Investigations into the Synthesis, Characterisation and Uranium Extraction of the Pyrochlore Mineral Betafite.

A thesis submitted for the fulfilment of the requirements for the degree of

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Document of authenticity

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is a result of work which has been carried out since the official commencement date of the approved research program; and, any editorial work, paid or unpaid, carried out by a third party is acknowledged.

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- Tim Minchin
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Terms and abbreviations

AE  Activation energy
BAM  Betafite Ambatofotsy Madagascar
BET  Brunauer, Emmett and Teller Theory
BMM  Betafite Miarinarivo Madagascar
BSC  Betafite Silver Crater
CIX  Continuous Ion Exchange
CPE  Carbon Paste Electrode
CV  Cyclic Voltammetry
CXA  Computer X-ray Analyser
E  Potential (V)
EDS/EDX  Energy Dispersive X-ray Spectroscopy
EPMA  Electron Probe Micro Analysis
eV  Electron volt (1.6×10^{-19} J)
FTIR  Fourier Transform – Infrared Spectroscopy
HT-XRD  High Temperature – X-ray Diffraction
\( h\nu \)  Photon energy from the X-ray source
IAEA  International Atomic Energy Agency
ICDD  International Centre for Diffraction Database
ICP-MS  Inductively Coupled Plasma – Mass Spectrometry
JCPDS  Joint Committee on Powder Diffraction Standards
KE  Kinetic Energy
LSV  Linear sweep voltammetry
MCC1  Standard test method for static leaching of monolithic waste forms long term method
MilliQ  Trademarked ultra-pure water brand
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tr>
<td>ORP</td>
<td>Oxidation-Reduction Potential</td>
</tr>
<tr>
<td>ppb</td>
<td>Parts Per Billion</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts Per Million</td>
</tr>
<tr>
<td>REE</td>
<td>Rare Earth Elements</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron microscopy</td>
</tr>
<tr>
<td>SNF</td>
<td>Spent Nuclear Fuel</td>
</tr>
<tr>
<td>SX</td>
<td>solvent extraction</td>
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<tr>
<td>Synroc</td>
<td>A portmanteau of “synthetic rock”</td>
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<tr>
<td>TGA</td>
<td>Thermo Gravimetric Analysis</td>
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<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
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Abstract

The usage of nuclear power, to generate base-load electricity, has steadily increased in acceptance as a more environmentally friendly alternative to fossil fuels since its first commercial introduction in the 1950s. Increasing consumption of uranium and the rising demand for nuclear fuel has led to a deficiency of high grade uraninite and pitchblende deposits. This has led to increased attention on the refractory uranium pyrochlore betafite due to its abundance in currently exploited uranium deposits.

In this document primary work was conducted on natural betafite from Ambatofotsy Madagascar, Miarinarivo Madagascar and Silver Crater Mine, Canada. These three samples were heat treated to 1200 °C to investigate the effect of recrystallization on uranium extraction. X-ray diffraction analysis showed that anatase was the only crystalline compound present in each of the unheated samples. After being heated to 1200 °C all samples exhibited diffraction lines characteristic of betafite and rutile, indicating that the betafite present in the preheated samples was amorphous (metamict). Electron probe microanalysis of the samples showed a high degree of compositional heterogeneity throughout each sample, most likely caused by aqueous fluid interactions forming secondary alteration products. All unheated samples were subject to a sulfuric acid leach over 6 h with the extent of uranium dissolution correlated with the degree of alteration. The most highly altered sample had 42% U dissolution while the least-altered exhibited only 7%.

Due to the differences in the degree of alteration observed in the natural samples it was decided to synthesise a pure betafite sample via a solid state synthesis route. The optimum conditions for the synthesis of betafite were found to be heating the reactants required at 1150 °C for 48 h under an inert gas atmosphere. Analysis via EPMA of a sectioned surface showed very small regions of Ca-free betafite on grain boundaries as well as minor rutile impurities. XPS analysis of the sample showed that the uranium in the synthesised betafite was predominately present in the U⁵⁺ oxidation state. A minor amount of U⁶⁺ was also detected which was possibly due to surface oxidation.
Dissolution studies were then conducted on the synthetic betafite to investigate the influence of various parameters on leaching. The results showed the uranium dissolution curves obtained over a range of time, temperature, [H\textsubscript{2}SO\textsubscript{4}], [Fe\textsubscript{TOT}] and redox potential conditions were similar with each having three discrete segments representing significantly different rates of uranium dissolution. The first segment occurred in the initial minute and involved extremely rapid dissolution. This segment made up for the majority of the overall uranium dissolution obtained over the test period (~2.0% U).

The second segment between 1 – 120 minutes was characterised by slow uranium dissolution rates which could be partially influenced by altering the experimental conditions. The uranium dissolution rate in the third segment was negligible due to passivation of the sample surface leaving no exposed uranium available for leaching. Investigations into leaching betafite using various iron salts showed the U dissolution more than doubled when iron fluoride was substituted for iron sulfate. The additional solubility was attributed to leaching of Nb, Ti, and Ta due to the \textit{in-situ} formation of HF. This caused removal of the passivating layers and allowed more uranium to be exposed to the leach solution.

Long term dissolution studies were also conducted on the synthetic betafite sample in order to determine the leach rate over a 90 day leach period. The results of these experiments showed very minor influences were observed when each of the standard parameters (temperature, [H\textsubscript{2}SO\textsubscript{4}], [Fe\textsubscript{TOT}] and redox potential) were studied. The increase in U leaching between no sulfuric acid added and 2.14 M [H\textsubscript{2}SO\textsubscript{4}] was only a 0.20% increase after the 90 day leach experiment. The influence of fluoride addition showed a slightly greater leach rate than that achieved with high acid concentration, though the main difference between this experiment and other experiments conducted with no fluoride was the solubilisation of the metals Ti, Nb and Ta which were not observed to leach in experiments where fluoride was not added.

Post leach characterisation of synthetic betafite identified only minor changes occurred in the sample. These changes included the formation of pyrochlore and a greater concentration of rutile was observed to be present. Analysis via XPS of the post leach residues showed the samples
contained similar U oxidation states to those observed in the preleached samples. Moreover, significantly greater Ta was observed via XPS in the post leach sample indicating that the Ta concentration had increased on the surface of the mineral. This indicated a possible passivation layer which caused the low rate of dissolution that was observed to occur.
CHAPTER 1

Introduction and Literature Review

This chapter provides a summary of the available literature on uranium minerals of interest to this project and the chemistry involved in extracting these minerals from ores. Areas which are covered in this chapter include the uranium fuel cycle from ore to radionuclide storage/disposal. An in depth review of the structure, composition, geochemical occurrences and dissolution chemistry of betafite is also covered. Further work showing dissolution studies of other uranium containing minerals was also summarised. The aims and scope of this thesis are provided in at the end of this chapter.
Chapter 1 – Introduction and Literature Review

1.1. Introduction

As more evidence into the influence of greenhouse gasses on climate change is reported there is increased focus on renewable and reliable sources of base load power which produce fewer greenhouse gasses such as CO₂ [1]. This has led to increased attention in the use of nuclear power to produce the energy needed to keep up with the growing demand for power whilst minimising the greenhouse gas production associated with fossil fuel power stations [2].

The technology of nuclear power production has been well established since the dawn of the nuclear age in the late 1930s where Hahn and Strassmann reported the discovery of nuclear fission by bombarding a uranium nuclei with neutrons resulting in the formation of lighter elements; barium, lanthanum and cerium [3]. The first commercial nuclear power station officially opened in June 1954 in the USSR, and since then there has been a steady increase in nuclear power plants opening to keep up with the ever-growing demand for energy [4]. As the usage of nuclear power has increased, the demand for nuclear fuel has also continued to grow [5].

This has led to new challenges since high grade uranium resources have become scarcer over recent years. For this reason, focus on minerals processing of more difficult to extract (refractory) uranium minerals such as betafite has become of increasing importance. Moreover, there is an emphasis on more targeted processing of lower grade deposits as the influence of gangue mineralogy is significantly more problematic in these deposits [6].

Betafite is currently only processed in significantly quantities in the Rössing uranium mine in Namibia [7] although several regions have been observed with trace to minor amounts of the mineral within each locality [8]. Betafite accounts for approximately 5% of the total uranium found in the Rössing uranium mine, the remainder of which is present as predominantly uraninite as well as some coffinite and uranophane [9]. The existing strategy at Rössing is to avoid processing regions of the Rössing deposit which contain high concentrations of betafite as very little uranium is leached due to the highly refractory nature of the mineral. For this reason, gaining a greater understanding into the
factors that influence betafite dissolution chemistry is important in improving the leach yield when processing deposits which contain a high concentration of betafite.

Another difficulty facing the nuclear power industry is the vast amount of highly radioactive waste produced from the fission reaction [10]. Research into long term disposal methods of radionuclides via means which have a minimal contamination risk is of increasing importance as the amount of high level waste continues to grow. The current methods of long term disposal of actinides involve reacting the metals with titanium, zirconium and various other elements to form insoluble ceramic oxides which can be then stored long term with a reduced risk of contamination to the environment [11]. The general focus of research in this area is to develop improved ceramic oxides which demonstrate more selectivity and durability. The design of improved storage materials has been strongly influenced by highly refractory minerals which have been found naturally. One such group which has been studied recently due to its highly refractory nature is the mineral super group – pyrochlore [12]. A minor component of this thesis will investigate the pyrochlore group mineral betafite for the purpose of actinide immobilisation.

Gaining a greater understanding of the structure and stability of minerals such as betafite will be beneficial to both the uranium minerals processing and spent nuclear fuel disposal industries.

1.2. Uranium minerals and uranium bearing ores

Uranium is relatively abundant in the earth’s crust (the average concentration of uranium in the earth’s crust is 2.8 ppm). Ore deposit U concentrations range from 0.03% (300 ppm) for a low grade deposit, to as high as 2% (20,000 ppm) for a high grade deposit, although concentrations have been recorded as high as 20% U in some very high grade deposits [5]. Uranium is typically found in 15 deposit types as classified by the International Atomic Energy Agency (IAEA). These deposit types are listed in Table 1.1 by their approximate economic significance [13].
<table>
<thead>
<tr>
<th>Deposit Type</th>
<th>Mineralisation</th>
<th>Uranium minerals</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unconformity-related deposits</td>
<td>Quartz rich sandstone</td>
<td>Uraninite, pitchblende</td>
<td>Athabasca basin (Cigar lake mine et al.)</td>
</tr>
<tr>
<td>Sandstone deposits</td>
<td>Medium course grain sandstone</td>
<td>Pitchblende, coffinite, secondary uranium minerals</td>
<td>Inkai uranium mine - Kazakhstan</td>
</tr>
<tr>
<td>Quartz-pebble conglomerate deposits</td>
<td>Quartz, chloritoid, rutile, pyrite</td>
<td>Uraninite, brannerite, coffinite</td>
<td>Elliot lake - Canada, Witwatersrand - South Africa</td>
</tr>
<tr>
<td>Breccia complex deposits</td>
<td>Iron oxide copper gold ore deposits (hematite rich)</td>
<td>Uraninite, brannerite, coffinite</td>
<td>Olympic dam - South Australia</td>
</tr>
<tr>
<td>Vein deposits</td>
<td>Quartz, carbonate, fluorite, dolomite</td>
<td>Uraninite, pitchblende</td>
<td>Jachymov - Czech republic</td>
</tr>
<tr>
<td>Intrusive deposits</td>
<td>Alaskite, granite, pegmatite, monzonites</td>
<td>Uraninite, coffinite, uranophane, betaifite</td>
<td>Rössing - Nambia</td>
</tr>
<tr>
<td>Phosphorite deposits*</td>
<td>Fluorite, apatite, pyrite</td>
<td>Autunite, torbenitie</td>
<td>USA, Jordan, Egypt</td>
</tr>
<tr>
<td>Collapse breccia pipe deposits</td>
<td>Limestone, sandstone, quartz</td>
<td>Uraninite, pitchblende, coffinite</td>
<td>Arizona breccia pipe mineralization - USA</td>
</tr>
<tr>
<td>Volcanic deposits</td>
<td>Felsic, quartz, feldspar</td>
<td>Pitchblende</td>
<td>McDermitt Caldera - USA</td>
</tr>
<tr>
<td>Surficial deposits</td>
<td>Calcrete (Mg,Ca carbonates)</td>
<td>Carnotite</td>
<td>Yeelirrie - Western Australia</td>
</tr>
<tr>
<td>Metasomatite deposits</td>
<td>Chlorite, pyrite, hematite, magnetite</td>
<td>Uraninite, brannerite</td>
<td>Valhalla - Australia, Ross Adams deposit, Alaska</td>
</tr>
<tr>
<td>Metamorphic deposits</td>
<td>Braunite, garnet</td>
<td>Uraninite</td>
<td>Mary Kathleen, Queensland</td>
</tr>
<tr>
<td>Lignite deposits*</td>
<td>Soft brown coal, Sandstone</td>
<td></td>
<td>Serres basin, Greece</td>
</tr>
<tr>
<td>Black shale deposits</td>
<td>Clay minerals, Quarts</td>
<td>Uraninite, Pitchblende</td>
<td>Ranstad, Sweden</td>
</tr>
<tr>
<td>Other</td>
<td>Varies</td>
<td>Varies</td>
<td>Varies</td>
</tr>
</tbody>
</table>

* sub economic deposit
Uranium bearing deposits generally contain several different uranium minerals depending on the ore genesis. Currently there have been over 200 uranium containing minerals that have been identified. These have been grouped into primary, secondary and refractory uranium minerals. The most common of the minerals are the reduced $U^{4+}$ primary minerals; uraninite ($UO_2$), pitchblende ($U_3O_8$) and coffinite ($USiO_4$) which are formed during crystallization of magma and are generally found in association with feldspar and quartz. The majority of the other exploitable uranium minerals are classified as secondary uranium minerals and are generally less common than the primary minerals in deposits. These minerals are commonly found in the $U^{5+}$ and $U^{6+}$ oxidation states and are more likely to be coloured and have fluorescent properties. The most common of these minerals include the uranyl vanadate mineral carnotite [$K_2(UO_2)_2(VO_4)_2.xH_2O$], the uranyl phosphate minerals; autunite [$Ca(UO_2)_2(PO_4)_2.xH_2O$], saleeite [$Mg(UO_2)_2(PO_4)_2.xH_2O$], torbernite [$Cu(UO_2)_2(PO_4)_2.xH_2O$] and the hydrated uranyl silicate; uranophane [$Ca(UO_2)_2(HSiO_4)_2.xH_2O$] [14]. The other less common, refractory uranium minerals are: brannerite ($UTi_2O_6$) and the more complex uranium titanates; davidite [(La,Ce,Ca)(Y,U)(Ti,Fe$^{3+}$)$_{20}O_{38}$] and betafilet [(Ca,U)$_2$(Nb,Ti,Ta)$_2O_7$] [6].

Gangue mineralogy of uranium baring ore bodies also differs significantly depending on the deposit type. These gangue minerals are known to considerably affect the leach yield of uranium from the host material. This will be discussed in further detail in subsequent sections.
1.3. **Uranium Processing**

There are several process steps which are involved in the uranium based nuclear fuel cycle. In this chapter subsection an overview of the main processes which are used throughout the nuclear fuel cycle will be covered. These steps include:

- Deposit type and uranium mining methods (Section 1.3.1)
- Ore processing to high purity U₃O₈ (Section 1.3.2)
- High purity U₃O₈ to enriched UO₂ nuclear fuel pellets for reactor fuel (Section 1.3.3)
- Spent nuclear fuel to reprocessing and short term storage/long term disposal (Section 1.3.4)
- Current methods for storage of radionuclides (Section 1.3.5)

1.3.1. **Deposit type and mining method**

Uranium mineralogy is one of several factors looked at when assessing whether a deposit is a viable mineral reserve. Some of the other factors include[8, 15]:

- Uranium grade,
- Degree of comminution required i.e. the required amount of crushing needed to liberate uranium from the ore,
- Preconcentration (if required) to improve uranium grade/decrease the gangue mineral concentration,
- Lixiviant for leaching i.e. alkaline or acidic
- Reagent consumption by uranium and gangue minerals,
- Deposit size, and
- Location.

Depending on these aforementioned factors various methods of mining/extraction are employed to efficiently extract the most uranium out of the ore with minimal expense. These extraction methods include:
- Underground and open cut mining – Where the ore is dug up via conventional mining techniques then taken to an onsite minerals processing plant where the uranium (and other target metals) are extracted. This will be explained in more detail in subsequent sections.

- In-situ leaching – Where the leach solution is pumped down into the ore deposit through boreholes. The solution penetrates the ore and is then pumped to the surface through separate boreholes. This pregnant leach solution which contains the dissolved uranium is then processed and reused [16].

- Heap leaching – Where the ore is mined via conventional processes then piled into a pad to form a large heap. This leap is then sprinkled with a leach solution which dissolves the target metal which is then collected in the bottom of the pad. The dissolved uranium is then extracted out of the pregnant leach solution and the solution is reused [5].

The process used to extract uranium at the Rössing uranium mine is discussed below. This process was chosen for discussion as the ore that is processed is known to contain the uranium mineral betafite which is of significant interest to this project (the occurrence of betafite will be discussed in greater detail in subsequent sections). The Rössing uranium ore deposit is a large low grade leucogranite hosted deposit in central Namibia where the ore is initially mined via an open pit method [15].

1.3.2. Ore to high purity U₃O₈

There are a range of processes that can be used to produce high purity U₃O₈. The processes that are used for a particular ore body depend on several factors such as the uranium ore type, grade and gangue mineralogy. Processing at Rössing, Namibia (Figure 1.1) initially starts with pre-treatment steps of comminution which are conducted on the unprocessed ore. In the Rössing uranium mine this is done in two steps, initially the unprocessed rock is crushed into <75 mm rocks. These are then fed into rod mills for further crushing down to <19 mm and mixed with water to form a mud like consistency slurry. This slurry then undergoes an oxidation and leach process in large mechanical
agitator tanks with sulfuric acid and ferric sulfate as the oxidant [9]. The uranium leaching process will be discussed in further detail later in the chapter.

It is important to note the influence of gangue mineralogy also plays a significant factor in the feasibility of uranium mineral processing. This occurs in many ways including; reagent consumption via neutralization with alkaline or acidic host rock and through dissolution of gangue [17]. This not only leads to the expected greater costs due to the replacement of reagents but also leads to downstream issues with Solvent Extraction (SX/CIX) recovery [18]. The role of gangue can also add additional costs to production by increasing comminution and preconcentration expenses in the extraction process. For these reasons, characterisation and understanding of the gangue minerals present in an ore deposited is significantly important in the overall leaching process [8]. Some of the most common and typical gangue minerals associated with the Rössing uranium ore body include: quartz, chlorite, rutile, fluorite and calcite [7, 19].

After the treatments to leach out the uranium have occurred, the feed solution undergoes a two-step separation where the insoluble material is either centrifuged out or gravity separated. The clear pregnant leach solution is then fed into a Continuous Ion Exchange (CIX) circuit where the solution comes into contact with a resin where the uranium is preferentially extracted from the leach liquor. The resin is then periodically removed and acid washed to extract the uranium out of the resin then put back into the CIX circuit. The acidic uranium containing eluent is then fed into the solvent exchange setup where uranium complexes with the organic tertiary amine Alamine® 336 in the organic phase while the acidic aqueous phase is fed back into the CIX step of the process. The uranium containing organic phase is added to a neutral pH ammonium sulphate aqueous solution which preferentially takes up the uranium. This solution is then added into large precipitation tanks where ammonia gas is bubbled through the solution to precipitate ammonium diuranate (ADU). This is then filtered out of the solution and roasted to form $\text{U}_3\text{O}_8$ which is then shipped for further processing (enrichment).
Figure 1.1 Process flow diagram for uranium extraction at Rössing uranium mine. Copyright John Wiley & Sons, 1987 [20]
1.3.3. **High purity U₃O₈ to enriched uranium hexafluoride (UF₆)**

The shipped product U₃O₈ is converted into UO₂ in a reducing hydrogen atmosphere at temperatures between 700 – 1100 °C.

The UO₂ is then reacted with HF in a kiln to form uranium tetrafluoride (UF₄). The purified UF₄ product is then oxidised with fluorine gas in a fluidised bed reactor to produce uranium hexafluoride (UF₆). The purified UF₆ subsequently undergoes an enrichment step to increase the fissile U-235 isotope concentration from its naturally occurring 0.72% to the desired amount required. This ratio is usually between 3-4% for fuel rods for commercial nuclear power plants, ~20% for fuel for naval nuclear propulsion reactors and as high as 90% for nuclear weapons [21]. Enrichment of uranium is conducted commercially using a gas centrifuge method where ²³⁵U and ²³⁸U are separated by their comparative density differences. After the enrichment step is completed the enriched uranium for nuclear fuel is then converted into palletised UO₂ and transported for use [22].

1.3.4. **Nuclear fuel storage/disposal**

Around a quarter of enriched UO₂ nuclear fuel is replaced with fresh nuclear fuel rods every 1 to 2 years [23]. Spent nuclear fuel is removed from the reactor core and transferred into spent fuel pools where it remains for a period of 10 to 20 years depending on the initial enrichment level as well as duration spent in the reactor core. While the fuel rods are in these pools they are highly radioactive and still produce significant heat and radioactive daughter products. Although this fuel still contains a similar concentration of fissile material, it is moved from the reactor core to the spent fuel pools due to the formation of a neutron absorbing barrier which coats the fuel rods and hence significantly decreases efficiency of the rod (and surrounding rods) [21].

Of the uranium initially inputted into the reactor core roughly 96% remains. This is mostly ²³⁸U, although the fissile ²³⁵U concentration has generally decreased from ~3-4% to 0.8% while a minor amount (0.4%) of ²³⁶U is also present. Around 1% of the remaining amount has been converted into plutonium (²³⁹Pu, ²⁴⁰Pu) as well as various other minor actinides including curium, americium and
neptunium [23]. Other radioactive daughter products that remain from the nuclear fission of $^{235}_{\text{U}}$ are generally separated into three categories (short, medium and long lived radionuclides).

- Short lived radionuclides are less stable and therefore produce more radiation than other more stable radionuclides. This category includes isotopes; $^{135}_{\text{I}},^{99}_{\text{Mo}},^{135}_{\text{Cs}}$ and $^{147}_{\text{Pm}}$ and have half-lives ranging from 48 hours to 15 years.

- Medium lived radionuclides are slightly more stable again and have half-lives between 30 and 90 years. The most abundant of these include: $^{90}_{\text{Sr}},^{137}_{\text{Cs}}$ and $^{151}_{\text{Sm}}$. The more stable radionuclides; $^{99}_{\text{Tc}},^{95}_{\text{Zn}},^{135}_{\text{Cs}},^{107}_{\text{Pd}}$ and $^{129}_{\text{I}}$ are considered long lived $^{235}_{\text{U}}$ daughter products, the half-lives of these range between two thousand years and two million years.

- The long lived radionuclides $^{99}_{\text{Tc}}$ and $^{129}_{\text{I}}$ are generally considered likely candidates for nuclear transmutation, where further nuclear bombardment is conducted on these radionuclides in order to form less hazardous waste [24]. The remaining long lived radioactive isotopes as well as $^{235}_{\text{U}},^{238}_{\text{U}}$ and plutonium nuclides are generally extracted out of the spent nuclear fuel waste then either reprocessed for use in future nuclear fuel cycles in mixed oxide reactors (MOX) or sent off for spent nuclear fuel long term disposal.

### 1.3.5. Methods for Radionuclide storage

Initial treatment steps are undertaken on the spent nuclear fuel before the waste is placed in long term storage/disposal. The purpose of the waste treatment is to limit the likelihood of any waste coming into contact with the environment which could pose a significant contamination problem. Currently several methods of processing the radioactive waste have been proposed all with varying degrees of practicality and success [25]. These methods include:

- Vitrification [26]. Vitrification is currently the most common and inexpensive method for long term storage of SNF. The method for production involves heating acidic solutions containing high concentrations of uranium, plutonium, neptunium and various other radioactive species to convert the metal nitrates into more stable oxide forms as well as
remove the water. This powdered residue is then heated in another furnace with fragmented glass to form a glass matrix containing the radioactive waste. This glass substance is then poured into stainless steel cylinders where the fluid solidifies forming a black glass material which is highly resistant to water. The stainless steel cylinder is then welded closed and inspected for any damage or external contamination. This vitrified waste can be stored in underground repositories or buried underground and safely immobilises radioactive waste for thousands of years.

- Ion exchange. This method is commonly used for concentrating medium level radioactive waste such as $^{137}$Cs and $^{90}$Sr into a small volume. Generally the uncontaminated bulk solution can then be safely discharged without risk of environmental contamination. In general, inexpensive ferric hydroxide flock is added into a radioactive waste stream where radioisotopes are absorbed onto the surface of the flock. The resultant sludge is then mixed in a steel drum with either concrete or cement depending on the desired mechanical stability required [27].

- Synroc. A portmanteau of “synthetic rock” is a more complex storage method for spent nuclear fuel which was first synthesised by Australian Ted Ringwood in 1978. The initial method published involved reacting radioisotopes with oxides of Ti, Ba, Si, Zr, Al, Ca and K to form stable and insoluble minerals: hollandite (BaAl$_2$Ti$_6$O$_{16}$), zirconolite (CaZrTi$_2$O$_7$) and perovskite (CaTiO$_3$) [28]. Further adaptations of synroc have been developed to target specific radioactive waste streams. I.e. weapons grade plutonium and differences in radioisotope concentration. Once the radioactive waste has been converted into synroc the product can be stored in a waste repository with a low likelihood of contamination to the environment. This technique for actinide disposal will be discussed in further detail later.
1.4. Occurrences and properties of betafite

1.4.1. Occurrences
As mentioned previously betafite is a refractory uranium mineral found in a number of uranium bearing ores which are currently being processed including Rössing uranium mine [15]. For this reason, there has been increased interest in gaining a greater understanding in the structure and chemical factors which influence U leaching from the mineral. This is important in developing more efficient leaching methods to improve production yields in betafite containing ore deposits.

Betafite [(Ca,U)₂(Ti,Nb,Ta)₂O₇] was initially discovered by French geologist, Antoine Lacroix, in 1912 and was named after the region where initial discovery of the mineral occurred; Betafo, Madagascar [29]. Occurrences of the mineral are primarily found in carbonatite, calcite-fluorite-apatite-amphibole veins as well as anorogenic granitic pegmatites [30]. There have been several additional occurrences of betafite that have been discovered since the initial find. These include several other localities in Madagascar [30-35] as well as; Australia [36], Canada [37], Czech Republic [38], France [39], Italy [40-42], Russia [43], USA [44] and the Luna 24 landing site on the moon [45]. These localities generally contained only minor amounts of the mineral at each site (Figure 1.2).

To date Betafite has only been found in appreciable concentrations in two ore deposits; Rössing uranium deposit, Namibia and Saima U-REE complex, China.
Figure 1.2 Approximate location of reported betaite localities throughout the world [32].
Rössing uranium mine is one of the largest and longest continuously operating uranium mines in the world. The commencement of minerals processing of the Rössing deposit begun in 1976 and currently it is the 5\textsuperscript{th} largest producer of uranium with a nominal production capacity of 4,000 tons/yr which accounts for approximately 8\% of the world’s uranium [9, 15]. Rössing uranium deposit is a large low grade deposit with an average uranium concentration of 250 ppm. The uraniferous material is hosted in an alaskaite matrix. Betafite accounts for between 4 - 6\% of the uranium containing minerals in the ore with predominantly uraninite and pitchblende making up the remainder of the uranium mineralogy [9].

Saima U-REE complex is one of four alkaline rock intrusions in the Fengcheng magmic massif. This complex covers an area of approximately 20 square kilometres and extends to a depth of more than 1000 meters. Approximately 5\% of the uranium reserves in this deposit occur in pyrochlore super group minerals (pyrochlore, microlite and betafite) which occur as veinlets in alkaline skarns in the upper part of the deposits which also contains pitchblende and base metal sulfides [46].

1.4.2. Structure and stability

Betafite is a part of the pyrochlore super group of minerals which have the general chemical formula \([A_{2-m}B_2O_6(O,H,F)_{1-n}pH_2O]\) where:

\(A = \text{Na, K, Ca, Mn, Fe}^{2+}, \text{Ce, Y, Th, U, Pb, Sr, Ba, Bi.}\)

\(B = \text{Nb, Ti, Ta, Zr, Sn, Fe}^{3+}, W.\)

The three subgroups of the pyrochlore super group differ by their \(B\) site cationic concentrations. Species with \([(\text{Nb}_a + \text{Ta}_a) > 2\text{Ti}_b]\) and \((\text{Nb}_a > \text{Ta}_a)\) are considered to be a pyrochlore mineral; similarly if \([(\text{Nb}_a + \text{Ta}_a) > 2\text{Ti}_b]\) and \((\text{Ta}_a > \text{Nb}_a)\) the mineral is considered to be a microlite subgroup. For betafite, the titanium dominant member of the pyrochlore super group the classification is \(2\text{Ti}_b \geq\)
However, further nomenclature rules state for betafite the A site must be $U\alpha$ dominant (>20 wt%) where the *calcio-* prefix is used to indicate $Ca\alpha$ dominance in the A site of the mineral [47]. Yaroshevskii et al. reported on the geochemical diversity of pyrochlore group samples which showed that niobium rich betafites (Nb>Ta) were the most stable phase of the mineral found naturally (Figure 1.3). Moreover, significant variation in the chemical composition was also observed between different natural betafite samples indicating that the mineral was generally non-stoichiometric and allowed significant variation in elemental concentrations without jeopardising the minerals crystal structure [34].

All pyrochlore super group minerals have the same isometric crystal system with space group $Fd\overline{3}m$ and unit cells between $a = 10.2 – 10.4 \text{ Å}$ [48-50], though typically the unit cell for betafite is $\sim10.30 \text{ Å}$ [33, 51].

Due to the presence of radioactive elements such as U and Th present in the mineral structure some degree of metamictisation is generally found in all naturally occurring samples. This is due to the release of alpha particles from radioactive species within the sample which damage the crystal structure of any of the minerals present in the sample [52]. For this reason uranium rich betafite minerals are generally found to be amorphous [30, 32, 35]; although instances of non metamict Ca-
rich betafite have been reported in the literature [41, 51]. However, it could not be determined whether the lack of metamictisation present was due to the low concentration of radionuclides or the relatively new age of the samples.

Frost et al. investigated correlations in Raman spectra of metamict uranium titanate containing minerals, namely betafite [35, 53]. Comparisons between the Raman spectra and the spectra of a uranyl oxyhydroxide hydrate where made and showed similar characteristic bands which were attributed to $\text{UO}_2^{2+}$, $\text{U}–\text{OH}$, $\text{H}_2\text{O}$ and $\text{OH}^-$ stretching and bending vibrations respectively. Moreover, the UO stretching bands observed via Raman spectroscopy in the metamict betafite were shown to be of lower intensity and broader than in a crystalline betafite sample.

Lumpkin and Ewing (1996) reported Thermo Gravimetric Analysis (TGA) of natural betafites and determined that the water content in the sample could help stabilize the mineral structure. The authors also determined the recrystallisation temperature of a metamict betafite to be 800 °C using X-Ray Diffraction (XRD) [33]. Further work conducted by Lumpkin and Ewing showed significant chemical and textural alteration occurred upon heating of the metamict samples they studied. The breakdown of the mineral was shown to occur in two steps, initially leaching of the $A$ site cations: $\text{U}_A$, $\text{Ca}_A$ and $\text{Na}_A$ occurred when $\text{H}_2\text{O}$ was incorporated into the minerals structure [41]. In this alteration step up to 20 – 30% of the uranium in the initial structure may be lost due to chemical alteration of the mineral. As $A$ site cations migrate from the structure the formation of pyrochlore ($\text{Ca}_2\text{Nb}_2\text{O}_7$) and microlite ($\text{Ca}_2\text{Ta}_2\text{O}_7$) occurs. This affects the $\text{U}:\text{Nb}:\text{Ti}$ ratio which consequentially destabilizes the remainder of the mineral which leads to secondary alteration where the formation of uranpyrochlore [($\text{U}_x\text{Ca}_{1-x}\text{Nb}_2\text{O}_7$), liandratite ($\text{UNb}_2\text{O}_8$), and rutile ($\text{TiO}_2$) occurs at different concentrations depending on the initial betafite elemental composition [33].

1.4.3. Synthesis

Pyrochlore group minerals such as betafite have been shown to be potential candidates for the storage of spent nuclear fuels [10]. The synthesis of pyrochlore structural compounds has been
shown to differ significantly depending on the target radionuclide chosen to immobilise. These methods range from solvothermal/hydrothermal to solid state synthesis depending on the composition of the mineral synthesised.

Modeshia and Walton (2010) synthesised pyrochlore (Ca₂Nb₂O₆OH) and microlite (Ca₂Ta₂O₆OH) using a two-step solvothermal synthesis. Initially calcium nitrate and the required niobium or tantalum ethoxide was reacted at 650 °C to form perovskite (Ca₈B₃O₉) where B = Nb or Ta. This product was then reacted solvothermally with a solution of KOH to form pyrochlore group minerals with a varying stoichiometry depending on the starting composition [54].

A high temperature hydrothermal synthesis of uranium and titanium containing pyrochlores was investigated by Redkin et al. (2013) [55]. These compounds were synthesised by adding the stoichiometric amount of the required metals to a 1M NaF solution with Co/CoO as an oxidation buffer. This solution was sealed inside a platinum vessel and heated to 800 °C for 7 days. This method was shown to be able to produce several pyrochlore samples with varying stoichiometric compositions; although most samples reported multiple mineral phases also being present in the samples [55].

Solid state synthesis is generally considered the least troublesome and most practical for the large scale synthesis of durable compounds required for immobilisation of spent nuclear fuel. Moreover, this method is advantageous due to the ability to immobilise more waste radiogenic nuclides than the aforementioned synthesis techniques. The fundamental studies by Ringwood et al. (1979) showed the solid state synthesis of a matrix designed for immobilising several radioactive species including: Zr, Mo, Ru, Cs, Pd Sr, Ba, Rb U, Th and various other actinides. These nuclides were incorporated into a matrix of hollandite (BaAl₂Ti₆O₁₀), zirconolite (CaZrTi₂O₇) and perovskite (CaTiO₃) synthesised by heating the waste nuclides with a mixture of TiO₂, ZrO₂, Al₂O₃, CaO and BaO to 1300 °C for 24 hours [28]. Further work conducted on solid state synthesis of pyrochlores was completed by Ball et al. (1989) and showed a SYNROC matrix containing Ti-betafite, hollandite perovskite and
uraninite was synthesised by mixing reprocessed radiogenic waste with finely divided titanium powder and heating the mixture to 600 °C for 1 hour under reducing conditions, followed by hot pressing under oxidising conditions at 1200 °C for 2 hours [56]. Variations of this solid state method have been conducted to synthesise several pyrochlores for specific radionuclide storage [57-59]. To date the synthesis of pure betafite for the use of actinide immobilization has not yet been completed although this will be covered in more detail in Chapter 4.

1.4.4. Stability in aqueous systems
There have been several publications discussing the dissolution of naturally occurring betafites. These publications have generally focused on studying the influence of metamictisation on uranium dissolution from the mineral. Eyal et al. (1986) reported long term uranium dissolution of natural betafite samples over a period of 50 – 100 days in 0.1M NaHCO₃ solutions to investigate the influence of metamictisation caused by alpha radiation in the samples. This paper showed regions of the sample where significant metamictisation was observed showed greater rates of leaching relative to more crystalline regions of the sample. Moreover, self-annealing (recrystallisation) of the metamict sample was shown to have occurred in regions of the sample where leaching of radioisotopes had taken place previously [60]. For betafite the estimated self-annealing time for metastable alpha recoil tracts was 2000 ± 1300 yr [61].

Leaching studies conducted to investigate the performance of betafite for long term storage of spent nuclear fuel were conducted by Ball et al. (1989), Gieré et al. (2003) and Icenhower et al. (2006)[56, 58, 62]. In these three studies variations of betafite were synthesised in matrices that consisted of several other uranium containing minerals. The dissolution rates for uranium and other radioactive species therefore differed as the host matrix changed. The leach rates for uranium were reported to vary between $10^{-1} – 10^{-4}$ g m⁻² d⁻¹ for a sample matrix containing Ti-betafite and uraninite [56] to approximately $10^{-3}$ g m⁻² d⁻¹ for a matrix containing: pyrochlore/betafite, rutile, monazite and perovskite [58]. Both of these experiments were conducted at 90 °C in deionised water using the standard test method for static leaching of monolithic waste forms long term method (MCC1) [63].
This therefore demonstrates that the overall leach rate is significantly influenced by the various mineral phases that make up the host matrix. This results in difficulties in determining the durability of betafite in a polyphase matrix troublesome due to the various minerals leaching at different rates.

There has been little research into the leaching of betafite under the conditions generally employed for commercial minerals processing. In the extractive metallurgy book written by Merritt (1971), the refractory nature of betafite is described. According to Merrit (1971) the leach conditions needed to achieve effective uranium leaching from a natural betafite sample from Betafo region in Madagascar are temperatures as high as 80 °C and \([\text{H}_2\text{SO}_4]\) of 100 g/L. Although these harsh leach conditions are impractical for commercial mineral processing plants [64]. Work by van Rensburg showed using similar conditions to those employed at the Rössing uranium mine (pH = 1.6, temperature = 35 °C, \([\text{Fe}^{3+}] = 3 \text{ g/L, } \text{Fe}^{3+}:\text{Fe}^{2+} \text{ ratio = 9:1, leach time = 7 h})\) showed half of the remaining uranium in the post leach residue was in the form of betafite while the other half was poorly liberated uraninite and coffinite [9]. This indicated that the majority of the uranium incorporated in betafite had not undergone leaching at the conditions employed at Rössing.

In a study conducted by Nettleton et al. (2015) natural betafite was leached at a range of conditions similar to that used in commercial uranium processing. Approximately complete dissolution was observed after 48 h at 214.5 g/L \([\text{H}_2\text{SO}_4]\), 2.0 g/L \(\text{Fe}^{3+}\) at 89 °C while refinement of the experimental conditions led to similar leach yields at 57.1 g/L \([\text{H}_2\text{SO}_4]\), 36.7 g/L \(\text{Fe}^{3+}\) at the same temperature. This work also showed recrystallisation of the metamict betafite reduced the uranium dissolution yield to less than 12% at the same conditions as previously described. Characterisation of the recrystallized betafite showed an enrichment of tantalum on the betafite surface which was hypothesised to cause this distinct drop in leaching [65].
1.5. Leaching mechanisms of uranium minerals

The dissolution mechanism of simple uranium oxides such as uraninite (UO₂) and pitchblende (U₃O₈) have been extensively studied since the commercialisation of uranium mining. The mechanism of dissolution occurs by an oxidation of tetravalent uranium to hexavalent uranium using ferric iron in an acidic medium (sulfuric acid). Laxen (1971) report this occurs initially by diffusion of Fe³⁺ species onto the UO₂ surface. The Fe³⁺ is then adsorbed onto the surface which then oxidises the surface uranium to UO₂⁺, further oxidation takes place to give UO₂²⁺ and Fe²⁺. These two aqueous products then desorb from the surface (Equation 1.1). The oxidised uranium in the form of a uranyl ion then binds to the sulphate ligand forming uranyl sulphate (UO₂SO₄) (Equation 1.2) [66]. The reacted ferrous iron then undergoes oxidation with the addition of a secondary oxidant (generally NaClO₃ or MnO₂) (Equations 1.3 & 1.4) [64]. The reintroduction of ferric ions into the system forms the continuous redox cycle which allows further tetravalent uranium to undergo oxidation. During commercial minerals processing, iron containing minerals in the ore generally provide the iron needed for ferric oxidation of uranium [67].

\[
\begin{align*}
\text{UO}_2(s) + 2\text{Fe}^{3+} & \rightarrow \text{UO}_2^{2+}(aq) + 2\text{Fe}^{2+} \quad (1.1) \\
\text{UO}_2^{2+}(aq) + \text{SO}_4^{2-} & \rightarrow \text{UO}_2\text{SO}_4(aq) \quad (1.2) \\
\text{Fe}^{3+} + \text{NaClO}_3 + 6\text{H}^+ & \rightarrow 6\text{Fe}^{2+} + \text{NaCl} + 3\text{H}_2\text{O} \quad (1.3) \\
2\text{Fe}^{2+} + \text{MnO}_2 + 4\text{H}^+ & \rightarrow 2\text{Fe}^{3+} + \text{Mn}^{2+} + 2\text{H}_2\text{O} \quad (1.4)
\end{align*}
\]

The leaching rates of uranium minerals can be influenced by various parameters. These can include ‘standard parameters’ which are commonly varied and monitored in a uranium minerals processing facility such as: [H₂SO₄], [Fe(TOT)], temperature, redox potential, % solids, particle size and residence time. Each of these aforementioned parameters influences the extent of leaching in uranium minerals to a varying degree.

Bharagava et al. (2015) describes the influence of standard parameters on the dissolution of both natural and synthetic UO₂. This work showed the dissolution of uraninite was not strongly influenced
by $[\text{H}_2\text{SO}_4]$ once the pH was below 1.8 (1.5 g/L). This was due to the role of sulfuric acid to be added to provide a low pH to allow for the formation of uranyl sulphate complexes while stopping the formation of jarosite which occurs at pH > 1.8. This work also provided optimal conditions of leaching uraninite bearing ores are: temperature range of 35 – 60 °C, pH – 1.5 – 1.8, % solids – 35 to 65% w/v, $[\text{Fe}_{TOT}] > 2$ g/L, Redox potential – 520 mV vs. Ag|AgCl and $\text{Fe}^{3+}:\text{U}^{4+}$ ratio > 4:1 [13].

When the aforementioned results are compared to the influence of standard parameters on the leaching of a more refractory mineral such as brannerite significant differences can be observed. Charalambous et al. (2013) demonstrated the dissolution of uranium increased from ~2% to 15~ when the sulfuric acid concentration was increased from 15 g/L to 200 g/L at 50 °C, 3 g/L $\text{Fe}_2(\text{SO}_4)_3$. Moreover the influence of $[\text{Fe}^{3+}]$ was reported to not be significant on uranium leaching from brannerite [68].

The aforementioned contradicting influences of parameters such as $[\text{H}_2\text{SO}_4]$ and $[\text{Fe}^{3+}]$ on uraninite and brannerite leaching clearly show that it cannot be assumed that the influence of various standard parameters will affect the leach rate in the same way for various uranium minerals.
1.6. **Summary of literature review**

Over recent years the usage of nuclear power has gained acceptance as a more environmentally friendly alternative to fossil fuels. This has led to further investigation into more effective methods for uranium extraction and targeted leaching for specific uranium minerals. The uranium pyrochlore mineral betafite has gained increased attention due to its refractory nature and abundance in Rössing uranium ore.

Betafite is a subgroup of the pyrochlore super group of minerals and has a general chemical formula of \([\text{[U,Ca]}_2(\text{Nb,Ti,Ta})_2\text{O}_7]\) although several other ions can substitute into the minerals structure as discussed previously. Characterisation of natural betafite samples showed uranium rich betafite samples are generally metamict (amorphous).

Dissolution studies have been conducted on betafite from two perspectives – minerals processing for commercial mining and actinide immobilisation. There is very little work conducted investigating uranium leaching from betafite; although the general consensus is to avoid treating ore containing high grades of betafite due to the low leachability leading to low leach yields. Leaching experiments conducted at similar conditions used to the Rössing uranium mine (pH = 1.6, temperature = 35 °C, \([\text{FeTOT}] = 3 \text{ g/L, Fe}^{3+:\text{Fe}^{2+}} \text{ ratio } = 9:1, \text{ leach time } = 7 \text{ h}) showed the majority of the uranium in the tailings was in the form of betafite; indicating that betafite could not be leached under these conditions.

Research into the durability of betafite (and other pyrochlore minerals) has been extensively studied previously. These studies have generally focused on pyrochlore group minerals for the purpose of immobilisation of spent nuclear fuel. These previous studies have demonstrated a range of radionuclides that can substitute into the betafite/pyrochlore structure for immobilisation as well as their respective aqueous durability.

While numerous publications have been conducted on characterisation of natural betafites and concluded the structure and chemical composition can vary considerably, there has been little work
conducted on correlating these changes to influences in dissolution. A greater understanding on the influence of various leaching parameters is important in considering betafite as a potential source of uranium to keep up with the growing demand for nuclear fuel. Furthermore, gaining a greater understanding of the chemical and structural properties of betafite is also important in assessing the potential for betafite for the use as a storage matrix for immobilisation for uranium and other radionuclides.
1.7. **Scope of project**

As previously discussed there has been very little research on certain aspects of the uranium bearing mineral betafite reported in literature. These areas included the stability of betafite at conditions commonly used in commercial uranium processing plants and the influence of structural and chemical properties of betafite on leaching.

The main aims of this study are to investigate the preparation of synthetic betafite (and to investigate its structure and composition), and to investigate the dissolution of synthetic and natural betafites (from a minerals processing perspective). Specific aims of this project include:

- Characterise natural betafite containing samples and investigate structural and chemical differences between naturally occurring betafites.
- Investigate how structural and chemical modifications influence the rate of dissolution of various naturally occurring betafites.
- Determine a fundamental understanding of how metamictisation and alteration/weathering of natural betafites influence their leachability under conditions of interest to commercial minerals processing.
- Prepare a method for synthesising pure betafite with no uranium containing impurities for the purpose of conducting characterisation and dissolution studies.
- Conduct dissolution studies to investigate the effect of varying standard dissolution parameters ([H$_2$SO$_4$], [Fe$_{TOT}$], redox potential, and temperature) on uranium dissolution from betafite.
- Investigate the influence of varying comminution, Fe counter ions, lixiviant, and secondary oxidants.
- Carry out long term (90 day) dissolution studies to investigate the aqueous durability of betafite over a long term leaching period.
• Furthermore, investigate both structural and chemical changes that occur after leaching of the sample has occurred.
1.8. References


9. van Rensburg, N.J., A value based approach to leach optimization at Rössing uranium limited, in Faculty of the Engineering and Built Environment. 2014, University of Cape Town: Rondebosch. p. 163.


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CHAPTER 2
Materials and Methodology

In this chapter technical information on the instruments used and the respective methodologies used in the subsequent chapter are presented.
2.1. Materials

2.1.1. Chemical reagents
The following chemicals were used as received for synthesis, characterisation and leaching studies:

Sulfuric acid \([H_2SO_4]\) (98% AR grade, Merck Ltd), nitric acid \([HNO_3]\) (70% AR grade, Merck Ltd),
hydrochloric acid \([HCl]\) (33% AR grade, Merck Ltd), hydrofluoric acid \([HF]\) (50% AR grade, Ajax
Chemicals), hydrogen peroxide \([H_2O_2]\) (30% AR grade, Merck Ltd), manganese dioxide \([MnO_2]\) (98% Lab
Reagent Merck Ltd), uranyl nitrate \([UO_2(NO_3)_2]\) (99% AR grade, Aldrich Chem. Co.), calcium carbonate
\([CaCO_3]\) (99.95% AR grade Aldrich Chem. Co.), titanium oxy sulphate \([TiOSO_4]\) (98% AR
grade, Riedel-de Haën), niobium(V) oxide \([Nb_2O_5]\) (99.9% AR grade Aldrich Chem. Co.), tantalum(V)
oxide \([Ta_2O_5]\) (99.99% AR grade Aldrich Chem. Co.), sodium fluoride \([NaF]\) (98% Lab Reagent Merck
Ltd), ammonium fluoride \([NH_4F]\) (>99% AR grade Aldrich Chem. Co.), potassium fluoride \([KF]\) (99.9%
AR grade Aldrich Chem. Co.), oxalic acid dihydrate \([HO_2CCO_2H\cdot2H_2O]\) (>99% AR grade Aldrich Chem.
Co.), glacial acetic acid \([CH_3CO_2H]\) (99.7% AR grade Aldrich Chem. Co.), hydrobromic acid \([HBr]\) (48%
AR grade Aldrich Chem. Co.), orthophosphoric acid \([H_3PO_4]\) (85% AR grade Aldrich Chem. Co.), ferric
sulfate \([Fe_2(SO_4)_3\cdot5H_2O]\) (99% Lab Reagent, Ajax Chemicals), ferrous sulfate \([FeSO_4\cdot7H_2O]\)
(>99.0%AnalaR Chem-Supply Ltd), ferric chloride \([FeCl_3]\) (97% AnalaR Chem-Supply Ltd), ferric
fluoride \([FeF_3\cdot3H_2O]\) (99.9% AR grade, Aldrich Chem. Co.), ferric bromide \([FeBr_3\cdot3H_2O]\) (98% AR
grade, Aldrich Chem. Co.), ferric nitrate \([Fe(NO_3)_3\cdot9H_2O]\) (99.95% AR grade, Aldrich Chem. Co.), ferric
phosphate \([FePO_4\cdot2H_2O]\) (29% Fe, Aldrich Chem. Co.), uranium ICP-MS standard [1000 mg/L U in
2% nitric acid] (AccuStandard), transition metal mix 2 for ICP [100 mg/L of Ti, Zr, Hf, Nb, Ta, Mo, W, Re in 2% nitric acid and 1% hydrofluoric acid] (TraceCERT), periodic table mix 1 for ICP (33 elements 10mg/L each), Millipore MilliQ water was used in the preparation of all solutions.

2.1.2. Natural samples
The three natural betafite samples used in this study were provided by Museum Victoria
(Melbourne, Australia), Australia Museum (Sydney, Australia) and an online mineral dealer. The
samples were sourced from unknown regions in Ambatofotsy, Madagascar; Miarinarivo, Madagascar.
and Silver Crater Mine, Canada respectively. Throughout this document the sample are hereafter referred to as BAM (Betafite Ambatofotsy Madagascar), BMM (Betafite Miarinarivo Madagascar) and BSC (Betafite Silver Crater).

2.2. Methodology

2.2.1. Preparation of synthetic betafite

Synthetic betafite was prepared via a solid state synthesis method (see Chapter 4 for further details). Prior to the reaction; all reactants were (in the required molar ratios) dry ground for 20 min in an agate mortar and pestle before passing the mixture through a 38 μm sieve. Reactants were then added to platinum lined alumina boats and placed into a quartz tube that was positioned inside a furnace. The reaction atmosphere was varied by passing different gases through the tube. As mentioned previously further details on the synthesis procedures investigated and the procedure used to produce high purity synthetic betafite are given in Chapter 4.

2.2.2. Multi acid digestion for ICP-MS analysis

Multi acid digestion was conducted on the natural and synthetic betafite samples in order to ascertain their elemental composition. The following procedure was used for all bulk multi elemental analysis results reported herein.

- 50 mg of crushed sample was weighed out into a Teflon vessel. The sides of this vessel were rinsed down with MilliQ water.

- 6 mL of concentrated HCl was slowly added and the reaction left to subside.

- 2 mL of conc. HNO₃ was then added and again the reaction was left to subside.

- 2 mL of conc. H₂SO₄ and 3 mL of conc. HF was then added.

- The Teflon vessel was then placed on an aluminium heating block at 110 °C and heated to incipient dryness. The temperature was then raised to 160 °C to bring the sample to complete dryness.
• A further 1 mL of conc. H$_2$SO$_4$ was subsequently added and the sample was heated at 160 °C to complete dryness.

• Once dry, an additional 1 mL of conc. HNO$_3$ and 2 mL of H$_2$O$_2$ was added and the reaction was left to subside.

• 19 mL of 10% HNO$_3$ and 2% HF was added, the vessel was then capped and placed in a drying oven at 180 °C for 5 hours.

The liquid samples were then diluted in MilliQ Water and acidified for full quantitative analysis via ICP-MS.

The ICP-MS analysis was completed using an Agilent HP 7700 series ICP-MS using a multi- element environmental standard (Aglient standard p/n: 5183-4682).

2.2.3. Dissolution Test Methodology

2.2.3.1. Short term dissolution test procedures

Short term (360 minute) dissolution studies were conducted to assess the leachability of betafite over a short leach duration. The following procedure was used for all short term dissolution tests throughout this document.

A 250 mL volume of the desired sulfuric acid concentration was added to a 250 mL three neck flask. The solution was then agitated using an overhead mechanical stirrer and heated to the required temperature using a heating mantle. Once at temperature, the desired amount of ferric and ferrous sulfate was added to create the required redox potential (ORP) and allowed to equilibrate for a period of 10 minutes. After this period 50 mg of the ground betafite sample was added to the leach vessel. The time upon addition of sample was determined to be 0 mins. Fifteen solution samples were then collected at pre-determined intervals throughout the experiment. The collected samples were filtered through a 0.45 µm nylon filter. Aliquots of 0.5 mL of the filtered sample were then diluted to 25 mL before being analysed via ICP-MS. The redox potential and pH was also measured...
and monitored with an Ag|AgCl electrode and a glass electrode respectively and kept within 10 mV of the desired redox potential by the addition of a 0.01 M NaMnO₄ solution (Figure 2.1).

Duplicate analysis of the diluted leach solution samples were conducted using an Agilent HP 7700 series ICP-MS. The instrument was calibrated using commercial uranium, niobium, titanium and tantalum standards. An in line internal standard containing Sc, Ge, Rh, In, Tb, Lu, Bi, was added to all calibration and test samples. The error in measurement on the instrument was calculated to be ± 2.5%.

![Figure 2.4 Leaching setup used for all short term dissolution experiments conducted.](image)

**2.2.3.2. Long term dissolution procedures**

The method used for long term dissolution studies was an adaptation of the standard test method for static leaching of monolithic waste forms for disposal of radioactive waste (formally MCC1) [1]. Dissolution studies were conducted by adding 30 mL of the desired concentration of sulfuric acid, iron sulfate and sodium fluoride or brine solution into a 30 mL Teflon sealed glass vial. The glass vials were placed in a rotary hybridization oven and heated to 50 °C. The vials were left in the oven for a
period of 2 hours to allow the solution to heat to 50 °C. The addition of 20 mg of sample added to each vial and the time upon addition was determined to be 0 minutes. A mass balance was conducted by weighing each vial with solution and betafite and recording the values to ensure the mass did not change throughout the duration of the experiment.

The brine solution was prepared using the method published in MCC1 [1]. The control dissolutions experiments were conducted in milliQ water.

Aliquots of each solution were collected at pre-determined intervals throughout the 90 day dissolution experiment. Each solution was refilled to the initial volume with fresh leach liquor with the same acid, iron and fluoride concentration and the leach liquor. Analysis of the leach solutions was then measured using the same ICP-MS method as previously described in Section 2.2.3.1.

2.2.4. Characterisation and analytical techniques

2.2.4.1. Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)

Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) is an analytical technique that can be used to determine the concentration of numerous elements in an aqueous solution. The technique employs a plasma (~10,000 °C) which ionises the elements (generally metals) present into charged elemental ions which are then passed through ion lenses which focus the charged species into the mass spectrometer. The mass spectrometer subsequently separates the ions by their respective mass-to-charge (m/z) ratio which is measured by the detector. A schematic diagram of the aforementioned components is given in Figure 2.2 [2]. The concentration of the species present is proportional to the measured signal intensity. The signal intensity, and hence calibration range can be affected by several factors which result in the production of charged ions. These factors include: the torch position, gas flow rate and the solution composition/matrix. The high temperature argon torch ionises the vast majority of the elements, however some elements may form neutrally charged species or interfering diatomic charged compounds which may interfere with species that are being analysed and hence affect the measurement. The maximum detectible concentration range for ICP-
MS is 10,000 ppb for major cations which are generally found in the environment and 1000 – 100 ppb for other elements [2, 3]. Minimum detection levels for the instrument vary significantly depending on the ability of the element to produce clean charged ions. Typically, concentrations below 1 ppb can be accurately measured with the appropriate methodology (Figure 2.3). ICP-MS analysis of the main elements targeted in this project (U, Ti, Nb, Ta) all lie between the 0 – 200 ppb detection range.

Figure 2.5 Schematic diagram of the components of an ICP-MS instrument [2]
Scott A. McMaster

Figure 2.6 Detection capabilities and isotopic ratio of a typical ICP-MS (ELAN 6000/6100 quadrupole ICP-MS [2]

Commercially purchased multi elemental standards were used to make the calibration curves for analysis. The calibration range was typically between 0 – 200 ppb for the minor cations analysed. Preparation of the samples from multi acid digestion and dissolution experiments was completed by initially diluting the samples to an appropriate concentration which fell within the aforementioned calibration range with MilliQ water (18 MΩ resistance) and nitric acid to ensure the overall nitric acid concentration was 2%. An in-line internal standard containing Sc, Ge, Rh, In, Tb, Lu, Bi, was added to all calibration and test samples. An Agilent HP7700 series ICP-MS with an auto sampler was used to carry out all of the elemental analysis experiments conducted.

2.2.4.2. X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD) is an important analytical tool for identification of crystalline substances. In this technique, electrons are emitted from an electron source at a metal target to produce X-rays [4]. The resultant wavelength is characteristic of the electron produced by the Cu Kα X-ray source used. The X-rays are then collimated and directed towards a flat region of the powered sample. The monochromatic X-ray beam interacts with the crystal lattice of any crystalline material in the
sample. This interaction is in the form of interference and hence diffraction. X-ray powder diffraction measures signal intensity of diffracted X-rays caused by interactions with the crystalline material in the sample [5]. These are measured at pre-determined angles and correlated to crystalline mineral matches. The X-rays diffract differently depending on the crystalline material present /atomic arrangement.

The Bragg Equation (Equation 2.1) must be satisfied in order for diffraction to occur [6]. This equation states that the path difference between the diffraction beam and the incident must be equal to a multiple of the wavelength of the X-ray source (Figure 2.4).

\[ 2d\sin\theta = n\lambda \]  

\( d \) = space difference between the adjacent planes of atoms  
\( \theta \) = angle of incidence of the X-ray beam (Bragg angle)  
\( n \) = order of diffraction  
\( \lambda \) = wavelength of X-ray source

Figure 2.7 X-ray diffraction at the atomic layers.

As previously described the X-ray source used for diffraction analysis in this project was the Cu K\( \alpha \) (1.5405 Å) to measure the \( \theta \) and therefore determine the d spacing of the crystal plane. Once a full range of diffraction data is collected, a diffraction pattern can be observed. This diffraction pattern is
characteristic for specific crystalline compounds/substances. This pattern can be interpreted by comparison with a standard reference crystallographic database such as the International Centre for Diffraction Database (ICDD) - Joint Committee on Powder Diffraction Standards (JCPDS) where the identification of known materials can be compared.

Preparation of samples for XRD analysis varied depending on the nature of the sample initially. Generally crushing of whole rock samples into <20 µm grains with a mortar and pestle was completed. The powdered sample was then placed evenly on a flat glass slide mounted on a circular poly methyl methacrylate holder and covered in Kapton film to reduce the likelihood of airborne contamination of radionuclides into the instrument. Diffraction patterns were obtained using a Brüker D4 Endeavour diffractometer fitted with a Cu Kα radiation source, incident beam monochromator and LYNXEYE detector. A 1° divergence slit was used to analyse between the 2θ range 5-90° with a step size of 0.02° 2θ and counting time of 2 s/step. The instrument was calibrated using quartz and corundum calibration standards prior to use.

### 2.2.4.3. Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is a useful tool in obtaining images of a material on the nanometre (nm) and micrometre (µm) scale length. This is beneficial in providing structural information such as morphological, crystallographic and the homogeneity of the sample. It does this by producing a magnified image of the sample by using electrons as a source instead of visible light. An accelerated beam of electrons with a pre-determined energy is thermionically emitted from an electron gun typically made of tungsten metal or lanthanum hexaboride (LaB₆) cathode filament which is directed towards the sample [7]. The electron beam travels through electromagnetic fields which are used to focus the beam on the sample. Once the electrons hit the sample, electrons and X-rays are ejected from the sample which is then picked up by detectors which determine the origin of the source of the backscattered electrons, secondary electrons and other photons of various energies and convert them into a signal which produces the final image (Figure 2.5). These signals
obtained from the sample can be used to determine characteristics of the sample including: morphology, grain orientation of the crystals and elemental composition of the sample surface [8].

Figure 2.8 Schematic of a Scanning Electron Microscope (Left). Cascade amplification process (Right) [9].

Preparation of samples for SEM analysis was completed by placing a small amount of the powdered sample on carbon tape mounted to a metal stub which was then carbon coated. Analysis was conducted using a FEI Quanta 200 SEM with EDAXSi (Li)X-ray detector under a vacuum of > 5×10^-5 Torr. An accelerating voltage of 30 kV was used with a spot size of 5 nm and probe current of ~1 nA.

2.2.4.4. Energy Dispersive X-Ray Spectroscopy (EDS/EDX)

Energy Dispersive X-Ray (EDX) spectroscopy is a valuable analytical tool for determining the elemental composition of the surface of a sample. This is undertaken by measuring the intensity of the X-ray signals generated by the electron beam previously described. X-rays omitted from the sample pass through a monochromator, which isolates the specimen chamber from the detector using a cooled reverse-bias Si (Li) crystal. Absorption of each X-ray onto the crystal leads to the ejection of a photoelectron which gives up the majority of its energy in the formation of electron
hole pairs (Figure 2.6) [7]. These are then converted into voltage pulses by a charge–to–voltage converter (pre-amplifier). These signals are then shaped by a linear amplifier and finally passed through to a Computer X-ray Analyser (CXA). The fundamental principle behind EDX is the proportional relationship between each voltage pulse to the energy of the incoming X-ray photon [9]. Moreover, as each X-ray is characteristic to the element from which it was emitted, this allows the determination of the elemental composition of the surface of the sample to be measured [8].

![Fundamental principles of Energy Dispersive X-ray Spectroscopy (EDX/EDS).](image)

Energy Dispersive X-Ray (EDX) analysis was conducted on a FEI Quanta 200 SEM with EDAXSi (Li)X-ray detector under a vacuum of > 5×10⁻⁵ Torr. An accelerating voltage of 30 kV was used with a spot size of 5 nm, probe current of ~1 nA. A step size of 0.5 µm and an acquisition time of 200 µs were used for all spot analysis points.

2.2.4.5. **Electron Probe Micro Analysis (EPMA)**

Electron Probe Micro Analysis (EPMA) differs from SEM as EPMA records emitted X-rays and differentiates them according to the Bragg spectrophotometer to determine elemental concentrations, whereas SEM records scattered electrons to produce an image of the sample (Figure 2.7). The advantage of EPMA is that the technique allows microstructural and chemical
characterisation of complex mineral specimens such as natural uranium baring minerals. This is completed by quantitative analysis of the sample picking up elemental distribution which is fed into an algorithm which determines the mineral composition of the sample. At the same time, a detailed image can be produced if the X-ray microspectrometer is part of the EPMA system [10].

Figure 2.10 various types of signal formation by electron bombardment of a solid sample. EPMA focuses primarily on the characteristic X-rays.

The electron microprobe uses a high energy electron beam to produce X-rays in a similar way to SEM. The produced X-rays are characteristic of the elements within the sample analysed. These electrons are produced by a low energy thermionic tungsten filament and accelerated by a positively biased anode plate to 10-30 keV. The electrons pass through a hole in the centre of the anode plate and are focused by a series of magnets that work as lenses. The X-rays are then produced from resultant beam interactions with the sample diffracted through analysing crystals (pentaerythritol,
lithium fluoride and thallium acid phthalate) and counted using gas-flow and sealed proportional detectors (Figure 2.8). The elemental composition was determined by comparing the X-ray intensity of known calibration standards and the samples after corrections for the effect of X-ray absorption and fluorescence in the sample [8].

The beam current used ranges from 10 – 200 nanoamps (nA) and has an electron beam which is roughly 1000× more sensitive than that used in a scanning electron microscope [11]. These higher current beams produce more X-rays from the sample and hence improve the accuracy and detection limits of the multi elemental analysis. The data obtained yields quantitative elemental composition and textural content of the regions analysed. Factors such as chemical composition of a mineral grain or metal are readily able to be determined using this technique for elements ranging in size from fluorine (Z = 9) to uranium (Z = 92) at concentrations as low as 100 ppm [12].

The specifics of the parameters used for EPMA analysis are discussed in the respective methodology sections of the results chapters.
2.2.4.6. **X-ray Photoelectron Spectroscopy (XPS)**

X-ray Photoelectron Spectroscopy (XPS) is an important tool in determining elemental composition and oxidation states of elements in the top ~5 nm depth of a substance. This is achieved by irradiating the sample with soft X-rays (generally AlKα or MgKα) which in turn results in the ejection of core level electrons from the targeted species. The identity of the elements present in the sample can be determined by the characteristic kinetic binding energies given off by the ejected photoelectrons (Equations 2.2) (Figure 2.9) [13]. Analysis of the minor variations in binding energy allows determination of oxidation states and other factors such as chemical bonding environment [12]. Moreover the relative concentrations of the elements present can also be determined by analysis of the photoelectron peak intensities and peak areas.

\[
KE = h\nu - E + \varphi
\]

(2.2)

Where KE = Kinetic energy

\(h\nu\) = photon energy from the X-ray source

E = Binding energy (unknown variable)

\(\varphi\) = spectrometer work function

In a solid sample, photoelectrons that are ejected from the bulk sample are generally absorbed by the sample and hence energies are too low to measure. Therefore XPS only proves electron coming from the top 5 nm which do not lose a significant amount of energy while penetrating the outer layers of the material. This penetration depth is dependent on factors such as density of the material, the energy of the photoelectrons measured and the angle between the sample and detector. Preparation of the sample for XPS was completed by pressing powdered sample at 7 tons under vacuum for 5 minutes using a hydraulic press. This pressed sample was mounted for analysis using carbon tape. XPS measurements were conducted on a Thermo Scientific K Alpha XPS instrument. A low energy flood gun was used to remove charge build up on the sample surface. Al Kα (1486.6 eV) X-ray source was used with constant analyser pass energy of 150 eV with a spot size
of 55 µm. Forty sweeps at scan rates of 80 seconds each were completed for the main elements associated with the sample (U, Ca, Nb, Ti, Ta). The binding energies were calibrated by fixing the C 1s binding peak to 284.8 eV [14]. Peak identification was conducted using literature data and is discussed in more detail in the results chapters (Chapters 3 – 6).

Figure 2.12. Electron ejection diagram showing of the fundamentals of XPS from a sample.

**2.2.4.7. Vibrational Spectroscopy**

**2.2.4.7.1. Fourier transform – Infrared Spectroscopy**

Fourier transform – Infrared Spectroscopy (FT-IR) is a characterisation technique used to obtain an infrared spectrum simultaneously over a range of wavelengths. The mathematical Fourier transform process is applied to the raw data to produce an absorbance or transmittance spectrum which can be used for interpretation [15]. An FT-IR spectrum can give a broad range of information about the chemical structure since absorbances/transmittances of specific functional groups are characteristic to known wavelengths. These absorbances can be therefore used to deduce structures (or parts of
structures) of compounds. These spectra can also be fed into spectral databases as a complementary conformation that a known chemical is present [16].

Diffuse Reflectance Infrared Fourier Transform (DRIFT) Spectroscopy was the method used in this project. This was performed using a Perkin Elmer Spectrum 100 FTIR instrument. The powered sample was diluted with potassium bromide (KBr) and ground until homogenous. Absorbance was recorded at room temperature between 400 and 4000 cm\(^{-1}\) with a resolution of 2 cm\(^{-1}\). Sixteen scans were completed on the sample to reduce the signal-to-noise ratio of the spectra.

2.2.4.7.2. Raman Spectroscopy

Raman spectroscopy is a spectroscopic technique that is used to study the vibrational changes in a material which can complement other characterisation methods to determine the structure of compounds [17]. This technique differs from FT-IR as changes in the polarisation potential are imperative for a compound to display Raman effect/absorbances. As monochromatic light interacts with a molecule photons produce bonding rotations and vibrations; this results in inelastic scattering (Raman scattering) [18].

Raman Spectroscopy was performed using a Perkin Elmer Raman station 400f. Raman excitation was achieved using a 785 nm laser. Acquisition was completed at room temperature between 100 and 3600 cm\(^{-1}\) with a resolution of 2 cm\(^{-1}\). Repeat acquisition was completed to improve signal-to-noise ratio. Spectra were compared to the RUFF Raman database. Manipulation such as baseline correction and signal normalization was completed on the data acquired.

2.2.4.8. Brunauer, Emmett and Teller Theory (BET)

Brunauer, Emmett and Teller Theory (BET) is an analytical tool used for measuring surface area and porosity of solid materials. Generally all solid surfaces attract gas molecules, this is known as gas sorption [19]. This property of materials is exploited by BET theory whereby physical adsorption of gasses onto the internal and external surfaces is quantified. The amount of gas adsorbed is dependent on the vapour pressure measured and is proportional to the total surface area of the
sample [20]. By monitoring the gas sorption onto the sample information which is characteristic for a sample such as surface area, porosity and pore size can be determined [19]. There are several methods that can be used to calculate the surface area from the gas absorption data measured. The most common of these methods is an expansion of the Langmuir equation which is most suitable for monolayer gas adsorption. This equation assumes adsorption starts on the strongest energy sites first then as the pressure increases adsorption occurs on the next energy level sites and so on until all sites have been occupied.

Surface area analysis was conducted using a Micromeritics ASAP 2000 Micropore Analysis instrument. The analysis was carried out on approximately 500 mg of the powdered sample. The sample was degassed at 250 °C for 24 hours prior to analysis.

2.2.5. Electrochemistry

2.2.5.1. Preparation of the Carbon Paste Electrode
Carbon Paste (CP) consisting of uniform graphite particles mixed with a paraffin binder, was purchased from Bioanalytical Systems (West Lafayette, USA), and used as received. To prepare the working formula, a 1:1 ratio of Carbon Paste: Synthetic uranium mineral (by weight) was freshly prepared by grinding in a mortar and pestle, to obtain a homogeneous paste. This paste was placed in a working electrode with a diameter of approximately 0.3 cm, levelled with a spatula and polished on low roughness paper to obtain a flat surface. All experiments were undertaken under a nitrogen atmosphere in a 50 mL temperature controlled glass reactor with a Pt wire as a counter electrode, an Ag|AgCl reference electrode held at ambient (22 °C) temperature by separation from the reaction vessel with a salt bridge, and a compressed and polished Carbon Paste-uranium mineral mixture as the working electrode. The reactor was maintained at the desired temperature with a circulating hot water bath. Electrochemical experiments were undertaken with a CH Instruments CH920D potentiostat. All solutions were prepared using analytical grade chemicals and MilliQ water and degassed with N₂ before analysis.
2.2.5.2. Linear sweep voltammetry

Linear sweep voltammetry (LSV) is an electrochemical method used to investigate oxidation or reduction of species on the surface of a material/substance. This is conducted by measuring the current of the working electrode while the potential of the counter electrode is swept in a linear fashion over time. As oxidation or reduction of a species occurs a peak in current signal is produced [21]. The voltage potential at which this peak occurs can be used to determine the oxidation/reduction of a specific species. Moreover, the peak size and shape can also be used to gain information on thermodynamic, kinetic and diffusion dissolution processes. The method used in this document utilises a Carbon Paste Electrode (CPE) as the working electrode for all experiments. This technique has been established to generate reproducible results on solid mineral samples which are mixed with carbon powder to form a homogenous mixture of carbon and the powdered sample [22].

2.2.5.3. Cyclic Voltammetry

In cyclic voltammetry (CV) the working electrode potential is ramped in a linear fashion at a given rate (scan rate). As the measured potential is increased between the reference and the working electrode, the current is measured between the working electrode and the counter electrode. The data obtained from this is plotted as current vs. potential (Figure 2.10) [23].
The initial scan (waveform) produces a current signal peak for any species that can be oxidised or reduced depending on the range of the potential scanned and the direction scanned. For processes which occur in solution, there is an increase in current as the potential reaches the point of reduction of a species onto the surface of the electrode, hence causing the concentration of the analyte to decrease as reduction occurs. As the potential is cycled several periods throughout the experiment the oxidation peak will be proportional to the aforementioned reduction peak when the process is electrochemically reversible. These cyclic voltammetry curves can give more detailed information on the mechanism of dissolution and the thermodynamic and kinetic process associated with leaching [24].

The heterogeneous nature of mineral samples affects the reproducibility of CV experimentation. For this reason the carbon paste electrode method described previously was used for all electrochemistry experiments conducted [22].
2.3. References


3. Thomas, R., Practical guide to ICP-MS. 2004, Marcel Dekker Inc: Maryland, U.S.A.


In this chapter, three natural betafite samples from various localities were characterised in order to gain a greater understanding of the chemistry of natural betafite. The focus of this work was to identify any structural and chemical changes which occur during weathering. It was demonstrated that all three samples had undergone significant metamictisation and resulted in very little crystalline material being present. Moreover, the samples were shown to have varying degrees of alteration due to chemical weathering. This degree of alteration was shown to significantly influence the dissolution of betafite, where the more highly altered sample showed a higher degree of leachability.
3.1. Introduction

Several types of uranium ore bodies are mined to supply uranium-based fuel for the world’s nuclear power industry [1]. The ore bodies vary significantly in their environment of formation (e.g. magmatic, hydrothermal, or sedimentary), their uranium and gangue mineralogy, and uranium grade. In recent years there has been increased attention on processing of more refractory uranium-bearing minerals due to the depletion of high grade easy to leach ores [2, 3]. Once such mineral which is receiving increased attention is the uranium pyrochlore mineral betafite, normally \([(\text{Ca},\text{U})_2(\text{Ti,Nb,Ta})_2\text{O}_6(\text{OH})]\).

As previously described in Chapter 1.3, betafite is part of the pyrochlore-group minerals which is a series of cubic Nb-Ta-Ti oxides that can contain substantial uranium. The structure of pyrochlore, \(A_2mB_x(O,\text{OH,F})_y\text{H}_2\text{O}\) is a defect derivative of the fluorite structure type with \(A = \text{Na, K, Ca, Sr, Sn, Ba, Pb, Bi, REE, U}\) and \(B = \text{Ti, Nb, Ti}\) [4, 5]. Charge balance is maintained in pyrochlores through cationic substitutions at either the \(A\) or \(B\) sites as well as through anionic substitutions. Pyrochlore minerals are classified into three subgroups on the basis of the \(B\)-site composition: pyrochlore is the Nb-dominant member, microlite is the Ta-dominant member and betafite is characterised by \(2\text{Ti}>(\text{Ta+Nb})\) and \(U\) usually >20% [4]. Betalite frequently shows chemical and textural alteration that mainly involves leaching of the \(A\)-site cations (U & Ca) coupled with the incorporation of water into the structure [6, 7]. Up to 20-30% of the original amount of U may be lost during alteration of the mineral [6]. Lumpkin and Ewing (1996) also showed that the breakdown of betafite occurs in two steps. Initially \(A\)-site cations Ca and Na migrate from the structure to form pyrochlore (\(\text{CaNb}_2\text{O}_7\)) and microlite (\(\text{CaTa}_2\text{O}_7\)). This consequentially affects the U:Nb:Ti ratio which destabilises the mineral. Secondary alteration of the remaining products forms liandratite (\(\text{UNb}_2\text{O}_7\)), uranpyrochlore (\((\text{U,Ca})\text{Nb}_2\text{O}_7\)) and rutile (\(\text{TiO}_2\)) depending on the initial elemental composition. U-rich betafite samples are nearly always metamict due to \(\alpha\)-decay radiation damage [4, 5, 8] although Mazzi and Munno [9], and Cámara [7] have both reported occurrences of non-metamict Ca-rich betafite. A comparison between chemistries of metamict and non-metamict samples shows that compositions
of radiation-damaged betafite samples are notably deficient in Ca and contain little or no Na and F [6, 10].

Betafite is currently processed in significant quantities from only one major deposit (Rössing, Namibia [11, 12]) although it is known to occur in trace to minor amounts in many other deposits, usually associated with intrusive or anatectic igneous rocks of different chemical composition (e.g. alaskite, granite, monzonite, pegmatite, peralkaline, syenite and carbonatite [13].

The difficulty in processing betafite, even under mild conditions [14] has meant that betafite is usually only processed from deposits where it is co-extracted along with the more dominant and easy to process uraninite. There is a distinct lack of research conducted on the dissolution of betafite. The majority of the research that has been conducted has focussed on investigating the influence of metamictisation. Eyal et al. (1986) reported results obtained from successive dissolution of natural betafite in alkaline conditions over a period of 50-100 days. This work showed similar results to those previously discussed for the uranium mineral brannerite where regions of the sample that were exposed to more alpha radiation damage leached at a faster rate than less metamict regions [15].

Investigations on the associated mineralogy, composition and microstructural features of betafite combined with leaching studies will be important in the development of any process to extract uranium from betafite ores. The aims of the research presented in this chapter were:

- To investigate the chemistry and mineralogy of three naturally occurring samples containing betafite using multiple characterisation techniques including; X-Ray Diffraction (XRD) analysis, Raman spectroscopy and Electron Probe Microanalysis (EPMA).
- To investigate the leaching of the aforementioned samples under conditions relevant to the uranium minerals processing industry.
• To conduct in depth leaching studies by varying a range of commonly varied leaching parameters such as: \([\text{H}_2\text{SO}_4]\), \([\text{Fe}_{TOT}]\), Temperature, and redox potential on the three natural betafite samples.

• To investigate any potential correlations between betafite composition and/or structure with observed leaching characteristics.

In addition, the samples were heat treated to examine the effect of temperature on the chemistry, texture and microstructural properties of the samples. Results provide an evaluation of the key differences between natural and heat treated betafite samples and variations in leachability associated with them.
3.2. Methodology

3.2.1. Natural Bafite Samples

The three samples containing betafite that were studied were sourced from Museum Victoria, Australia and the National Museum of Australia. The Museum Victoria sample was originally collected from the Ambatofotsy region in Madagascar and is referred to as BAM hereafter (Figure 3.1a). The National Museum of Australia sample was from the Miarinarivo region in Madagascar (referred to as BMM) and the sample purchased online was sourced from the Silver Crater Mine in Bancroft, Ontario, Canada (BSC) (Figure 3.1b).

![Whole rock samples BAM (a) and BSC (b). Both samples show defined cubic hexacontahedral Pm3n crystals.](image)

3.2.2. Procedure used to heat treat samples

Samples were heated from 100 °C to 1200 °C at 100 °C intervals. All samples were placed in a platinum lined alumina boat and heated to the desired temperature at a rate of 15 °C/min, held at the required temperature for 2 h, before being cooled to room temperature. A Lindberg Blue programmable furnace was used for heat treatment of the three betaite samples.
3.2.3. Characterisation Methods
The following methods that were used to conduct the research presented in this chapter:

Dissolution test procedure, acid digestion procedure, XRD analysis, ESEM analysis, XPS analysis,
elemental mapping analysis and ICP-MS analysis) are given in Chapter 2.

3.2.4. Dissolution methods
The dissolution method used to conduct leaching experiments on the three natural betafite samples
was given in Section 2.2.3.

3.2.5. Electron Probe Micro-analysis (EPMA)
Two types of EPMA information were obtained. Initially, the three samples were each mapped using
a high resolution Field Emission Gun (FEG) equipped EPMA (JEOL 8500F Hyperprobe) to examine the
chemical homogeneity of the betafite. Following mapping by FEG-EPMA, the samples were analysed
by quantitative EPMA techniques to determine the chemistry of the betafites. The operating
conditions for each of the techniques are described separately below.

3.2.5.1. EPMA mapping
The polished samples were initially inspected using high contrast back scattered electron (BSE)
imaging to locate regions of high uranium concentration and then selected areas were mapped using
a combination of wavelength dispersive (WD) and energy dispersive (ED) spectroscopic techniques.
The elements mapped using the WD spectroscopic techniques were U, Nb, Ca, Ti and Ta. Standards
used to calibrate the EPMA WD spectrometers prior to mapping were: wollastonite (CaSiO$_3$ - for Ca),
synthetic uranium oxide (UO$_2$ - for U), natural rutile (TiO$_2$ - for Ti), niobium metal and tantalum
metal. Elements that were not measured by WD spectroscopy were measured using two energy-
dispersive (ED) spectrometers operating in parallel. Measuring both ED and WD signals
simultaneously ensured that the complete chemical spectrum, at each step interval in the map, was
obtained. This additional information was important when trying to identify phases that contained
elements not present in the main WD element map suite. Operating conditions for the microprobe
during mapping were an accelerating voltage of 10 kV, a current of 50 nA, a step size of 0.5 µm and
counting times of 20 msec per step. The choice of step size was based on a compromise between maximising the area analysed and ensuring any fine-grained U-rich mineral phases were located.

3.2.5.2. Quantitative EPMA

The chemical composition of the natural betafite samples was quantitatively determined using a JEOL 8500F Hyperprobe Electron Probe Microanalyser (EPMA, JEOL 8500). The accelerating voltage and beam current were 15 kV and 46 nA, respectively. All analysis positions were verified as being homogeneous and flat by viewing the secondary electron image of the area to be analysed (at 5000× magnification). The electron beam diameter was defocused to 2 µm for all analyses. The following suite of elements was analysed: Ca, Nb, Si, Fe, Na, Ti, U, Ta, Mg, Mn, Pb, Al and Ce. A separate Energy Dispersive (ED) X-ray detector system was used during the analyses to check for the presence of other elements. For each element, the standards used for calibration, the X-ray peak used, and the calculated detection limits (2σ, listed in ppm) were as follows: synthetic hematite (α-Fe₂O₃) for Fe(Kα), 1200 ppm, natural UO₂ for U(Mα), 4000 ppm, natural wollastonite (CaSiO₃) for Si(Kα), 1200 ppm, natural rutile for Ti(Kα), 3500 ppm, synthetic Ca₂Ta₂O₇ for Ca(Kα), 1600 ppm, synthetic Ca₂Ta₂O₇ for Ta(Mα), 2400 ppm, synthetic magnesium aluminate spinel (MgAl₂O₄) for Al(Kα), 580 ppm, natural anglesite (PbSO₄) for Pb(Mα), 1400 ppm, synthetic yttrium vanadate (YVO₄) for Y(Lα), 420 ppm, cerium oxide (CeO₂) for Ce(Lα), 1900 ppm, synthetic magnesium aluminate spinel (MgAl₂O₄) for Mg(Kα), 660 ppm, natural MnSiO₃ for Mn (Kα), 850 ppm, synthetic NbPO₅ for Nb (Lα), 5000 ppm and natural albite (NaAlSi₃O₈) for Na (Kα), 970 ppm. Oxygen was calculated by difference based on valence. All elemental analyses were corrected for atomic number (Z), absorption (A) and fluorescence (F) using the CITZAF Phi-Rho-Z matrix correction procedure implemented on the JEOL 8500F EPMA [16].
3.3. Results and Discussion

3.3.1. Characterisation of Natural Bettafite Samples

3.3.1.1. X-Ray Diffraction Analysis

X-ray Diffraction analysis was conducted on all of the as received samples (Betafite Ambatofotsy region in Madagascar (BAM), Betafite Miarinarivo, Madagascar (BMM) Betafite Silver Crater Mine, Ontario, Canada (BSC)). Samples were heated at varying temperatures between 100 – 1200 °C in an attempt to crystallise any amorphous compound(s) present / investigate the temperature at which this process started to occur.

The XRD patterns obtained for sample BAM that had been treated at different temperatures (refer to Section 3.2.2) are presented in Figure 3.2a. The XRD pattern obtained for the as received BAM sample showed that it contained mostly metamict minerals / compounds as the pattern contained very few intense diffraction lines and also had a broad weak intensity region consistent with the presence of non-crystalline material. A small number of sharp diffraction peaks were observed at ~25° and ~47° 2θ corresponding to the presence of crystalline niobium-rich anatase (Nb-TiO₂).

Anatase is the low-temperature polymorph of TiO₂ and is often found as a minor constituent of igneous and metamorphic rocks, in veins associated with granitic pegmatites, and as an alteration product of other Ti-bearing minerals such as titanite and ilmenite. The pattern obtained for the as received sample BAM also contained low intensity diffraction lines matching the major diffraction lines for Nb-rich anatase (Nb-TiO₂). Upon heat-treatment; the crystalline Nb-TiO₂ underwent a phase transition to Nb-rich rutile (Nb-TiO₂) between 800-900 °C. The diffraction pattern at 900 °C also showed the presence of weak characteristic peak matches for betafite, indicating the thermal recrystallisation of betafite. This was consistent with Eyal et al. (1986) who previously observed the crystallisation of natural betafite at similar temperatures [15]. Upon further heating to 1000 °C, the Nb-anatase completely converted to Nb-rutile and additional heating to 1200 °C resulted in sharper, more intense betafite diffraction lines indicating increased crystallinity (Figure 3.3).
The XRD patterns obtained for BMM heated at different temperatures are presented in Figure 3.2b. The diffraction pattern obtained for the as received sample showed the absence of significant diffraction lines indicating that the sample contained mainly amorphous/metamict compounds. Weak, low intensity diffraction lines matching major diffraction lines for anatase (TiO$_2$) were the only lines that could be resolved for the as received sample. Heat treatment to 700 °C resulted in broad, weak intensity diffraction lines corresponding to the crystallisation of a uranium titanium niobium oxide (UTiNb$_2$O$_{10}$) phase. These peaks became sharper and more intense at 900 °C and beyond. Anatase persisted to ~900 °C although conversion of the anatase to rutile began at temperatures as low as 700 °C. Weak diffraction peaks characteristic of betafite phase were detected at 900 °C. These were initially broad in profile but gradually increased in sharpness with increasing temperature, consistent with progressive recrystallisation. At 1200 °C, the final diffraction pattern contained sharp diffraction lines characteristic of UTiNb$_2$O$_{10}$, rutile and betafite phases.

The XRD pattern obtained for the as received BSC sample showed no significant diffraction lines indicating that any minerals / compounds in this sample were amorphous. Weak intensity diffraction lines matching betafite were first observed when the sample was heated to 300 °C, while some rutile was also observed to be present. Upon further heating the diffraction lines for the aforementioned minerals became more defined and intense indicating higher crystallinity occurring in the sample.

The XRD data obtained indicated that except for the presence of secondary phases, all the samples were rendered amorphous by natural α-decay of $^{235}$U incorporated in the A-site and therefore XRD analysis was unable to provide confirmation of the existence of betafite in the as received metamict samples. Upon heating, of the three samples only sample BSC was shown to be comprised primarily of single phase betafite with a trace amount of accessory rutile detected. The other two samples had only minor betafite and were contaminated by significant amounts of other phases including rutile (BAM and BMM) and a uranium titanium niobium oxide phase (sample BMM). The results suggest that samples BAM and BMM would have likely undergone significant alteration causing depletion and migration of A site cations and breakdown of the original betafite into secondary alteration
phases. Heating to re-constitute the betafite was therefore unsuccessful. In comparison, it appears that sample BSC whilst having undergone some alteration, has not been affected to the same degree and betafite was able to be successfully recrystallised during high temperature heating.
Figure 3.15 X-ray Diffraction patterns for samples (a) BAM (b) BMM and (c) BSC. ICDD Diffraction Matches for: Betafite $[(\text{U,Ca})_2(\text{Nb,Ti,Ta})_2\text{O}_7.x\text{H}_2\text{O}]$ (PDF 008-0300), Rutile $[\text{TiO}_2]$ (PDF 034-0180), Uranium titanium niobium oxide $[\text{UTiNb}_2\text{O}_{10}]$ (PDF 085-0597), Anatase $[\text{TiO}_2]$ (PDF 085-0597) are presented below each sample.
Figure 3.16 XRD patterns for as received (unheated) and heat treated samples containing natural betafite BAM (Bottom), BMM (Middle), BSC (Top) with diffraction matches: Betafite [(U, Ca)$_2$(Nb, Ti, Ta)$_2$O$_{x}$xH$_2$O] (PDF 008-0300) (Pink), Nb-Anatase (Nb-TiO$_2$) (PDF 046-1391) (Orange), Nb-Rutile (Nb-TiO$_2$) (PDF 002-0494) (Light blue), Rutile [TiO$_2$] (PDF 034-0180) (Green), Uranium titanium niobium oxide [UTiNb$_2$O$_{10}$] (PDF 085-0597) (Red), Anatase [TiO$_2$] (PDF 085-0597) (Blue).
3.3.1.2. **Bulk Elemental Analysis**

Bulk elemental analysis of all samples was conducted and the results obtained compared with the mineralogy of the samples determined based on XRD analysis. Elemental analysis of BAM showed all major elements necessary for the sample to be classified as containing beta-fite were present (i.e. U 23.15%, Nb 17.91%, Ti 11.46%, Ta 2.69%). Apart from the aforementioned elements that are generally associated with beta-fite, sample BAM also contained sodium, aluminium and iron in appreciable quantities (Table 3.1). Hogarth (1961) reported that metals such as sodium which has an atomic radius similar to calcium can be substituted into the $A$ site of the beta-fite structure. Similarly, iron was also reported in the same study to be able to substitute into the $B$ site of the beta-fite structure [10]. Amorphous aluminium silicate from the host rock (pegmatitic granite) could explain the high amount of aluminium in the sample although none was identified via XRD in either the unheated or heat treated samples.

The elemental composition of sample BMM was relatively similar to BAM. Calcium however was shown to not be present in this sample. Lumpkin and Ewing (1988; 1996) showed calcium and sodium deficiencies are typical in beta-fites that have undergone significant secondary alteration. Sample BMM contained ~17% uranium which is less than the nomenclature requirements for beta-fite of >20% U. It is unclear from the chemical data if this is due to an incorrect classification of the sample or due to additional impurities. Thorium was also present in the sample at 1.15% which is known to be a daughter product of alpha decay of uranium and can also be substituted into the beta-fite $A$ site [10].

The elemental composition of sample BSC shows similar trends to BAM and BMM, with concentrations of aluminium, titanium niobium, tantalum and uranium all present in appreciable quantities. Trace amounts of the uranium daughter products thorium and lead were also present in the sample. Again, the substantial amount of aluminium in the sample could be due to the presence of gangue aluminium silicates in the beta-fite sample.
It is important to note that only 60-80% of the sample mass was detected via ICP-MS. This difference was most likely due to various other elements which were not able to be detected via ICP-MS. It was assumed the most abundant of these undetected elements was oxygen which is not able to be quantitatively measure via ICP-MS in a water matrix (and is also know to make up a significant amount of pyrochlore group minerals).
Table 3.2 ICP-MS elemental compositions of the bulk natural betafite samples BAM, BMM and BSC. The uncertainty of the bulk composition is ± 3% of the value given. n.d = not detected.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
<th>Sample</th>
</tr>
</thead>
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<tr>
<td></td>
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<tr>
<td>Na</td>
<td>4.65</td>
<td>3.25</td>
</tr>
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<td>Mg</td>
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<td>0.16</td>
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<td>Al</td>
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</tr>
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<td>Ti</td>
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</tr>
<tr>
<td>Zn</td>
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<td>n.d</td>
</tr>
<tr>
<td>Nb</td>
<td>17.91</td>
<td>18.36</td>
</tr>
<tr>
<td>Ba</td>
<td>n.d</td>
<td>0.19</td>
</tr>
<tr>
<td>Ta</td>
<td>2.69</td>
<td>2.21</td>
</tr>
<tr>
<td>Pb</td>
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<td>0.26</td>
</tr>
<tr>
<td>Th</td>
<td>0.88</td>
<td>1.15</td>
</tr>
<tr>
<td>U</td>
<td>23.15</td>
<td>16.97</td>
</tr>
<tr>
<td>Total</td>
<td>77.51</td>
<td>60.30</td>
</tr>
</tbody>
</table>

Geochemical alteration of betafite can be shown by the significant variation in composition between the three samples analysed. An example of this is the sub-stoichiometric amount of sodium and calcium possibly due to their high solubility relative to other betafite containing elements. Table 3.2 shows the three natural samples had $2\text{Ti:}(\text{Nb+Ta})$ mole ratios of 2.3 (BAM), 1.9 (BMM) and 1.9 (BSC) respectively. Analysis of the $\text{Nb:Ta}$ ratio also showed significantly more niobium in each sample than
tantalum. This indicates stability of betafite occurs when Nb>Ta and therefore close to the pyrochlore/betafite binary join, confirming results previously reported by Yaroshevskii et al. [17].

Table 3.3 ICP-MS molar elemental compositions calculated for the bulk natural betafite samples. The uncertainty of the molar elemental composition is ± 3% of the calculated value given.

<table>
<thead>
<tr>
<th>Molar Comp.</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
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<td>BAM</td>
</tr>
<tr>
<td>U</td>
<td>0.10</td>
</tr>
<tr>
<td>Ca</td>
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</tr>
<tr>
<td>Na</td>
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</tr>
<tr>
<td>Nb</td>
<td>0.19</td>
</tr>
<tr>
<td>Ti</td>
<td>0.24</td>
</tr>
<tr>
<td>Ta</td>
<td>0.01</td>
</tr>
<tr>
<td>2Ti</td>
<td>0.48</td>
</tr>
<tr>
<td>Nb+Ta</td>
<td>0.21</td>
</tr>
</tbody>
</table>

3.3.1.3. X-ray Photoelectron Spectroscopy (XPS) of natural betafites

The oxidation state of surficial uranium in the natural betafite samples was determined via XPS. The data shown in Figure 3.4 shows two intense peaks located at ~381 and 392 eV, these are attributed to the excitation states U4f7/2 and U4f5/2 respectively. Deconvolution of the U4f5/2 excitation peak reveals 3 peaks, 2 of weak intensity at 390.88 and 391.48, as well as a more intense peak at 392.48 eV. Chadwick (1973) demonstrates that as the oxidation state of uranium increases the binding energy (BE) of the deconvoluted U4f peaks also increases by approximately 1.7 eV between U4+ and U6+ [18]. The deconvoluted peaks can also be used to determine the U oxidation state by calculating the Binding Energy (BE) difference between the deconvoluted peaks and higher energy U4f5/2 satellite peaks which occur at >395 eV. This difference indicates the U oxidation state present in the sample. For U4+ species the BE difference is between 6-7 eV, for U5+ between 7.7-8.5 eV, and two
peaks at ~4 and 10 eV for U$^{6+}$. Satellite peaks occur for both U4f$_{7/2}$ and U4f$_{5/2}$ peaks but due to overlap of the U4f$_{7/2}$ satellite peaks and the U4f$_{5/2}$ excitation peak the U4f$_{7/2}$ satellite peaks are generally not used for analysis of oxidation states. The spectrum presented in Figure 3.4 shows two small satellite peaks at 396.68 and 402.48 eV. Since the gap between the deconvoluted peak at 390.88 eV and the satellite peak at 396.68 was 5.8 eV this peak was assigned to U$^{4+}$. The difference between the peak at 392.48 eV and the highest binding energy of 402.48 eV was shown to be 10.0 eV. For this reason it was assumed that the peak at 396.68 eV was made up of 2 peaks, one being assigned to a U$^{4+}$ satellite peak, the other peak assigned to a U$^{6+}$ satellite peak. The smallest deconvoluted U4f$_{5/2}$ peak at 391.48 eV was assigned to U$^{5+}$ since the BE is in between the U$^{4+}$ and U$^{6+}$ deconvoluted peaks. Due to the small magnitude of the deconvoluted U$^{5+}$ peak the satellite peak which is expected to occur between 7.7 and 8.5 eV higher (~401 eV) could not be seen in the spectra.

![Figure 3.17 XPS Spectra of U4f orbital of natural betafite BAM](image-url)
The XPS spectra measured from the U4f orbital of the uranium in the BMM sample showed two intense asymmetric peaks with binding energies of 380.68 and 392.08 eV which were due to the excitation of the U4f_{7/2} and U4f_{5/2} orbitals in the sample (Figure 3.5). Deconvolution of the two U4f_{5/2} peak showed two uranium excitation states with varying intensities. Analysis of the spectra between 395 – 405 eV showed two clear excitation satellite peaks at 396.58 and 399.78 eV. The binding energy difference between the deconvoluted U4f_{5/2} peaks at 391.08 and 392.48 eV and the satellite peaks was calculated to be 8.7 eV from the lowest binding energy U4f_{5/2} deconvoluted peak (391.08 eV) indicating that the sample contained U^{5+}. The difference between the remaining U4f_{5/2} deconvoluted peak and the remaining satellite peak was shown to be 4.1 eV which is indicative of U^{6+} present in the sample. A satellite peak with a great binding energy of approximately 402.5 eV due to the presence of U^{6+} in the sample was not observed; this was most likely due to the minor amount of U^{6+} present and hence making the satellite peak (which is a fraction of the intensity of the U^{6+} U4f_{5/2} peak) difficult to observe.
The XPS spectra for the natural betafite sample BSC contained two intense peaks at 381 and 392 eV which were due to U4f\(_{7/2}\) and U4f\(_{5/2}\) excitation states respectively (Figure 3.6). Deconvolution of the U4f\(_{5/2}\) reveals 2 excitation peaks at 391.08 and 392.28 eV. Analysis of the U4f\(_{5/2}\) satellite peak showed three weak intensity peaks at 396.28, 399.68 and 402.98 eV. The binding energy difference between the lower energy deconvoluted U4f\(_{5/2}\) and the middle satellite peaks was calculated to be 8.6 eV and therefore assigned to the U\(^{5+}\) oxidation state. The energy difference between the U4f\(_{5/2}\) deconvoluted peak at 392.28 eV and the remaining two satellite peaks at 396.28 and 402.98 eV had a BE difference of 4.0 and 10.7 eV and were therefore assigned to U\(^{6+}\). A weak intensity peak at 407.08 eV which is too high to be a satellite peak of the U4f\(_{5/2}\) excitation state was assigned to Cd3d\(_{5/2}\) excitation state which was shown by Gulino et al. to have a similar binding energy [19]. Although bulk analysis of the BSC sample showed the cadmium concentration was below the detection limit of
this technique (Section 3.3.1.2); it is possible for this metal to be present in measurable concentration via XPS as this technique only measures the top ~5 nm of the sample [20].

Figure 3.19 XPS Spectra of U4f orbital of natural betafite BSC

3.3.1.4. Raman Spectroscopy

Raman spectroscopy was conducted to investigate any potential changes in the functional groups present by heating the samples (Figure 3.7). The Raman spectra obtained for the as received sample BAM showed broad overlapping peaks at 810 and 893 cm\(^{-1}\) which were assigned to symmetric and anti-symmetric UO\(_2^{2+}\) stretching vibrations (Figure 3.7a). The intense peak at 149 cm\(^{-1}\) is most likely due to O-Ti-O vibrations which are consistent with the presence of anatase observed in the XRD analysis. The broad overlapping peaks between 1000 and 1700 cm\(^{-1}\)s were previously observed in a Raman study of natural betafite by Frost and Reddy (2010) and these were assigned to U-OH and \(\delta U-OH\) bending vibrations and their overtones respectively [21]. Several peaks below 1000 cm\(^{-1}\)
were assigned to anatase [22]. Upon annealing of the BAM sample at 1,200 °C, the majority of the peaks below 1000 cm\(^{-1}\) disappeared due to the anatase/rutile phase transition. The remaining broad peak at 384 cm\(^{-1}\) was assigned to O-Ti-O (rutile) bending vibrations [23]. Negligible variation in intensities of peaks between 1000 and 1700 cm\(^{-1}\) was observed.

Raman analysis of the as received BMM sample (Figure 3.7b) revealed unassignable broad peaks of low intensity which roughly corresponded to the peaks observed in the sample after being heated to 1200 °C. The differences in the Raman spectra obtained for the as received and heated sample were most likely due to the differences in molecular stacking due to the amorphous nature of the natural sample leading to a variation in wavelength and intensity for the peaks characteristic for specific bending and stretching vibrations. Tomasic et al. reported similar observations where broad unassignable Raman bands are present in the metamict Nb-Ti-Ta complex oxide due to the distortion in polyhedral stacking. Upon annealing, the Raman bands became sharper and more intense due to the more ordered structure of the mineral [24]. When BMM was heated to 1,200 °C the Raman bands showed regions consistent with the heated BAM sample. The O-Ti-O assigned peak at 380 cm\(^{-1}\) appeared broader and the intensity of the U-OH peaks at 1350 cm\(^{-1}\) were observed to be more intense than those present in the heated BAM sample. All assigned peaks from the previous sample were also present in BMM except for a small peak at 1880 cm\(^{-1}\). This was assigned to a U-O-Nb bending mode presumably in the uranium niobium titanium oxide phase which was shown to be present in the heated sample via XRD analysis.

Raman analysis of the as received BSC sample gave a spectrum with no readily assignable Raman bands (Figure 3.7c). Broad bands of low intensity roughly corresponding to the bands observed in the same sample after heat treatment at 1200 °C were due to disordered molecular stacking which was previously described for the BMM sample. When the sample underwent heat treatment, the characteristic peaks observed in the previous two betafite samples developed; a broad peak at 380 cm\(^{-1}\) assigned to O-Ti-O, a sharp group of bands between 1100 and 1800 cm\(^{-1}\) which can be assigned to U-OH bending modes and its overtones [21, 23]. Consistent across the three samples was the
presence of a broad band between 3200 cm\(^{-1}\) and 3500 cm\(^{-1}\). These bands were assigned to water and hydroxyl bond stretching. Overall, results were broadly comparable to a previous study on heated and unheated betafite conducted by Frost and Reddy (2010). Any differences observed were most likely due to either the different composition of the betafites studied or the degree of metamictisation of the samples. Moreover, the sample that showed the most similarity to the results obtained by Frost and Reddy (2010) was sample BAM which was sourced from a similar region in Madagascar. The unheated sample was shown to contain a high amount of crystalline anatase and the majority of the Raman bands were assigned to this compound.
Figure 3.20 Raman spectra measured for BAM (a), BMM (b) and BSC (c) samples pre-heating and after being heated to 1200 °C in air.
3.3.1.5.  **Electron Probe Micro-analysis**

3.3.1.5.1.  **EPMA Mapping - as received samples**

The three natural samples (BMM, BAM and BSC) were mapped using EPMA to determine the key minerals associated with the betafite, to examine the distribution of phases, and to examine the textures of individual particles. Results are shown in Figure 3.8 in the form of back-scattered electron (BSE) images over the mapped areas with corresponding maps showing the distribution of the elements Nb, Ti and U.

The BMM and BAM samples both exhibited complex, heterogeneous microstructural features including extensive evidence for alteration. This was most likely through interaction with an aqueous fluid resulting in the formation of secondary alteration products, and the presence of pores, cracks, fractures and micro-veinlets throughout the samples. The patchy contrast evident in the BSE images for these two samples (Figures 3.8a and 3.8c) correlate with significant mobility of elements leading to the formation of irregular U-rich patches (red areas), Ti-rich and U-depleted irregular patches (green areas) and Nb-rich, U-depleted regions (blue and mauve areas). These are seen by comparing the BSE images with corresponding three-element overlay maps showing the distribution of elements Nb, U and Ti (Figures 3.8b and 3.8e). Preliminary Energy Dispersive (ED) analysis and follow-up quantitative EPMA analysis of these areas indicated that, for both samples, any betafite that may have been originally present was now extensively altered to secondary phases. These included mineral phases such as liandratite \((\text{UNb}_2\text{O}_8)\), uranpyrochlore solid solution, and a Ti-rich oxide, most likely anatase.

The back-scattered electron image of sample BSC (Figure 3.8e) showed that alteration was also present with areas of low contrast localised along voids and micro-fractures, some of which contained precipitates of galena. Galena appears to be less common in the brighter contrast regions. Accessory phases present in fractures and voids included apatite and calcite. The localised and low concentrations these accessory phase minerals were present in meant that they were well below the
detection limits of XRD. The light and dark patches evident in Figure 3.8e are associated with differences in concentrations of the elements Nb, U and Ti.

Based on the EPMA map results we believe samples BAM and BMM have been subject to at least two stages of alteration as defined by Lumpkin and Ewing (1996). Stage 1 alteration involves chemical alteration and loss of Na, Ca, F and O while Stage 2 involves major element mobility and re-crystallisation leading to breakdown of the betafite into a three phase field involving defect betafite compositions lying within the stability field of rutile, liandratite and uranpyrochlore. Loss of up to 20-30% of the original amount of uranium may occur at this stage, although some uranium may be retained in the form of secondary phases e.g. as U\(^{6+}\) in liandratite [6]. When the more highly altered BMM undergoes heating to 1200 °C a stoichiometric reaction occurs between liandratite and anatase forming the UTiNb\(_2\)O\(_{10}\), which was shown to be present based on the XRD analysis (Figure 3.2b, and 3.3) (Equation 3.1).

\[
\text{UNb}_2\text{O}_8 + \text{TiO}_2 \rightarrow \text{UTiNb}_2\text{O}_{10} \quad (3.1)
\]

This indicates that once complete Ca loss has occurred due to the alteration mechanism reported by Lumpkin and Ewing (1996) sintering the sample will lead to the formation of uranium titanium niobium oxide (UTiNb\(_2\)O\(_{10}\)) as well as betafite. It should be pointed out that in this case where the complete loss of Ca has occurred, it is assumed Na takes its place in the A site of the betafite structure.

A marked contrast with the previous two samples is that sample BSC does not appear to have been as pervasively altered to different mineral phases. The effects of alteration on the BSC sample has largely been to partially re-distribute/leach U, Nb and Ti and cause the loss of radiogenic lead from both long term diffusion and secondary alteration aided by radiation damage-induced volume expansion and microfracturing. The sub-micron to micron-sized PbS thus forms within the voids and fractures, presumably in the presence of an S-bearing hydrothermal fluid.
Figure 3.21 BSE and corresponding Nb/Ti/U element distribution maps for samples BAM (a,b), BMM (c,d) and BSC (e,f).

In each image the scale bar represents 100 micron. Brightest phases in Figure 3.8e represent precipitates of galena, PbS.
3.3.1.5.2. Quantitative EPMA

Data from the quantitative EPMA examination of the natural betafite samples are listed in Table 3. Results are provided for the key alteration phases present in samples BMM and BAM as well as data for the light and dark zones previously identified as being present in sample BSC. All data in Table 3 (including analyses used to calculate the average analyses) have been plotted on ternary Nb-Ta-Ti and Nb-U-Ti plots in Figures 3.9 and 3.10, respectively to illustrate the compositions according to the standard pyrochlore nomenclature and also to demonstrate the changes in composition that have occurred through geochemical alteration processes.

The data for sample BAM (Table 3.3, Figures 3.9a and 3.10b) show that secondary alteration has resulted in the betafite sample being composed of at least three different phases. A comparison of the BAM plotted data with a ternary Nb-U-Ti plot showing the phases developed after secondary alteration of betafite (Figure 3.9a) indicates that the phases present include; unaltered (or only partially altered) betafite, a U-rich composition close to the liandratite-uraninite solid solution compositional space and a uranpyrochlore-rutile solid solution phase.

The data for sample BMM (Table 3.3, Figures 3.9b and 3.10c) is unexpected based on the extent of alteration that appeared evident when examining the EPMA map data for the sample (Figure 3.8d). The map data suggested pervasive secondary alteration of the sample had occurred giving rise to at least three different phases that were identifiable by their differences in BSE contrast when conducting the quantitative EPMA analyses. In contrast, the EPMA results suggest that although some alteration has occurred resulting in the formation of a uranpyrochlore-rutile solid solution phase, for the most part the composition data indicate that the sample still retains a considerable proportion of material that remains close to betafite in composition. The data is spread however, suggesting that some alteration has occurred but not to the same extent as observed for sample BAM. It is noteworthy that the 2Ti:(Nb+Ta) mole ratios of 2.3 (BAM), 1.9 (BMM) and 1.9 (BSC)
derived previously indicate that sample BAM is very different in composition from samples BMM and BSC which both exhibit similar ratios (and BSC appears to be betafite with only minimal alteration). The quantitative data thus confirms the bulk chemistry results.

The quantitative EPMA data for sample BSC (Table 3.3, Figures 3.9c and 3.10d) confirms the EPMA map results in that the sample is composed of mainly betafite. Although some alteration is evident leading to minor depletion of some elements and causing a slight scatter of data, the results indicate the sample is a Nb-rich, Ta-poor form of betafite.
Figure 3.22 Proportion (at%) of Ti, Nb and Ta in the natural betafite samples analysed by EPMA. Samples: (a) BAM, (b) BMM and (c) BSC. The orange points correspond with light regions in the BSE images, light blue with grey regions, and dark blue with dark regions analysed. The total regions analysed in for BAM, BMM and BSC was 13, 10 and 33 respectively.
Figure 3.23 (a) Stage two alterations reported by Lumpkin and Ewing (1996) involving major element mobility and redistribution into a 3 phase solid-solution of uraninite, uranpyrochlore and rutile. Proportion (at%) of U, Nb and Ti in the natural beta-fite samples: (b) BAM, (c) BMM and (d) BSC. The orange points correspond with light regions in the BSE images, light blue with gray regions, and dark blue with dark regions analysed.
Table 3.4 Representative EPMA data from the three betafite samples. Totals below 100% are assumed due to hydration as previous work by Lumpkin and Ewing (1996) indicated up to 9-13 wt% H₂O in betafite and altered products.

<table>
<thead>
<tr>
<th>Sample/Phase</th>
<th>Na</th>
<th>Si</th>
<th>Fe</th>
<th>Nb</th>
<th>Ca</th>
<th>Ta</th>
<th>Mg</th>
<th>Mn</th>
<th>U</th>
<th>Ti</th>
<th>Al</th>
<th>Ce</th>
<th>Pb</th>
<th>O</th>
<th>Total</th>
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<tbody>
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<td><strong>Sample BAM</strong></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>Uranpyrochlore-TiO₂ss</td>
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<td>n.d.</td>
<td>1.97</td>
<td>25.32</td>
<td>0.02</td>
<td>3.39</td>
<td>0.01</td>
<td>0.05</td>
<td>3.00</td>
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<td>0.14</td>
<td>2.93</td>
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<td>88.24</td>
</tr>
<tr>
<td>Liandratite-uraninite</td>
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<td>n.d.</td>
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<td>13.61</td>
<td>0.28</td>
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<td>0.00</td>
<td>0.01</td>
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<td>2.59</td>
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<td>88.39</td>
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<tr>
<td>Unaltered betafite</td>
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<td>0.09</td>
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<td>2.35</td>
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<td>0.05</td>
<td>20.50</td>
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<td>21.49</td>
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<td><strong>Sample BMM</strong></td>
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<tr>
<td>Partially altered betafite</td>
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<td>0.58</td>
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<tr>
<td>Uranpyrochlore-TiO₂ss</td>
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<td>0.15</td>
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<td>4.98</td>
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<td>0.92</td>
<td>22.56</td>
<td>87.56</td>
</tr>
</tbody>
</table>
3.3.1.5.3. **EPMA Mapping- heated samples**

All of the natural samples were heated to 1200 °C to examine the phases formed upon re-crystallisation from the metamict state. Only sample BSC however was re-mapped by EPMA to determine changes in texture, element distribution and/or mineralogy. Results presented in Figure 3.11 show a BSE image (Figure 3.11a) with a corresponding map showing the distribution of the elements Nb, Ti and U (Figure 3.11b) and a phase-patched mineral map (Figure 3.11c). Texturally, the sample appeared no different from the unheated sample with areas of light and dark contrast (Figure 3.11a) still visible. While re-crystallisation of the sample has occurred (as confirmed by XRD analysis) there appears to have been no effect of heating on the mobility of cations within the beta-fite.
Figure 3.24 BSE and corresponding Nb/Ti/U element distribution map for the heated sample BSC. The final image is a phase-patched map showing the distribution of mineral phases within the heated sample. In each image the scale bar represents 100 micron.
3.3.2. Dissolution studies on natural betafite samples

The influence of various parameters on the dissolution of the three natural betafites characterised in the previous sections were investigated to examine any association between compositional and structural variations on their dissolution.

3.3.2.1. Dissolution of natural betafite samples under conditions similar to those used in the Rössing leach circuit

The conditions used for these studies were chosen to reflect similar conditions to those currently used in the Rössing uranium leach circuit [25]. These conditions were as follows: \( \text{[H}_2\text{SO}_4] = 50 \text{ g/L (0.51 M)} \), temperature = 35°C, \( \text{[Fe}^{\text{TOT}}] = 3\text{ g/L} \), \( \text{Fe}^{3+}:\text{Fe}^{2+} \) ratio = 9:1, initial [Betalite] = 200 ppm, leach time = 6 hours. The dissolution results obtained for the three as received betafite samples are presented in Figure 3.12. Over the 6 hour period studied ~42 %, 20 % and 7% U extraction was observed respectively for the BAM, BMM and BSC samples. As discussed in Section 3.1.4.2, all three samples contained significant amounts of metamict betafite; although each had undergone varying degrees of the two stage alteration mechanism [6]. The most highly altered sample was BAM which contained a high degree of heterogeneity in elemental distribution throughout the sample that led to the formation of solid solutions of the alteration products liandratite, uranpyrochlore and titanium oxide (Figures 3.9 & 3.10). The higher uranium dissolution for BAM as compared to BMM and BSC as shown in Figure 3.12 can most likely be attributed to the enhanced dissolution of uranium from the more soluble \( \text{U}^{6+} \) alteration products liandratite and uranpyrochlore. The least altered sample, BSC showed a homogeneous elemental distribution and the dissolution of this sample at the same conditions as BAM and BMM was significantly lower. The presence of a primarily betafite sample with minimal alteration products was attributed to the decreased U extraction rate for sample BSC. The disruption of the crystal lattice either through alteration forming secondary alteration products or through metamictisation appears to be a key factor in improving the uranium extraction from betafite. This will be discussed in more detail in subsequent sections.
3.3.2.2. Influence of $[\text{H}_2\text{SO}_4]$ on dissolution of natural betafites

Four experiments were conducted to study the influence of sulphuric acid concentration on natural betafite dissolution. The results presented in Figure 3.13 for sample BAM show as the concentration of acid is increased the rate of dissolution also increases. In the first minute of each experiment ~2.0% of the uranium from the natural sample was found to have dissolved at each acid concentration used, whereas after this period the rate of dissolution varied significantly for the different acid concentrations used. This initial rapid dissolution within the first 15 min for all tests is possibly due to surface $\text{U}^{6+}$ being present from the weathering process and hence dissolving instantaneously. The highest sulphuric acid concentration used was 100 g/L (1.02 M), this lead to 57.7% uranium dissolved from BAM after 6 hours.
The results from the influence of acid tests conducted on sample BMM are presented in Figure 3.14. The results of these experiments showed similar leaching trends as the previously discussed BAM sample. The extent of leaching was however slightly less than what was observed for the BAM sample. This is most likely due to the different degree of alteration observed in this sample though this will be discussed in more detail in the subsequent section. Approximately 3% of the uranium was observed to leach when no sulphuric acid was added. It was assumed that this dissolution was observed to be significantly lower due to the higher pH allowing the formation of jarrosite which stopped the ferric oxidation of uranium from occurring and hence limiting the dissolution. These results also demonstrated as the acid concentration increased the dissolution rate also increased. In each case the leach rate was observed to be consistent for the duration of the 360 minute experiment, indicating that the leaching had not leached equilibrium.
The dissolution data presented in Figure 3.15 shows the influence of sulphuric acid on uranium dissolution from BSC. The dissolution experiment conducted with no addition of acid was shown to leach a negligible amount of uranium from the sample over the dissolution period. As the acid concentration increased the leach yield was also observed to increase, although at the highest acid concentration used (100 g/L) only ~4.7% of the uranium was dissolved out of the sample.
The influence of sulphuric acid concentration on uranium dissolution showed similar trends to those previously discussed for the initial dissolution experiments. The extent of dissolution after 6 hours showed significantly more uranium was leached out of BAM than BMM at both 50 and 100 g/L \([\text{H}_2\text{SO}_4]\). This was most likely due to the higher amount of pores, cracks, fractures and micro-veinlets present in the BAM sample which led to easier extraction of uranium from the materials. In comparison, the extent of dissolution for BSC over the 6 hours ranged from 0.11 to 4.70% over the acid concentrations studied. The lower dissolution at all acid concentrations relative to the BAM and BMM samples was due to the unaltered nature of the sample resulting in low concentrations of the more soluble betafite decomposition/weathering products present in the sample.

### 3.3.2.3. Influence of temperature on U dissolution of natural betafites

The influence of temperature on uranium dissolution from BAM was studied between 35 and 95 °C. The results presented in Figure 3.16 show as the temperature increases, the rate of uranium dissolution also increases presented in Section 3.3.1.2. The highest temperature experiment conducted was at 95 °C, this yielded ~35% of the uranium dissolved out of the BAM sample after 360 minutes. The difference in dissolution yield was shown to increase at a similar amount between 35, 50 and 65 °C; whereas a noteworthy difference in the amount of U leached between 65 and 80 °C was observed. This may indicate that a second competing dissolution mechanism occurs at temperatures of 80°C and above.
Figure 3.29 Influence of temperature on uranium dissolution from natural betafite BAM. $[\text{H}_2\text{SO}_4]$: 5 g/L, $[\text{Fe}]_{\text{TOT}}$: 3 g/L, Redox Potential: 510 mV vs. Ag/AgCl.
The influence of temperature on dissolution of uranium from the BMM sample is presented in Figure 3.17. The results of this experimental series show the dissolution of uranium was very similar over the first 30 minutes for the three experiments conducted at the highest temperatures after this period the results showed the leaching rate was significantly influenced by temperature. The extent of dissolution was relatively similar to what was observed in the BAM sample under the same experimental conditions. It is important to note no experiment was conducted at 65 °C due to the limited amount of sample available.

![Graph showing the influence of temperature on uranium dissolution from natural betafite BMM.](image)

**Figure 3.30** Influence of temperature on uranium dissolution from natural betafite BMM. \([H_2SO_4]: 5 \text{ g/L}, [Fe]_{TOT}: 3 \text{ g/L}, \text{Redox Potential: } 510 \text{ mV vs. Ag/AgCl.}\)

The influence of temperature on uranium dissolution from BSC shown in Figure 3.18 demonstrates similar trends to the BAM and BMM temperature experiments where increasing the temperature increased the leach yield. The major difference noted when comparing the influence of temperature on the three natural betafite samples was the extent of dissolution for BSC was significantly lower than the other two samples. At 95 °C only 9.1% of the uranium from the sample was leached out after 360 mins whereas 38 and 39% was leached out of BAM and BMM respectively. This difference in the extent of dissolution between BAM and BSC was most likely due to the alteration factor which will be discussed in the subsequent section.
The data obtained from the aforementioned tests on the influence of temperature was also used to determine the activation energies for the dissolution of the three natural betafite samples.

Activation energies were calculated for the three samples using kinetic data calculated from the dissolution experiments (Figure 3.19). The first order kinetic rates used to determine activation energies were calculated using the dissolution data obtained in the 15 – 360 minute period for each sample as the dissolution of uranium observed in the first 15 minutes, which was very similar for all samples, was most likely not representative of the dissolution of bulk betafite. The calculated activation energies were; 8.61, 7.64 and 12.42 kJ/mol for BAM, BMM and BSC respectively. These activation energies are significantly lower than previously reported values for the refractory uranium titanate mineral brannerite (30.3kJ/mol) which was calculated from small scale leaching studies under similar experimental conditions to those used in this study [26].
3.3.2.4. Influence of total Fe concentration

The influence of total iron concentration was investigated between 0 and 12 g/L in the form of ferric and ferrous sulphate at a ratio of 9:1 (Figure 3.20). Ferric iron has been shown to be important in the uranium leaching process as it is used as an oxidant to oxidise tetravalent and pentavalent uranium into the more soluble hexavalent uranyl ion according to the following Equation 3.2 [27]:

\[
\begin{align*}
UO_2(s) + 2Fe^{3+}_{(aq)} &\rightarrow UO_2^{2+}_{(aq)} + 2Fe^{2+}_{(aq)} \\
\end{align*}
\]  

(3.2)

The influence of total iron on dissolution of uranium from the BAM sample was shown to be significantly different to the generally excepted ferric oxidation mechanism of U leaching [28]. In this experimental series the highest amount of dissolution occurred when there was no addition of iron; indicating that the ferric oxidation of uranium described previously was not the favoured mechanism for dissolution for this sample.

The difference in uranium at varying Fe_{TOT} concentration between 1.5 to 12 g/L was shown to be negligible within experimental error. The influence of total iron concentration has been shown to affect the dissolution amount in two ways. The initial effect as previously discussed where increasing the total iron concentration generally increases the likelihood of uranium(IV and V) being oxidised to
U(VI) by ferric which increases the dissolution rate. Moreover, Gogoleva described passivation of brannerite by the precipitation of iron sulphate onto the brannerite surface at high iron concentrations [26]. It is likely that a similar mechanism is happening with betafite and hence resulting in the lower leach rate at higher Fe\textsubscript{TOT} concentrations.

Four experiments were conducted to investigate the influence of total iron on the natural betafite sample BMM (Figure 3.21). The results of this experimental series showed a similar trend to the previously discussed BAM sample where the highest amount of dissolution occurred when no iron was added. The dissolution rate of this experiment with 0 g/L [Fe\textsubscript{TOT}] was shown to have the highest and most consistent rate of the experiments conducted in this experimental series. This higher rate of dissolution and consistent rate over the leach duration was assumed to be due to the reasons discussed previously for the BAM sample and proves further consistency these unusual trends previously described. The dissolution experiment conducted at 3 g/L Fe\textsubscript{TOT} was shown to have the second highest rate of leaching. The extent of dissolution at 6 and 12 g/L total Fe were shown to have the same influence as each other, and lower rates of dissolution than the experiments conducted at 0 and 3 g/L. These results indicate that as the total iron is increase the dissolution rate
decreases up until 6 g/L where increasing the iron concentration has no further influence on the result. Unfortunately the reason for this result could not be determined and due to that lack of sample further experiments could not be conducted in order to confirm this trend. Although the cause of this trend is most likely similar to that described by Gogoleva where increasing the total iron concentration was shown to hinder dissolution by the target mineral acting as a seed for precipitation of iron sulphate[26].

Figure 3.34 Influence of total iron concentration on uranium dissolution from natural betafite BMM. [H₂SO₄]: 5 g/L, Temperature: 35°C, Redox Potential: 510 mV vs. Ag/AgCl.

The degree of dissolution of BSC at various total iron concentrations was shown to be significantly lower than the previous two betafite samples discussed (Figure 3.22). In this experimental series the tests conducted at 0, 1.5, 3 and 6 g/L [Fe_TOT] were shown to have the same dissolution curve where initially a high rate of dissolution occurred over the initial 30 minutes followed by a slow leach rate for the remainder of the experiment. Uranium leaching at 9 and 12 g/L showed less dissolution than the experiments conducted at the lower total iron concentrations. The leach rate over the initial 120 minutes was shown to be lowest at the highest total iron concentration experiment conducted (12 g/L). Although the dissolution rate was lower for this experiment the extent of leaching was similar to the 9 g/L experiment after 120 minutes. The difference between the lower total iron...
concentrations and experiments conducted at the two higher concentrations could be due to passivation of the sample due to the betaïte particles acting as places for seeding of ferric oxide (Fe₂O₃) as described in Gogoleva [26] for the uranium titanate mineral brannerite. The dissolution rate between 120 and 360 minutes was shown to be similar for all the leach tests conducted in this experimental series. The difference between the previous two samples discussed and BSC was the BSC sample showed a low dissolution rate between 120 – 360 minutes whereas both BAM and BMM showed a consistently high rate throughout the whole dissolution experiment, moreover the current sample showed a significantly lower extent of dissolution than the BAM and BMM samples. This indicates the BSC sample is more refractory than the previous two samples discussed. This is most likely due to the lower level of alteration in this sample shown via EPMA (Figure 3.11) meaning the sample contains less micro fractures and fissures which allow solution to penetrate further into the structure allowing more uranium to leach.

![Figure 3.35 Influence of total iron concentration on uranium dissolution from natural betaïte BSC. [H₂SO₄]: 5 g/L, Temperature: 35°C, Redox Potential: 510 mV vs. Ag/AgCl.](image)

**3.3.2.5. Influence of redox potential**

Investigation into the influence of solution redox potential was conducted in 5 experiments using redox potentials between 350 – 570 mV vs. Ag|AgCl. Throughout the 6 hour experiment the redox
potential was measured and adjusted with the addition of sodium permanganate to maintain the ORP with +/− 10 mV of the initial value. The results of the experiments using sample BAM are presented in Figure 3.23. The experiment conducted at 350mV had the highest dissolution while the remaining four experiments showed similar dissolution curves where less uranium was observed to have leached. Since the dissolution rate for the experiment conducted at 350 mV (100% Fe²⁺) was the highest and showed a similar trend to the experiment conducted at 0 g/L Fe (Figure 3.21) it was assumed that the greater dissolution could be attributed to no Fe³⁺ being present in the leach system. This was assumed to be due to the previously discussed reason where betafite grains were acting as a seed for the formation of jarosite with aqueous Fe³⁺ on the surface which limited the dissolution rate. Once experiments were conducted with ferric sulphate present the dissolution yield was drop from 10% to 5% U leached over the 6 hour dissolution period. If the test at 330 mV is disregarded due to the aforementioned reason, no further difference in leaching rate was observed between 465-570 mV. It can therefore be deduced that redox potential did not have an influence in U dissolution from BAM.

![Figure 3.36 Influence of redox potential on uranium dissolution from natural betafite BAM. [H₂SO₄]: 5 g/L, [Fe_total]: 3 g/L Temperature: 35°C.](image)
The influence of redox potential on uranium dissolution from the BMM sample was conducted over a period of 6 hours (Figure 3.24). The results of this experimental series showed similar dissolution curves for each of the leaching experiments conducted. In each case approximately 3% U was observed to leach in the initial minute; this was followed by a consistent leach rate for all tests for the remainder of the experiment. Approximately 11.4% uranium was shown to be leached after 6 hours in all of the redox potential experiments conducted. Since the leach rates and extent of dissolution were similar it was determined that redox potential had no influence in leach rate over the remainder of the experiment provided there was iron present in the leaching system.

The influence of redox potential was shown to have a negligible influence on dissolution of betafite dissolution from BAM and BMM samples. The reason for this is most likely due to dissolution of uranium not occurring via the generally accepted leaching mechanism given in Section 3.3.2.4 where ferric iron is used to oxidise U⁴⁺ to the soluble uranyl species; and instead via a diffusion mechanism where the only role of iron sulphate is as a source of sulphate ions for the formation of the UO₂SO₄ aqueous species. Though verifying this is difficult due to the limited amount of the natural samples acquired.

![Figure 3.37 Influence of redox potential on uranium dissolution from natural betafite BMM. [H₂SO₄]: 5 g/L, [Fe₅⁺]: 3 g/L Temperature: 35°C.](image-url)
The influence of redox potential on U leaching of the BSC sample is shown in Figure 3.25. The results of these experiments showed similar dissolution curves for the five experiments conducted with redox potential being found to have no significant effect on the U dissolution and similar leaching to the total iron experiments conducted between 0 and 6 g/L [FeTOT]. In each case the dissolution rate started at a high rate then slowly decreased over the duration of the experiment. This decrease in leach rate indicates the sample became passivated as the experiment progressed as discussed in Section 3.3.2.4. Since this sample was shown to be the least altered of the three natural beta-fites, passivation of the sample is most likely caused by the lack of microfractures and vainlets within the beta-fite structure inhibiting dissolution once the easier to leach uranium has been liberated from the structure.

![Figure 3.38 Influence of redox potential on uranium dissolution from natural beta-fite BSC. (H₂SO₄): 5 g/L, [FeTOT]: 3 g/L. Temperature: 35°C.](image)

3.3.2.6. Influence of heat treating on U dissolution of natural beta-fites

The influence of heat treating on U dissolution was conducted over four experiments at two different acid concentrations (0 g/L and 50 g/L). These experiments were designed to investigate the effect of metamictisation on uranium dissolution from beta-fite. The dissolution results presented in Figure 3.26 show two significantly different dissolution curves occur between when the sample is
unheated and heated to 1100 °C. In the unheated sample the dissolution rate stays constant throughout the experiment whereas in the heated sample the rate slows significantly after 120 mins. The two experiments conducted with no acid show more dissolution occurs when the sample is heated over the initial 120 mins. This could be due to oxidation of the uranium during the annealing process as well as structural alterations allowing a higher amount of U^{6+} to be accessible for leaching (Figure 3.26a). This would explain why the rate decreases as the experiment progresses. Comparison between the unheated and heated 50 g/L H_2SO_4 experiments show the initial rate is significantly higher over the initial 120 mins in the heated sample (Figure 3.26b). After this point the dissolution rate slows considerably. This could be due to the aforementioned reasons; more U^{6+} could be found in the heated sample, or a structural transformation has led to the leachable uranium being more accessible to the leach solution. The decrease in rate after this point is most likely to be due to the heat treating leading to recrystallization of the betafite and hence the stronger mineral structure needing more energy to breakup and dissolve the uranium from the mineral.

Figure 3.39 Influence of heat treating on uranium dissolution from natural betafite BAM. Figure 3.26a 0 g/L [H_2SO_4], Figure 3.26b 50 g/L [H_2SO_4]. All other conditions were held at the following values: Temperature: 35 °C, [Fe]_tot: 3 g/L, Redox Potential: 510 mV vs. Ag/AgCl

Similar trends are present in BSC as were shown previously in BAM when studying the influence of heat treating. The results presented in Figure 3.27a shows a higher amount of uranium was
dissolved in the heated sample than the unheated sample when no sulphuric acid was added. As described previously a greater amount of U⁶⁺ could be present or the U⁶⁺ could more exposed to be leached. Comparison between the headed and unheated BSC dissolution curves when 50 g/L H₂SO₄ was added shows a significantly higher dissolution rate in the heated sample over the initial 30 mins. After this point the rate slows for the remainder of the 360 min experiment. This initial fast rate over the first 30 minutes is due to the reasons explained previously, but is shown to be more prominent due to the compounding effect of the high acid concentration (Figure 27b). The dissolution rate of the heated sample is slower than the unheated sample after the initial spike for the first 30 mins. Again this influence is attributed to the stronger mineral structure gained from annealing the unheated sample leading to more energy needed to dissolve uranium from the mineral.

Figure 3.40 Influence of heat treating on uranium dissolution from natural betaite BSC. Figure 3.27a 0g/L [H₂SO₄], Figure 3.27b 50g/L [H₂SO₄]. All other conditions were held at the following values: Temperature: 35 °C, [Fe]₉₀₉: 3 g/L, Redox Potential: 510 mV vs. Ag/AgCl
3.4. Conclusions

Three natural betafite samples were characterized to investigate their textural, chemical and mineral properties. The techniques used were XRD and multi acid digestion ICP-MS analysis for bulk characterization and Raman spectroscopy and EPMA for microstructural analysis. The samples were heated *ex situ* and XRD analysis was completed at different temperature intervals. The XRD results show crystallization of betafites occurred at ~900 °C in the 3 samples investigated. Other minerals found to be present in the heated samples were UTiNb$_2$O$_{10}$ (formed from liandratite + TiO$_2$) in BMM and anatase/rutile in the other unheated and heated sample respectively. Bulk elemental concentrations showed all samples contained similar concentrations of U, Ti, Nb and Ta, whereas the concentration of Ca varied significantly between the 3 samples. The samples with lower Ca concentration were shown to be more highly altered and more heterogeneous by EPMA. This alteration was caused by aqueous fluid interaction causing formations of secondary alteration products. BAM was shown to be the most highly altered sample and showed at least three different phases when the quantitative EPMA data was plotted on a Nb-Ta-Ti ternary diagram. BSC was shown to be the least altered sample. EPMA mapping of the heated BSC showed the sample was predominantly betafite though had minor apatite and galena phases.

Higher dissolution quantities were observed in the more highly altered betafite samples due to the presents of the more soluble U$^{VI}$ decomposition products liandratite and uranpyrochlore, whereas the least alter sample BSC showed significantly less dissolution over the 6 hour leach period. Activation energies of uranium dissolution for the three samples showed higher values for the less altered betafite samples. The influence of acid concentration was shown give similar rates for each sample for the various acid concentrations studied. The maximum dissolution rate observed for all samples was achieved at 50 g/L H$_2$SO$_4$ concentration, beyond this point increasing the acid concentration did not increase dissolution rate any further.
3.5. References


25. van Rensburg, N.J., *A value based approach to leach optimization at Rössing uranium limited*, in *Faculty of the Engineering and Built Environment*. 2014, University of Cape Town: Rondebosch. p. 163.


The work conducted in the previous chapter demonstrated alterations in the natural betafites resulted in several impurities and significantly influenced the leachability of the mineral. It was therefore decided to synthesise a pure betafite sample in order to better study the structural and chemical properties of a pure betafite sample. The following chapter provides literature on the synthesis of pyrochlore group minerals via solid state and hydrothermal synthetic methods. The synthesis of betafite was examined using a high temperature solid state synthetic procedure. The sample was then characterized using X-ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), vibrational spectroscopy, and Electron Probe Micro Analysis (EPMA).
4.1. Introduction

In the previous chapter, characterisation and dissolution studies were conducted on natural betafite samples. The results of these experiments demonstrated that the alteration and the presence of other uranium-containing minerals had a significant influence in the leachability of the betafite. For this reason, it was decided to synthesise a pure betafite sample for the purpose of characterisation and dissolution studies.

As previously described in Chapter 3, betafite is a subgroup mineral of the pyrochlore supergroup. For this reason, studies on the synthesis of betafite were conducted by investigating pyrochlore structural compounds as a starting point. In a study by Garviea et al., a mixed calcium and cerium pyrochlore \([\text{Ca,Ce}_2\text{Ti}_2\text{O}_7]\) was synthesised by calcining stoichiometric amounts of \(\text{Ca(OH)}_2\) and \(\text{Ce(NO}_3\) \(_4\) with rutile at 1300 °C [1]. Although this pyrochlore did not contain U, Nb, or Ta, the resulting cubic structure was similar to that of betafite. The use of a hydrothermal method to synthesise pyrochlore compounds was suggested by Modeshia and Walton [2]. They investigated the synthesis of niobates and tantalates pyrochlore of the formulae \(\text{A}_2\text{B}_2\text{O}_6\text{OH}\), where \(\text{A} = \text{Ca}\) and \(\text{B} = \text{Nb}\) or \(\text{Ta}\). The synthesis method involved initially a firing step at above 650 °C to convert calcium nitrate and group V ethoxides to form pervoskite \((\text{CaBO}_3)\) where \(\text{B} = \text{Nb}\) or \(\text{Ta}\). The mixture was then heated between 100 and 200 °C in a KOH solution. Varying the Nb/Ta concentration changed both the stoichiometry of the pyrochlores as well as the products formed [2].

A method for synthesising brannerite \((\text{UTi}_2\text{O}_6)\), a uranium titanate mineral similar to betafite, was investigated by Amin et al.; [3]. The method used involved heating stoichiometric amounts of uranium nitrate \([\text{UO}_2\text{(NO}_3\) \(_2\)]\) and \(\text{TiO}_2\) to 1200 °C under reducing conditions \((\text{Ar}/5\% \text{H}_2)\). The product of this method was however found to contain both uraninite \(\text{UO}_2\) and rutile impurities. More recently, Charalambous et al. successfully prepared high purity synthetic \(\text{UTi}_2\text{O}_6\) (and REE-doped versions) using an initial wet chemistry step, which involved mixing stoichiometric amounts of uranyl acetate and titanyl sulphate dihydrate in an oxalic acid solution. The dried precipitate collected from the aforementioned solution was heated at 1200 °C under reducing conditions \((\text{Ar}/5\% \text{H}_2)\) for 96
hours [4]. This procedure was a modified version of the method described by Hussein et al. (2008) [5].

Redkin et al. reported on the hydrothermal synthesis of a range of pyrochlore group minerals including a Ti-rich betafite [6]. This was synthesised by the addition of stoichiometric amounts of the starting metal oxides to a 1M NaF solution using Co-CoO as an oxygen buffer which was then heated for 7 days at 800 °C in a sealed platinum vessel. The diffraction data provided by Redkin et al. to support the synthesis of betafite did however show that the betafite produced was not pure as there were numerous diffraction lines missing or of different intensities than expected.

Another reason for the investigation into the synthesis of betafite is to study the feasibility of using betafite as a potential material for storage of spent nuclear fuel. Several methods for storing spent nuclear fuel (SNF) have been developed since the initial advancement of SYNROC (synthetic rock) by Ringwood et al. [7]. As previously described in Section 1.3.5 the majority of these methods involve waste actinide fission products being bound in the crystal lattices of mixtures of the titanate-based minerals; hollandite nominally Ba(Al,Ti)₂Ti₆O₁₆, zirconolite (CaZrTi₂O₇) and perovskite (CaNbO₃). The first SYNROC material synthesised was composed of hollandite, zirconolite, perovskite, and rutile, together with a few percent of minor phases and metal alloys [8]. Other variations of SYNROC include; SYNROC-D, a multiphase ceramic consisting of nepheline, zirconolite, perovskite, and spinel (ABO₄) designed for storage of defence high level waste and; SYNROC-F which was designed for storage of SNF where actinides are incorporated into pyrochlore (A₂B₂O₆[OH,F]), perovskite and hollandite [9]. The storage of SNF has also been investigated using synthetic versions of naturally occurring uranium bearing minerals such as brannerite (UTi₂O₆) [10] and betafite [11].

In this chapter, the preparation of a synthetic betafite with composition [(Ca,U)₂(Ti,Nb,Ta)₂O₇] was investigated. The development of a method(s) for the preparation of synthetic version(s) of betafite will enable a pure betafite sample to be studied. This will be beneficial in understanding various factors that may influence dissolution which can be applied to commercial mineral processing of
betafite containing ores. Moreover, studies on this mineral may be beneficial in determining the feasibility of betafite as a potential storage material for radioactive waste.

To the best of our knowledge no previous method for preparing a synthetic form of betafite has been reported that contains an element suite that is characteristic of the main elements present in naturally occurring betafite.

4.2. Materials and Methodology

4.2.1. Materials

The following reactants were used as received; uranyl nitrate, $\text{UO}_2(\text{NO}_3)_2$, (99% AR grade, Aldrich Chem. Co.), calcium carbonate, $\text{CaCO}_3$, (99.95% AR grade Aldrich Chem. Co.), titanium dioxide, $\text{TiO}_2$, (99.99% AR grade Aldrich Chem. Co.), niobium (V) oxide, $\text{Nb}_2\text{O}_5$, (99.9% AR grade Aldrich Chem. Co.), tantalum (V) oxide, $\text{Ta}_2\text{O}_5$, (99.99% AR grade Aldrich Chem. Co.).

Synthetic betafite was prepared via reactions between several solid state reactants (see results and discussion for details). The preparation method for synthesis given was described in further detail in Chapter 2.2.

4.2.2. Characterisation methods

The following characterisation methods that were conducted in this chapter: Elemental analysis (ICP-MS) Powder X-ray diffraction, X-ray photoelectron spectroscopy, Raman spectroscopy and FTIR are described in detail in Chapter 2.

4.2.2.1. Scanning Electron Microscope (SEM)

Samples were prepared for SEM analysis by either placing granules of the sample onto a stainless steel holder that was covered in carbon tape or by dispersing the granules in epoxy resin and mounting into a 2.5 cm round block. The resin block was cured overnight, sectioned to expose a fresh surface, and then polished flat using successively finer diamond paste cutting compounds down to a final cutting size of 1 µm. Immediately prior to analysis, the sample was coated with a 15 nm thick carbon film to prevent charge build-up on the surface when probed by the electron beam.
Scanning electron microscopy was performed using an FEI Quanta FEG 400 Environmental Scanning Electron Microscope (ESEM) instrument equipped with a single Bruker XFlash® silicon drift detector for conducting Energy Dispersive X-ray spectroscopy (EDX) and Esprit v.1.9 analytical software. The ESEM was operated at an accelerating voltage of 15 kV, a probe current of ~1 nA and a vacuum of >5x10⁻⁵ Torr.

4.2.2.2. Electron Probe Micro-Analysis (EPMA)

EPMA examination of the synthetic betafite was performed using a high resolution Field Emission Gun (FEG) equipped EPMA (JEOL 8500F Hyperprobe). Two types of EPMA information were obtained. Initially, the sample was mapped in order to examine the chemical homogeneity of the betafite grains. Following mapping, the sample was examined by quantitative EPMA techniques to determine the chemistry of the synthetic betafite. Operating conditions for each of the techniques are described in Section 3.2.5.

4.3. Results and Discussion

4.3.1. Synthesis Results

The two routes commonly used to synthesise pyrochlore group minerals are: (1) hydrothermal-based processes (which generally involve a mild calcination step) and, (2) solid state processes where high temperatures are used to fuse starting materials together to form the desired product. It was decided to investigate the synthesis of betafite using a solid state based approach as this has been shown to be successful previously for the synthesis of a similar mineral, brannerite, UTi₂O₆ [4]. Moreover the use of a hydrothermal route would most likely have been hindered by the fact that all of the main elements present in betafite are difficult to keep in a soluble form simultaneously (e.g. Nb and Ta are only soluble in HF, whereas Ca forms the sparingly soluble CaF₂ species under acidic conditions).

The syntheses of betafites with two distinct elemental compositions were investigated. The elemental composition’s that were targeted were: Betafite A = (U₀.₄⁹Ca₀.₁₇)(Nb₀.₈₈Ti₁.₂₂Ta₀.₁₀)O₇ and
Betafite $B = (U_{0.32}Ca_{0.42})(Nb_{0.41}Ti_{1.76}Ta_{0.10})O_7$. The composition of Betafite A is based on literature values that have been reported on the stoichiometry of natural betafite [12] whereas the composition of Betafite B is based on a stoichiometry calculated from nomenclature guidelines reported by Hogarth [13].

An initial experiment to synthesise betafite was conducted by heating the amounts of reactants required to produce a betafite of composition A in air for 24 hours (run number B1, Table 4.1). XRD results of the run products showed that the following compounds were present: rutile, $UTiNb_2O_{10}$, $UNb_2O_{10}$, Uranmicrolite $[(U,Ca)Ta_2O_7]$ and a minor amount of betafite (Figure 4.1). Based on the results obtained it was decided to firstly investigate the influence of the reaction atmosphere as a number of the products obtained in the initial test contained $U$ in the 6+ oxidation state which is not the state in which $U$ is commonly found in betafites – where the $U$ oxidation state is commonly reported as predominantly 4+ with some 6+ due to surface oxidation however there is no XPS data to confirm these finding and it was assuming this assignment was based on the refractory natural and lack of solubility of uranium in betafite [14-16].
Figure 4.41 XRD pattern (labelled B1) of synthesis products after heating the mixture with molar ratio Betafite A at 1150°C for 24hrs in air. Standard patterns from the ICDD JCPDS XRD database for other phases identified in the sample are included for comparison. Betafite \([\text{(U,Ca)}_2(\text{Nb,Ti,Ta})_2\text{O}_7.\text{xH}_2\text{O}]\) (PDF 008-0300), Rutile \([\text{TiO}_2]\) (PDF 034-0180), Uranmicrolite \([\text{(U,Ca)}_2\text{Ta}_2\text{O}_7]\) (PDF 043-0693), UNb₃O₁₀ (PDF 088-0138), UTiNb₂O₁₀ (PDF 085-0597).

The results obtained from XRD analysis of the products formed using composition Betafite A under a reducing gas environment (5%H₂/Ar) are listed in Table 4.1 with corresponding diffraction patterns shown in Figure 4.2. When the reactants required to produce Betafite A were heated under a reducing atmosphere (run number B2) the products generated were predominantly rutile, UNb₃O₁₀ and TiTaO₄ as well as minor betafite (Table 1, Figure 2). This sample also showed an XRD pattern match for \((\text{Ca,U})_2\text{Ti}_2\text{O}_5\text{OH}\), a betafite mineral devoid of group 5 elements Nb and Ta. This was possibly due to Nb and Ta being reduced and preferentially forming their corresponding oxides rather than substituting into the betafite structure. Based on the aforementioned results it was
decided to investigate formation of betafite under an inert atmosphere (N₂). Characterisation of the reaction products after conducting the reaction in an inert (N₂) atmosphere (run number B3) showed the sample contained a greater amount of betafite, however significant amounts of UTiNb₂O₁₀ and rutile remained as impurities (Table 4.1, Figure 4.2). Based on the results obtained it is most likely that synthesis of betafite with composition A cannot be synthesised using a simple solid state based process. This is most likely due to this composition, which was based on natural betafite data, is influenced by a number of processes such as metamictisation, cationic substitution and alteration, and hence is the product of a number of complex processes. Hence it was decided to focus on the synthesis of Betafite B, whose composition is based on a stoichiometry calculated from nomenclature guidelines.

Figure 4.42 XRD patterns of synthesis products after heating the mixture with molar ratio Betafite A at 1150°C for 24hrs in Ar/5% H₂ (pattern B2) and in high purity N₂ (pattern B3). Standard patterns from the ICDD XRD database for other

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{xrd_patterns.png}
\caption{XRD patterns of synthesis products after heating the mixture with molar ratio Betafite A at 1150°C for 24hrs in Ar/5% H₂ (pattern B2) and in high purity N₂ (pattern B3). Standard patterns from the ICDD XRD database for other}
\end{figure}
phases identified in the sample are included for comparison. Betafite \([(U, Ca)_{2}(Nb, Ti, Ta)_{2}O_{7+x}H_{2}O]\) (PDF 008-0300), Rutile \([TiO_{2}]\) (PDF 034-0180), Betafite* \([(U, Ca)_{2}Ti_{2}O_{7}]\) (PDF 045-1477), TiTaO\(_{4}\) (PDF 081-0912) UNb\(_{3}O_{10}\) (PDF 088-0138), UTiNb\(_{2}O_{10}\) (PDF 085-0597).

The products obtained from the reaction to synthesise Betafite B under the following conditions (T = 1150 °C, time = 24 hrs, inert atmosphere) are given in Table 4.1 (run number B4) and Figure 3. At these conditions, results for the Betafite B sample showed the formation of predominantly betafite, as well as minor amounts of pyrochlore \((Ca_{2}Nb_{2}O_{6}OH)\) and rutile (Table 4.1, Figure 4.3). The experiment was repeated and allowed to run for a further 24 hr (48 hr in total) which resulted in the formation of betafite with only a trace amount of rutile (around the XRD limit of detection of <1-2%). Hereafter, all characterisation results refer to the product of run number B5.

![Figure 4.43 XRD patterns of synthesis products after heating the mixture with molar ratio Betafite B at 1150°C for 24hrs (pattern B4) and 48 hours (pattern B5) in high purity N\(_2\). Standard patterns from the ICDD JCPDS XRD database for other phases identified in the sample are included for comparison. Betafite \([(U, Ca)_{2}(Nb, Ti, Ta)_{2}O_{7+x}H_{2}O]\) (PDF 008-0300), Rutile \([TiO_{2}]\) (PDF 034-0180), Pyrochlore \([Ca_{2}Nb_{2}O_{6}]\) (PDF 073-0597).](image-url)
Table 4.5 Results from solid state synthesis experiments examining the effects of element ratio, time and gas atmosphere on the formation of synthetic beta-fite. All experiments were conducted at 1150 °C.

<table>
<thead>
<tr>
<th>Run Number</th>
<th>Element Ratio</th>
<th>Atmosphere</th>
<th>Time (hrs)</th>
<th>Compounds detected by XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>Beta-fite A</td>
<td>Air</td>
<td>24</td>
<td>UTiNb2O10, UNb3O10, Uranmicrolite, Beta-fite, Rutile</td>
</tr>
<tr>
<td>B2</td>
<td>Beta-fite A</td>
<td>Ar/5%H2</td>
<td>24</td>
<td>Rutile, Beta-fite*, UNb3O10, TiTaO4</td>
</tr>
<tr>
<td>B3</td>
<td>Beta-fite A</td>
<td>N2</td>
<td>24</td>
<td>Beta-fite, UTiNb2O10, Rutile</td>
</tr>
<tr>
<td>B4</td>
<td>Beta-fite B</td>
<td>N2</td>
<td>24</td>
<td>Beta-fite, Pyrochlore, Rutile</td>
</tr>
<tr>
<td>B5</td>
<td>Beta-fite B</td>
<td>N2</td>
<td>48</td>
<td>Beta-fite</td>
</tr>
</tbody>
</table>

4.3.2. Characterisation of Synthetic Beta-fite

Duplicate analysis of the synthetic beta-fite by ICP-MS gave an average composition of: U (25.48%), Ca (7.03%), Nb (20.95%), Ta (15.33%) and Ti (10.75%). Using the elemental composition data and charge balancing to satisfy the oxide portion of the beta-fite formula, the composition is calculated to be [(U0.42Ca0.69)(Nb0.88Ti1.10Ta0.33)O7].

The unit cell parameters were refined using refinement software based on Holland et al. [17]. The refined unit cell parameters indicated the synthetic beta-fite had cubic symmetry with a = 10.289 Å. This was within the range reported by Hogarth of 10.27 -10.39 Å for naturally occurring beta-fites [16].

4.3.2.1. X-ray Photoelectron Spectroscopy (XPS)

The oxidation state(s) of U in the synthesised beta-fite were investigated using XPS. Analysis of the XPS data shows two intense peaks between 375 and 410 eV (Figure 4.4). One peak has a binding energy (BE) centred around 380-381 eV and the second, smaller peak is located at 391-392 eV. These peaks correspond to the excitation of U4f7/2 and U4f5/2 spin orbitals splits, respectively [18]. The BE of the U4f7/2 peak is directly related to the oxidation state of uranium and previous studies have shown that as the oxidation state of uranium increases from U4+ (UO2) to U6+ (UO3), the BE of the
U\textsubscript{4f}\textsubscript{7/2} peak increases by about 1.7-1.8 eV [19, 20]. Deconvolution of the U\textsubscript{4f}\textsubscript{5/2} peak showed two peaks at 391.48 and 392.98 eV respectively. Analysis of higher energy satellite peaks was shown to reveal three low intensity peaks. Satellite peaks occur for both the U\textsubscript{4f}\textsubscript{7/2} and U\textsubscript{4f}\textsubscript{5/2} spin orbitals splits, but due to overlap of the U\textsubscript{4f}\textsubscript{5/2} peak, U\textsubscript{4f}\textsubscript{7/2} satellite peaks are generally not observed. The U\textsubscript{4f}\textsubscript{5/2} satellite peaks are located at higher energies and the difference of the binding energies between the main photoelectric peaks and the satellite peaks can be used as an indicator of the uranium oxidation states [6]. These peaks are located at the higher binding energies of 6-7 eV for U\textsuperscript{4+}, 7.7-8.5 eV for U\textsuperscript{5+}, and ~4 and 10 eV for U\textsuperscript{6+} [21]. Analysis of the satellite peaks from the deconvoluted U\textsubscript{4f}\textsubscript{5/2} peak revealed three satellite peaks with binding energies of 3.6, 8.1 and 10.0 eV respectively. Since the energy gap between the 391.48 eV and the middle satellite peak is 8.1 eV this satellite peak is due to U\textsuperscript{5+} in the synthetic betafite sample while the two remaining peaks with binding energies of 3.6 and 10.0 eV most likely belong to the U\textsuperscript{6+} oxidation state. Based on the peak areas of the uranium valence peaks of the U\textsubscript{4f}\textsubscript{5/2} peak the uranium in the betafite sample can be proposed to consist of predominantly U\textsuperscript{5+} with a minor amount of U\textsuperscript{6+} possibly due to surface oxidation from exposure to air. As mentioned earlier uranium in natural betafite has been reported to exist predominantly as U\textsuperscript{4+} although some U\textsuperscript{6+} may also be present [15, 21]. In the publications where the aforementioned was reported the oxidation state was predicted by measuring the solubility of betafite under acidic conditions, and not measured using a direct method such as that used in this study. Hence it is possible that natural betafite does actually contain U in the 5+ oxidation state.
4.3.2.2. Vibrational Spectroscopy

FTIR analysis of the synthesised betafite produced 9 peaks all with relatively low intensities shown in Figure 4.5 and Table 4.2. The broad peak at 700 cm$^{-1}$ is most likely due to Nb-O bond flexing [22]. The sharp weak peak at 890 cm$^{-1}$ is most likely due to in plane U$^{6+}$-OH vibrations [15]. The peak at 1386 cm$^{-1}$ was assigned to Ti-O bond vibrations as observed in Lopez et al [23]. A sharp weak peak at 1650 cm$^{-1}$ and a broad peak at 3500 cm$^{-1}$ were possibly due to chemically bound water/hydroxide in the sample. This water is mostly likely to have come from the starting compounds UO$_2$(NO$_3$)$_2$ and CaCO$_3$ or the synthetic product being slightly hydroscopic.

Raman analysis of the synthetic betafite sample showed several peaks the majority of which were due to variations of U-O, Ti-O and Nb-O vibrations (Figure 4.5, Table 4.2). The sharp peaks at 220 and 294 cm$^{-1}$ were shown to be due to O-U-O bonding when a comparison was made between Frost (2010) and the acquired spectrum. The intense peak at 542 cm$^{-1}$ and shoulder at 620 cm$^{-1}$ was also described in Frost et al. as elongation of U$_2$O bonding and Ti-O bonding respectively [24]. The intensities of the aforementioned peaks were all similar to what was reported in Frost (2010). McConnell et al. showed Raman bands of Nb-O in Nb$_2$O$_5$ occurring at 704 cm$^{-1}$, this is consistent with observed bands in the synthetic betafite spectrum [25].
Figure 4.45 Fourier Transformed Infrared (black) and Raman spectroscopy (gray) of synthetic betafite from 100 – 4000 cm⁻¹.
Table 4.6 Assignment of absorption spectral bands.

<table>
<thead>
<tr>
<th>FTIR (cm⁻¹)</th>
<th>Raman (cm⁻¹)</th>
<th>Assigned:</th>
</tr>
</thead>
<tbody>
<tr>
<td>114</td>
<td></td>
<td>Not assigned*</td>
</tr>
<tr>
<td>220</td>
<td>OUO [24]</td>
<td></td>
</tr>
<tr>
<td>294</td>
<td>OUO [24]</td>
<td></td>
</tr>
<tr>
<td>434</td>
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<tr>
<td>542</td>
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<td></td>
</tr>
<tr>
<td>620</td>
<td>TiO [24]</td>
<td></td>
</tr>
<tr>
<td>685</td>
<td></td>
<td>Not assigned*</td>
</tr>
<tr>
<td>700</td>
<td>Nb-O [22]</td>
<td></td>
</tr>
<tr>
<td>704</td>
<td>Nb-O [25]</td>
<td></td>
</tr>
<tr>
<td>804</td>
<td>UO₂²⁺ [26]</td>
<td></td>
</tr>
<tr>
<td>890</td>
<td>δU-OH [15]</td>
<td></td>
</tr>
<tr>
<td>1116</td>
<td></td>
<td>Not assigned*</td>
</tr>
<tr>
<td>1184</td>
<td></td>
<td>Not assigned*</td>
</tr>
<tr>
<td>1386</td>
<td>Ti-O [23]</td>
<td></td>
</tr>
<tr>
<td>1650</td>
<td>δH₂O [15]</td>
<td></td>
</tr>
<tr>
<td>2946</td>
<td>OH [27]</td>
<td></td>
</tr>
<tr>
<td>3492</td>
<td>OH [28]</td>
<td></td>
</tr>
</tbody>
</table>

* No confident match was found

4.3.2.3. Scanning Electron Microscopy (SEM) and EPMA Mapping

The synthetic betafite was examined by SEM and also mapped by EPMA to examine the distribution of elements and homogeneity. Results are shown in Figure 4.6 for the SEM analysis and Figure 4.7 for the results from the EPMA mapping.

SEM examination indicated that the synthetic betafite was composed of clusters of euhedral crystals up to ~3 μm in size and with characteristic cubic/isometric (hexaoctahedral) morphology (Figure
Examination of a sectioned surface comprising an aggregate of crystals indicated the presence of a minor amount of a Ca-free phase that was identified using EPMA mapping (bright phase in Figures 4.6b and 4.6c). The Ca-free phase was typically sub-micron in grainsize and characteristically had higher uranium and lower Ta (reduced by about 20%) and Nb (reduced by about 50%) contents compared to the surrounding betafite. The material exhibited anhedral morphology consistent with having undergone incomplete reaction. A minor (<1% by area) amount of unreacted rutile was also observed to be present in the sample (image not shown). The rutile was present as either; a) relatively coarse grains reaching 8-10 µm in size and surrounded by smaller betafite crystals which appeared to be growing on the surface of, or partially reacting with, the rutile, or, b) as small, isolated grains. In some areas of the sample it was observed that the betafite was polyphase consisting of a dark phase surrounding a slightly lighter euhedral phase (Figure 4.6b). EDX analysis indicated the primary difference between the two phases was in the ratio of Nb:Ta with the darker phase containing more niobium. While this texture is indicative of incomplete synthesis, it is noted that this texture made up only a small proportion of the sample and for the most part the betafite was homogeneous in composition (Figure 4.6c).
Figure 4.46 Back-scattered electron (BSE) images showing; a) the euhedral morphology, and, b)-c) the degree of inhomogeneity of the synthetic betafite crystals. In the latter two images, EDX analysis indicates the small, bright inclusions are un-reacted UO$_2$ while for image b), the mid-grey euhedral material is associated with high Ta and the surrounding dark-grey material is Nb-rich. The latter two phases both contain approximately the same amount of U but differ only in Nb:Ti ratio.

EPMA map results from two areas of the synthetic betafite sample are shown in Figure 4.7 in the form of classified mineral maps. The maps show the single phase nature of the betafite, forming large sintered aggregates of grains. Interspersed with the betafite is a small amount of the Ca-free ‘betafite’ phase previously discussed as well as some unreacted rutile.
Figure 4.47 Three element maps (a and b) showing the distribution of Nb (blue), U (green) and Ti (red) within two mapped areas on the synthetic betafite. Clustering of the element distribution data produces classified mineral maps (c and d) showing the distribution of phases within the synthetic betafite sample.

4.3.2.4. Quantitative EPMA

Quantitative point analyses were measured on a number of grains within the synthetic betafite sample in order to assess the degree of homogeneity. Results are provided in Table 4.3 while a ternary diagram of the three predominant components occupying the B site: Nb, Ta and Ti is shown as Figure 8. The proportions of these elements are used to recognise the main mineral species within
the pyrochlore group with the betafite subgroup defined by $2\text{Ti} \geq \text{Nb} + \text{Ta}$ for the B-site cation population [13].

The data in Table 4.3 and Figure 4.8 indicate that complete homogeneity during synthesis has not been obtained with at least three chemically distinct compositional groups evident. The bulk of the analyses belong to a population containing, on average, 20.42%Nb, 26.71%U, 9.43%Ca, 12.39%Ta and 8.49%Ti which plots within the betafite subgroup field of the Nb-Ta-Ti ternary (Figure 4.8). The second group consists of a suite of analyses with slightly different Nb:Ta ratio caused by a depletion in Nb and a concomitant increase in Ta and also lower Ti and Ca contents. The average composition for this group of analyses is: 18.07%Nb, 26.85%U, 8.47%Ca, 17.35%Ta and 7.38%Ti and this group also plots within the betafite subgroup. The final group represents only a small part of the synthesised material (only two analyses obtained), is characterised by much higher Nb contents, and falls within the pyrochlore subgroup. Individual grains of the Ca-free phase previously observed in the EPMA map results were unable to be analysed due to their fine grainsize.

The above results suggest that while the synthesis of betafite was largely successful, problems of homogeneity were encountered. These were primarily manifest in variation of the Nb:Ta ratio.
Figure 4.48 Proportion (at%) of Nb, Ta and Ti in synthetic betaite grains analysed by EPMA (refer to data in Table 1). The bulk of the sample lies in the betaite subgroup although there is some variation in Nb:Ta ratio. A small number of grains appear to off-composition and plot within the pyrochlore subgroup (nomenclature based on the pyrochlore classification scheme of Hogarth, 1977).
Table 4.7 Electron probe microanalysis data from the synthetic betafite sample.

<table>
<thead>
<tr>
<th>Nb</th>
<th>U</th>
<th>Ca</th>
<th>Ta</th>
<th>Ti</th>
<th>O</th>
<th>Total</th>
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<td>21.20</td>
<td>26.96</td>
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<td>11.48</td>
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<td>8.47</td>
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<td>13.55</td>
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<td>13.71</td>
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</tr>
<tr>
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<td>9.43(21)</td>
<td>12.39(1.61)</td>
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<td>27.78</td>
<td>8.32</td>
<td>17.13</td>
<td>7.53</td>
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### 4.4. Conclusions

High purity betafite was formed by a solid state synthetic method. XRD characterisation showed the formation of betafite and several synthetic products such as various uranium niobium oxides and rutile depending on the starting elemental ratio, gas atmosphere and heat duration. The successful synthesis of high purity betafite was completed by heating stoichiometric amounts of the starting metal nitrates, carbonate and oxides in nitrogen gas at 1150 °C for 48 hrs. Complementary characterisation of the high purity betafite was conducted via FTIR, Raman, XPS, and SEM/EPMA. FTIR and Raman spectrums showed several consistent peaks matching that of natural betafite samples as well as associated natural pyrochlore minerals. EPMA mapping showed the synthetic sample was predominantly betafite however small regions of Ca-free betafite and rutile were also observed. Quantitative EPMA showed some heterogeneity between the Nb:Ta ratio throughout the sample, though this variation was still within nomenclature requirements for betafite. Interpretation of the XPS spectrum showed uranium was predominantly found as $U^{5+}$ though small amounts of $U^{6+}$ were also observed; this was possibly due to surface oxidation of the uranium.

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</tbody>
</table>
4.5. References


In this chapter, dissolution studies of synthetic betafite were conducted where a number of leaching parameters were investigated. Initial work was conducted where the influence of the most commonly varied parameters in commercial scale leaching (temperature, $[\text{H}_2\text{SO}_4]$, $[\text{Fe}_{\text{tot}}]$ and redox potential) were investigated. Investigations were also carried out on the influence of other parameters which included non-uranium bearing ions (which are commonly leached out of gangue minerals), lixiviant, and surface re-oxidation.
5.1. Introduction

5.1.1. Introduction

Understanding how various parameters influence the U leaching rate of betafite is extremely important in determining the feasibility and viability of U extraction from betafite containing ores. There is very little literature on the dissolution of betafite with acid ferric sulfate leaching. Small scale dissolution studies conducted on Rössing ore by van Rensburg (2014) under conditions similar to those used in the uranium leaching circuit (ORP - 500 mV, [Fe$_{TOT}$] - 4 g/L, pH - 1.6, Temperature - 35°C, wt % solids - 70%), showed that ~80% of the uranium in the ore was leached after a 13 hour resonance period. The remaining unleached uranium was shown to be present in the betafite, coffinite and poorly liberated uranophane [1].

McMaster et al. studied the dissolution of a natural betafite sample at similar dissolution conditions to that used in Rössing uranium processing plant. They showed only ~5% of the uranium leached out of the betafite. Maximum U dissolution was achieved by varying the ‘standard’ parameters with conditions of; 74°C with 5 g/L [H$_2$SO$_4$], 3 g/L [Fe] (510 mV vs Ag/AgCl) for 24 hrs giving 45% uranium dissolution. The authors noted, however, that these samples contained other uranium minerals such as studtite which is significantly more soluble than betafite and hence a proportion of the U dissolution was attributed to the presence if this mineral [2].

In a further study, McMaster et al. (2014) investigated the dissolution of two natural betafite samples over a range of processing conditions. The results of this work showed significant differences in dissolution between the two samples. The conditions under which the maximum amount of uranium was dissolved (~58% U for sample A and 5%U for sample B) were; 100 g/L [H$_2$SO$_4$], 3 g/L [Fe$_{TOT}$], ORP (510 mV vs Ag/AgCl), 35°C, 6 hours. The degree of chemical alteration/weathering was shown to significantly influence the rate of dissolution and in all dissolution tests conducted the more highly altered samples were shown to leach more readily. A decrease in dissolution extent was also shown when annealing of the metamict samples was completed [3]. This was further supported by work conducted in Chapter 3 where it was shown that
the microstructure and composition of natural betafite can vary significantly which results in drastically different leach rates. These variations (in conjunction with the fact that obtaining very high purity natural betafite samples (particularly samples that do not contain other uranium bearing minerals)) make it very difficult to accurately determine the influence of key parameters on betafite dissolution. Hence it was decided to investigate the influence of key parameters on the dissolution of synthetic betafite.

The aim of this chapter is to conduct a systematic study of the parameters that affect the dissolution of uranium from betafite in acid sulfate media and compare leaching trends to those observed previously for natural betafite samples. The approach is to initially prepare a synthetic betafite sample and then to determine the uranium dissolution over a range of time, temperature, \([H_2SO_4]\), \([Fe_{TOT}]\) and redox potential conditions. The dissolution matrix chosen for the current work was selected based on leaching parameters which are commonly varied in a commercial scale uranium leaching circuit.

5.1. Materials & Methodology

5.1.1. Synthesis

The procedure used to prepare synthetic betafite was given in greater detail in Section 4.3.1. Briefly, synthetic betafite was prepared via a solid state reaction between uranyl nitrate, calcium carbonate, titanium dioxide, niobium (V) oxide and tantalum (V) oxide in amounts required to achieve the following stoichiometry; \((U_{0.32}Ca_{0.42})(Nb_{0.41}Ti_{1.78}Ta_{0.10})O_7\). The appropriate metal salts and oxides were dry ground for 20 minutes and then added into a platinum lined alumina boat. The boat was placed in a tube furnace for 48 hours at 1150°C in a dry \(N_2\) atmosphere. Approximately 8 grams of the synthetic material was prepared in multiple batches and dry sieved through a 63 \(\mu\)m sieve prior to use.
5.1.2. Dissolution studies

Dissolution tests were conducted as follows: 250 mL of the desired sulfuric acid concentration was added to a 250 mL three-neck flask. The solution was then agitated using an overhead mechanical stirrer and heated to the required temperature using a heating mantle. Once at temperature, the desired amount of ferric and ferrous sulfate was added to create the required redox potential (ORP) (Table 5.1). The solution was then allowed to equilibrate for 10 min before 0.05 g of <63 µm synthetic betafite was added. The time upon addition of sample was determined to be 0 mins and solution samples were collected at pre-determined intervals throughout the experiment.

Analysis of the diluted leach solution samples were conducted using an Agilent HP 7700 series ICP-MS the instrument was calibrated using commercial uranium, niobium, titanium and tantalum standards. An internal standard containing Sc, Ge, Rh, In, Tb, Lu, Bi, was added to all calibration and test samples. The error in measurement on the instrument was calculated to be ±2.5%.

5.1.3. Pre and post leach characterisation

The following characterisation techniques were used throughout this chapter: X-ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), Multi acid digestion/ICP-MS analysis. The methods that were used with each of these techniques are given in Chapter 2.

5.1.4. Electrochemical leaching of betafite

The method used for electrochemical leaching studies is given in Section 2.2.5.
5.2. Results and Discussion

5.2.1. Overview of dissolution tests

All samples of synthetic betafite were characterised prior to use to ensure no significant impurities were present. An XRD pattern of one of the samples used is presented in Figure 5.1 and shows only a minor amount of rutile present.

The dissolution of synthetic betafite was investigated over a range of conditions with parameters selected to reflect those encountered in commercial scale processing of uranium ores. The specific reaction conditions that were used in the individual dissolution tests that were conducted are given in Table 5.1, which cover the following range of conditions: Temperature (35-95 °C); [H$_2$SO$_4$] (0-50 g/L [0-51 M]); [Fe$_{TOT}$] (0-12 g/L); Redox potential (330-730 mV vs. Ag/AgCl); Fe$^{3+}$ (added in form of F$^-$, Cl$^-$, Br$^-$, PO$_4^{3-}$, NO$_3^-$ and SO$_4^{2-}$ salts); F$^-$ (added in form Na$^+$, K$^+$, NH$_4^+$ salts); and lixiviant (H$_2$SO$_4$, C$_2$H$_2$O$_4$, HCl, CH$_3$COOH, HNO$_3$, HBr, H$_3$PO$_4$).
Table 5.8 Experimental conditions used in the dissolution experiments conducted. For tests 1-20, iron was added in the form of the sulfate salt. * indicates equivalent normalized proton concentration were used for each respective acid.

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<th>Test No</th>
<th>$[\text{H}_2\text{SO}_4]$ (M)</th>
<th>$[\text{Fe}_{\text{tot}}]$ (mM)</th>
<th>Fe$^{3+}$ : Fe$^{2+}$</th>
<th>ORP (mV vs. Ag/AgCl)</th>
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</tr>
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Figure 5.49 X-ray Diffraction pattern of synthetic betaite sample used in leaching experiments.
5.2.2. Dissolution of synthetic betaifite using Rössing uranium leach circuit conditions

An initial dissolution experiment was conducted at similar conditions to those used at the Rössing uranium mine [1]. These conditions were: \([H_2SO_4] = 0.051 \text{ M (5 g/L)}, [Fe_{TOT}] = 53.6 \text{ mM}, Fe^{3+}:Fe^{2+} = 9:1, \text{ Redox Potential} = 520 \text{ mV}, \text{ Temperature} = 35^\circ \text{C (Test 1 in Table 5.1).}

The results of this experiment showed ~0.5% of the total uranium in the sample dissolved in the initial 1 min of leaching (Figure 5.2). Further significant leaching occurred until approximately 30 mins into the dissolution experiment after which time a total of ~1.4%U had been leached. The dissolution rate then decreased significantly remaining essentially constant for the remainder of the experiment. After a total leach time of 6 h, 2.04 ± 0.03 % of the U had been leached.

The extent of leaching observed in the current study was significantly lower than previously observed in Chapter 3 of this document. In Section 3.3.2, leach studies conducted at conditions similar to Test 1 but using three natural betaifite samples with varying degrees of alteration, the %U dissolution was shown to be between 2.61 and 37.3% depending on the degree of alteration in the metamict samples. The very low extent of leaching observed for synthetic betaifite is discussed in detail in subsequent sections.
5.2.3. Effect of Temperature, \([\text{H}_2\text{SO}_4]\), \([\text{Fe}_{\text{TOT}}]\) and redox potential

The dissolution of synthetic betafite was investigated by varying standard leaching parameters (temperature, \([\text{H}_2\text{SO}_4]\), \([\text{Fe}_{\text{TOT}}]\) and redox potential). These parameters were studied as they are the most commonly varied when commercial mineral processing (for conditions see Tests 1 – 20, Table 5.1).

5.2.3.1. Temperature

The influence of temperature on uranium dissolution was investigated by conducting tests at 35, 50, 65, 80 and 95°C (all other parameters were kept constant excluding ORP due to the interrelationship between this parameter and temperature - see Table 5.1, Tests 2-6). Results of the tests are presented in Figure 5.3. The extent of uranium dissolution in these 5 experiments was shown to vary between 1.97% (Test 2 at 35°C) and 2.16% (Test 6 at 95°C) after 6 hrs. Analysis of the leaching data from Figure 5.3 showed that temperature had a noticeable effect with the overall %U dissolution gradually increasing as the leach temperature was increased. Temperature also had a significant
effect on the dissolution rate, particularly in the first 15-20 mins where the greatest rate of dissolution occurred in this period. Beyond this time, the rate of dissolution decreased to a similar extent in all tests.

The kinetics for betafite dissolution most closely fitted a first order rate between the interval 15-75 mins where increasing temperature resulted in an increased dissolution rate. The range between 15-75 mins was chosen for rate kinetic analysis as the dissolution rate was significantly different either side of this range. The differing rates observed over the period of testing are discussed in detail later in the chapter. Within the 15-75 mins time range, an activation energy for betafite dissolution was calculated to be 2.49 kJ mol\(^{-1}\). This value is considerably lower than determined for other synthetic uranium containing minerals under similar conditions (i.e. \([\text{H}_2\text{SO}_4]\), \([\text{Fe}^{3+}]\) and redox potential) to that used in this study (e.g. brannerite - 30.3 kJ mol\(^{-1}\) [4] and uraninite - 15.2 kJ mol\(^{-1}\) (6.7×10\(^{-3}\) M [Fe\(_{TOT}\]) [5]). The activation energy for the synthetic sample is also much lower than the values of 7.64 – 12.42 kJ mol\(^{-1}\) derived for natural betafite samples leached at the same experimental conditions [6]. The differences in activation energy can be attributed to the range of minerals having significantly different structures and compositions, both of which will influence the leaching rate. Moreover, the higher activation energy for the natural betafite samples was most likely due to their amorphous nature and degree of chemical weathering leading to alteration and the formation of other, more easily leached uranium mineral impurities [6].
5.2.3.2. Sulfuric acid concentration

Dissolution studies were conducted to investigate the influence of sulfuric acid concentration on the dissolution of uranium by varying the acid concentration while other parameters remained constant as per Table 5.1. The sulfuric acid concentrations used in these studies were between 0-0.51M (pH 1.81-0.29). The results showed that the total amount of uranium leached over the duration of the experiment increased from 1.91 to 2.12% leached as the sulfuric acid concentrations was increased (Figure 5.4).

Furthermore, in this series, three uranium dissolution segments corresponding to different uranium dissolution rates were observed in a similar manner as observed in Section 5.2.3.1 (Figure 5.3). These can be approximately partitioned into the following time intervals; 0-30, 30-120 and 120-360 minutes.

The initial 30 minutes of reaction had the highest rate of uranium dissolution in all $[H_2SO_4]$ experiments. The leach rate over the initial minute increased as the acid concentration increased –
this change in rate with increasing acid concentration (where the dissolution that occurs is most likely due to oxidised uranium on the surface of the betafite) is consistent with the influence of acid concentration on the dissolution of oxidised uranium. In contrast, the dissolution rate after this initial 1 minute period showed a minor difference in rate was observed for the subsequent 120 minutes of leaching at varying acid concentrations (Figure 5.5). This minor difference was inversely correlated to acid concentration, indicating at lower acid concentration a slightly higher leach rate was observed over the period from 30 to 120 minutes. This was attributed to the slower release of surface oxidised uranium at lower acid concentrations and hence a minor amount of this oxidised uranium was still being liberated from the betafite after 30 minutes of leaching.

After 120 minutes the extent of uranium leached was shown to be ~2.0% in all experiments. Since a similar amount of uranium was leached in all of the experiments in this series, it appears that changing the sulfuric acid concentration does not have an influence on the uranium dissolution rate between 120 – 360 minutes.

This therefore demonstrates that increasing the acid concentration only increases the liberation rate of surface oxidised uranium, and does not increase the overall dissolution rate of uranium once the surface oxidised uranium has been leached from the sample.
Figure 5.52 Effect of $[\text{H}_2\text{SO}_4]$ on the dissolution of betafite over the 360 minute period compared against standard Rossing leach circuit conditions (Test 1). For all other parameters, refer to Table 5.1.

Figure 5.53 Effect of $[\text{H}_2\text{SO}_4]$ on uranium dissolution rate between 0 - 0.51M over the period of 30 – 120 minutes. All other parameters were kept constant as per Table 5.1.
5.2.3.3. **Total iron ([Fe\text{TOT}]\))

The effect of changing [Fe\text{TOT}] on synthetic betafite dissolution is shown in Figure 5.6. All experiments were conducted at a constant Temperature, [H\text{2SO}_4] and ORP – see Table 5.1.

For the test conducted at 0 mM [Fe\text{TOT}] all of the leaching occurred within the initial 1 minute of the dissolution. The uranium concentration then remained constant for the duration of the experiment. This represents the initial solubility of surface oxidised uranium followed by no further dissolution. According to Merritt [7] when the sample is added to the leachant the Fe^{3+}/U oxidation process required to convert the U(V) in betafite to U(VI) cannot occur due to the lack of iron. This demonstrates why no further dissolution was observed after the liberation of the surface oxidation uranium had occurred.

The amount of U leached after 15 mins was indirectly proportional to Fe\text{TOT} concentration; this could indicate that a lower Fe\text{TOT} concentration initially increases the rate of dissolution. Lexan et al. report that for electron transfer between Fe^{3+} and UO_2, complexes such as FeSO_4^{2-} and Fe(SO_4)_2^{2-} are highly effective. An iron sulfate speciation diagram reported in their study showed that at ~44.6-89.3 mM [Fe\text{TOT}] (i.e. for tests 3, 12, and 13) these complexes for electron transfer are more likely to be present [8]. Thus the higher rate of dissolution for experiments conducted with lower [Fe\text{TOT}] over the initial 15 minutes could be due to a faster rate of electron transfer between U species and the iron/sulfate matrix via FeSO_4^{2-} and Fe(SO_4)_2^{2-} complexes as well as the dissolution of surface oxidised uranium. Although any trends observed due to these aforementioned effects were demonstrated to be quite minor and therefore hard to determine the true cause for these results. In each of the experiments conducted with iron present the leaching yield was shown to increase until approximately 120 minutes. Beyond this point the amount of uranium leached remained consistent at ~2.1% for the remainder of the experiment duration.

Rate kinetic data calculated for the interval 15-75 minutes most closely followed a first order rate with the exception of the 0 mM [Fe\text{TOT}] experiment (Figure 5.7). These rates were shown to very
roughly increase as the \([\text{FeTOT}]\) increased until the maximum rate of \(5.60 \times 10^{-3} \text{ mol}^{-1}\) was observed at 107.1 mM \([\text{FeTOT}]\) (Test 14). It is important to note that the increasing trend in dissolution rate as \([\text{FeTOT}]\) increases is only observed up until 107.1 mM, beyond this point no increase in dissolution rate are displayed over the conditions studied.

Figure 5.54 Effect of \([\text{FeTOT}]\) as iron (II,III) sulfate salts of the dissolution of betafite over a 360 min period. All other parameters were kept constant as per Table 5.1.
Redox potential

Five experiments were conducted to investigate the influence of redox potential on betafite dissolution. A range of Fe$^{3+}$/Fe$^{2+}$ ratios were used (ranging from 0:1 (330 mV vs. Ag|AgCl) to 1:0 (610 mV)) while the [Fe$_{TOT}$] was kept constant.

As the ratio of Fe$^{3+}$/Fe$^{2+}$ was increased, the amount of U dissolved was mostly increased (Figure 5.8). The results of the 420 and 475 mV experiments (Tests 18 & 19) showed a significantly lower amount of U leaching in the initial minute of dissolution relative to the other experiments conducted. Ram et al. describe lower dissolution of UO$_2$ at redox potentials of 470 mV due to excess sulfate present leading to the formation of less reactive iron sulfate complexes [9]. This would result in less sulfate ligands that are available to form the soluble uranyl sulfate species which is liberated from the betafite structure. At the end of the 360 minute period both Tests 18 & 19 still had a very slight positive rate of U dissolution, indicating that the extent of dissolution had not reached a maximum.

The two dissolutions conducted at the highest redox potential showed that 2.1% dissolution of uranium was achieved in both cases although when the ORP was 610 mV the dissolution reached a
maximum within 15 minutes, whereas at 560 mV it took approximately 90 minutes to reach a similar point.

Note however, that Test 17 conducted at 330 mV (~100% Fe²⁺) showed no increase in dissolution from ~15 minutes onwards. Although auto-oxidation of Fe²⁺/Fe³⁺ will occur, the duration it takes to reach equilibrium at the acid concentrations and temperature used is significantly longer than the duration of the experiment and hence any influence of Fe³⁺ oxidation of uranium was most likely negligible [10]. It can be therefore assumed no redox oxidation takes place and hence the dissolution amount can be attributed to the presence of surface oxidised U(VI).

Figure 5.56 Effect of redox potential (ORP) on the dissolution of synthetic betafite over a 360 minute period. All other parameters were kept constant as per Table 5.1.

5.2.3.5. Influence of particle size

The influence of particle size was investigated by conducting experiments at various particle size fractions. These size fractions were obtained by dry sieving the synthetic betafite sample through sieves of varying size then leached at the conditions given in Table 5.1. Similar dissolution curves to those previously described in Sections 5.3.3.1-4 were observed. In all cases, rapid dissolution of
uranium occurred in the initial minute of leaching. The extent of leaching over the initial period was shown to be influenced by the particle size of the sample where decreasing the particle size increased the initial dissolution until the particle size was less than 63 µm.

After the initial dissolution period the dissolution rate was observed to slow down until approximately 120 min where almost no further leaching was observed. These dissolution curves are similar to those observed previously and discussed in more detail in Section 5.3.2.

The results presented in Figure 5.9 shows the largest particle size experiment conducted was shown to only dissolve 0.80 % of the U from betafite over the 360 minute experiment. As the particle size was decreased the extent of dissolution increased. This trend was similar to the initial leaching extent discussed previously, where the three experiments conducted at the smallest particle sizes (38-63 µm, 20-38 µm and <20 µm) showed similar leaching curves and extents of dissolution of approximately 2.10%. This indicates that the influence of particle size is only important up until the particle size is <63 µm.

The results of this work showed as the particle size decreased from 106 to 63 µm a greater amount of U was observed to have leached. As the particle size was decreased beyond 63 µm a very minor influence in particle size was observed, indicating that the predominant mechanism influencing dissolution was no longer controlled by the number of active sites. It was therefore hypothesised that the controlling factor of leaching at the smaller particle sized was passivation. As the oxidised uranium leaves the mineral the insoluble Nb, Ti, Ta remain meaning that sub surface uranium becomes less exposed to the solution due to a Nb, Ti, Ta passivation layer further hindering dissolution. As the experiment continues the dissolution rate stops, this point occurs earlier in the experiments at larger particle sizes as there is less active dissolution sites available and hence complete passivation of these sites occurs more quickly.
5.2.4. Effect of Fe counter ion, fluoride ion and lixiviant

5.2.4.1. Fe counter ion

The influence of different Fe counter ions (SO₄²⁻, NO₃⁻, PO₄³⁻, Br⁻, Cl⁻ and F⁻) on betafite dissolution was investigated under the following conditions: 53.6 mM [Fe_{TOT}], 9:1 Fe³⁺:Fe²⁺ (560 mV ORP) T = 95°C. The different counter ions that were investigated were chosen as they are commonly found in gangue minerals (and/or leached from gangue minerals) typically associated with uranium-containing ores.

The dissolution results presented in Figure 5.10 show similar extents of dissolution were obtained when different Fe counter ions were used, except in the case of fluoride where the use of FeF₃ increased the uranium dissolution significantly. In general, a weak trend showed higher dissolution was observed over the initial minute for iron halides; bromide, chloride and fluoride than for the oxyanions; sulfate, nitrate and phosphate. The redox potential was shown to be lower with iron halide salts than the oxyanions. This demonstrates the higher rate of dissolution over the initial period is not due to a higher oxidation potential in the solution and is most likely due to
monodentate halides forming more reactive complexes in solution compared to the bidentate or polydentate oxyanions [8, 11]. It is important to note that although the iron chloride test (Test 27) does slightly decrease in U concentration over the initial 30 minute period, this decrease was within experimental error.

The results from Test 29 showed the effect of iron phosphate on U dissolution resulted in a lower dissolution rate over the initial 120 minute followed by a similar extent of leaching relative to iron sulfate leaching discussed previously. Nicol et al. reported electrochemical studies on the influence of PO$_4^{3-}$ on the dissolution of UO$_2$. They report complexes FeH$_2$PO$_4^{2+}$ and FeHPO$_4^+$ were shown to be more reactive than Fe$^{3+}$, FeOH$^{2+}$ and Fe$_2$OH$_4^{4+}$ complexes [12]. Although the more highly reactive complexes occur, the underlying insolubility of FePO$_4$ (shown by the significant amount of precipitate in the leach solution), negated any influence these complexes had on the uranium dissolution. Moreover, the slower rate of dissolution over the initial 120 minutes was assumed to be due to the betafite grains acting as seeds for the precipitation of FePO$_4$ and hence passivating the surface temporarily and resulting in limited active sites available for leaching.

The effect of nitrate on uranium dissolution was shown to have no substantial impact (Figure 5.10 Test 30). Ram et al. examined the effect of NO$_3^-$ on the dissolution of uraninite and showed that increasing the concentration of NO$_3^-$ increased the rate of UO$_2$ dissolution. This was attributed to the increase in redox potential due to oxidation of Fe$^{2+}$ from NO$_3^-$. Moreover the excess NO$_3^-$ could form uranyl nitrate complexes with the solubilized UO$_2^{2+}$ [9]. Although this had a positive influence on dissolution of uraninite, the influence of the aforementioned factors were shown to have negligible effect on betafite dissolution.

While the effect of iron halides had a positive effect on U dissolution from betafite over the initial 30 minutes, it is known that the initial rate of dissolution for the anions studied can be influenced by several factors. These include the reactivity of the species formed at the Fe$^{3+}$/Fe$^{2+}$ ratios and [Fe$_{TOT}$] studied, the redox potential effect of the anion ligand, the stabilized complexes formed with the
uranyl ion, the solubility of the Fe salts and their stability constants [8, 9, 11-13]. For this reason deducing the influence of the Fe counter ion is significantly difficult in this limited data set. All dissolution experiments conducted except F showed the dissolution rate remained constant after approximately 45 mins. This was most probably due to causes explained previously for the effects of acid strength, [Fe$_{TOT}$], T and ORP; U(IV) from active surface sites is readily solubilised whereas U(IV) within the bulk pyrochlore structure remains insoluble (Sections 5.2.3). This structure is impenetrable by the solution and hence any differences caused by the counter ion are negated by the diffusion controlled reaction.

The influence of fluoride counter ion showed similar instantaneous dissolution followed by increasing dissolution over the duration of the experiment where approximately 4.5% of the uranium was dissolved. Solubility of niobium, titanium and tantalum has been shown to only occur in acidic fluoride solutions [13, 14]. Moreover, Kabangu and Crouse showed >50% dissolution of Nb and Ta oxides can be achieved using a 2 M sulfuric acid/ammonium fluoride salt solution [15]. Analysis of the leach solution showed dissolution of Nb, Ti, Ta had occurred when fluoride was added. This demonstrates that most likely HF generated from the fluoride counter ion dissolves the Nb, Ti, and Ta from the mineral and hence allows more U to be exposed to the solution and enabling it to be solubilised.
5.2.4.2. **Fluoride ion**

Three fluoride salts were used to further investigate the influence of fluoride on the dissolution of betafite. The fluoride salts chosen were NaF, KF and NH₄F which were added at levels sufficient to generate 0.5 M F⁻ concentrations in each experiment. Experiments were conducted using the different fluoride salts with either 53.6 mM Fe (as the sulfate salt) or no Fe added. The results of these experiments are presented in Figures 5.11 and 12 and both series of experiments show the addition of fluoride has a positive influence on uranium dissolution with a greater extent of dissolution observed in all tests as compared to tests conducted under the same conditions with no F present. When fluoride was added to the iron-containing leach solution the results showed 2.6, 3.25 and 3.25% of the U was leached for the experiments conducted with NaF, KF and NH₄F respectively (Figure 5.11, Tests 32-34). Furthermore, when fluoride was added to the leaching system with no iron present, the dissolution rate was shown to still be positive after the final 360 minute sample was taken (Figure 5.12).

The U dissolution observed over the initial 30 minute period was shown to be due to the liberation of surface oxidised uranium in the same was as observer previously in Section 5.2.3. Additional
dissolution which was observed was due to the presence of fluoride ions which was formed from
dissociation of NaF into F⁻ ions. These ions then generate HF in situ in the acidic solution (Equation
5.1) which caused the dissolution of Nb, Ti and Ta, and hence allowed more uranium to be exposed
to the solution surface and hence undergo dissolution. Over time, the HF most likely reacts with Fe³⁺
forming more stable and less reactive complexes (e.g. Equation 5.2) leading to a gradual decrease in
the dissolution rate [16] although the magnitude of which is difficult to determine. For this reason it
was assumed that the dominant factor which resulted in the slowing in leaching rate observed is
most likely caused by passivation of the mineral surface instead of the formation of less reactive iron
fluoride complexes.

\[ 2NaF + H_2SO_4 = 2HF + Na_2SO_4 \quad (5.1) \]
\[ 3HF + Fe^{3+} = FeF_3 + 3H^+ \quad (5.2) \]

Ferric fluoride (FeF₃) will preferentially form when ferric sulfate is added to a dilute hydrofluoric acid
solution [17]. Moreover, the octahedral Fe³⁺ complexes with fluoride and H₂O ligands stabilise the
ferric iron and hence direct Fe³⁺/U⁴⁺ oxidation is less likely to occur. Levanon et al. (1969) reports
species [Fe(H₂O)₂F₃]⁻ and [Fe(H₂O)F₄⁻] are likely to be present at the 1.02 M sulfuric acid
concentration and ~9.3 : 1 F/Fe ratio used in this experimental series [11]. This explains the lower
extent of dissolution when iron is present in comparison to experiments conducted with no iron
present (Figures 5.11 and 12).

When no iron is present in the system the formation of the ferric fluoride complexes does not occur.
Therefore the greater extent of dissolution is primarily due to the formation of a greater amount of
hydrofluoric acid since no competing complication with iron occurs. Niobium, titanium and tantalum
are known to be easily dissolved in HF [18]. It can be therefore assumed that the increase in
dissolution compared to sulfuric acid/iron sulfate dissolution is due to increased Nb, Ti and Ta being
leached in the HF solution, causing more uranium to be exposed to the solution allowing more U
dissolution. It is important to note that even though the group 4 and 5 metals are dissolving, the rate of their dissolution also slows throughout the experiment indicating that some degree of passivation occurred. This shows that the higher rate of uranium dissolution was not due to congruent dissolution of $B$ site metals in the beta-fite structure and hence indicated that the dissolution mechanism is still quite similar to those previously discussed, where the uranium dissolution is more heavily influenced by the solid/liquid interface reactions through a series of ligands exchange allowing effective electron transfers to solubilise the uranium.

The type of fluoride salt used also had an effect on the dissolution rate of uranium. Over the initial 30 minutes NaF showed a higher U solubility rate when either iron or no iron was present. This was assumed to be due to the NaF dissociating into HF at a quicker rate than the other two fluoride salts used. Experiments conducted with 53.6 mM ferric iron present showed the dissolution rate when KF or NH4F were added stayed relatively consistent after ~30 minutes, whereas when sodium fluoride was added almost no increase in dissolution was noted beyond 60 minutes. This is most likely due to the aforementioned less reactive ferric fluoride complexes $[\text{Fe(H}_2\text{O)}_2\text{F}_3]$ and $[\text{Fe(H}_2\text{O)}\text{F}_4]$ forming preferentially, which have been shown to reduce the rate of dissolution [9]. When no iron is present, the dissolution rate remained relatively constant after the initial 30 mins in all three fluoride salt experiments conducted. The highest extent of U dissolution occurred when 0.5 M ammonium fluoride was added. The redox potential when ammonium fluoride was added was ~650 mV whereas for NaF and KF it was ~620 and ~630 mV respectively. This indicates that the added dissolution was not due to any substantial change in redox potential. It was therefore assumed that the cause of the higher rate of dissolution when NH₄F was present was due the salt being known to be a weak acid.
5.2.4.3. **Lixiviant**

The influence of lixiviant was studied to investigate the effect of the conjugate base on uranium dissolution. In this experimental series the proton equivalent of 0.51N (1.02M) $\text{H}_2\text{SO}_4$ for the respective acids was used (Figure 5.13).
The results show the majority of the mineral acids used resulted in a dissolution curve similar to that observed previously (Figure 5.4). The amount of dissolution observed in these experiments roughly followed a similar trend to the acid dissociation constants (lower pKa = greater dissolution; values are given in the figure legend). Sulfuric acid however caused a higher rate of dissolution than the other acids used even though it has the 3rd highest pKa. This was most likely due to the increased concentration of the sulfate oxo-anion which reacts with iron and forms the more reactive iron sulfate complexes, FeSO₄⁺ and Fe(SO₄)₂⁻, which increase the rate of dissolution.

Phosphoric acid produced the lowest rate and amount of U dissolution from betafite. Other dissolution experiments conducted showed the majority of the dissolution occurs in the initial 45 minutes, whereas this point occurred significantly later in the experiment with phosphoric acid. Phosphoric acid reacts with Fe³⁺ to form insoluble FePO₄ which decreases the redox potential and prohibits the Fe³⁺/U⁴⁺ oxidation reaction (Equation 5.3) [19].

\[
2H₃PO₄(aq) + Fe₂(SO₄)₃(aq) = 2FePO₄(s) + 3H₂SO₄(aq)
\]  (5.3)

In this experiment the slow rate of dissolution over the initial period is most likely due to solid betafite particles seeding the precipitation of the sparingly soluble FePO₄ (which was confirmed via XRD). Over the duration of the experiment however, FePO₄ will dissolve and re-precipitate allowing newly exposed un-leached areas of the sample to undergo dissolution. The maximum dissolution (\(~1.3\%U\)) was reached after approximately 120 minutes. This was significantly lower than in the other experiments since the solution contained excess \([H₃PO₄]\) relative to \([Fe₂(SO₄)₃]\) (0.34 mol, 0.053 mol respectively) and therefore the majority of the ferric iron would have precipitated as FePO₄. This inhibits the redox process from occurring and hence the only uranium dissolved is the surface oxidised uranium which does not need to undergo oxidation before dissolution. Huang et al. showed the precipitation of FePO₄ occurred quicker when a seeding compound was added to the phosphate containing effluent [20]. It was assumed a similar mechanism occurred in this dissolution experiment where betafite acted as the seed; although confirming that FePO₄ had coated the
surface was difficult due to the vast excess of FePO₄ precipitate with respect to betafite in the leach solution.

The amount of uranium dissolution was observed to be 50% less when oxalic acid was used for dissolution relative to sulfuric acid. The majority of the dissolution occurred in the initial minute of the dissolution indicating that the uranium species present did not need to undergo oxidation in order to become soluble. Oxalic acid is known to be a reducing agent and forms insoluble Fe²⁺ and Fe³⁺ salts [FeC₂O₄ and Fe₂(C₂O₄)₃] [19]. Moreover, soluble ferrioxalate ion [Fe(C₂O₄)₃]³⁻ will form when Fe²⁺ reacts with oxalic acid [21]. Initially, no precipitate was observed indicating that the iron was present as [Fe(C₂O₄)₃]³⁻, [Fe(C₂O₄)₂]²⁻ complexes or [Fe₂(SO₄)₃]. These soluble ferric species will be used in the redox process to solubilise the uranium. The results show a very similar dissolution curve to that conducted with 53.6 mM ferrous iron (Figure 5.8, Test 17) where no Fe³⁺ was present and hence the U/Fe³⁺ oxidation does not take place. This suggests that the reduction of Fe³⁺ by C₂O₄²⁻ has occurred and hence no oxidation of U follows which results in the small amount of uranium dissolved.
Figure 5.61 Effect of varying the lixiviant on the dissolution of synthetic betafite over a 360 minute period. Experiments were conducted with different acids at equivalent proton concentration relative to 1.02 M H$_2$SO$_4$ (0.51 N). All other parameters’ were kept constant as per Table 5.1.

### 5.2.4.4. **Influence of surface re-oxidation**

Based upon previous investigations in the preceding sections, the betafite appears to be passivated beyond a period of 120 minutes, with minimal U dissolution observed beyond this period. Therefore, these tests were conducted to determine if exposing the surface of the residues to air would lead to further leaching (as based on the previous results showing surface uranium exposed to air leached readily). Repeated leach tests were run on subsequent residues obtained to ascertain whether surface re-oxidation would result in further leaching. This was conducted via three experiments conducted at varying conditions. In each experiment five successive leaching tests were conducted at the conditions given in Table 5.3 in order to investigate the influence of drying the leach residues in different gas atmospheres as well as increased acid concentration.
Table 5.9 Experimental leach conditions for surface re-oxidation re-leaching experiments.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>[H\textsubscript{2}SO\textsubscript{4}] (M)</th>
<th>[Fe\textsubscript{TOT}] (mM)</th>
<th>Fe\textsuperscript{3+}:Fe\textsuperscript{2+}</th>
<th>ORP (mV)</th>
<th>Temperature (°C)</th>
<th>Particle size (µm)</th>
<th>Drying atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>0.153</td>
<td>107.1</td>
<td>9:1</td>
<td>560</td>
<td>50</td>
<td>&lt;75</td>
<td>Air</td>
</tr>
<tr>
<td>46</td>
<td>2.04</td>
<td>214.2</td>
<td>1:0</td>
<td>610</td>
<td>50</td>
<td>&lt;75</td>
<td>Air</td>
</tr>
<tr>
<td>47</td>
<td>2.04</td>
<td>214.2</td>
<td>1:0</td>
<td>560</td>
<td>50</td>
<td>&lt;75</td>
<td>N\textsubscript{2}</td>
</tr>
</tbody>
</table>

The results of the initial test shows a similar dissolution curve to those obtained previously under the same conditions (Test 45, Figure 5.14). Of the 500 mg of betafite added in initially in the aforementioned test approximately 400 mg was recovered and used for the following experiment. As multi elemental analysis was conducted and showed negligible Ca, Nb, Ti and Ta in solution, this loss was determined to be due mostly due to unrecoverable fines which were visually observed.

After the recovered sample was dried for 2 hours in air, re-leaching of the post leached residue was conducted. The results of this showed a further 0.1% uranium had leached from the residue of the previous experiment (Test 45B-D). In the following 3 experiments, releaching of the dried leach residue from the previous experiments showed a similar trend where a further ~0.1% of the U was leached in each successive experiment. After the 5\textsuperscript{th} re-leaching experiment (Test 45E) the sample was left to dry for a period of 24 hrs before the final experiment was commenced. In the final releaching experiment a further 1.3% of the U was leached from the 5 times releached betafite sample (leading to 4% of the total uranium present leached over the successive leaching experiments.)

The dissolution curves in each experiment showed the majority of the dissolution occurred in the initial minute of leaching demonstrating that the dissolution was due to liberation of surface oxidised uranium which will be described in further detail in Section 5.3.6. The amount of uranium leached from the sample in each experiment was consistent when the sample was dried for the
same period of time. Moreover when the sample was left to dry for 24 hours significantly more
dissolution was observed. This demonstrates that the leaching of uranium can be roughly correlated
with the time the sample was dried; indicating that it is likely that structural or chemical changes
that occur in the dried samples cause the increase in dissolution yield. This will be explained in more
detail in subsequent sections.

Figure 5.62 Successive releaching of synthetic betafite experiment. Each residue was dried in air for a period of time
between releaching experiments at identical conditions given in Table 5.2.

The results of the experimental Test 46 (Figure 5.15) conducted at 2.04 M $[\text{H}_2\text{SO}_4]$ showed the initial
test in the series had a greater amount of dissolution when compared with the initial leach in the
Test 45 experimental series which was conducted at 0.153 M $[\text{H}_2\text{SO}_4]$ (Figure 5.14, Test 45). This is
consistent with the findings discussed in Section 5.3.3.2 where increasing the acid concentration was
shown to lead to greater U dissolution. The successive re-leaching tests showed similar results to the
previous experimental series; although the amount leached in each dissolution experiment was
slightly higher due to the aforementioned acid influence. This led to approximately 0.5% more
uranium leached compared to the previously discussed experimental series.
The final experiment in the experimental series (Test 47) was conducted at the same conditions to Test 46 ([H$_2$SO$_4$] = 2.04 M, [Fe$_{TOT}$] = 214.2 mM, Fe$^{3+}$:Fe$^{2+}$ ratio = 1:0, ORP = 610 mV, Temperature = 50 °C). The extent of dissolution after the initial 120 minute experiment was shown to be the same as the previous experiment. This sample was then dried in a nitrogen atmosphere between each successive leach experiment. The amount of dissolution in each case was shown to be significantly less than when the sample was dried in oxidising conditions (Figure 5.16). This demonstrates that drying the samples under oxidising conditions most likely led to oxidation of the sample and hence a greater amount of dissolution.
Figure 5.64 Successive releaching of synthetic betafite experiment. Each residue was dried in N₂ for a period of time between releaching experiments at identical conditions given in Table 5.2.

When the total time the residue is exposed to the respective atmosphere is plotted against the total amount of U leached the results show a linear trend (Figure 5.17) indicating that oxidation of uranium occurred at a constant rate in the dried betafite samples. The extra dissolution that was shown to occur in the initial minute could be due to destabilisation of the mineral structure once water has evaporated from the sample in the same way that was reported by Lumpkin and Ewing for natural betafite sample [22], or oxidation of the dried mineral. The above mentioned results indicate the latter as no further dissolution was observed when the sample was dried in an inert atmosphere. In supporting work by Gorman-Lewis complex uranium minerals such as uranium carbonate and silicates were shown to undergo oxidation when exposed to air for a brief period of time [23].
5.2.5. Influence of Thermal pre-treatment

5.2.5.1. Thermal pre-treatment characterisation

The influence of pre-treatment was conducted in order to determine whether a high temperature oxidation or reduction step would aid in uranium recovery for synthetic betafite. In this experimental series pre-treatment of the synthetic betafite was conducted in 2 gas atmospheres (oxidising and reducing). This was completed by separately heating the synthetic betafite to 1150 °C in air and 5%H₂/95% Ar for 2 hours respectively.

X-ray characterisation was conducted on the annealed product and presented in Figure 5.18. The diffraction patterns for the annealed samples show very little change to the sample when sintered at 1150 °C in air. X-ray diffraction lines for this sample showed the sample was predominantly betafite, with minor amounts of rutile and pyrochlore (Ca₂Nb₂O₇). The diffraction pattern of the sample sintered at the same temperature in 5% H₂/Ag shows the sample contained predominantly betafite with minor amounts of pyrochlore, rutile and 2 other reduced uranium minerals uranmicrolite [(Ca,U)₂Ta₂O₇] and uraninite (UO₂).
Figure 5.66 X-ray diffraction pattern of the untreated, sintered in air, and sintered in H$_2$/Ar samples. ICDD JCPDS XRD database for other phases identified in the sample are included for comparison. Betafite [(U,Ca)$_2$(Nb,Ti,Ta)$_2$O$_7$.xH$_2$O] (PDF 008-0300), Pyrochlore [Ca$_2$Nb$_2$O$_7$] (PDF 073-0597), Rutile [TiO$_2$] (PDF 034-0180), Uranmicrolite [Ca, U]$_2$Ta$_2$O$_6$OH] (PDF 043-0693) and Uraninite, syn [UO$_2$] (PDF 009-0206).

Dissolution studies were conducted on the thermally treated betafite samples. The conditions studied were chosen to investigate two main parameters: sulfuric acid concentration and iron concentration. These two parameters were chosen as there alteration were demonstrated to have the most substantial influence on betafite dissolution of any of the standard parameters studied. The specific conditions used for this experimental series are given in Table 5.4.
Table 5.10 Experimental leach conditions used for thermal pre-treatment experiments

<table>
<thead>
<tr>
<th>Test No</th>
<th>$[\text{H}_2\text{SO}_4]$ (M)</th>
<th>$[\text{Fe}_{TOT}]$ (mM)</th>
<th>$\text{Fe}^{3+} : \text{Fe}^{2+}$</th>
<th>ORP (mV vs Ag/AgCl)</th>
<th>Temperature (°C)</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>48</td>
<td>0</td>
<td>53.6</td>
<td>9:1</td>
<td>N/A</td>
<td>50</td>
<td>Unheated</td>
</tr>
<tr>
<td>49</td>
<td>0</td>
<td>53.6</td>
<td>9:1</td>
<td>N/A</td>
<td>50</td>
<td>$\text{H}_2/\text{Ar}$</td>
</tr>
<tr>
<td>50</td>
<td>0</td>
<td>53.6</td>
<td>9:1</td>
<td>N/A</td>
<td>50</td>
<td>Air</td>
</tr>
<tr>
<td>51</td>
<td>0.51</td>
<td>53.6</td>
<td>9:1</td>
<td>520</td>
<td>50</td>
<td>Unheated</td>
</tr>
<tr>
<td>52</td>
<td>0.51</td>
<td>53.6</td>
<td>9:1</td>
<td>520</td>
<td>50</td>
<td>$\text{H}_2/\text{Ar}$</td>
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</tbody>
</table>

5.2.5.2. Influence of sulfuric acid on sintered betafite

The results from the tests on the influence of thermal pre-treatment on betafite dissolution are presented in Figure 5.20. Similar dissolution curves were observed between the untreated and annealed in air samples indicating that no chemical alterations occurred which changed leachability of the sample. This was most likely due to the high resistivity to high temperatures once synthesis of betafite had occurred.

Dissolution experiments conducted on the betafite heated under $\text{H}_2/\text{Ar}$ showed similar dissolution occurred in the initial minute of leaching with respect to the untreated betafite samples. The leach rate was shown to be greater over the initial 30 minutes of leaching relative to the unheated
experiment (Figure 5.19). Beyond this point the dissolution rates for the H₂/Ar and unheated experiment were shown to be similar, although due to a greater rate of leaching in the initial 30 minutes observed in the H₂/Ar sample this sample showed a significantly greater extent of leaching overall. This added dissolution was assumed to be due to the presence of uranmicrolite and uraninite which have been shown to have greater leachability than betafite [12, 24, 25].

Similar dissolution results were observed when leach experiments were conducted using a higher acid concentration (0.51 M [H₂SO₄]). In the experiments a very similar dissolution curve was noted between the untreated and air heat treated samples. As previously discussed this is indicative of very little chemical change occurring in the sample when heat treatment was conducted.

The experiment conducted with the sample sintered under a reducing atmosphere showed in the initial minute approximately 2% of the uranium leached from the mineral matrix. After this period the dissolution showed a consistent rate from ~20 minutes onwards (Figure 5.20). After the completion of the 120 minute experiment ~5.1% U was observed to be leached. This steady rate of dissolution between 15 – 120 minutes was attributed to the more soluble uranium pyrochlore microlite being present in the sample. In the untreated experiments discussed previously the high
rate of leaching initially was shown to be due to surface oxidised uranium in the sample. When the sample was heated in a reducing atmosphere at high temperature this oxidised uranium would have been reduced and hence no high rate of initial dissolution should have been observed. However, this experiment showed approximately double the amount leaching in the initial minute relative to the untreated betafite. This greater amount of initial dissolution is most likely due to the dissolution of the more reactive uranium containing minerals uraninite initially which was observed to be present via XRD (Figure 5.19).

Figure 5.68 Influence of sintering in various atmospheric conditions with 0.51 M sulfuric acid present. Experimental conditions were given in Table 5.3.

5.2.5.3. Influence of total iron concentration

Dissolution studies were also conducted with no iron added into the system. This was completed to investigate whether the extra dissolution observed was due to liberation of already oxidised uranium or oxidation of uranium through the ferric oxidation mechanism discussed previously. The results of this experimental series show similar results to those reported in the acid experiments previously (Figures 5.19 and 5.20) where similar dissolution amounts were reported for both the untreated and sintered air samples. The reason for this was discussed in more detail in Section 5.3.3.3 (influence of iron on U dissolution). The dissolution experiment conducted on the sintered
sample in reducing conditions showed a similar amount of uranium leached over the initial minute as the other two leaching experiments in this series (Figure 5.21). Beyond this point U dissolution increased steadily for the remainder of the experiment. This steady rate was attributed to chemical changes when the sample was annealed leading to the formation of uraninite and uranmicrolite. Although no ferric iron was present to be used in oxidation of the sample it was assumed that the high [H$_2$SO$_4$] (0.51 M) would be sufficient to liberate uranium from the more soluble uraninite and uranmicrolite minerals [5].

![Graph showing the influence of sintering in various atmospheric conditions with no iron present.](image)

**Figure 5.69** Influence of sintering in various atmospheric conditions with no iron present. Experimental conditions were given in Table 5.3.

Experiments conducted with 0.51 M [H$_2$SO$_4$] and 214.3 mM [Fe$_{TOT}$] on the synthetic samples heated under the aforementioned gas atmospheres were presented in Figure 5.22. Once again similar dissolution results for the untreated and air sintered samples were observed. These results have been discussed in further detail previously in the chapter (Section 5.3.5.2).

The dissolution curve for the sample sintered under a reducing atmosphere showed substantially more U leached over the initial minute relative to the untreated sample. Since this initial leach amount was greater than that reported in Figure 5.9 (53.6 mM [Fe$_{TOT}$]) it can therefore be attributed...
to dissolution caused through ferric oxidation which has been shown to occur at faster rates at higher iron concentrations in minerals such as uraninite [26]. A fast rate of U dissolution was observed for the following 20 minutes before the rate slowed to a similar rate to that observed in the untreated and air sintered samples. At this point it was assumed that all of the more soluble uranium containing betafite decomposition products such as uraninite and uranmicrolite had leached leaving only betafite in the sample to be leached and hence a very slow dissolution rate was observed.

Figure 5.70 Influence of sintering in various atmospheric conditions with 214.3 mM [Fe₅OT₄³⁺] present. Experimental conditions were given in Table 5.3.

5.2.6. Discussion of dissolution

In experiments to determine the solubility of betafite under varying conditions, similar uranium dissolution curves were observed for the majority of the tests. The dissolution curves were typically comprised of three relatively distinct regions, which are described below and shown in Figure 5.23.

1. 0-1 mins: A period of initial rapid leaching which accounts for the majority of the dissolution of uranium (~80% of the total dissolution). In each experiment ~1.8% of the uranium in the sample was leached out in the initial minute (segment 1). This instantaneous dissolution is proposed to be
due to the liberation of oxidised surface uranium U(IV) from the sample (or in some cases due to the presence of any non beta-fite uranium containing compounds such as UO₂).

2. 1-120 mins: A very slow dissolution rate interval that continues to slow until ~90 minutes. Of all periods, this was the one where changes in dissolution rate were most closely influenced by variations in experimental conditions. The second segment of dissolution was most likely due to the more traditional ferric oxidation/sulfate liberation reactions.

3. 120-360 mins: No further leaching occurs – zero rate of uranium dissolution (120-360 mins). The third segment showed very little dissolution in most cases. By this stage it is likely that the surface of the beta-fite has become passivated. A passivation layer is most likely caused by dissolution of the exposed uranium sites leaving behind a uranium-depleted layer which is impermeable to the leach solution. In a mineral such as UO₂, stoichiometric release of the oxidised uranyl ion leaves the structure allowing new exposed uranium sites to be available for oxidation.

In the synthetic beta-fite sample there are two possible explanations for this low yield of leaching. The first explanation is as the oxidised uranium leaves the mineral structure the insoluble metals Nb, Ti and Ta remain causing the new uranium sites to become less exposed to the solution. The other explanation is leaching and re-precipitation of the sparingly soluble metals Nb, Ti and Ta could be forming an insoluble layer coating the beta-fite and hence creating a passivation layer. This therefore limits the leaching by creating a diffusion controlled mechanism between 1-120 minutes which is discussed in the previous results sections. This dissolution rate approaches zero due to two possible factors. These factors include:

- The overall change in the speciation of uranium as dissolution occurs.
- Passivation due to re-precipitation of semi soluble group 4 and 5 metals or structural rearrangement of mineral once some uranium has been liberated.
Figure 5.71 The 3 segments of dissolution observed for uranium dissolution from betaite (using Test 3 as an example). Segment 1: 0 – 1 minutes (yellow), segment 2: 1 – 120 minutes (green), segment 3 120 – 360 minutes (blue). Dissolution was conducted at 0.51M \([\text{H}_2\text{SO}_4]\), 50°C, 53.6mM \([\text{Fe}_{\text{TOT}}]\), 9:1 \(\text{Fe}^{3+}:\text{Fe}^{2+}\) ratio, redox potential 520 mV.

In order to investigate the cause of the high rate of dissolution in the initial 0-1 minute segment, pre- and post-leach characterisation by X-ray Photoelectron Spectroscopy (XPS) was conducted in order to investigate the oxidation state(s) of the uranium. Work presented in Section 4.3.2.1 showed that pre-leached synthetic betaite contained predominantly U(V) with a small amount of U(VI) which was assumed to be derived from surface oxidation [27] (Figure 4.4).

Post leach residue XPS analysis on the Test 3 residue was conducted to determine whether the U(VI) present in the pre-leached sample had been removed from the surface. Test 3 was chosen for post-leach analysis because the sample had undergone the 3 stages of uranium dissolution previously discussed (Figure 5.23).

Analysis of the \(\text{U}^{4f_{5/2}}\) satellite peaks show both hexavalent and pentavalent uranium is present in the post leach sample (Figure 5.24). In each sample the peak intensities were normalized with respect to the C1s peak. When a comparison is made between the pre- and post-leached samples it can be seen that the \(\text{U}^{4f_{5/2}}\) peak which corresponds to U(VI) is larger relative to the same peak in the post-
leached sample. Qualitative comparison between the peak intensities show the U(VI) approximately halved in the post leach sample, indicating that significant U(VI) has been leached (Table 5.2). It can therefore be assumed that this loss in U(VI) from the post leach sample corresponds to the initial fast liberation step betafite undergoes in the initial minute of dissolution.

Using the normalised, deconvoluted U4f5/2 peak intensities measured for each sample it can be noted there is a 13% decrease in the U4f5/2 peak sum for the post leach sample. This indicates qualitatively that there is ~13% less uranium in the 8-10 nm surface depth analysed in the post leach sample when compared to the pre-leached betafite.

<table>
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<th>Post-leach</th>
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<td></td>
</tr>
<tr>
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<td>92.1 (11650)</td>
</tr>
<tr>
<td>U4f5/2 U6+</td>
<td>20.7 (3000)</td>
<td>7.9 (1000)</td>
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<tr>
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<td>25.1 (470)</td>
<td>12.2 (220)</td>
</tr>
<tr>
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<td>48.1 (900)</td>
<td>71.1 (1280)</td>
</tr>
<tr>
<td>U6+ Sat</td>
<td>26.7 (500)</td>
<td>16.7 (300)</td>
</tr>
</tbody>
</table>

Table 5.11 Normalized XPS peak intensities showing qualitative % pentavalent and hexavalent uranium and their actual intensities (show in brackets) in the pre- and post-leach samples relative to their corresponding satellite peaks.
Studies were conducted on synthetic betafite to investigate the dissolution of uranium electrochemically. This is essential in gaining a mechanistic understanding of under potential bias mineral leaching by studying the redox interactions between an electrode and electrolyte, and how these measuring processes change at varying redox potentials.

These experiments were conducted using a similar method to the batch leaching experiments reported previously in this chapter. The potentials are applied by a bipotentiostat rather than an iron sulfate solution, to induce redox reactions.
5.2.7.1. Influence of scan rate

Cyclic voltammetry (CV) experiments were conducted at three different step rates (10 mV/s, 50 mV/s and 100 mV/s) to investigate the oxidation and reduction of species within the synthetic beta-fite sample in a 1 M sulfuric acid matrix. The results presented in Figure 5.25 show CVs successively recorded at each of the 3 step rates. In each case the initial cyclic voltammogram started at 0.197 V vs. SHE showed no anodic current peak between 0.50 – 1.20 V (p1), indicating that no anodic oxidation of the sample occurred in the initial pass over this voltage. Charalambous et al. showed the oxidation of uranium in brannerite occurred at ~0.75V in a 15 g/L (0.153 M) \([\text{H}_2\text{SO}_4]\) electrolyte [28]. This is consistent with the previously discussed findings where the sample was shown to contain an abundance of oxidised U(VI) on the mineral surface. The experiments conducted at 50 mV/s and 100 mV/s showed the anodic current for each experiment increased as the scan number increased while the peak maximum shifted to the more positive potentials. This indicates that oxidation of uranium was diffusion controlled. The second oxidation process observed between 1.50 and 1.70 V (p2) of \(\text{HSO}_4^-\) formation in the solution [29]. The formation of this species was demonstrated to form more rapidly than the oxidation reaction of U discussed previously in Section 5.3.3.3 (p1).

In the cathodic region of the voltammogram two peaks were observed; p3 at 0.62 V and p4 between -0.25 to +0.15 V. The peak at 0.62 V (p3) is due to the formation of \(\text{SO}_2^{2-}\) in the leach solution [29]. The final peak in this scan (p4) is the corresponding uranium reduction peak to p1. In the initial cycle a reduction peak was shown to occur whereas no oxidation peak was observed. This further demonstrated the previous finding reported in Section 5.3.6 which showed the exposed uranium was in the U(VI) oxidation state when added into the electrochemical leach setup.
5.2.7.2. Influence of electrolyte and temperature

Three electrolytes were chosen to investigate their effect on electrochemical leaching of betafite at 10 °C. The electrolytes studied were HCl, HNO₃ and H₂SO₄ at a concentration of 1 N and were selected as these are the most common acid mediums that could be used for dissolution of uranium minerals such as betafite. The results presented in Figure 5.26 show the electrochemical dissolution of betafite in the three aforementioned acids. In the sulfuric acid CV experiment two oxidation peaks (p₁, p₂) and two reduction peaks (p₆ and p₇) were observed. Discussion of the cause of these peaks is given in the previous section (Section 5.3.7.1). The CV of the redox process when HCl is used as the electrolyte is also presented in Figure 5.26. The CV exhibits a low current oxidation peak occurring at 0.74 V which represents the oxidation of uranium in the sample, as observed in the sulfuric acid test. This peak was observed to be 5 fold less in magnitude than the final CV in the sulfuric acid test, indicating that oxidation of uranium does not occur as readily in HCl solutions relative to H₂SO₄. Ikeda et al. showed reduction of the uranyl chloride UO₂Cl₂ species occurs at 0.71 V in a concentrated HCl solution [30]. The reduction peak observed at a similar value (p₅) was therefore assigned to the reduction of UO₂Cl₂. One further reduction peak was observed which was at a similar
The CV conducted in nitric acid also showed two oxidation peaks and two reduction peaks. The redox couple peaks for uranium were observed at 0.7 V ($p_1$) and 0.0 V ($p_2$). The magnitude of these peaks was significantly less than that observed when sulfuric acid was used. One further oxidation peak was observed at 1.70 V; this peak was assigned to the oxidation of the NO$_3^-$ complex within the electrolyte. The reduction peak for this reaction was observed to occur at 0.10 V and was demonstrated to be due to the reduction of the NO$_3^-$ species to NO$_2$ [31]. It is important to note that the peak intensity of the electrolytic experiments was significantly greater when sulfuric acid is used. This is due to the greater proton diffusion efficiency with sulfuric acid due to its diprotic nature.

![Figure 5.74 Cyclic voltamagram of synthetic betafite at 10 °C in a 1 N acid matrix with varying step rate of 10 mV/s.](image)

Electrochemical studies conducted at 35 °C showed similar redox couple peaks to that observed in the previous experimental discussion (Figure 5.27). One notable difference between the previous test at 10 °C and this experiment was consistent current is observed for each CV pass over the U oxidation/reduction peaks. This indicates that the more rapid diffusion rate which occurs at the higher temperature caused the reaction to go to completion more quickly. Additionally, all redox
process were shifted less positive by ~100 mV when heated to 35 °C as expected with a temperature dependent process.

Electrochemistry studies conducted on synthetic betafite showed a number of interesting findings that were discussed in more detail previously. Some of these findings include:

- No anodic oxidation was reported in the initial CV pass, indicating that any uranium present was found in an already oxidised form. This was consistent with results discussed previously in Section 5.2.6
- The oxidation reaction of uranium in betafite was shown to be diffusion controlled when experiments were conducted at 35°C in a 1 M sulfuric acid solution.
- A second redox coupled reaction was observed to occur at 0.62 and 0.20V respectively. This was assigned to be due to the $\text{SO}_2^{2-}$ dissociating in solution.
- The magnitude of oxidation was observed to be greater in a sulfuric acid medium than hydrochloric or nitric acids.
- Increasing the temperature was shown to result in a greater amount of U oxidation observed in the three mediums studied.
5.3. Conclusions

High purity betafite was synthesised and used for dissolution studies. The parameters investigated were: temperature, [H$_2$SO$_4$], [Fe$_{TOT}$], redox potential, iron salt, fluoride salt and lixiviant. The results showed that in most cases synthetic betafite leaching involves three distinct periods of differing dissolution rate. The first period which had a relatively high rate of dissolution occurred in the initial minute. This dissolution was shown to be due to liberation of surface oxidised uranium in the sample. The second dissolution period where the dissolution rate was very slow relative to the first period occurred between 1~120 minutes. This period was shown to be most influenced by the typical redox reaction between ferric and uranium. This segment was also most affected by changes in dissolution parameters such as acid concentration, total iron concentration and redox potential. As the experiments progressed the dissolution rate in the second period decreased which was most likely due to the sample becoming passivated. By the start of the third segment the dissolution rate had slowed to a negligible rate and remained negligible for the remainder of the experiment. The extent of U dissolution in the majority of the experiments was demonstrated to be less than 2.1% demonstrating the highly refractory nature of the mineral over the range of conditions studied ([H$_2$SO$_4$] = 0 – 2.03 M, [Fe$_{TOT}$] = 0 – 214.3 mM, Temp = 35 – 95 °C).

The addition of fluoride was also shown to increase the dissolution rate of synthetic betafite. In a series of experiments conducted at varying fluoride concentrations the results showed an increase from 2% to over 3.5% U leached was observed when fluoride was added to the leaching experiments.

Releaching experiments were conducted on dried leached residues to investigate any changes that occurred when the leached sample was dried in various gas atmospheres. The results of this work showed that when the leached residue was dried in nitrogen no surface oxidation was observed to occur and hence significantly less U was observed to leach out of this sample when compared to dissolution of residue that was dried in air.
Investigations into heat treatment of the betafite sample revealed when the synthetic betafite was heated in air no mineralogical change was observed, whereas when the sample was heated in a reducing atmosphere (H\textsubscript{2}/Ar) the sample was demonstrated to decomposed into pyrochlore, rutile and 2 other reduced uranium minerals uranmicrolite \([(Ca,\text{U})\text{Ta}_{2}O_{7}]\) and uraninite \((\text{UO}_{2})\). This resulted in increased dissolution of the heat treated in reducing gas atmosphere which was most probably due to leaching of the betafite decomposition products uranmicrolite \([(Ca,\text{U})\text{Ta}_{2}O_{7}]\) and uraninite \((\text{UO}_{2})\).
5.4. References

1. van Rensburg, N.J., *A value based approach to leach optimization at Rössing uranium limited,* in *Faculty of the Engineering and Built Environment.* 2014, University of Cape Town: Rondebosch. p. 163.


In this chapter, ninety day dissolution experiments were conducted where parameters ([H$_2$SO$_4$], [Fe$_{107}$] and redox potential were varied. Further experiments were conducted in MilliQ water and brine solutions in order to determine the feasibility of betafite as a potential host matrix for nuclear fuel storage/disposal. Post leach characterisation of the betafite samples was conducted with a number of techniques to investigate any structural and/or chemical changes which occur during leaching.
6.1. Introduction

Globally, ~10,000 metric tons of heavy metal nuclear waste are produced per annum, adding to the cumulative stockpile of ~300,000 tons [1]; 96% of which consists of $^{238}\text{U}$ and $^{235}\text{U}$, about 1% of the mass is $^{239}\text{Pu}$ and $^{240}\text{Pu}$ and the remainder minor actinides [2]. The disposal and long term storage of this high level radioactive waste is one of the greatest challenges facing the nuclear power industry.

While there is a current push to reprocess Spent Nuclear Fuel (SNF) for use in mixed oxide (MOX) type reactor designs there is still a significant shortfall in demand for the SNF waste. This has led to the majority of SNF being scheduled for disposal in geological repositories throughout the world [3]. The majority of research towards developing methods of storing actinides generated from the nuclear fuel cycle has focused on compounds which demonstrate long-term durability and chemical variability [4]. In work by Smith et al. (2001) suitable actinide-containing mineral candidates were ranked based on their aqueous durability through various long term leaching experiments as follows: perovskite < hollandite < brannerite < pyrochlore < zirconolite [5]. Based on this analysis, the pyrochlore group of minerals could potentially be suitable for SNF storage applications.

Dissolution studies presented in Chapter 3 on three natural betafite samples showed the dissolution rate and extent of U leaching from natural betafite samples varied significantly even though each sample was determined to be aperiodic and metamict. This work showed that the more highly altered samples containing secondary alteration products such as liandratite ($\text{UNb}_2\text{O}_6$), uranpyrochlore ($\text{U,Ca})\text{Nb}_2\text{O}_7$ were more readily leachable. The least altered of the samples studied only showed minor leaching even though the sample was completely metamict. It was therefore concluded that disruptions in the crystal lattice through secondary alteration appeared to be the key factor in uranium dissolution from natural betafite.

In comparison, work presented in Chapter 5 examined the dissolution of synthetic betafite over a range of conditions. The baseline conditions used were: $[\text{H}_2\text{SO}_4]$ – 0.51 M, $[\text{Fe}_{\text{TOT}}]$ – 53.6 mM, Redox potential – 560 mV vs. Ag|AgCl, and temperature 50 °C. Under these conditions uranium dissolution
was shown to leach in three differing stages. Approximately 2% of the uranium was leached in the initial minute of the experiment, which was most likely due to liberation of surface oxidized uranium. The next segment from 1 – 120 minutes was controlled by an electrochemical redox reaction mechanism during which time a further ~0.4% U was leached. Beyond 120 minutes, negligible uranium was determined to leach over the remainder of the 6 hour experiment although the short duration of the experiment could not fully discount the possibility of further dissolution occurring at a very slow rate.

Previous work reported in Chapter 3 investigating the stability of betafite showed that although natural betafite is generally found to be amorphous, the leachability of uranium remains low in unaltered samples. Moreover, U dissolution studies using well crystallised synthetic betafite also indicated minimal solubility. Thus the stability of the pyrochlore structure appears to be very high even under conditions that for most uranium-bearing minerals would lead to high solubilities. This supports the possibility that pyrochlore-structured betafite may prove to be a suitable candidate material for long-term disposal of uranium and other radionuclides.

In this chapter long term dissolution studies were completed on synthetic betafite over a ninety day dissolution period. These studies were conducted in order to gain a greater understanding of leaching chemistry at commercial minerals processing conditions beyond the 6 hour dissolution period which was extensively studied in Chapter 5. Additional aims in this chapter were to investigate the potential for betafite to be used as a host material for actinide disposal.

These aims were studied by leaching a synthetically prepared betafite using an adapted method for static leaching of a monolithic waste forms. Following the long term leach tests, the residue was characterised via multiple techniques including X-ray diffraction (XRD), X-ray Photoelectron Spectroscopy and Electron Probe Microanalysis (EPMA) to investigate any structural and chemical changes. Such data may provide valuable information in determining the cause for the slow leach
rate over extended periods which will be beneficial in both minerals processing and actinide immobilisation applications.

6.2. Methodology

6.2.1. Characterisation methodology
The following methods that were used to conduct the research presented in this chapter: Acid digestion/ICP-MS procedure, XRD analysis, XPS analysis are given in Chapter 2.

6.2.2. Long Term Dissolution Procedure
The method used for long term dissolution was an adaption of the Standard Test Method for static leaching of monolithic waste forms for disposal of radioactive waste (formally MCC1) [6].

Dissolution studies were completed by adding 30 mL of the desired lixiviant, iron sulfate and sodium fluorides into a 30 mL Teflon sealed glass vials. The vials were placed in a rotary hybridization oven and heated to 50 °C and left in the oven for a period of 2 hours to allow the solutions to heat to temperature. Twenty milligrams of powdered synthetic betafite was accurately measured then added to each vial and the time upon addition was determined to be 0 minutes. The mass of each vial with solution and betafite was also recorded to ensure the mass did not change throughout the duration of the experiment.

The brine solution was prepared using the method published in MCC1 [6]. The control dissolutions experiments were conducted in milliQ deionised water. Aliquots of each solution were collected at pre-determined intervals throughout the experiment and the solution was refilled to the initial volume with fresh solution with the same acid, iron, and fluoride concentration.

6.2.3. Post Leach Residue Acquisition
Post leach characterisation was conducted on the residue from three of the dissolution experiments. After the dissolution studies were conducted the solutions were allowed to settle for a period of 5 hours before the leaching solution was removed and the residue was washed with a mixture of
milliQ water and ethanol in order to separate the fines from the solution. These samples were then
dried in an inert environment before post leach analysis was conducted.
6.3. Results and Discussion

6.3.1. Influence of Temperature, $[\text{H}_2\text{SO}_4]$, $[\text{Fe}_{\text{TOT}}]$ and redox potential

A series of experiments were conducted over a period of ninety days to investigate the dissolution rate and % U extraction of betafite under conditions of relevance to commercial processing of betafite. Following these, experiments were conducted under simulated environmental conditions using standardised brine and deionised water solutions to evaluate the long term aqueous stability and feasibility of betafite as a potential actinide disposal material.

In each experiment one parameter was altered while other parameters remained constant while duplicate experiments at the same experimental conditions were completed. The base conditions set for each parameter were chosen based on the most efficient experimental conditions demonstrated in Chapter 5 of this document. These conditions were: $[\text{H}_2\text{SO}_4] = 0.153$ M; $[\text{Fe}_{\text{TOT}}] = 0.107$ M; $\text{Fe}^{3+}:\text{Fe}^{2+}$ ratio of 9:1; a redox potential of 560 mV (vs. an Ag/AgCl reference electrode) and; a particle size of <75 µm.

The conditions used in each experiment are reported in Table 6.1.

Table 6.12 Long term dissolution conditions.

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<th>Test No.</th>
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<th>Redox Potential (mV vs. Ag/AgCl)</th>
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</table>
6.3.1.1. Effect of sulfuric acid concentration

In Section 5.3.3.2 the influence of sulfuric acid concentration on the dissolution of synthetic betafite was investigated over a 6 hour period. Approximately 2.14% of the uranium was shown to leach out of the sample in the 6 hour dissolution. The uranium was largely solubilised within the first minute of the dissolution experiment and this was attributed to the dissolution of surface oxidised uranium U(VI). The dissolution rate thereafter was negligible and it was assumed that either the sample surface became passivated or the uranium, when present in the U(IV) within the pyrochlore structure, was essentially unable to be leached. Dissolution of Nb, Ti and Ta was shown to be below the detection limit for ICP-MS (<0.004%) over the range of sulfuric acid concentrations studied.

Results for the 90 day dissolution experiments using different sulfuric acid concentrations (Figure 6.1) show similar levels of uranium solubility were obtained over the range of concentrations studied. The extent of dissolution after 1 day was 2.10%U for the 0 M experiment while slightly higher dissolution levels of ~2.30%U were observed for the three experiments which contained sulfuric acid.

The dissolution data for the experiments conducted showed the leach rates were between $\sim 3.0 \times 10^{-9}$ and $4.1 \times 10^{-9}$ g m$^{-2}$ d$^{-1}$ for all of the experiments conducted between 0 – 2.14 M [H$_2$SO$_4$] (Figure 6.2). It should be noted that these rates are likely to be influenced by factors such as metamictisation and decomposition of the mineral structure leading to formation of more soluble uranium containing

<p>| | | | | |</p>
<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>0.153</td>
<td>0.107</td>
<td>1:0</td>
<td>640</td>
</tr>
<tr>
<td>9</td>
<td>0.153</td>
<td>0.107</td>
<td>0:1</td>
<td>350</td>
</tr>
<tr>
<td>10</td>
<td>0.153</td>
<td>0.107*</td>
<td>1:0</td>
<td>620</td>
</tr>
<tr>
<td>11</td>
<td>2.040</td>
<td>0.214</td>
<td>1:0</td>
<td>640</td>
</tr>
<tr>
<td>12</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* added as FeF$_3$
species will increase the leach rate over time. This is a significantly slower leach rate when compared to other uranium minerals under similar conditions. For example, Ram et al. (2013) showed 100% dissolution of uraninite occurs after only 3 hours [7] while the more refractory mineral brannerite took 50 hours to achieve a similar extent of dissolution at the same dissolution at conditions to test 3 [8].

![Graph showing the influence of [H\textsubscript{2}SO\textsubscript{4}] on the dissolution of betafite over a 90 day period. Refer to Table 6.1 for the experimental conditions used.](image)

Figure 6.76 Influence of [H\textsubscript{2}SO\textsubscript{4}] on the dissolution of betafite over a 90 day period. Refer to Table 6.1 for the experimental conditions used.
6.3.1.2. Effect of total iron concentration

Four experiments were conducted to examine the effect of total iron concentration on dissolution over a period of 90 days. These experiments were conducted between 0 and 0.214 M [Fe$_{TOT}$] which is the range of variation of total iron concentrations used in commercial uranium mineral processing plants [9]. The acid strength was kept constant at 0.153M. All other experimental parameters are listed in Table 6.1. Approximately 2.1% of the uranium was leached out in the initial 1 day period in the experiments conducted using different total iron concentrations (Figure 6.3). These results were similar to that observed for the experiments in which the acid concentration was varied. The amount of uranium solubilised was identical to that measured in Section 5.2.3.3 where short term leach studies were conducted at the same conditions.

Dissolution rates between $2.79 \times 10^{-9}$ and $4.12 \times 10^{-9}$ g m$^{-2}$ d$^{-1}$ were calculated for the long term study, with a slightly greater dissolution rate observed for higher total iron concentrations (Figure 6.4). Since these dissolution rates are low and similar in magnitude it is difficult to speculate with certainty why the dissolution rate changed when the iron concentration was increased. The dissolution mechanism reported in Section 5.3.3.3 described the effect of iron sulfate species leading
to a higher rate of dissolution over the initial 75 minutes. In this section total iron concentrations of greater than 0.107 M produced similar rates of dissolution before passivation of the sample began to become rate limiting factor. The current work shows the contrary, where increasing the total iron concentration increased the dissolution rate, although the difference between 0 – 0.214 M [Fe\text{TOT}] was minor in magnitude (Figure 6.4). The dissolution of Nb, Ti and Ta over these experimental conditions studied were shown to be below the detection limit of the instrument (0.005%).

Figure 6.78 Influence of [Fe\text{TOT}] on the dissolution of betafite over a 90 day period. Refer to Table 6.1 for the experimental conditions used.
6.3.1.3. Effect of varying redox potential

Dissolution studies were conducted at three different redox potentials. These were: 330 mV (100% Fe$^{2+}$), 560 mV (9:1 Fe$^{3+}$:Fe$^{2+}$) and 640 mV (100% Fe$^{3+}$). Since autoxidation/reduction was a significant problem over the 90 day experiments, the redox potential was adjusted with the addition of sodium sulfite or sodium permanganate solutions to ensure the redox potential was kept within 10 mV throughout the duration of each experiment. Results shown in Figure 6.5 indicate between 2.1 and 2.3%U was leached out in the initial 24hr period. The dissolution yield was shown to be slightly lower for the dissolution at 330 mV than the dissolutions conducted at higher redox potentials.

The calculated dissolution rates showed only minor variation from $3.15 - 3.46 \times 10^9$ g/m$^2$/day indicating the influence of redox potential on the dissolution of uranium was minimal when compared to the effects of total iron and sulfuric acid concentration.
6.3.2. Effect of Fluoride Addition

Dissolution of betafite with 0.107 M $[\text{Fe}_{\text{TOT}}]$ as $\text{FeF}_3$ was conducted over the 90 day period. Fluoride was added to the leaching solution since work conducted in Section 5.3.4.1-2 showed significantly more uranium leached in the presence of fluoride. In this section the additional solubility was shown to be due to the dissolution of Nb, Ti and Ta which allowed more U dissolution to occur. Similar results were observed in this study where greater dissolution of U (up to 2.6 %) was measured when compared to baseline conditions (2.1%). As well, Nb, Ti and Ta were all observed to have undergone dissolution which was observed not to have occurred in any of the previous tests (Tests 1-9, Table 6.1). The majority of the dissolution was shown to occur in the initial 1 day period with approximately 2.55% U, 0.08% Nb, 1.20% Ti and 0.38% Ta compared to 2.62% U, 0.09% Nb, 1.21% Ti and 0.41% Ta leaching after 90 days (Figure 6.6). The dissolution of Nb, Ta and Ti was most likely due to the formation of fluoride complexes with these metals which would not occur under baseline conditions.
The most notable observation in the experiment with fluoride added was that after the initial period where the surface oxidised uranium and Nb, Ti and Ta were observed to have leached, the sample became passivated and the dissolution rate slowed to approximately zero for the remainder of the experiment. Even though passivation was observed, slow dissolution rates were able to be calculated for the four metals analysed. Leach rates for these metals are given in Table 6.2 which shows that the U dissolution rate when ferric fluoride was added to the leach solution was approximately one third greater than dissolution at the base conditions. The differences in leaching rates indicate that congruent dissolution occurred over the period studied. It was noted however, that dissolution rates, although positive for Nb, Ti and Ta, were not as large in magnitude compared to U. This was most likely due to passivation of the surface over time as a result of the increasing ratio of the less soluble group 4 and 5 metals within the betafite structure.

The group 5 metals Nb and Ta were shown to have the lowest dissolution rates of $0.38 \times 10^{-9}$ and $1.06 \times 10^{-9}$ g m$^{-2}$ d$^{-1}$ for Nb and Ta respectively. Lumpkin and Ewing (1996) proposed that the decomposition mechanism of betafite due to chemical weathering initially involved the loss of Ca and U. This charge destabilises the structure which in turn leads to the loss of Ti and Ta and the formation of the uranium containing minerals liandratite ($\text{UNb}_2\text{O}_8$) and uranpyrochlore ($[\text{U, Ca}_2\text{Nb}_2\text{O}_7]$). In the current work, dissolution of the group 4 and 5 metals shows results consistent with Lumpkin and Ewing’s work where the least soluble metal (Nb) was the metal most likely to form insoluble uranium minerals as the mineral charge destabilises due to Ti and Ta being removed.
Figure 6.81 % leached of various elements over 90 days in an 0.107 M \( \text{FeF}_3 \) leach solution (Test 10). All other parameters are indicated in Table 6.1.

Table 6.13 Leach amounts and rates of U, Nb, Ti and Ta over the 90 day leach experiment (Test 10).

<table>
<thead>
<tr>
<th>Element</th>
<th>Initial dissolution (%)</th>
<th>Leach rate ( \times 10^{-9} \text{ g m}^{-2} \text{d}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>2.60</td>
<td>5.46</td>
</tr>
<tr>
<td>Nb</td>
<td>0.09</td>
<td>0.38</td>
</tr>
<tr>
<td>Ti</td>
<td>1.20</td>
<td>2.45</td>
</tr>
<tr>
<td>Ta</td>
<td>0.40</td>
<td>1.06</td>
</tr>
</tbody>
</table>

6.3.3. *Aqueous Durability in DI Water and Brine*

The aqueous durability of betafite was studied over a period of 90 days in DI water and brine solutions according to Standard Test Method for static leaching. The dissolution of uranium in the brine solution showed ~0.33%U was leached over the initial 1 day period. After this time the extent of U dissolution was shown to increase only slightly more than the experimental error of 0.002% for the remainder of the experiment.
Negligible dissolution was observed when leaching experiments were conducted in DI water. Although the sample was shown to contain surface oxidised uranium very little was liberated due to the solution not containing suitable ligands to complex the oxidised uranium. The initial dissolution of uranium was less than $0.024 \pm 0.002\%$ which remained constant throughout the remainder of the experiment. Dissolution of Ti, Nb, and Ta was also examined however concentrations were below the limit of detection of $0.002\%$ w/w for each of these elements.

The data presented in Figure 6.7 shows that the leach rate of uranium from betafite in both brine and deionised solutions significantly decreases over time. The initial higher dissolution rate was due to liberation of surface oxidised uranium from the mineral sample and was approximately 10 times greater when the sample was dissolved in brine compared to deionised water. Extrapolation of the exponential dissolution rate curve gives the dissolution rate of uranium in brine and deionised water to be $4.32 \times 10^{-10}$ and $3.43 \times 10^{-11}$ g m$^{-2}$ d$^{-1}$ respectively.

![Graph showing dissolution rate of uranium from betafite over a period of 90 days in brine and deionised water at 50°C.](image)

**Figure 6.82** Dissolution rate of uranium from betafite on over a period of 90 days in brine and deionised water at 50°C. The exponential rate curve for brine was $y=38.601x^{-1.002}$ ($R^2 = 0.9992$) and deionised water $y=2.9707x^{-1.009}$ ($R^2=0.9991$).
6.3.4. Post Leach Characterisation

In each dissolution experiment approximately 15 mg of the sample was recovered and used for the corresponding characterisation experiments. The residue of these experiments was rinsed with Milli-Q water to remove any soluble compounds that remained from the leach liquor and then dried in an inert environment to reduce the likelihood of chemical or physical changes to the residues.

6.3.4.1. X-ray Diffraction

X-ray diffraction analysis of the leach residue from three experiments was conducted to investigate any mineralogical changes that the samples had undergone as a result of leaching. These three tests: Test 2 (baseline conditions refer to Table 6.2), Test 10 (test conducted using FeF\textsubscript{3}), and Test 11 (test using high acid and high iron concentrations) were chosen to compare the difference between a baseline leaching experiment and Tests 10 and 11 which showed the greatest amount of leaching. The results presented in Figure 6.8 show the diffraction patterns for the pre-leached and three post-leached samples.

The pre-leached sample was highly crystalline and exhibited peak matches for betafite with a very minor amount of rutile and pyrochlore. The post-leach residue from Test 2 (baseline conditions) was less crystalline and contained betafite (major), rutile (minor) and pyrochlore (Ca\textsubscript{2}Nb\textsubscript{2}O\textsubscript{7} - minor). The high abundance of betafite in the residue was expected as very little dissolution was observed in this sample. The rutile and pyrochlore detected due to the uranium-depleted betafite undergoing decomposition although it is difficult to deduce the extent of formation of these minerals. Since metals other than uranium were not observed in solution it was assumed that Ta was present within the pyrochlore.

Analysis of the leach residue from Test 10 which included FeF\textsubscript{3} showed similar results to Test 2. Although the fluoride led to an increase in the rate of dissolution as well as minor solubility of Nb, Ti and Ta the extent of dissolution of all elements was low and hence the diffraction pattern did not change significantly when compared against Test 2.
The diffraction pattern for the leach residue from Test 11 (highest acid strength, highest total Fe) indicated the presence of amorphous material. Diffraction peaks were matched to betafite, rutile and pyrochlore, at similar relative concentrations as were observed in the previous samples. Although this sample was shown to leach out slightly less uranium than test 10 and none of the group IV and V metals, the XRD pattern remained similar due to the non-stoichiometric nature of the sample.

![X-ray diffraction patterns for pre-leached betafite and post-leach residues from Test 2, Test 10 and Test 11. Peak diffraction matches were taken from the ICDD JCPDS XRD database: betafite [(U, Ca)2(Nb, Ti, Ta)2O7·xH2O] (PDF 008-0300; blue), rutile [TiO2] (PDF 034-0180; red), and pyrochlore [Ca2Nb2O7] (PDF 073-0597; green).](image)

**6.3.4.2. X-ray Photoelectron Spectroscopy (XPS)**

XPS analysis of the three samples analysed via XRD was conducted in order to determine the change(s) in oxidation state of uranium in the post leach betafite residue. The XPS spectra for the
pre-leached synthetic betafite used in this study contained predominantly U(V) with a minor amount of U(VI) due to surface oxidation (Section 4.3.2.1).

Analysis of the XPS spectra from the Test 2 post-leach residue is shown in Figure 6.9a. Deconvolution of the peak corresponding to the U4f orbital reveals two peaks with varying peak heights. Four shakeup peaks were revealed at higher binding energies than the U4f$_{5/2}$ peak. These peaks had binding energies of 396.78, 399.08, 401.48 and 405.78 eV. The three lower binding energy peaks were correlated to pentavalent and hexavalent uranium by measuring the binding energy difference between the deconvoluted U4f$_{5/2}$ peaks and the 3 satellite peaks where a difference of 6-7 eV correlates to U$^{IV}$, 7.7-8.5 eV for U$^{V}$, and ~4 and 10 eV for U$^{VI}$ [11]. One further shakeup peak with a peak intensity of 405.78 eV was revealed in the deconvoluted XPS spectra; the difference between this peak and the U4f$_{5/2}$ peak was ~14 eV which is significantly greater than where any U4f$_{5/2}$ shakeup peaks would occur. This is likely indicating the presence of Ta as XPS for Ta$_2$O$_3$ has a similar peak at ~14 eV due to excitation of the Ta4p$_{3/2}$ orbital [12]. The penetration depth of electrons via XPS, while dependent on the sample matrix, is ~10 nm [13]. Since a Ta4p$_{3/2}$ peak wasn’t evident in the pre-leached sample it is concluded that the post-leach surface contains a greater amount of tantalum.

An intense Ta peak between 25 – 28 eV caused by excitation of electrons in the Ta4f$_{7/2}$ orbital was peak height normalised to the C1s orbital peak at 385 eV. The results show the peak intensity was approximately double the intensity of the pre leached betafite (Table 6.3). Since the signal intensity is proportional to the elemental concentration it can be further deduced that there is a greater concentration of tantalum in the outer layer of the post-leached residues than the pre-leached sample.

Deconvolution U4f$_{5/2}$ excitation peak in the leach residue of Test 10 (with FeF$_3$) showed two peaks were present (Figure 6.9b). These peaks were shown to have corresponding satellite peak characteristic to U(V) and U(VI). The dissolution of this sample was shown leach slightly more
uranium than the previous sample; moreover increased dissolution of Nb, Ti and Ta was also observed to occur at these conditions. This difference in dissolution from the previous sample could be why U(V) was observed to be present in the leach residue but not in the other residues analysed. Two further shakeup peaks were observed between 395 and 405 eV which did not correlate to characteristic satellite peaks for the $\text{Uf}_4\frac{3}{2}$ orbital. The higher binding energy peak was assigned to excitation of the $\text{Ta}_4\text{p}_{3/2}$ orbital as discussed previously although the lower binding energy at $\sim$395 eV could not be matched to excitation of any of the elements known to be present in the sample.

Analysis of the XPS spectra from the leach residue from Test 11 showed two deconvoluted peaks which make up the $\text{U}_4\text{f}_{5/2}$ excitation peak at $\sim$391 eV (Figure 6.9c). Five excitation shakeup peaks with higher binding energies were shown to occur between 394-405 eV. Of these, three were correlated to the presence of U(V) and U(VI) in the post leach residue. The two remaining peaks at 395 and 405 eV had binding energies which were outside the characteristic ranges expected for uranium oxidation satellite peaks. As per Test 10, the higher peak with a binding energy of 405 eV was assigned to $\text{Ta}_4\text{p}_{3/2}$ which was further confirmed by the greater normalised peak intensity for the $\text{Ta}_4\text{f}_{7/2}$ excitation peak given in Table 6.3. The shakeup peak at 385 eV was unable to be assigned to an appropriate match for in the leach residue sample.
Figure 6.84 XPS of post-leach residues of the uranium U4f excitation orbital. Spectra A (bottom) corresponds to the post-leach residue from Test 2, Spectra B (middle) post-leach residue from Test 10, spectra C (top) post-leach residue from Test 11.
Table 6.14 Normalised peak intensities of the Ta4p3/2 excitation orbital

<table>
<thead>
<tr>
<th>Sample</th>
<th>Binding energy (eV)</th>
<th>Normalised peak intensity (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preleached</td>
<td>25.68</td>
<td>4099.37</td>
</tr>
<tr>
<td>Test 2</td>
<td>25.87</td>
<td>7363.76</td>
</tr>
<tr>
<td>Test 10</td>
<td>25.58</td>
<td>4877.48</td>
</tr>
<tr>
<td>Test 11</td>
<td>25.59</td>
<td>7966.39</td>
</tr>
</tbody>
</table>

6.3.4.3. Bulk elemental analysis

The bulk elemental composition of the three samples chosen for detailed post-leach analysis was conducted via multi elemental digestion followed by ICP-MS analysis. All samples were shown to contain all the elements that were present in the pre-leached sample. The dissolution results for the baseline dissolution experiment conducted (Test 2) showed approximately 2.3% of the uranium was leached out after 90 days while the other elements showed negligible dissolution (Table 6.4). The results of the bulk elemental analysis showed minor differences in concentration of the group 4 and 5 metals as well as similar amount of uranium leaching. The concentrations of Nb, Ti and Ta were within experimental error which indicates that negligible amounts of these elements were leached under these experimental conditions.

The bulk elemental composition of the leach residue from Test 10 showed more of each metal was leached in this experiment than any other dissolution experiment conducted. When a comparison was made between the mass balanced composition (leach residue composition + dissolution yield) the results showed slightly more uranium was reported to be leached in the bulk elemental composition data. This discrepancy could be due to the small sample size used for bulk elemental analysis due to the limited amount of post-leach data obtained. A further notable difference
between this sample and the other post-leach bulk analysis is the 6% decrease in total mass. This difference in mass is most likely due to the formation of insoluble fluoride compounds which would account for some of this mass difference although none were identified via XRD.

The post-leach residue from Test 11 showed similar results to Test 2. A mass balance for this experiment showed very similar results to the initial dissolution data conducted. It is important to note that although there was a change in elemental concentration of the sample, the X-ray diffraction pattern for the post leach residue experiments only showed minor differences in diffraction pattern. This indicated that these differences lead to the formation of a betafite with varying stoichiometry relative to the initial betafite leached.

**Table 6.15 Elemental composition of leach residue.**

<table>
<thead>
<tr>
<th></th>
<th>Preleached</th>
<th>Test 2</th>
<th>Test 10</th>
<th>Test 11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uranium</td>
<td>25.48</td>
<td>23.16</td>
<td>22.37</td>
<td>22.96</td>
</tr>
<tr>
<td>Calcium</td>
<td>7.03</td>
<td>6.77</td>
<td>2.42</td>
<td>6.78</td>
</tr>
<tr>
<td>Niobium</td>
<td>20.95</td>
<td>20.90</td>
<td>20.71</td>
<td>20.95</td>
</tr>
<tr>
<td>Titanium</td>
<td>10.75</td>
<td>10.74</td>
<td>9.75</td>
<td>10.61</td>
</tr>
<tr>
<td>Tantalum</td>
<td>15.33</td>
<td>15.17</td>
<td>14.76</td>
<td>14.97</td>
</tr>
<tr>
<td>Total</td>
<td>79.54</td>
<td>76.73</td>
<td>70.01</td>
<td>76.27</td>
</tr>
</tbody>
</table>
6.4. Conclusions

Long term dissolution studies were conducted to investigate the aqueous durability of synthetic betafite over a ninety day dissolution period. The aim of this work was to investigate any trends in leaching beyond the 6 hour experiments conducted in Chapter 5. The influence of the standard leaching parameters \([H_2SO_4], [Fe_{TOT}]\) and redox potential were initially investigated. The results of this work showed very minor trends in leaching when each parameter was varied. The U leaching yield was shown to only increase by 0.20% when the acid concentration was increase from 0 to 2.14 M \(H_2SO_4\) over the 90 day leach period. The influence of fluoride was conducted by adding \(FeF_3\) instead of \([Fe_2(SO_4)_3]\) and showed a higher yield of leaching in the initial period, followed by a greater rate of leaching \((5.46 \times 10^{-9} \text{ g } \text{ m}^2 \text{ d}^{-1})\) over the ninety day experiments. Moreover, in the fluoride addition experiments the dissolution of the group 4 and 5 metals Ti, Nb and Ta were observed to have leached. This could also have attributed to the greater rate of U leaching under these experimental conditions.

Post leach characterisation of the leached residue showed changes to the mineralogical composition via XRD. These changes included the formation of pyrochlore and rutile but were only observed to be minor due to the low amount of leaching in the sample. The XPS results of the post leach sample showed similar U in the same oxidation states as observed in the preleached samples. These results also showed significantly greater amount of tantalum via XPS in the post leach sample, indicating that the Ta concentration had increased on the surface of the mineral. This therefore indicates a possible passivation layer which could be attributed to the low rates of dissolution that were observed.
6.5. References


7. Conclusions and Future Research

7.1. Conclusions

7.1.1. Synthesis of betafite

A method for producing very high purity synthetic betafite was developed in this project. The uranium containing pyrochlore betafite was synthesised via a solid state synthesis method using uranyl nitrate, calcium carbonate, titanium dioxide, niobium(V) oxide and tantalum(V) oxide. The synthesis was shown to be sensitive to several parameters including: initial reactant ratio, gas atmosphere used (oxidising, neutral or reducing) and the heat duration. The successful solid state synthesis method was achieved using a starting elemental ratio of $U = 0.32$, $Ca = 0.42$, $Nb = 0.41$, $Ti = 1.78$, $Ta = 0.10$. This mixture was ground for 20 minutes and sieved through a 68 µm sieve. The powered mixture was then placed in a platinum lined alumina boat and heated in a dry nitrogen atmosphere for 48 hours at 1150 °C. X-ray characterisation of the products obtained revealed that it was mostly betafite with a minor rutile impurity. Electron Probe Microanalysis (EPMA) analysis of a sectioned region of the sample showed small inclusions of Ca-free betafite on the grain boundaries as well as minor rutile impurities within the sample. Quantitative EPMA showed some heterogeneity between the Nb:Ta ratio but this was generally within the nomenclature requirements for betafite. SEM morphology analysis of the synthetic sample showed the sample was comprised mostly of hexaoctahedral crystals of ~3 µm in diameter. XPS analysis of the betafite showed the uranium in the sample was predominantly in the $U^{5+}$ oxidation state. A minor amount of $U^{6+}$ was also detected which was attributed to surface oxidation of the sample.

7.1.2. Characterisation of natural betafites

Samples of natural betafite from Ambatofotsy Madagascar, Miarinarivo Madagascar and Silver Crater Mine, Canada were characterized using a range of techniques. X-ray diffraction analysis of the unheated betafite samples showed the samples were almost completely amorphous with only minor
matches for anatase (TiO\textsubscript{2}) observed. Upon heat treatment of the samples at 1200 °C all samples exhibited diffraction lines matching to beta-fite and rutile. This indicated that the beta-fite in the sample was amorphous in the preheated samples. The EPMA data showed a high degree of heterogeneity throughout each natural sample which was most likely caused by aqueous fluid interactions forming secondary alteration products; pyrochlore (CaNb\textsubscript{2}O\textsubscript{7}), uranpyrochlore [(Ca,\text{U})\textsubscript{2}Nb\textsubscript{2}O\textsubscript{7}], liandratite (UNb\textsubscript{2}O\textsubscript{8}), microlite (Ca\textsubscript{2}Ta\textsubscript{2}O\textsubscript{7}), and rutile (TiO\textsubscript{2}).

The Ambatofotsy beta-fite was observed to be the most altered sample while the Silver Crater Mine sample was observed to be the least altered. Quantitative EPMA showed that in each sample the niobium concentration was greater than the tantalum concentration indicating that preferential formation of beta-fite occurs in Nb abundant environments. The EPMA results further showed the formation of liandratite was favourable as the sample became more highly altered. When these more highly altered samples were heated the formation of uranium titanium niobium oxide (UTiNb\textsubscript{2}O\textsubscript{10}) was observed due to a solid state reaction between liandratite and rutile. EPMA mapping of the least altered sample (Silver Crater) showed the sample was predominantly beta-fite with minor amounts of apatite and galena, both of which are gangue generally found with beta-fite.

Bulk analysis of the natural samples showed the more metamict beta-fites generally contained more sodium, potassium and the uranium daughter products lead and thorium; indicating that the more highly altered samples could be geologically older. X-ray Photoelectron Spectroscopy (XPS) showed each sample varied in mixture of pentavalent and hexavalent uranium.

### 7.1.3. Dissolution studies on natural beta-fite

Dissolution of the three natural beta-fite samples was conducted in order to study the influence of several parameters which are commonly varied in commercial minerals processing plants.

Initial dissolution investigations were conducted to determine any significant differences in the dissolution of the natural samples at conditions commonly used in commercial processing of uranium ores. In the natural characterisation section discussed previously (Section 7.1.2) varying
degrees of alteration were observed for the three betafite samples analysed. In leach experiments that were conducted at similar conditions to that currently used at the Rössing uranium mine \([\text{H}_2\text{SO}_4] = 0.051 \text{ M (5 g/L), temperature} = 35 \, ^\circ\text{C}, \text{[Fe}_{\text{TOT}}] = 53.5 \text{ mM (3 g/L), Fe}^{3+}:\text{Fe}^{2+} \text{ ratio} = 9:1, \text{initial [Betalite]} = 200 \text{ ppm, leach time} = 6 \text{ hours}\) approximately 42 %, 20 % and 7% U was leached from the most highly altered betafite sample to the least. This demonstrates that as the samples become more heavily altered the mineral leaches more readily.

Experiments conducted where the solution temperature was changed were used to determine the activation energies of the natural samples. These results showed the more highly altered samples had lower activation energies. Moreover, increasing the acid concentration was observed to more readily leach the more highly altered samples. These greater U leach rates in the more altered samples were most probably caused by uranium leaching out of other uranium containing minerals such as uraninite and uranmicrolite which were shown to be were present in the highly altered samples.

Heat treating of the metamict samples at 1,200 °C for 2 hours showed a greater rate of dissolution was observed over the initial 100 minutes in the heat treated sample, which was followed by almost no further dissolution. This higher rate of dissolution initially was most likely due to the formation of more soluble uranium containing minerals such as pitchblende (U\(_3\)O\(_8\)) and uranium titanium niobium oxide (UTiNb\(_2\)O\(_{10}\)). After these more soluble uranium containing minerals were leached the dissolution rate slows due to the crystallinity of the betafite making it more difficult to leach the uranium.

Since the natural betafite sample were demonstrated to be highly altered and impure, it is difficult to discern whether the uranium is leaching from betafite or other uranium containing minerals within the sample. This leads to inaccuracies when determining what influence the various parameters studied has on the U dissolution from betafite. For this reason it was decided to conducted extensive dissolution studies on a high purity synthetic betafite sample.
7.1.4. Dissolution of synthetic betafite

As previously described dissolution of synthetic betafite was conducted in order to determine the influence of several leaching parameters which are most commonly varied during commercial minerals processing. These include the parameters: Temperature, \([H_2SO_4]\), \([Fe_{TOT}]\), redox potential, and comminution. Other parameters investigated to study their influence on betafite dissolution were: Fe counter ion, presence of fluoride, different lixiviants, secondary oxidants, and heat pre-treatment.

The results of dissolution experiments conducted under similar conditions to those used in the Rössing uranium mine (conditions given in Section 7.1.3) showed that only \(~2\%\) of the uranium in synthetic betafite dissolved after 6 hours as compared to \(42\%\), \(20\%\) and \(7\%\) for natural betafite samples. This significant difference in leachability between natural and synthetic betafites was due to namely the degree of alteration and metamictisation leading to the formation of more soluble secondary uranium minerals.

Analysis of the dissolution results obtained showed three distinct segments of dissolution rate during the experiments. The first segment occurred in the initial minute and involved extremely rapid U leaching. This dissolution made up the majority of the total extent of leaching observed over the total dissolution period. XPS of the pre and post leach sample showed that this was most likely due to the liberation of surface oxidised \(U^{6+}\) in the synthetic sample. The second segment occurred between 1 – 120 minutes and was shown to be most influenced by altering the experimental conditions (i.e. changes in temperature, \([H_2SO_4]\), etc). The final segment occurred from 120 minutes onwards; during this period negligible U dissolution was observed.

The influence of temperature showed very similar dissolution curves over the duration of the leaching experiments. In each experiment the majority of the U leaching was shown to leach in the initial minute of dissolution. The dissolution rate in segment two was shown to be influenced by the
solution temperature. In each of the 5 experiments no further dissolution was observed after 120 minutes.

Experiments conducted where the influence of total iron was studied demonstrated the characteristic high rate of dissolution over the initial minute of leaching when no iron was present. This was due to liberation of the surface oxidised uranium present which required no ferric oxidation. Beyond this point no further dissolution was observed indicating that the remainder of the uranium needed to undergo oxidation to leach it out of the minerals structure. The influence of $[\text{Fe}_{\text{TOT}}]$ at concentrations greater than 0 was shown to positively influence the leach rate over the initial 120 minutes until 107 mM $[\text{Fe}_{\text{TOT}}]$ was added. Beyond this point increasing the $[\text{Fe}_{\text{TOT}}]$ did not increase the rate of dissolution. Fluoride was shown to significantly increase dissolution of uranium from betafite. This increase was most likely due to the in situ formation of HF which solubilised the group 4 and 5 metals Ti, Nb and Ta which are known to be soluble in HF solutions. The liberation of these metals allowed uranium to undergo ferric oxidation without the hindrance of Ti, Nb and Ta passivating the mineral structure. The overall amount of leaching observed was shown to almost double when fluoride was added into the leaching system.

Experiments conducted using different lixiviants demonstrated relatively similar leaching results with the exception of oxalic acid and phosphoric acid which were shown to cause precipitation of iron which resulted in the $U$ oxidation step not occurring and hence leading to a reduced amount of $U$ dissolution.

Further experiments were conducted on the synthetic betafite to investigate the influence of releaching on the sample. These studies were conducted on the synthetic betafite by collecting the leach residue and exposing the sample to various gas atmospheres. The results of these successive leaching experiments showed when the sample was dried under inert conditions the leach rate was lower than that when dried in air. This demonstrated that the sample was undergoing a structural change or oxidation when dried in air resulting in greater dissolution.
The influence of two different heat pre-treatments (1150 °C in H₂/Ar or air) was investigated. The results of the dissolution experiments conducted on the heat treated samples showed similar dissolution amounts were observed for the sample that was heated in air. When the synthetic betafite was heated in H₂/Ar the XRD results showed some of the betafite had reacted to form uranmicrolite. This resulted in roughly double the amount of dissolution to occur over the 120 minute experiment.

7.1.5. Long term dissolution of synthetic betafite

Long term dissolution studies were conducted to investigate the aqueous durability of betafite over an extended leach period in order to determine the feasibility of using betafite as a potential material for actinide immobilisation. These dissolution experiments were conducted using an agitated leaching technique over a 90 day dissolution period. The influence of the standard parameters [H₂SO₄], [Fe(II)] and redox potential were investigated over the leach period. The results of these experiments showed very minor influences were observed with each of these parameters investigated. The increase in U leaching between no sulfuric acid added and 2.14 M [H₂SO₄] was only a 0.20% increase after the 90 day leach experiment. The influence of fluoride addition showed a slightly greater leach rate than that achieved with high acid concentration, though the main difference between this experiment and other experiments conducted with no fluoride was the solubilisation of the metals Ti, Nb and Ta which were not observed to leach in experiments where fluoride was not added.

Post leach characterisation of synthetic betafite identified only minor changes occurred in the sample. These changes included the formation of pyrochlore and a greater concentration of rutile was observed to be present. These changes were only minor due to the small amount of dissolution that was observed. The XPS analysis of the post leach residues showed the samples contained similar U oxidation states to those observed in the preleached samples. Moreover, significantly greater Ta was observed via XPS in the post leach sample indicating that the Ta concentration had increased on
the surface of the mineral. This indicated a possible passivation layer which caused the low rate of dissolution that was observed to occur.
7.2. Future research

Several areas of potential research have been identified from work contained in this thesis. This research should focus on the following areas:

- Synthesis of doped forms of betafite with other radionuclides substituted into the mineral structure. Further synthesis of doped forms of betafite with the commonly associated substituted metals would also be beneficial.

- Electrochemical leaching studies to investigate the dissolution of betafite. This will be beneficial in understanding the electrochemical role of dissolution of uranium from betafite. Moreover, factors such as diffusion and passivation would be able to be more thoroughly investigated via this technique.

- Further studies on the physical and chemical differences between natural and synthetic betafite would aid in correlating the leaching data conducted on synthetic betafite with natural occurrences.

- More detailed studies investigating the influence of anions, cations and gangue minerals on the dissolution of betafite. This would be beneficial in understanding how a complex mineral system such as an ore body influences the dissolution of betafite.

- Further investigation into the formation of a passivation layer which was demonstrated to hinder dissolution. By understanding this layer possible methods can be implemented to hinder the formation and hence allowing more uranium to leach.

- Long term aqueous durability studies to further investigate the potential of betafites and doped betafite for the use in radionuclide immobilisation. This area of research is gaining greater importance as the amount of radioactive waste increases.

- Investigations into the formation of amorphous synthetic betafite would be valuable in further determining the influence of metamictisation on leaching. This knowledge would also be advantageous in any long term aqueous durability studies that were conducted.