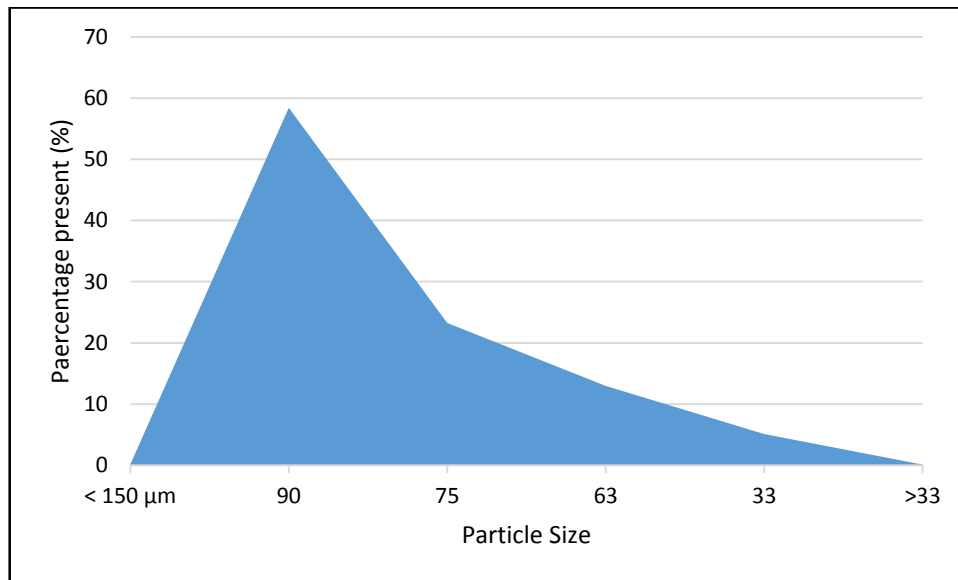


Figure B-9: Particle size distribution for a monazite sand sample

In order to simulate a continuous flow, a batch of 500, 120 μm monazite particles, were released every 10 ms for a period of 100 ms. The model ran for a total of 600 ms. The monazite particle which attained the highest maximum particle temperature was generally found in the centre, henceforth referred to as Centre, and the monazite particle with the lowest maximum particle temperature was found along the side of the plasma, henceforth referred to as Side (Figure B-10). The monazite particles in the 6 kW attained temperatures between 2162 and 2852 $^{\circ}\text{C}$. These temperatures are in excess of what is required and confirms that the 6 kW RF plasma can heat a small quantity of monazite to a high enough temperature at which monazite can be decomposed in the presence of carbon.

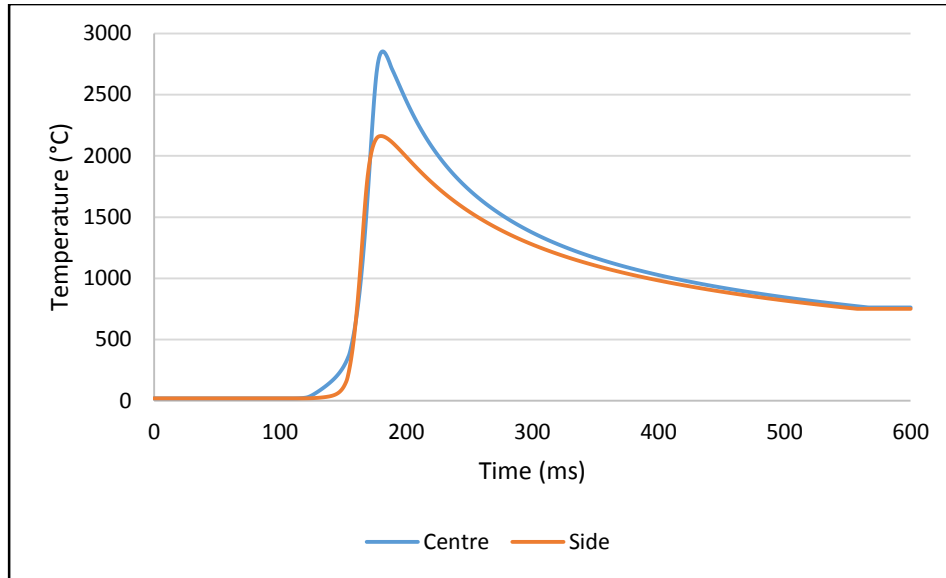


Figure B-10: Simplified particle temperature relation of monazite sand in a 6 kW plasma presenting a 120 μm particle travelling in the centre and along the side.

In order to obtain the minimum plasma power required to decompose all of the monazite to determine how much additional energy is available to decompose the particles, the particle at the side must attain a minimum temperature of 1400 °C, which is the decomposition temperature of monazite in the presence of carbon (Xing et al., 2010). The plasma power was varied by 0.1 kW between 5.0 and 6.0 kW. For each power level, the particle temperature on the side and the centre was determined (Figure B-11). This resulted in a near linear relationship between the power input, the particle temperature and the gas temperature. The linear relationship is presented with T as the temperature in °C and P , the plasma power, in kW for a 120 μm monazite particle. An R-squared value of 0.9989 was obtained for Equation B-6, indicating an accurate fit for the specified temperature range.

$$T(^{\circ}\text{C}) = 1094.P(\text{kW}) - 4417$$

Equation B-6

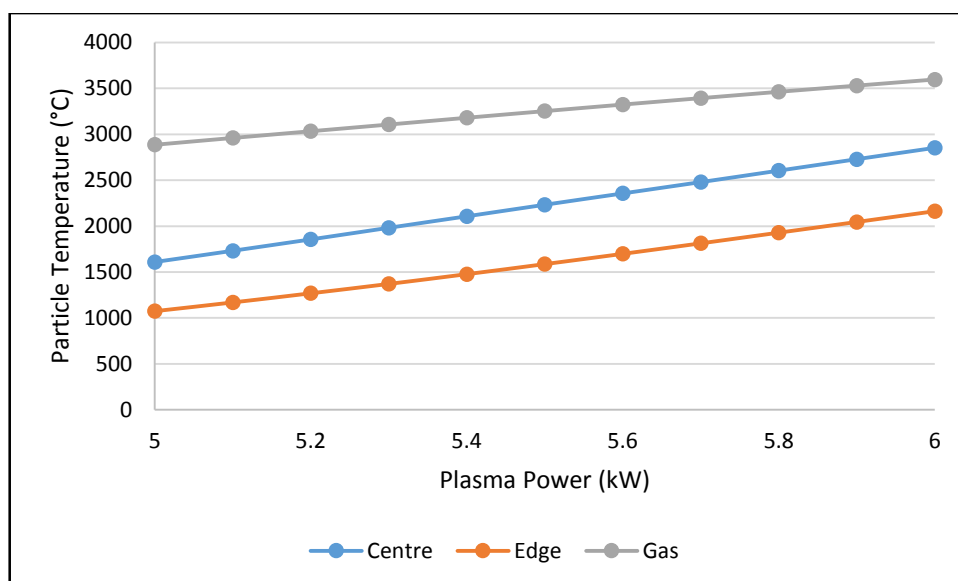


Figure B-11: Particle and gas temperatures as a function of plasma power for the 120 µm monazite particles

Using Figure B-11, the optimum power required to decompose monazite is 5.4 kW. At this power level the plasma will deliver a maximum particle temperature along the side of 1477 °C, a maximum particle temperature in the centre of 2107 °C, and an average monazite particle temperature of 1966 °C, with a maximum gas temperature of 3179 °C and an average graphite temperature of 1676 °C. This is the minimum power required to heat all 120 µm monazite particles to the decomposition temperature. Additional energy requirements for a higher mass flow will be discussed later.

Analysis over the various power inputs with the particle temperature indicate that the particle temperature and gas temperature increase almost in relation with each other with a temperature difference of between 1434 and 1811 °C in the designated power range. The gap between the two temperatures become wider the lower the plasma power. This temperature difference can be used in future plasma development to more quickly optimize the plasma and, by measuring the plasma temperature during operation, establish whether the plasma is hot enough to decompose monazite.

B.3.2 The 5.4 kW Plasma

The 5.4 kW plasma with 120 µm monazite particles were subsequently developed further. The 5.4 kW plasma's gas velocity presents the same laminar flow structure

and gas velocities of the 6 kW plasma. The gas velocity does not change relative to the plasma power due to the low quantity, heat capacity and pressure of the argon gas. The 5.4 kW plasma temperature profile showed the formation of an oval shaped ball of high temperature gas in the centre which is similar to other RF plasmas and the 6 kW plasma (Figure B-7). As the gas enters the plasma zone it is rapidly heated up to its maximum temperature of 3091 °C at the end of the plasma zone at a height of 505 mm (Figure B-12). The gas temperature drops rapidly along the axis of the plasma to the reactor wall which is water cooled to 20 °C. The drop in temperature along the edges of the plasma validates the need to feed the monazite particles in the centre of the plasma where it will attain the maximum particle temperature and to concentrate the majority of the particles in the centre of the plasma to attain maximum dissociation.

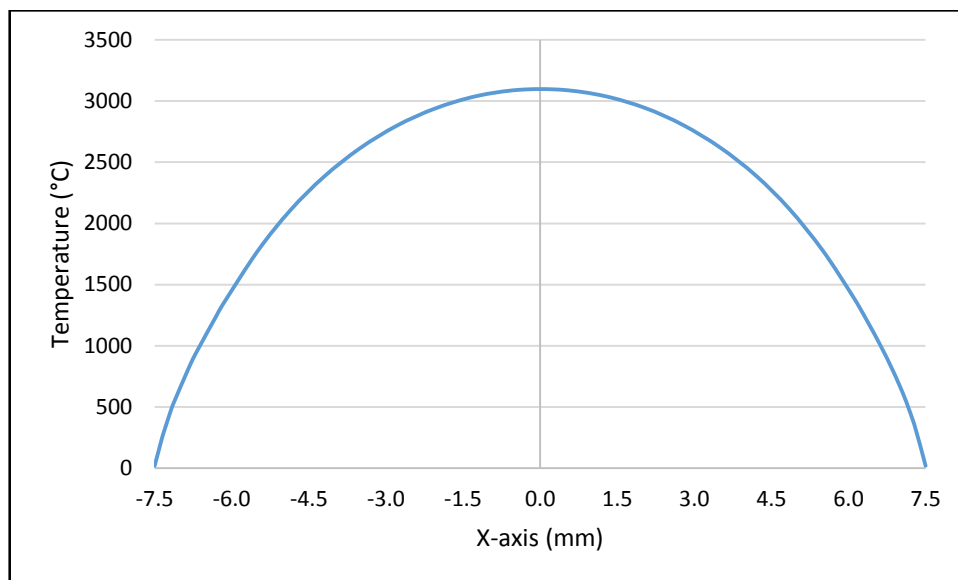


Figure B-12: Temperature as a function of the x-axis of the 5.4 kW plasma at a height of 5 mm

After the plasma gas has passed through the plasma zone it enters a section called the “Distance to Exit” at 500 mm. This section is 100 mm in length and water cooled along the sides to 20 °C. The gas loses heat rapidly in this section due to the close proximity of the walls and the large temperature gradient between the gas particles. As the gas leaves the “Distance to Exit” section it will enter the larger reactor vessel at 400 mm. Here the cooling rate of the gas is reduced due to the poor heat conductance of the argon gas, the distance to the cooling wall has increased and a smaller temperature gradient between the cooler particles is present (Figure B-13).

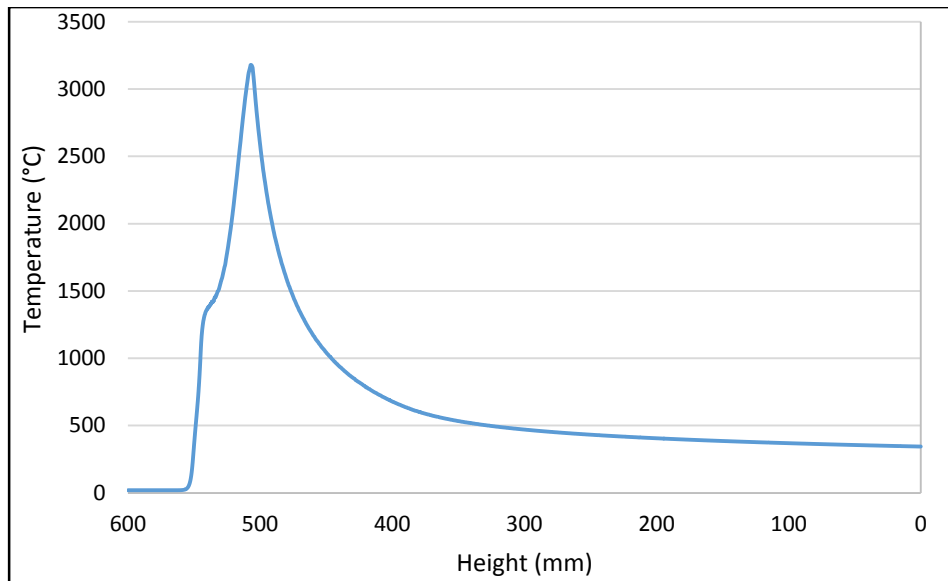


Figure B-13: Gas temperature along the centreline of the 5.4 kW plasma

When the particles fall through the plasma the profile starts off in a u-shape. As it passes through the plasma zone this shape is inverted into an upside down V-shape. The inversion occurs due to the velocity of the gas in the side inlets which is faster than the gas in the centre where the particles enter. The faster gas on the side speeds up the particles along the side of the plasma which decreases the residence time of the particles along the side and decreases the time to heat the particles. This reduces the maximum attainable temperature of the particles (Figure B-14). Decreasing the plasma inlet length will not flatten the particles but rather disperse the monazite particles and make them cling to the plasma wall. This will reduce the number of monazite particles which can be decomposed as more particles would travel along the edge of the plasma where there is no heat (Figure B-12).

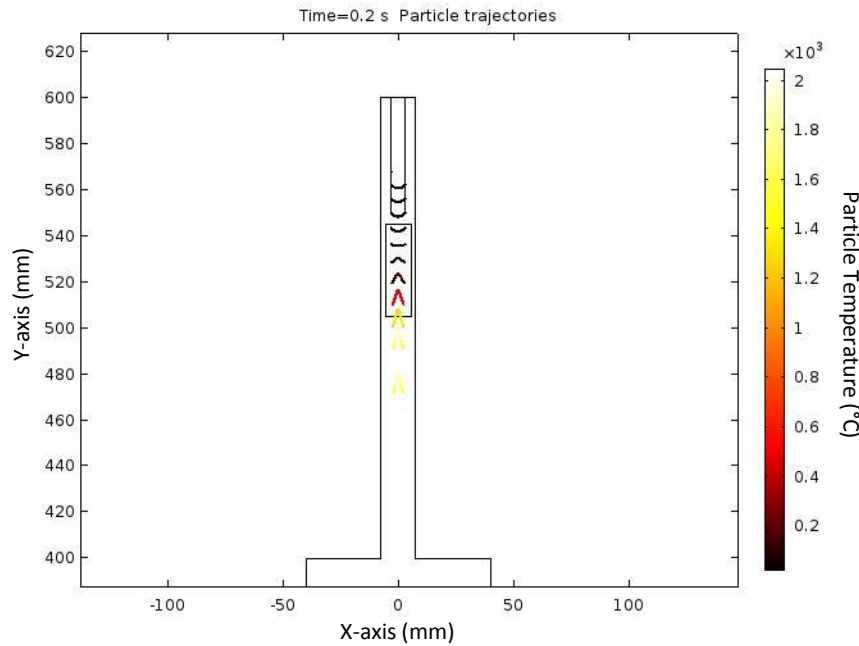


Figure B-14: Visual representation of the temperature of the monazite particles as they pass through the plasma

The temperature profile of the particles as they pass through the plasma shows a rapid increase in temperature followed by a gradual decline in temperature (Figure B-15), similar to the gas temperature (Figure B-13). The monazite particles were heated to a temperature of between 1477 and 2107 °C which is high enough to attain the minimum decomposition temperature of monazite. Both the particle in the centre and the particle on the side attained their maximum temperatures within 2 ms of each other. This is due to the highest temperatures in the plasma, which is concentrated in the centre of the plasma, and the cooler portions of the plasma along the sides. The maximum rate of heating of the particle in the centre is 111 553 °C/s and the particle along the edge is 92 731 °C/s. the cooling rate of the particle in the centre reached a maximum rate of 9989 °C/s and 3795 °C/s for the particle along the edge (Figure B-16). These rates are in line with values found by Boulos (1985).

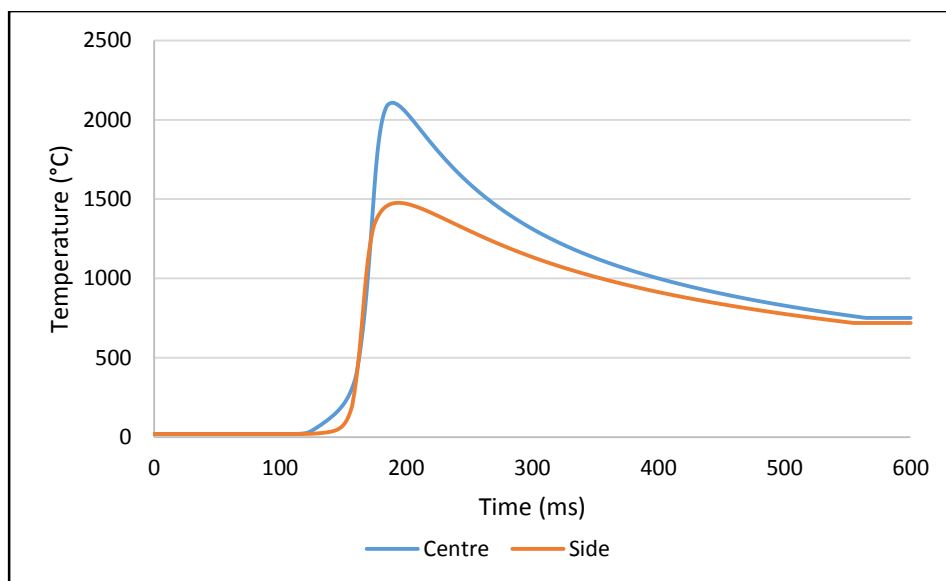


Figure B-15: Particle temperature profile of monazite as a function of time in a 5.4 kW plasma

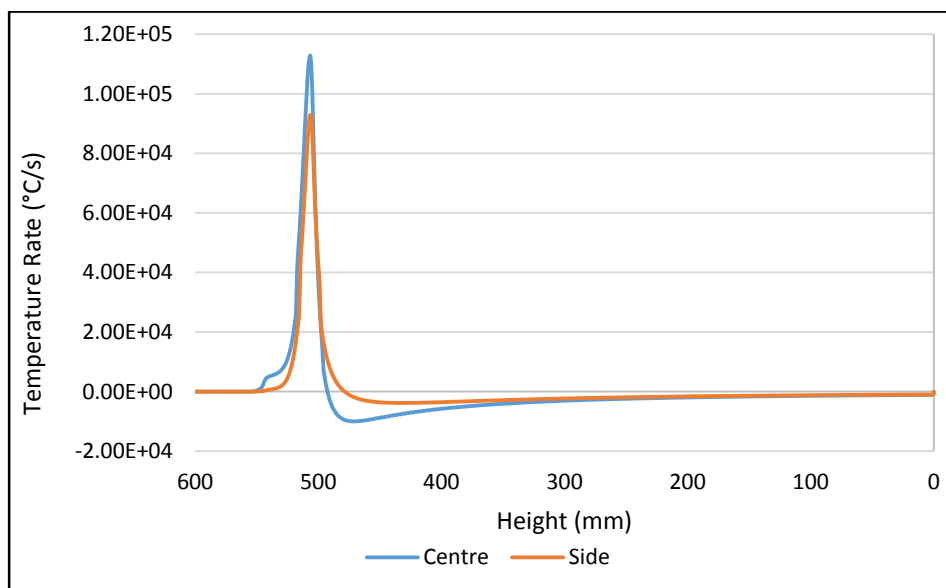


Figure B-16: Rate of monazite particle heating as a function of height of the 5.4 kW plasma on 120 µm monazite particles

As the particles travel through the plasma in relation to the temperature of the gas, it attains its maximum temperature in the plasma flame and not in the plasma zone when the plasma gas temperature is at its maximum (Figure B-17). If the particle can be slowed down in order to reside longer in the plasma zone or as it leaves the plasma zone it would result in higher particle temperatures. The reason is that the temperature gradient, which is at its highest at this point, would be able to heat the particles to a

higher temperature without the need to increase the plasma power. The simplest method is to reduce the mass flow of the plasma to permit more energy to be absorbed per particle and to slow down the gas and particle velocity.

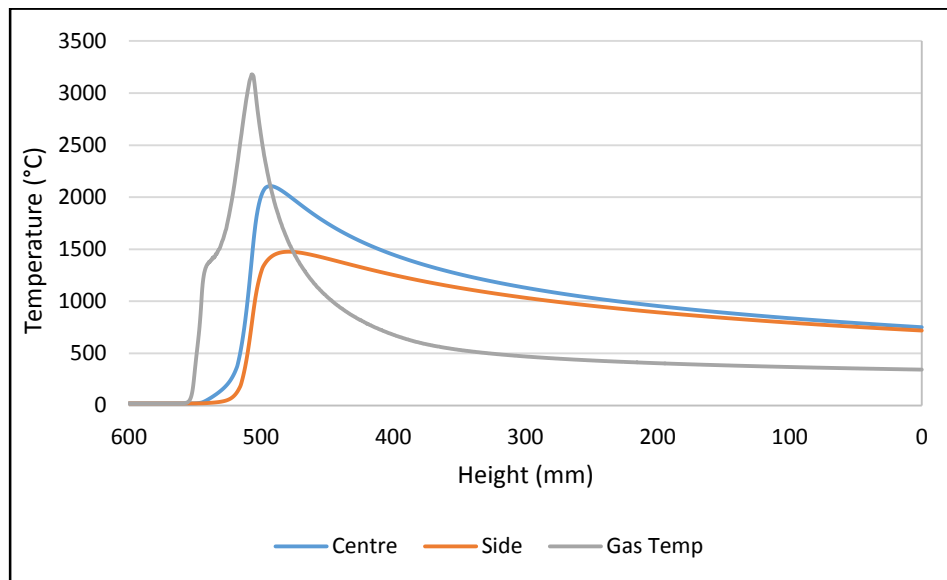


Figure B-17: Particle temperature profile of monazite as a function of height in a 5.4 kW plasma

An alternative in slowing down the particles is to redesign the plasma to naturally slow down the gas as it leaves the plasma zone. This can be accomplished by rapidly increasing the surface area through which the gas needs to travel. The plasma reactor does this naturally when the gas enters the reactor chamber. By decreasing the distance between the plasma zone and the entrance to the reactor, henceforth referred to as Distance to Exit, the gas and particle velocity would be reduced which would increase the residence time of the particles in the plasma flame. To theoretically evaluate the validity of this theory, the distance to the exit was changed from the standard 100 mm to 150, 50 and 0 mm.

Increasing the Distance to Exit had no significant effect on gas temperatures. However, by decreasing the distance by 50 %, the particle temperature was decreased by 35 °C or 2.4 %. This drop in temperature is due to the long narrow chamber of the wall, which concentrates the heat, which is very short and the hot plasma gas which flows too fast to permit for a reasonable residence time to sufficiently heat the particle as it passes through the plasma. When the particle enters the reactor chamber the

heat is dispersed into the cooler surrounding gas which reduces the maximum temperature of the gas.

When the distance to exit is set to the minimum of 0 mm, then a temperature increase of 97 °C, or 6.57 %, was attained. This increase in temperature in the particle on the side indicate that an increase in the maximum temperature is attained when the distance to the exit is at a minimum (Figure B-18). This change in temperature increases when the plasma power is decreased. For this reason this effect would have a more profound impact when smaller, less energy intensive plasmas are used.

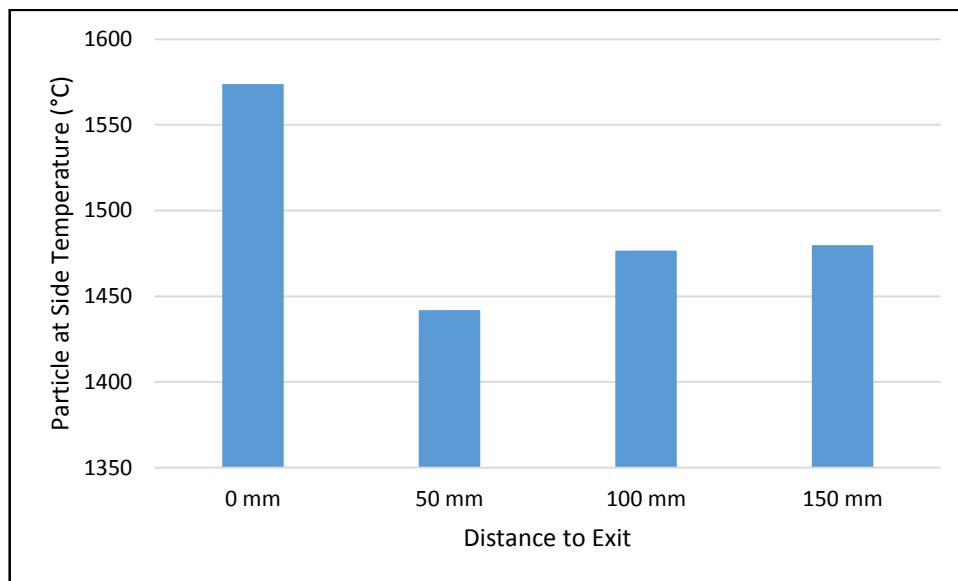


Figure B-18: Particle temperature at the side as a function of a change in the distance from the plasma to the exit for a 5.8 kW plasma

The reduction in the distance to the exit has the intended effect on the gas velocity (Figure B-19) when it expands and slows down in the plasma flame. When compared to the temperature profile (Figure B-20), the speed reduction concurs with the plasma flame as it has extended the residence time of the particles in the plasma flame.

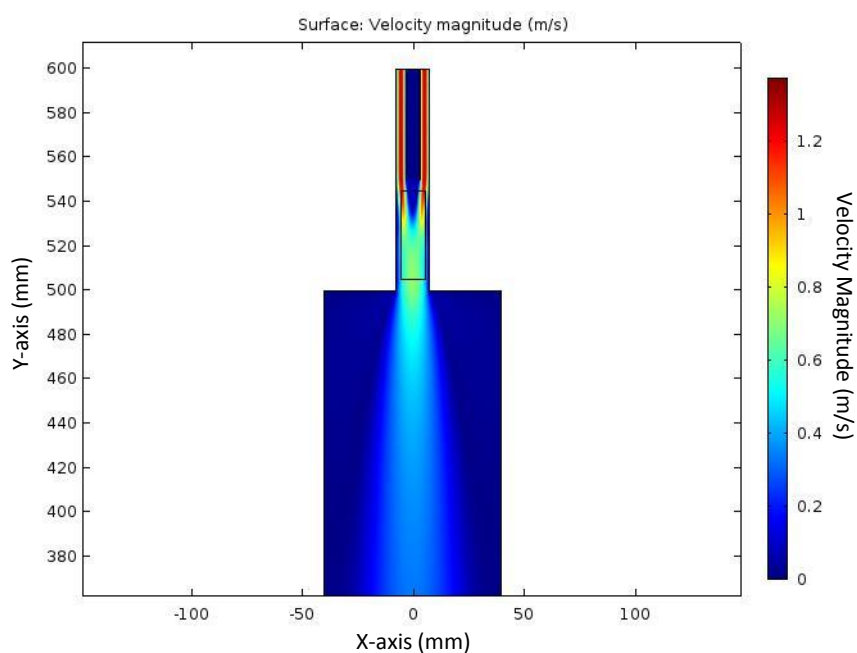


Figure B-19: Velocity profile of the plasma gas of the 5.4 kW plasma with a distance to exit of 0 mm

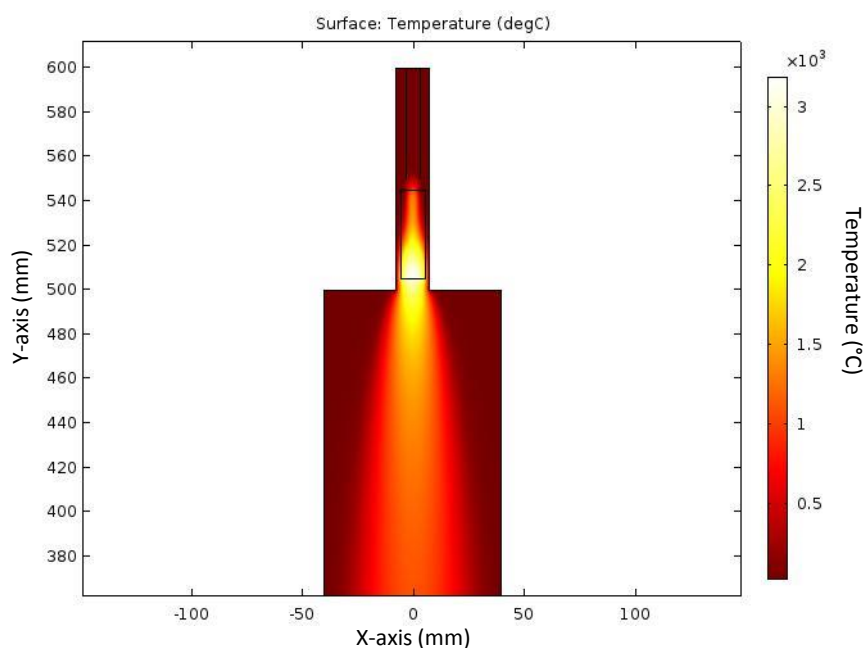


Figure B-20: Temperature profile of the plasma gas of the 5.4 kW plasma with a distance to exit of 0 mm

The particle temperature as it travels along the plasma, with the “Distance to Exit” at 0 mm, shows that the monazite could not reach the exit of the plasma (Figure B-21). This confirms that the monazite particles have slowed down in the course of being fed to the plasma and would require more than 600 ms to reach the bottom of the plasma.

The reduction in speed corresponds to an increase in the particle temperature which would be a consequence of the longer residence time in the plasma. This confirms that the particle's temperature can be increased without changing the plasma's operating conditions like the plasma's power or gas flow.

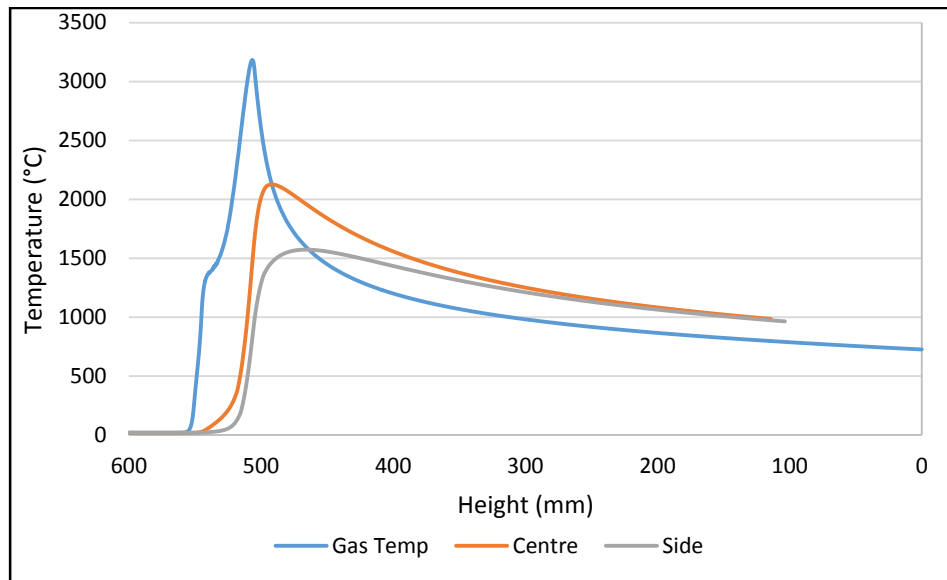


Figure B-21: Particle temperature as a function of plasma height in a 5.4 kW plasma with a distance to exit of 0 mm

B.3.3 Variable Sized Particles

The particle size distribution indicates that a small portion (0.14 %) of the monazite sand contained particles which are bigger than 150 μm . The temperature of the particles as a function of plasma power for 150 μm particles was determined and indicated that 5.8 kW of power for the plasma would be required (Figure B-22), which is still within the permissible range of the 6 kW plasma. The maximum particle size which can be decomposed in a 6 kW plasma was calculated by extrapolating from the results of the 120 and 150 μm particles. The maximum particle size which can be used, and still be expected to decompose, is 163 μm but with no additional energy available to heat the particle.

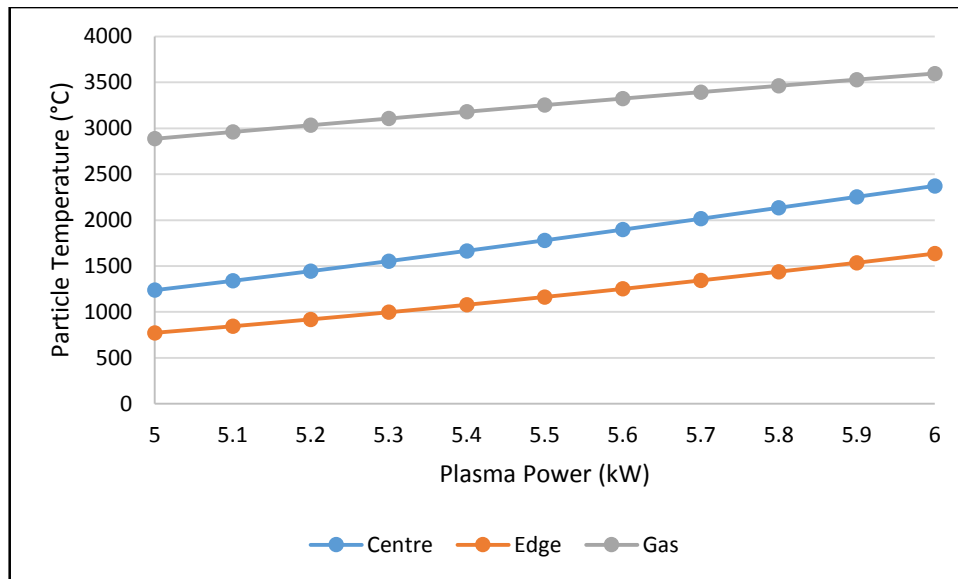


Figure B-22: Particle and gas temperatures as a function of plasma power for the 150 µm monazite particles

By using a smaller monazite particle, the plasma gas temperature can be lowered which would reduce the energy required to heat the particles to 1400 °C. The use of the smaller 60 µm monazite particle is impractical. When the particle is fed to the plasma and enters the plasma zone, it stops and floats atop of the plasma zone (Figure B-23). The particle remains there while the plasma is in operation. The reason for the particle stopping at the start of the plasma zone is the flow of the gas around the plasma zone which forms a vortex (Figure B-24). This vortex circulates the particle within, due to its low mass and momentum, and explains the rise in the gas magnitude along the centreline (Figure B-6). The particle, due to its low mass and momentum, cannot break through this gaseous barrier and will remain at this location until an exterior force pushes it out or the plasma operating conditions have been altered.

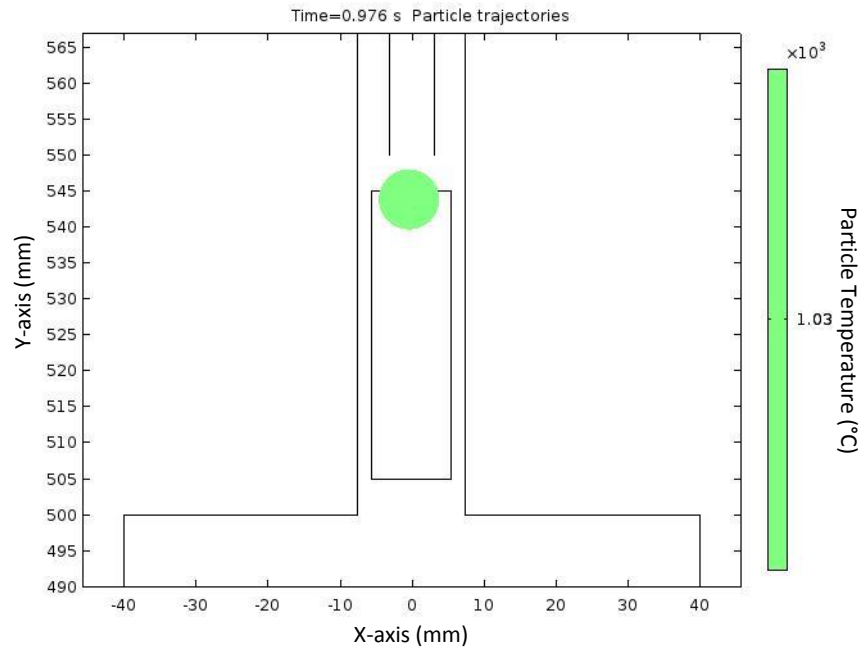


Figure B-23: Particle profile of a 60 μm monazite particle in a 4.5 kW plasma

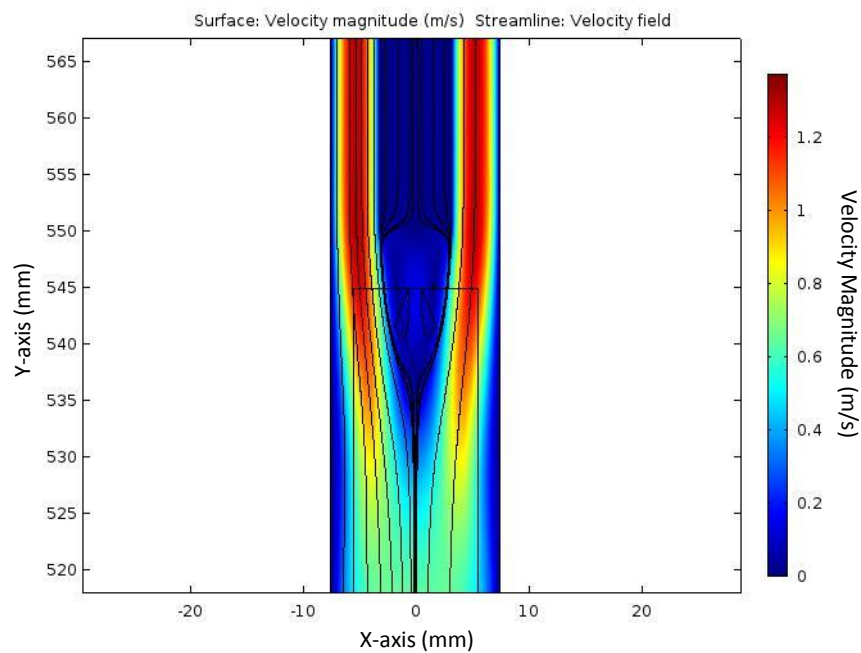


Figure B-24: Close-up of the velocity profile at the top of the plasma zone using streamlines to display the vortex which retains the 60 μm particles

This effect can be properly observed when the particle temperature and height is plotted as a function of time (Figure B-25). The result shows that the particle remains at a height of 544 mm and obtains a maximum particle temperature of 951 °C which is too low for the monazite to be decomposed. When the particle size was increased from 60 to 70 μm , which is a 58 % increase in mass, the particle had enough mass

and momentum to break through the vortex and attain the required temperatures on the side of 1490 °C (Figure B-26). The simulation indicates that the minimum size of the monazite particle, for the purpose of this model, is 70 μm and that anything smaller would simply remain at the top of the plasma and would not be decomposed.

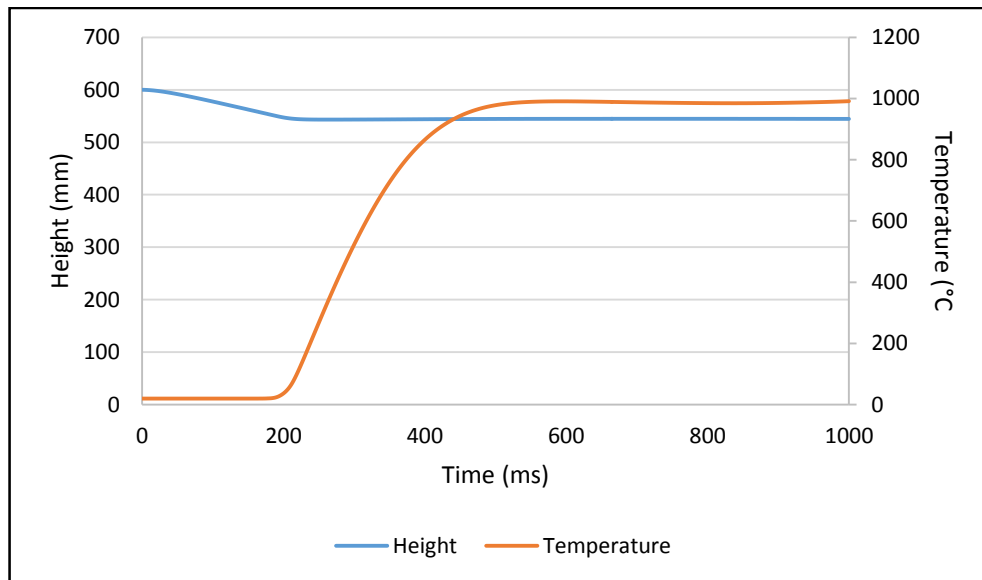


Figure B-25: Particle height and temperature of a 60 μm monazite particle in a 4.5 kW plasma as a function of time

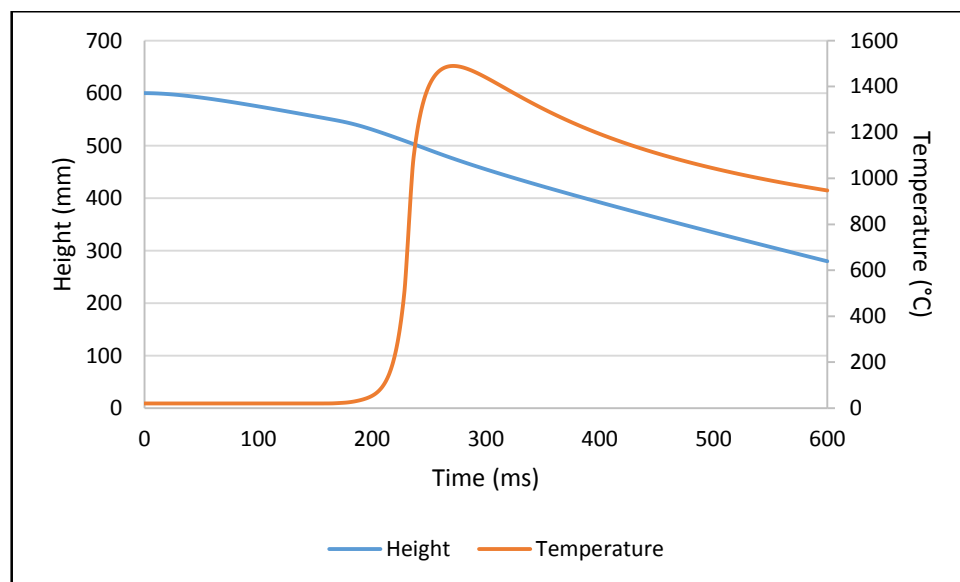


Figure B-26: Particle and temperature profile of the 70 μm monazite particles in a 4.5 kW plasma as a function of time

When the particle size of graphite was reduced to compensate for the reduction in size in plasma power and the monazite particles, then the smallest graphite particle which passed through the system was 100 μm , however the smaller particles did obtain the decomposition temperature of 1250 K (977 $^{\circ}\text{C}$) (Yugeswaran et al., 2015) at which carbon combusts and forms CO. This will release the heat required to decompose monazite at 1400 $^{\circ}\text{C}$. However, the formation of the gas, the vortex barrier and the release of heat above the plasma zone, may be ineffective as the gas and the energy released would be contained and cannot partake in the decomposition of the monazite. Further analysis of this is beyond the scope of this research.

B.3.4 Energy Required to Heat the Particles

Comsol was able to determine the temperature the particles would reach in the plasma as described. The problem is that the gas temperature in Comsol is not affected by the loss in energy from the particles which gain that energy and lower the plasma flame temperature. To compensate for this, the energy required to heat the monazite particles to their respective temperatures need to be included. The problem is that each of the particles have their own maximum particle temperature. In order to calculate the average energy required the average maximum particle temperature of the monazite and carbon particles, respectively, will be used.

When the monazite and carbon particles on the side have been heated to at least 1400 $^{\circ}\text{C}$, which is the decomposition temperature as previously stated, the average maximum particle temperature for monazite is 1966 $^{\circ}\text{C}$ and 1676 $^{\circ}\text{C}$ for carbon. The energy required to heat monazite to 1966 $^{\circ}\text{C}$ is 309.55 kJ/mol and to heat carbon to 1676 $^{\circ}\text{C}$ is 52.92 kJ/mol. The energy required for carbon was calculated for carbon from 298 K to 1250 K, for CO from 1250 K to 1500 K and for CO₂ from 1500 K to 1949 K (1676 $^{\circ}\text{C}$). This heating of carbon is in line with what is described by Yugeswaran et al. (2015).

The monazite to carbon molar ratio is 2:5 to produce the rare earth oxides. This equates to an energy requirement of 883.7 kJ for 2 moles of monazite and 5 moles of graphite. Converting the molar values to mass presents an energy requirement of 1.64 kJ/g of the monazite-carbon mixture to be delivered to the plasma. The actual

particles which will be fed into the plasma will have a particle size distribution (Figure B-9) between 70 and 163 μm . This variation in particle size would similarly have an effect on the mass of monazite and carbon which can be fed to the plasma. Using the current plasma design as specified, an additional 600 W of energy is available. Due to the variation in size of the monazite and graphite particles, the average feed rate of the mixture is 0.37 g/s or 1.32 kg/h. The mass rate which has been calculated would merely serve as a guide from which further refinement of the system needs to be completed.

Necsa has developed a 450 kW plasma reactor which can feed zircon, in the absence of carbon, at a rate of 100 kg/h. The energy required to heat zircon to its dissociation temperature of 2250 K (1977 °C) (Yugeswaran et al., 2015) was calculated to be 1.48 kJ/g zircon which is 10.81 % less than monazite and carbon. For this reason, the plasma which was used for dissociating zircon can process 90.24 kg/h of the monazite-carbon mixture.

B.4 Conclusion

Monazite dissociation in a plasma was modelled using a 10 kW RF plasma with a thermal efficiency of between 40 and 60 %. A particle size distribution of monazite showed that the majority of the particles are between 90 and 150 μm . An average size of 120 μm was used in all simulations.

The plasma power was varied between 5 and 6 kW to determine the particle temperature from which a linear relationship was determined. The difference between the particle on the side and the gas temperature was between 1434 and 1811 °C for lower powered plasmas. The optimum plasma was a 5.4 kW plasma which delivered particles at a temperature of between 1477 and 2107 °C. The maximum temperature of the particles can be increased by 6.58 % when the distance between the plasma zone and the reactor vessel is kept to a minimum. This gap increases with a reduction in plasma power and gas temperature.

It was determined that if the plasma can only deliver 6 kW then the maximum monazite particle size which can be treated is 163 μm but with no additional energy available to heat the particle. CFD simulation determined that the smallest monazite particle which

can be treated is 70 μm . The 6 kW is sufficient to heat a monazite carbon mixture with a molar ratio of 2:5 with a mass feed rate of 1.32 kg/h. Using the current design and assuming all monazite particles are between the sizes of 70 and 163 μm , the current plasma at Necsa is sufficient to decompose monazite into the rare earth oxides in the presence of carbon.

B.5 References for Appendix B

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