SYNTHESIS, CHARACTERISATION AND DISSOLUTION STUDIES OF THE URANIUM MINERAL COFFINITE

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DECLARATION 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.

______________________________
Hailey Sonja Reynolds

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The most exciting phrase to hear in science, the one that heralds new discoveries, is not “Eureka!” but “That’s Funny”

Isaac Asimov
PUBLICATIONS


ABSTRACT

The field of uranium chemistry is of current interest, especially with the push for low green-house gas emissions technology. To meet the potential growing uranium demand, lower grade and/or “difficult to process uranium minerals” will need to be mined and processed. In order to achieve improvements in uranium minerals processing, a greater understanding of the chemistry occurring in a number of the currently used processes is essential. The lack of understanding pertaining to the specific dissolution of uranium from the mineral coffinite, primarily due to the limited research conducted on this mineral with respect to dissolution and leaching, lead this thesis to focus on gaining an increased knowledge of the chemistry of the uranium mineral coffinite – composition, structure and dissolution chemistry.

The objectives of this study include, trying to gain quantitative mineralogical information of naturally forming coffinite to, among other things, aid in the synthesis of a synthetic analogue which could be used for comprehensive dissolution studies.

Two natural uranium bearing samples were analysed (1) a uranium bearing ore sample from Olympic Dam (known to contain coffinite) and (2) a natural sample containing coffinite acquired from the Museum of Victoria, were analysed via multiple techniques and were found to contain non stoichiometric coffinite which varied in the uranium:silicon ratio across the coffinite grain.

Coffinite was successfully synthesised when 10 mL of 5 mmol UCl₄(aq) was added to 25 mL of equimolar Na₂SiO₃ (in a dry and inert atmosphere of N₂) and 2 M of degassed NaOH was added until gelling occurred (pH ≈ 8). The solution was buffered to between a pH of 8.5 and 9 with NaHCO₃ and placed into a sealed in a Teflon lined autoclave vessel, which was heated to 250 °C for 24 Hr.

The successful coffinite appeared to be consistent with other reported analysis of synthetic coffinite where the unit cell parameters were calculated (a=b 6.99795±0.0002 Å and c 6.27197±0.0002 Å) which is within 1 % of previously reported values (of both natural and synthetic coffinites).
The synthetic coffinite was found to have a low surface area (78.44 m²/g) and the acquired TGA data supports the theory that coffinite contains water in a number of different varieties, with the water content being found to between 1 and 1.5 moles.

EPMA mapping indicated that the synthetic coffinite was very similar to that of the coffinite found in the natural sample (patchy, polycrystalline aggregates with heterogeneous BSE contrast). Quantitative analysis found that the weight percent of both uranium and silicon varied throughout the sample, 62.72 – 65.44 wt % and 8.93 – 11.33 wt % respectively (as was observed in the natural coffinites), with the edge of some coffinite grains being classified as low U coffinite (containing greater amounts of Si). The overall uranium to silicon ratio was low (0.73) compared to the theoretical value of 1.0 (although higher than the 0.6 previously reported for synthetic coffinite).

The dissolution studies carried out on the prepared synthetic coffinite (similar to natural coffinite samples) resulted in trends that were different than what has been observed for the most common uranium mineral, uraninite.

Temperature was found to have a significant effect once the temperature was raised to 80 °C or higher. The activation energy was calculated as 64.6 kJ/mol and an Arrhenius parameter of 220. Increasing the concentration of sulfuric acid resulted in an unusual increase and subsequent decrease in the extent of uranium dissolution, with maximum uranium dissolution occurring after 90 minutes when 1.5 g/L of sulphuric acid was used. Increasing the [Fe]_{Total} appeared to have little effect on the extend or rate of uranium dissolution from coffinite when the Fe^{2+}:Fe^{3+} ratio is maintained, however it is highly dependent on the solution ORP. Increasing the solution ORP resulted in an increase in the dissolution of uranium from coffinite. Fe^{2+} was found to have a significant effect on the uranium dissolution, where as soon as trace amounts of Fe^{2+} were present in the system a significant depression of the amount of uranium dissolved was observed. The Fe^{2+} effect was greater in systems containing the lowest amounts of Fe^{3+} (0.1 g/L). Under relatively mild conditions (1g/L of Fe^{3+}; 3 g/L of Fe^{2+}; 15 g/L of sulphuric acid and at 50 °C) 100 % uranium dissolution from can be achieved between 36 and 48 hours.
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GLOSSARY OF TERMS AND ABBREVIATIONS

A

ADU Ammonium Diurantate

a.u Arbitrary Units

B

BET A theory which explains the physical adsorption or gas molecules on a solid surface used in surface area analysis and is an extension of the Langmuir theory. BET named after the three scientists Brunauer, Emmett and Teller who first published this theory

BJH Barret-Joyner-Halenda calculation scheme for calculating mesopore distribution from nitrogen adsorption data

BSE Back Scatter Electron

C

CCD Counter Current Decantation

E

EDAX Energy Dispersive Spectroscopy

EPMA Electron Probe Micranalysis

ER Electrefining; A process for purifying metals using electrolysis

eV electron Volts (units for the measure of Binding Energy)

EW Electrowinning; the electrodeposition of metal which are in solution or have been liquefied

F

Feed The sample which is to go into that process.
FTIR Fourier Transform Infrared Spectroscopy

G
Gangue The commercially valueless minerals in which ore is found (Oxford online dictionary)

H
HT-XRD High Temperature X-ray Diffraction
Head Grade The average grade of the ore which is fed into a mill

I
ICP-MS Inductively Coupled Plasma Mass Spectrometry
IR Infrared

L
Lixiviant The liquid medium used in hydrometallurgy to selectively extract the desired metal from the ore and or mineral. The lixiviant may be acidic or alkaline in nature

M
Metamict material affected by metamictisation - A mineral whose crystal structure has been disrupted by radiation from contained radioactive particles
Metamictisation A natural process resulting in the gradual and ultimately complete destruction of a mineral's crystal structure leaving the mineral amorphous. (also known as metamiction)

O
Ore Mineral A mineral which is of economic importance
ORP Oxidation-Reduction Potential
Paragenesis  The science which treats of minerals with special reference to their origin. The sequence in which the minerals are formed in an ore deposit. The order in which minerals occurring together in rocks and veins have developed. The formation of minerals in contact, so as to affect one another's development.

PLS  Pregnant Leach Solution

ppm  Parts per Million

Raffinate  the pregnant leach solution with a commodity of value removed. i.e. copper raffinate is the pregnant leach solution after the copper has been removed.

REE  Rare Earth Elements

SCE  Saturated Calomel Electrode

SEM  Scanning Electron Microscope/Microscopy

SX  Solvent Extraction (Cu and U refers to Copper and Uranium respectively)

TGA  Thermogravimetric Analysis

ULF  Uranium Leach Feed

UOC  Uranium Oxide Concentrate
X

XRD          X-ray Diffraction

XPS          X-ray Photoelectron Spectroscopy
CHAPTER 1

INTRODUCTION
Uranium based fuel is used to generate approximately 13-14% of the world's current electricity supplies [1]. It has been projected that uranium based fuel could be used to generate up to 38% of the world's electricity by the year 2050. With the push for low green-house gas emissions technology and potential benefits to reducing future CO₂ emissions there is a potentially attractive future for fission based nuclear energy. The significant interest in generating a greater proportion of electricity using nuclear technology can be observed by future plans of countries such as China, India and the USA to increase their nuclear energy facilities and outputs.

To meet potential growing uranium demand, lower grade and/or “difficult to process uranium minerals” will need to be mined and processed. To reduce the processing impacts and to reduce costs, improved processes for processing uranium minerals will need to be developed. To achieve improvements in uranium minerals processing, a greater understanding of the chemistry occurring in a number of the currently used processes is essential. Areas where there is room for improved understanding include; the structure/composition of uranium minerals (and how this influences their processing), the dissolution of refractory uranium minerals and the influence of gangue mineralogy with respect to individual uranium minerals as well as the uranium speciation in solution.

The focus of this thesis was to generate an improved understanding of the composition, structure and dissolution chemistry of the commercially important uranium mineral coffinite.

1.1 A Brief History of Uranium

In 1789, a new element was discovered by M. H. Klaproth in a pitchblende ore. This element was to be known as Uranit, named after the newly found planet, Uranus [2, 3], and for fifty years this element was believed to be the metallic uranium. A French chemist by the name of Peligot showed that the element Uranit was in fact uranium dioxide (UO₂) and not a single element. In 1841, Peligot was able to isolate true
elemental Uranium as a black powder by reducing uranium tetrachloride (UCl4) with potassium [2-4]. The radioactivity of uranium was not discovered until many years later (1896) when Becquerel noticed that the one of his photographic plates had been darkened with exposure to the uranium salts during his studies of the fluorescence behaviour of potassium uranyl sulfate. Upon further investigation Becquerel found that all uranium salts exhibited the same behaviour, concluding this new radioactivity was a property of uranium [3]. In 1934 Fermi and his colleague bombarded uranium with neutrons to discover a whole new range of radioactive elements [3].

During the 19th Century though uranium metal was tried as an alternative to tungsten it was mined almost exclusively for thorium. After the presence of radium was found in uranium ore, uranium mining increased as the demand for radium increased [2].

The nuclear age began in 1939 after Hahn and Strassmann discovered nuclear fission [3]. It was not until 1942 that the uranium mines were mined primarily for the production of uranium, before this uranium was used almost exclusively as a pigment in glass and ceramics. It was during WWII that the United States of America gathered an abundance of new data on the chemistry of uranium under the “Manhattan Project”, however much of this information was not generally available until the first “conference on the peaceful uses of atomic energy” in Geneva, 1955 [2].

1.1 Uranium Chemistry

Uranium is a naturally occurring element and is fourth in the actinide series. It has an atomic number of 92 and mean atomic mass of 238.03 atomic mass units (amu). There are 24 recorded isotopes of uranium with masses ranging from 217-219 amu, 222-240 amu and 242 amu, which have half-lives as short as 1ms ($^{222}$U) to as long as 4.468x109 years for the most predominant isotope ($^{238}$U) [3]. Uranium is the precursor for two natural decay series: $^{238}$U (4n+2) and $^{235}$U (4n+3) (Figure 1.1 and Figure 1.2). In nature uranium contains only three of the 24 known isotopes: $^{238}$U (99.276 %), $^{235}$U (0.718 %) and $^{234}$U (0.0056 %) [2]. The abundance of uranium found in the earth’s crust is on
average 2-3 ppm, which is more than other elements such as cadmium, gold, silver and mercury and equal to that of tin. Naturally, uranium is not found in its elemental state but rather incorporated into minerals [3].

Uranium exhibits a range of oxidation states III, IV, V and VI, since uranium has a larger spatial extension of 5f orbitals where these electrons are less effective at shielding both the 7s and 7p electrons when compared to the lanthanide series. This increase in spatial extension of the 5f orbital results in a small energy difference between 5fn7s2 and 5fn-16d7s2 electron configurations and thus allows for a wider range of oxidation states. Although there are four possible oxidation states of uranium, it is only the IV and VI oxidation states that are stable enough to be of any significant importance, although the inclusion of various other elements within the mineral assemblage enables many uranium-bearing minerals to carry a uranium oxidation state of V by providing a charge balance [3].

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Formula</th>
<th>CAS Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uranium</td>
<td>U</td>
<td>7440-61-1</td>
</tr>
<tr>
<td>Uranium Dioxide</td>
<td>UO2</td>
<td>1344-57-6</td>
</tr>
<tr>
<td>Uranium Tetrachloride</td>
<td>UCl4</td>
<td>10026-10-5</td>
</tr>
<tr>
<td>Uranyl Sulfate</td>
<td>USO6</td>
<td>14972-01-1</td>
</tr>
<tr>
<td>Uranyl Nitrate</td>
<td>UN2O8H2</td>
<td>36478-76-9</td>
</tr>
</tbody>
</table>
Figure 1.1: Uranium-238 natural decay series

Figure 1.2: Uranium-235 natural decay series
1.2 Uranium Minerals

Currently, there are approximately 200 to 250 known minerals in which uranium is an essential or major constituent, and another 60 which contain uranium as a minor constituent or impurity [3, 5-8]. Approximately, only a third of the known uranium minerals have defined structures, primarily due to the difficulties associated with analysing these minerals using conventional techniques such as X-Ray diffraction (a number of uranium minerals absorb large amounts of X-rays and often do not form crystals of a reasonable size required for analysis). Some minerals also undergo dehydration or transformation during analysis, making structure determination and elucidation difficult or even impossible with current technologies [7].

Though there are multiple classifications and groupings used to discuss uranium minerals with similar characteristics, at the most basic level, uranium minerals can be divided into two broad classifications: reduced minerals and oxidised minerals [2, 3, 5, 7]. Reduced minerals are those minerals whereby the uranium is found as U⁴⁺ and were previously known (and sometimes still referred to) as primary minerals because of their abundance in uranium ore deposits. Oxidised minerals are those minerals where the uranium is found in the U⁶⁺ oxidation state and were termed secondary minerals because of the belief they were formed from the oxidation of pre-existing “primary minerals”. It is now known that oxidised minerals can precipitate from solution without the reduced species precursor [7]. It is also interesting to note that while most uranium minerals fall easily into the category of either reduced or oxidised minerals, there are some known uranium minerals where the uranium is found in a mixed oxidation state (U⁴⁺ and U⁶⁺) and at least one mineral known to contain uranium in the U⁵⁺ oxidation state [2, 3, 5, 7].

Reduced uranium minerals such as coffinite (which as mentioned earlier is the main focus of this thesis), are generally formed during the final stages of magma solidification and are found in pegmatites, which are coarse grained igneous rocks with a grain in
excess of 20 mm (with the exception of pitchblende) [2, 3, 5, 7]. Reduced minerals are usually highly symmetrical with regular co-ordination of polyhedra that contain six to eight ligands around the uranium cation. The effective ionic radii for reduced minerals are \(\{6\} \text{U}^{4+}, 0.89 \text{ Å} \) and \(\{8\} \text{U}^{4+}, 1.00 \text{ Å}\), which gives a predicted \(\text{U}^{4+}\)-O bond length of 2.25-2.36 Å opposed to 2.28-2.47 Å for oxidised minerals, dependent upon the number of ligands bonded to the uranyl ion. Reduced minerals (such as coffinite) are also often iso-structural with non-uranium analogues and the uranium cation can be substituted with other cations such as Th\(^{4+}\) and Rare Earth Elements (REE\(^{3+}\)). In nature, many of the reduced minerals are partially oxidised, often containing both \(\text{U}^{4+}\) and \(\text{U}^{6+}\) and occasionally \(\text{U}^{5+}\) [7, 8].

### Table 1.2: Some reduced minerals with known crystal structures [7]

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Space group</th>
<th>(a) (Å)</th>
<th>(b) (Å)</th>
<th>(c) (Å)</th>
<th>(\beta) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uraninite</td>
<td>((\text{U}^{4+})<em>{1-x} \cdot \text{REE}^{3+} \cdot \text{M}^{2+} \cdot \text{M}^{2+} \cdot \text{O}</em>{2+x \cdot \text{y} \cdot \text{z} \cdot \text{v}}))</td>
<td>Fm3m</td>
<td>5.470-</td>
<td>5.443</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coffinite</td>
<td>USiO(_4)</td>
<td>I41/amd</td>
<td>6.979</td>
<td>6.253</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brannerite</td>
<td>((\text{U},\text{Ca},\text{Ce})(\text{Ti},\text{Fe})_2\text{O}_6)</td>
<td>C2/m</td>
<td>9.79</td>
<td>3.72</td>
<td>6.87</td>
<td>118.4</td>
</tr>
<tr>
<td>Uranmicrolite</td>
<td>((\text{U},\text{Ca},\text{Ce})_2(\text{Nb},\text{Ta})_2\text{O}_6(\text{OH},\text{F}))</td>
<td></td>
<td>10.40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Uranpyrochlore</td>
<td>((\text{U},\text{Ca},\text{Ce})_2(\text{Ta},\text{Nb})_2\text{O}_6(\text{OH},\text{F}))</td>
<td>Fd3m</td>
<td>10.44</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Considerably more oxidised minerals have been identified compared with reduced minerals and can be broadly categorised as uranyl - oxyhydroxides, carbonates, silicates, phosphates, arsenates, vanadates, molybdates, tungstates, sulfates, selenites and tellurites. Refer to Table 1.2 for common oxidised minerals. This has been proposed to be due to oxidised minerals being formed from alterations of reduced minerals during weathering, hydrothermal activity, possible transport or re-deposition and metathesis [2, 3, 5, 7]. Oxidised minerals are also more diverse and complex than reduced minerals, which is due to the unusual crystal chemistry of the \(\text{U}^{6+}\) cation. These minerals are also rarely iso-structural with any other minerals and are highly coloured [7].
<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carnotite</td>
<td>$K_2(UO_2)V_2O_8\cdot 3H_2O$</td>
</tr>
<tr>
<td>Tyuyamunite</td>
<td>$Ca(UO_2)V_2O_8\cdot 8H_2O$</td>
</tr>
<tr>
<td>Autunite</td>
<td>$Ca(UO_2)_2(PO_4)_2\cdot 10-12H_2O$</td>
</tr>
<tr>
<td>Uranophane</td>
<td>$Ca(UO_2)_2(SiO_3OH)_2\cdot 5H_2O$</td>
</tr>
<tr>
<td>Torbernite</td>
<td>$Cu(UO_2)_2(PO_4)_2\cdot 8H_2O$</td>
</tr>
</tbody>
</table>

From a processing perspective, the chemistry of each individual mineral, the location within the host rock as well as the mineralogy it is associated with is important. All of these factors will influence the choice of what is the most appropriated process technology. The chemical formula and structure of the minerals will influence the processes which are best suited to extract the uranium from the host mineral. Some minerals such as coffinite are best suited for acid leaching (most commonly sulfuric acid) whereas others (such as carnontite) are best suited to alkaline dissolution (most commonly sodium carbonate). Reduced minerals require the presence of an oxidant in order to leach the uranium, whereas oxidised uranium ($[UO_2]^{2+}$ uranyl ion) is readily soluble in both acidic and alkaline conditions. Almost all of the data currently available for understanding what processes are most appropriate for what mineral are based on commercial processing information. Though this data may be accurate, it cannot be directly transferred from ore body to ore body since the most appropriate process for that particular ore is not always the most appropriate process for a particular mineral within the ore. This is because for each process there are a number of advantages and disadvantages, and with such a complex assemblage there is always a trade off in order to achieve the best possible overall outcome. Because the majority of data currently available is from industry, the optimal processing conditions for a specific uranium mineral such as coffinite are unknown.

Since being discovered in 1954, there have been a few studies presented in the open literature on the composition and/or structure of coffinite. Although a crystal structure was first given for this mineral over 50 years ago in 1955 [9] there is still controversy
over the true chemical formula of coffinite, with regards to water or hydroxyl being incorporated or attached in the structure. This conjecture is discussed in more detail in Chapter 2.1.1.1. There are a number of factors which have led to the conjecture surrounding the chemical formula of coffinite (and other uranium minerals).

Coffinite is often found as fine grained inclusions and intimately mixed with other minerals in very complex assemblages and can also be encapsulated by the other minerals. This results in three major difficulties in analysis; 1) Isolating and extracting coffinite from the host rock can be very difficult and extremely time consuming, if at all possible, 2) If coffinite can be separated, there may not be enough for quantitative or extensive analysis to be conducted, 3) If coffinite is analysed in situ, the resolution of, for example, electron beams is too coarse to distinguish fine coffinite grains from the matrix.

Almost all minerals (including coffinite) found in nature are not stoichiometrically “pure” as they have endured many geological events over time, resulting in the elemental substitution and/or inclusion of other elements into the mineral structure, hence complicating any analysis which can be done on natural samples.

As coffinite is a uranium mineral, over time the uranium will decay. During this decay process various particles are released disturbing the crystal lattice of the mineral. This process of crystal structure degradation due to natural radiation is known as metamictisation and may cause the mineral to become wholly or partially amorphous.

The inability to solidly define the chemical structure of coffinite is significant from a processing point of view, as to truly understand the speciation and the kinetics of any process, the starting material (in this case coffinite) must be known. This problem is then enhanced during full scale processes as natural coffinite is not the only mineral present during the process. Understanding the fundamentals of a process which uses natural samples is extremely difficult due to the enormous variation of the samples. In actual processing plants, the majority of the ore (or feed) is not the many uranium minerals that could be present (which include) coffinite but the vast array of gangue minerals. With current technologies it is impossible to identify every single mineral
present within any particular ore body, especially as there may be large variation in the mineralogy of relatively small distances, even in one ore body. The large variation in chemical composition of coffinite and the mineralogy it is surrounded in results in the inability to transfer results from the studies of ore containing coffinite from one ore body to another.

In order to overcome the problem with natural variation of coffinite and the ore it is hosted in, researchers have begun investigating synthetic versions of the mineral coffinite. Though coffinite was first published as being synthesised in 1956 [10], each synthesis publication after that has altered the method, and in all cases impurities of UO₂ and/or SiO₂ have been observed in the product. It was not until recently (2010) that a reproducible method for producing high purity coffinite was published. (More information regarding the synthesis of coffinite is given in Chapter 3)

### 1.3 History of Uranium Mining / Processing in Australia

In Australia, the history of uranium mining dates back to about the same time as the discovery of uranium's radioactivity and coincides with the discovery of torbinite (Cu(UO₂)₂(PO₄)₂·12H₂O) in 1894. Uranium exploration/mining and production in Australia each occurred in two distinct periods or phases.

- **Exploration phase I** – 1944 to the late 1950’s
- **Exploration phase II** – 1966 to the Present Date
- **Production phase I** – 1954 to 1974
- **Production phase II** – 1976 to the Present Date

In the first phase of production, uranium was produced from Rum Jungle (NT), Radium Hill (SA), Mary Kathleen (QLD) and the South Alligator Valley (NT), producing a combined total of 5 947 tonnes of Uranium [11]. During the second production phase, five mines have primarily contributed to uranium production: Mary Kathleen (QLD),
Nabarlek (NT), Ranger (NT), Olympic Dam (SA), and Beverley (SA), where the combined total uranium production as of the end of 2000 was 8 3425 tonnes of Uranium [11]. There are many other known deposits in Australia, and feasibility studies into the establishment of new mines are constantly under review. To date, there are currently three mines in operation in Australia; Olympic Dam (SA), Ranger (NT) and Beverley (SA). The Honeymoon and Four Mile projects in South Australia have the potential to be operational within 18 months. There are a number of deposits in Western Australia that are currently under development, though not likely to being production until 2014 or later; these include Yeelirrie and Kintyre [12].

During this time, Australia has seen many changes in the public’s attitude towards uranium. Factors such as wars and global warming influence the policies outlined by the federal governments of the time, and in turn impact mining, the treating and processing of uranium as well as its exportation. Outlined below are the major events (including political policies) that make up the history of uranium mining in Australia. More comprehensive details of this field can be found in many publications [11, 13-15].

<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>1894</td>
<td>Torbinite (Cu(UO2)2(P04)2 ⋅12H2O) found with cobalt at Carcoar (NSW).</td>
</tr>
<tr>
<td>1906</td>
<td>Uranium found in significant quantities at Mount Painter (SA).</td>
</tr>
<tr>
<td>1910</td>
<td>Uranium found in significant quantities at Radium Hill (SA).</td>
</tr>
<tr>
<td>1930s</td>
<td>Uranium ores were mined at Radium Hill, SA, and Mount Painter (SA).</td>
</tr>
<tr>
<td>1944</td>
<td>The systematic exploration of uranium began.</td>
</tr>
<tr>
<td>1949</td>
<td>Ore bodies discovered at Rum Jungle (NT).</td>
</tr>
<tr>
<td>1950-59</td>
<td>Major exploration resulted in five uranium ore deposits being discovered.</td>
</tr>
<tr>
<td></td>
<td>Mining began at three deposits and Radium Hill was reopened as a uranium mine.</td>
</tr>
<tr>
<td></td>
<td>Tax concessions were offered to those who earned profits from the</td>
</tr>
</tbody>
</table>
mining and treatment of uranium.
- A standstill in the exploration of uranium exploration occurred when the existing sales contracts were fulfilled and there seemed little prospect of further sales.

1960-64 Four mines ceased production.

1965-69  
- Late in this decade a second wave of exploration began initiated by the development of nuclear power, and another three ore deposits were discovered.
- Experts believed that the use of nuclear power as an energy source would increase dramatically.

1970-79  
- Twelve ore deposits were discovered and Rum Jungle was closed.
- Government opinions and policies swung to and fro throughout the decade with respect to uranium mining, processing and exporting.
- Mary Kathleen (QLD) began recommissioning its mine and mill and later in the decade recommenced production of uranium oxide which the Commonwealth Government held a 42% share of the company.

1980-88  
- Pilot plant operations commenced at deposit and ceased three years later.
- Two more ore bodies were discovered, two mines closed or ceased production and three mines opened.
- The “Three Mine Policy” was introduced.

1994  
Native Title Act 1993 introduced by the commonwealth government making prospectors notify and negotiate with native title owners before tenements were granted. This particularly impacted exploration in much of WA.

2000  
Beverley Mine (SA) commenced operations.

2001  
Prominent Hill (SA) Ore deposit discovered.

2007  
The three-mine-policy (though it survived a change in government in 1996) was abandoned as public opinion changed over the rising concerns of global warming.

2009  
- Work began on the Honey Moon Mine (SA).
- Approval for the establishment of the Four Mile Mine (SA) was granted.
1.3.1 Australia’s Largest Single Uranium Deposit

In 2010, Australia supplied the world with 11% of the world’s Uranium [14] and is currently the third largest producer of uranium behind Kazakhstan and Canada [16]. Australia’s largest single uranium deposit is Olympic Dam, which is an integrated metallurgical facility situated in central South Australia located 16 km south of the Roxby Downs Township and 560 km north west of the state’s capital, Adelaide. This deposit is also the largest single uranium deposit in the world. Olympic Dam was previously owned by WMC Resources Ltd and is now owned by BHP Billiton Ltd. It is designed to produce copper (as copper cathodes), uranium (as uranium oxide), gold and silver (as bullions) as final products on site and contains the world’s only hybrid solvent extraction (SX) circuit for the recovery of both copper and uranium. Olympic Dam is the fourth largest copper deposit in the world, fifth largest gold deposit and largest single deposit of uranium (refer to Table 1.6 for the breakdown of commodities found in the ore and the weight percentage of final products [17-19]).

Table 1.5: Olympic Dam uranium ore reserves and resources as of 30/6/2009 [13]

<table>
<thead>
<tr>
<th>Ore or Resource (million tones)</th>
<th>Grade U₃O₈ (%)</th>
<th>Contained U₃O₈ (tones)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proved Ore Reserves</td>
<td>188</td>
<td>0.060</td>
</tr>
<tr>
<td>Probable Ore Reserves</td>
<td>401</td>
<td>0.059</td>
</tr>
<tr>
<td>Total Reserves</td>
<td>589</td>
<td>0.059</td>
</tr>
<tr>
<td>Measures Resources</td>
<td>1250</td>
<td>0.033</td>
</tr>
<tr>
<td>Indicated Resources</td>
<td>4623</td>
<td>0.028</td>
</tr>
<tr>
<td>Inferred Resources</td>
<td>3207</td>
<td>0.023</td>
</tr>
<tr>
<td>Total Resources</td>
<td>9080</td>
<td>0.027</td>
</tr>
</tbody>
</table>

*NB. Resources include Reserves.

Table 1.6: Head-grade and production at Olympic Dam operations [17]

<table>
<thead>
<tr>
<th>Commodity</th>
<th>Average Ore Head Grade</th>
<th>Wt % of Final Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>2.4wt%</td>
<td>97.883</td>
</tr>
<tr>
<td>Uranium</td>
<td>650g/t</td>
<td>2.104</td>
</tr>
<tr>
<td>Gold</td>
<td>0.57g/t</td>
<td>0.001</td>
</tr>
<tr>
<td>Silver</td>
<td>4.3g/t</td>
<td>0.012</td>
</tr>
</tbody>
</table>
Olympic Dam is a polymetallic, haematite-rich, breccia complex deposit comprised within granite located approximately 350 m below the surface of the Grawler Craton district [11, 17, 20]. There have been many studies done on constructing an age and geological genesis of the deposit. The mineralisation of the Olympic Dam deposit is believed to have occurred during the Grawler Range thermal event and is reported to be of a similar age to some large Proterozoic iron rich deposits including Kiruna iron ore deposit (Sweden) and iron ore deposits in South Eastern Missouri (USA) [11, 20]. Detailed information regarding the geology and genesis of Olympic Dam can be found in work published by Reeve et al (1990) [21], Oreskes and Einaudi (1990) [22] and Davidson et al (2007) [23].

The Olympic Dam site was discovered in 1975, however development did not begin until December of the next year, and production commenced in August 1988. Olympic Dam is Australia’s largest underground mine and utilises long-hole open stoping methods. Initially Olympic Dam treated 2.2 Mt of ore per annum resulting in the production of 1 400 t U₃O₈ (1 190 t U), 65 000 t copper as well as silver and gold. In March of 1999 the Olympic Dam Operation underwent an expansion that saw between 8.7 and 9.2 Mt of ore treated every year, by 2003 the miner was producing 10 Mt of ore per annum with the capacity to produce 235,000 t of refined copper cathode, 4,500 t of uranium oxide (U₃O₈), 78,000 oz (2 211 kg) of refined gold and 850 000 oz (24 097 kg) of refined silver each year. [11, 17]. The latest figures (FY 2011) show that Olympic Dam produces 194.1 kt of copper cathode, 4 050 t of uranium oxide, 111 368 oz of refined gold and 982 koz of refined silver [24].

1.4 Uranium Minerals Processing

Around the world, uranium minerals are processed in a variety of ways. The process used is dependent on many factors including the geography, geology/mineralogy of the deposit, as well as the economic and legal influences of the region.
Chapter 1

Uranium processing encompasses a wide range of more specific processes;

- Ore Preparation
- Leaching
- Solid-Liquid Separation
- Solution Purification
- Product Recovery

The ore preparation may include processes such as grinding, beneficitation and roasting. Grinding is required to expose and/or liberate the uranium enabling further processes to be more effective. This process also allows a more manageable ore with respect to slurry handling and pumping. Beneficitation is a process which is not always employed though is used to bring ores up to a grade which is considered economically viable. Roasting may be employed to improve the leachability of an ore by changing the chemical and/or physical properties of the ore and hence how they behave in the leach circuit.

There are many options available for Leaching, depending on the nature of the ore being treated. The first option is whether to leach in acid or alkaline solution. As for the leaching system itself there are five main processes available;

1) Agitation (atmosphere) leaching – may be acid or alkaline
2) Pressure leaching – may be acid or alkaline
3) Strong acid pugging and curing – acid
4) Heap leaching – acid or alkaline
5) In-situ leaching (acid or alkaline)

The ore grade, amount of ore, uranium mineralogy and gangue mineralogy usually determine which of options 1-5 are chosen. Heap leaching is usually reserved for low grade ore where other systems are not as economically viable. This system sometimes uses bacteria to oxidise ferrous ions to create ferric ions and is used on low grade stockpiled heaps. In-situ leaching is very dependent on the host rock and its
permeability, though it can be economically viable as there are savings on the mining and crushing operations.

Choosing between systems 1, 2 and 3 is reliant primarily on the mineralogy of both the uranium and gangue minerals. Agitation leaching at atmospheric pressure is the most common leach system in practice, though pressure leaching is common when refractory uranium minerals are present. The use of alkaline solutions is employed when the gangue minerals cause an excessively high acid consumption.

Solid liquid separation is a very important aspect of uranium minerals processing as this is where the valuable liquid is separated from the invaluable solid material. This section of processing usually includes processes such as thickening, filtration and flocculation. The dominant processes for solution purification are ion exchange in conjunction with solvent extraction, followed by stripping and precipitation. There are other processes such as direct precipitation and two stage precipitation. The processes, equipment, ion exchange resins and or solvents used are highly dependent on type of solution (which is primarily determined by the mineralogy and leaching solution).

As the final set-up and operating conditions of any uranium processing facility is completely dependent on the particular ore that is to be processed, it is not possible to discuss all variations. This thesis is concerned with the uranium mineral coffinite and hence only one process overview of the Olympic Dam facility, which is known to process coffinite containing ores is discussed.

### 1.4.1 Olympic Dam Entire Process Overview

The entire metallurgical process which occurs at the Olympic Dam (Figure 1.3) can be divided into four areas [17]:

1) Mill/Concentrator/Feed Preparation
2) Hydrometallurgical Plant
3) Smelter/Acid Plant
4) Refinery

Though each of these areas is independently important, each section is required to operate with respect to the other sections and hence a brief understanding of the entire process is required. As this thesis is primarily focused with the leaching aspect of uranium minerals processing, the hydrometallurgical plant and the chemistry involved in the process is the most relevant to this research.

Figure 1.3: Schematic of Olympic Dam’s metallurgical process [17]

1.4.1.1 Mill/Concentrator/Feed Preparation

The mined ore is milled to 80 % passing 75µm in two single stage, fully autogenous mills (a 38 ’ diameter Svedala mill and a 34 ’ diameter Fuller Mill) [17].

The flotation circuit produces copper concentrate with small amounts of uranium. Concentrate from the smelter slag is blended with the standard concentrate and in the feed preparation area and fed back through the circuit (refer to Figure 1.3).
The uranium is removed from the standard concentrate by an agitated leaching process under what is considered relatively moderate conditions [17, 25].

- Temperature: 55-70 °C
- Free acid concentration: approximately 6-15 g/L
- Solids Loading: 55%

Lawson and Dudly summarise the mineral/elemental constituents of interest that enter and exit the leach circuit [17]. As the majority of the copper has already been removed during the flotation, there is only 0.23 % of copper in the system when it enters the uranium leach circuit, where 77.4 % of uranium is recovered. The leached concentrate is then filtered, neutralised and pumped to the feed preparation where it is then dried and transferred to the smelter feed storage silos [17].

1.4.1.2 Hydrometallurgical Plant

This area can be further divided into three main process areas:

- Tails leach/solid-liquid separation
- Copper solvent extraction (Cu SX)
- Uranium Solvent Extraction/Precipitation (U SX/ppt)

The tails from the concentrator are pumped through a series of agitated leach vessels to recover the remaining copper and uranium. The resulting slurry is then sent to the solid-liquid separation process which involves counter-current decantation (CCD), clarification stages (thickeners) and a series of sand filters to separate it into a copper/uranium rich pregnant leach solution (PLS) and a washed leach tailings slurry. The washed leach tailings slurry is disposed into the tailings retention system [17].

The copper solvent exchange stage consists of two copper solvent extraction plants in parallel and is designed to concentrate and purify the copper prior to uranium solvent extraction. The copper is extracted from the pregnant leach solution by transferring it through a solvent medium and stripping it into a copper rich electrolyte. This
The chemistry behind uranium minerals processing is discussed in section 1.2.2 “Chemistry involved in the production of uranium ore concentrate at OD”

1.4.1.3 Smelter/Acid Plant

The smelter uses the only one of its kind, direct-to-blister process. The dried copper concentrate goes to a flash furnace where it is trapped to remove the molten blister. The molten blister is then transferred via launders to the anode furnaces for fire-refining. The anode copper, which has 99.6 % purity and still contains both gold and silver is cast into moulds using twin casting wheels [17].

The slag from the flash furnace is also tapped into an electric furnace to collect any residual copper. The gasses produced during the smelting process are cooled via a
waste heat boiler and go through a gas cleaning process before going into the acid plant. In the acid plant, the SO₂ gases are converted to sulfuric acid to be used for the leaching of both concentrate and tailings leach in the hydrometallurgical circuit [17].

1.4.1.4 Refinery

There are three components to the refinery operation, these include:

- Electrorefining (ER)
- Electrowinning (EW) to produce copper cathode

Precious metals recovery and refining producing gold and silver bullions

The copper anodes (from the smelter) are taken to the ER tank-house, which uses the ISA PROCESSTM to produce copper cathodes with a purity of greater than or equal to 99.999 % (LME grade). The slimes produced in this process are then treated in Australia’s most complex gold and silver refining process, producing premium quality gold and silver [17].

The copper rich electrolyte (from the Cu SX plant) becomes the feedstock for the EW process, which also utilises the ISA process. The EW copper has a purity of 99.999 % [17].

1.4.2 Chemistry involved in the production of Uranium Ore Concentrate at Olympic Dam

Though the processes used at OD for converting uranium minerals into UOC are well established, there a number of areas in which scientific research can contribute to improvement in these processes. As one of the main foci of this thesis is the chemistry of coffinite dissolution only the dissolution/leaching chemistry of uranium minerals is discussed here in detail. As there is a lack of knowledge surrounding the dissolution chemistry of coffinite, the information given below is the published understanding of uranium dissolution based around the findings of uraninite studies.
Current leach practices at Olympic Dam use dilute aqueous sulphuric acid to achieve dissolution of the uranium minerals in the ranges of 20-90 % dependent upon the ore [17].

For dissolution, uranium is required in the hexavalent state and can then leach directly into solution according to the following equation:

\[
UO_3^+ + 2H^+ \rightarrow UO_2^{2+} + H_2O
\]

Equation 1

In solution, sulphuric acid ionises to form sulphate, bisulphate and hydrogen ions. Uranium in the hexavalent form can react with ionised sulphuric acid to form uranyl sulphate (Equation 2) and complex uranyl sulphate anions (Equations 3 and 4). Dissolved uranium can be found in any of these forms dependent on a number of variables including uranium concentration and temperature [26].

\[
UO_2^{2+} + SO_4^{2-} \leftrightarrow UO_2SO_4
\]

Equation 2

\[
UO_2SO_4 + SO_4^{2-} \leftrightarrow UO_2(SO_4)_2^{2-}
\]

Equation 3

\[
UO_2(SO_4)_2^{2-} + SO_4^{2-} \leftrightarrow UO_2(SO_4)_3^{4-}
\]

Equation 4

If uranium is present in the non-soluble tetravalent form, it requires oxidation to produce the hexavalent ion (Equation 5). To do this, iron is used as the oxidant (Equation 6) as it is always present in the system as either part of the ore or introduced as metallic iron through wear and abrasion of equipment during the milling and grinding process.

\[
UO_2 \rightarrow UO_2^{2+} + 2e^-
\]

Equation 5

\[
UO_2 + Fe^{3+} \rightarrow UO_2^{2+} + 2Fe^{2+}
\]

Equation 6

In an acid medium, rapid oxidation of the uranium ion occurs and hence reduction of the ferric ion to ferrous ion. The rate of this step will differ for each uranium mineral; the operating conditions will also have a significant effect on this rate. To ensure continued dissolution of UO₂ (or any other tetravalent uranium species), the ferric ion must be regenerated. A subsequent oxidation reaction is required to maintain the ferric
ion concentration in solution by oxidising the ferrous ions (Equation 7). There are many oxidants which may be used for this purpose in the uranium acid leach process including; manganese dioxide, (or pyrolusite its mineral equivalent), sodium chlorate, air oxidation and agitation, chlorine, potassium permanganate and oxidation by biological activity [26]. Olympic Dam employs the use of sodium chlorate [17, 27].

\[
6Fe^{2+} + NaClO_3 + 6H^+ \rightarrow 6Fe^{3+} + NaCl + 3H_2O \quad \text{Equation 7}
\]

The Oxidation Reduction Potential (ORP) of the leach solution is known to influence the leaching of uranium and is related to the ferric-ferrous ratio [26, 28, 29]. Typically, leach solutions are maintained at ORP values in the range of 450 mV to 550 mV vs Standard Calomel Electrode (SCE); however it has been found that an ORP of 320 mV vs SCE is sufficient to convert all uranium to the hexavalent form [17, 25].

As mentioned earlier, sulphuric acid is the lixiviant used for leaching uranium minerals at Olympic Dam. There have been reports of other acid lixivants being used such as nitric and hydrochloric acids [26, 28]. A suitable pH (and free acid concentration) is required to keep uranium and copper in solution. At Olympic Dam, the free acid concentration target range is between 6 – 15 g/L of H$_2$SO$_4$ (pH around 1.0 - 1.3) [17, 25]. As acid can be consumed during the leaching process, additional acid is often required to maintain the desired free acid concentration. Acid consumption is usually as a result of gangue minerals being present in the ore and not as a result of the reactions featured in Equation 7 [17, 26]. At Olympic Dam, siderite, hematite and metallic iron consume acid according to the reactions featured in Equations 8 to 10.

At low acid concentrations and ambient temperatures:

\[
FeCO_3 + H_2SO_4 \rightarrow FeSO_4 + CO_2(g) + H_2O \quad \text{Equation 8}
\]

At increased temperature and elevated acid concentrations:

\[
Fe_3O_4 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O \quad \text{Equation 9}
\]

\[
Fe + H_2SO_4 \rightarrow FeSO_4 + H_2(g) \quad \text{Equation 10}
\]
1.5 Objectives

There is a lack of understanding pertaining to the dissolution of uranium from the mineral coffinite primarily due to the limited research conducted on this mineral. One of the biggest challenges in trying to understand the dissolution chemistry is trying to establish the chemical equilibrium in solution in the absence of a defined chemical composition of coffinite. This itself is near impossible in a natural system where there are so many different variables and unknowns (composition of solution is constantly changing).

One of the objectives of this thesis was to gain quantitative mineralogical information on naturally forming coffinite and aid in the discussion over the uncertainty surrounding the coffinite chemical and structural formula. The thesis will also study the gangue mineralogy which hosts natural coffinite within an ore body. The aforementioned was conducted using a large number of techniques that are discussed in detail in chapter 2.

Another objective of this thesis was to prepare synthetic coffinite, which could be used as an analytical comparison to the naturally forming coffinite and be used for further comprehensive studies. Synthetic coffinite is imperative to gaining an in-depth understanding of coffinite, only a synthetic sample is void of all impurities allowing for strong theoretical and experimental data to be collected forming a solid foundation to which impurities and dopants found in naturally occurring samples can then be tested in a precise scientific and logical manner. A more in-depth look at the previous literature regarding synthetic coffinite as well as the preparation and analysis of synthetic coffinite prepared for this thesis can be found in Chapter 3: Preparation and Characterisation of Synthetic Coffinite.
The third major objective of this PhD project was to investigate the dissolution chemistry of coffinite using the above mentioned prepared synthetic coffinite. The use of synthetic coffinite for the study of the dissolution chemistry may improve mineral processing of uranium ores containing coffinite as each individual parameter may be tested and analysed independently, without the extremely complex matrix variations found in natural samples. The results of these investigations can be found in Chapter 4: Investigations on the Dissolution of Synthetic Coffinite.

1.6 References


CHAPTER 2

CHARACTERISATION OF A URANIUM BEARING ORE AND A NATURAL COFFINITE SAMPLE
2.1 Introduction

As mentioned in the previous chapter there are a number of factors that can influence the dissolution of uranium minerals such as coffinite. Basically these factors can be split into two main types:

- Internal – these include composition (including oxidation state) and structure of the uranium mineral
- External – these include minerals/compounds at uranium mineral grain boundaries, species present in the dissolution matrix and the general reaction conditions (temperature, pH, Eh)

In order to investigate the influence of some of the aforementioned factors on the leaching of minerals such as coffinite detailed characterisation studies are required. There have however been very few detailed characterisation studies conducted on coffinite bearing ore samples. More specifically there have been very few studies on the following aspects of such samples:

- Composition of coffinite
- Location of coffinite within the bulk material
- Grain boundary of coffinite and the mineralogy of its surrounds

Coffinite is a naturally occurring uranium ore mineral broadly classified as a reduced tetravalent $U^{4+}$ species (see Chapter 1.1: Uranium Minerals for more details on classification). It is commonly only found as microscopic inclusions where the crystal size is $< 5 \, \mu m$ and most samples are too small for conventional structural analytical techniques [1-5]. There are however localities where coarse grained material has been located and data on such samples have been reported in literature.
2.1.1 Occurrence and Composition

Coffinite is the major uranium mineral in the unoxidised ores of the Colorado Plateau, the location it was first discovered. By 1956 (one year after discovery) coffinite had been identified in more than 25 mines and since then has been found in many other deposits across 37 countries [2, 6-15] (Figure 2.4). Though coffinite has not always been considered a uranium ore mineral [16] today it is said to be the second most important uranium ore mineral behind uraninite [1, 4, 17].

The age of coffinite varies from location to location, the youngest coffinite is found to be “fresh” and well crystallised and the oldest coffinite is largely metamict or is pseudomorphously replaced by quartz or pitchblende. A study on the paragenesis of coffinite from New Mexico found that pyrite, cobaltite and coffinite generations overlap in time [7].

![Figure 2.4: Countries of the world which have documented coffinite occurrences](image-url)
Chemically coffinite is classified as a simple uranium silicate mineral, belonging to the most abundant group of tetravalent uranium minerals (uranyl silicates) [1, 5, 18]. Coffinite is primarily found as fine grained crystals less than 10 µm, or as a very fine-grained mineral intimately associated with other minerals. The fine-grained, intergrown nature of coffinite typically causes overestimations of elements such as Al, Si, U, rare earth elements (REE) and P during chemical analysis. Though coffinite is found around the world it has been stated that the largest dataset for the chemical composition of coffinite comes from a few areas; 1) uranium deposits in Oklo, Gabon; 2) Cigar Lake, Canada and 3) Grants uranium region, Colorado, USA [19]. The coffinite in regions 1 and 2 are both alteration products of uraninite and the crystal size is usually <5 µm, whereas the coffinite found in region 3 is considered course grained (>10 µm) [19]. The compositional data on the coffinite in these areas varies quite significantly [19]. Though initially and simplistically written as USiO₄, it is universally recognised that coffinite is never found in this form in nature. Table 2.7 lists the various chemical formulas for coffinite that have been reported in the literature.

<table>
<thead>
<tr>
<th>Coffinite Formula</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>USiO₄</td>
<td>[20, 21]</td>
</tr>
<tr>
<td>U(SiO₄)₁₋ₓ(OH)₄ₓ</td>
<td>[3, 22]</td>
</tr>
<tr>
<td>USiO₄·ₙH₂O (where n =0 &lt; 2)</td>
<td>[19]</td>
</tr>
<tr>
<td>(U⁴⁺₁₋ₓU⁶⁺ₓ)Si₁₋ₓO₄·ₙH₂O (where 0 &lt; x &lt; 0.2 and 0 &lt; n &lt; 2)</td>
<td>[19]</td>
</tr>
<tr>
<td>(U,Ca,Y)(Si,P)(O₄)₁₋ₓ(OH)₄ₓ</td>
<td>[23]</td>
</tr>
</tbody>
</table>

The first appearance in the literature of a compound having the chemical formula USiO₄ was proposed by Goldschmidt, when U⁴⁺ was substituted for the Th⁴⁺ in thorite (ThSiO₄) [24]. Since then, there have been numerous other chemical formulas proposed for coffinite (Table 2.7). The most commonly used is U(SiO₄)₁₋ₓ(OH)₄ₓ, which was derived from the presence of water observed in chemical analysis results. Stieff et al [3] analysed a high purity natural coffinite and found that the samples contained up to 61 % uranium, with varying amounts of silicon, arsenic and vanadium. The amount of SiO₂ found in these samples was not sufficient for this mineral to be a simple uranous silicate (USiO₄), and the chemical data coupled with infrared (IR) analysis in which two OH
absorption bands were observed, led Stieff et al. to the conclusion that some \((\text{OH})_4^{-4}\) was substituting for the silicate, and that the true chemical formula of coffinite was \(\text{U} (\text{SiO}_4)_{1-x} (\text{OH})_{4x}\) \([3, 22]\).

Since the work of Stieff et al. \([3]\), further compositional and IR studies have rebuked the conclusion of hydroxyl \((\text{OH})_4^{-4}\) substitution, and suggested that the water bound to coffinite is of a molecular nature which led to the proposal of the chemical formula \(\text{USiO}_4 \cdot n\text{H}_2\text{O}\), with \(n \approx 2\) by Jeneczek and Ewing \([1, 4, 19, 24, 25]\).

Deditius et al. \([19]\) investigated the chemical stability of coffinite; conducting a case study on samples from the Grants uranium region in New Mexico, USA. They determined that coffinite in the region was found in three different populations according to chemical composition and the way in which the coffinite was formed. These were:

1) Primary coffinite
   - \((\text{U}_{0.924}\text{Ca}_{0.218}\text{Y,REE}_{0.021}\text{Zr}_{0.001})_{1.163}(\text{Si}_{0.835}\text{P}_{0.033}\text{As}_{0.010})_{0.878}\text{O}_4 \cdot n\text{H}_2\text{O}\)

2) Recrystallised coffinite
   - \((\text{U}_{0.805}\text{Ca}_{0.156}\text{Y,REE}_{0.022}\text{Zr}_{0.001})_{0.984}(\text{Si}_{0.954}\text{P}_{0.036}\text{As}_{0.005})_{0.995}\text{O}_4 \cdot n\text{H}_2\text{O}\); the uranium in this coffinite was depleted approximately by 13%.

3) Coffinite formed under oxidising conditions during extensive alteration
   - \((\text{U}_{0.619}\text{Ca}_{0.117}\text{Y,REE}_{0.018})_{0.754}(\text{Si}_{1.127}\text{P}_{0.040}\text{As}_{0.004})_{1.171}\text{O}_4 \cdot n\text{H}_2\text{O}\); where the uranium was depleted by approximately 23%.

Based upon the data obtained from the coffinite found to be in group 1 and 2 (above) the amount of \(\text{U}^{6+}\) within the coffinite structure was estimated to be within the range 0.1-0.19 atoms per formula uni (apfu) with an upper limit of 0.2 apfu and hence the authors proposed the “ideal chemical formula of coffinite” as \((\text{U}^{4+}_{1-x}\text{U}^{6+}_x)\text{Si}_{1-x}\text{O}_4 \cdot n\text{H}_2\text{O}\) where 0<x<0.2 and 0<n<2. The authors also believed from their high totals in chemical analysis that the water associated with coffinite is most likely of a molecular nature, and is not an essential component of coffinite although minor amounts of \(\text{OH}^-\) may be
incorporated into the structure. The compositional variations of the coffinite seen in nature is governed by a number of substitutions [19];

- \( \text{U}^{4+} + \text{Si}^{4+} + \text{U}^{6+} + [2(\text{OH})·0.5\square] \)
- (n.b – \( \square \) indicates a vacancy in the mineral structure)
- \( \text{REE}^{3+} + \text{As}^{5+} + \text{U}^{4+} + \text{Si}^{4+} \)
- \( \text{Ca}^{2+} + (\text{As,P})^{5+} + \text{REE}^{3+} + \text{Si}^{4+} \)

1.2.1.1 Structure

Coffinite is iso-structural with zircon (ZrSiO₄), and though the crystal structure has not yet been refined, it is generally accepted that coffinite is a tetragonal orthosilicate forming a distorted cube-like polyhedron. It has a tetragonal unit cell with space group symmetry I\(4\)1/amd (141) and each uranium atom is surrounded by 8 oxygen atoms, exhibiting two different bond lengths, 0.238 nm and 0.236 nm [21, 24]. The \( \text{UO}_8 \) polyhedron shares its edge with the \( \text{SiO}_4 \) tetrahedron along the c-axis [19]. Refer to Figure 2.2 for an image of the coffinite unit cell.
As well as being iso-structural with zircon, coffinite is also iso-structural with hafnon (HfSiO₄) and thorite (ThSiO₄) as well as other synthetic actinides (Np, Pu and Am) [1, 4, 19]. Several common substitutions are discussed in the literature, such as 4(OH)-substituting (SiO₄)²⁻ and phosphorus replacing silicon providing a charge balancing mechanism allowing REE to be incorporated into the structure [1, 4, 22].

In addition to the aforementioned substitutions U⁶⁺, Zr⁴⁺, Hf⁴⁺, Ca²⁺, Y³⁺ and REE³⁺ can substitute the U⁴⁺ site, while P⁵⁺, As⁵⁺, V⁵⁺, S⁶⁺, F⁻ and OH⁻ groups can replace the Si site. There is also the possibility of vacancies at the tetrahedral site [19]. The X-ray powder diffraction pattern of coffinite resembles that of thorite, with the unit cell parameters lying between those of zircon and thorite [1, 4, 19, 22, 24], please refer to Table 2.8 for unit cell parameters of coffinite previously reported in literature.
Table 2.8: Crystallographic unit cell data for coffinite reported in literature

<table>
<thead>
<tr>
<th>Coffinite sample</th>
<th>a=b (Å)</th>
<th>C (Å)</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural (Arrowhead mine)</td>
<td>6.94†</td>
<td>6.31†</td>
<td>[3, 20, 22]</td>
</tr>
<tr>
<td>Natural (Jack Pile mine)</td>
<td>6.951†</td>
<td>6.298†</td>
<td>[20]</td>
</tr>
<tr>
<td>Natural (Grants uranium region, New Mexico)</td>
<td>6.946</td>
<td>6.268</td>
<td>[7]</td>
</tr>
<tr>
<td>Synthetic (hypergenic) (Dubinchuk et al 81)</td>
<td>6.98</td>
<td>6.30</td>
<td>[2, 26]</td>
</tr>
<tr>
<td>Synthetic (hydrothermal) (Dubinchuk et al 81)</td>
<td>6.93</td>
<td>6.30</td>
<td>[2, 26]</td>
</tr>
<tr>
<td>Natural (Dubinchuk et al 82)</td>
<td>6.98</td>
<td>6.24</td>
<td>[2, 27]</td>
</tr>
<tr>
<td>Natural (Belova et al 80)</td>
<td>6.90</td>
<td>6.21</td>
<td>[2, 28]</td>
</tr>
<tr>
<td>Natural (Nord 77)</td>
<td>6.938</td>
<td>6.291</td>
<td>[2, 29]</td>
</tr>
<tr>
<td>Natural (Bayushkin 69)</td>
<td>6.92</td>
<td>6.25</td>
<td>[2, 30]</td>
</tr>
<tr>
<td>Natural (Taylor et al 66)</td>
<td>6.97</td>
<td>6.22</td>
<td>[2, 31]</td>
</tr>
<tr>
<td>Natural (Darnley at al 65)</td>
<td>6.95</td>
<td>6.26</td>
<td>[32]</td>
</tr>
<tr>
<td>Natural (Darnley at al 65)</td>
<td>6.98</td>
<td>6.19</td>
<td>[32]</td>
</tr>
<tr>
<td>Natural (Dymkov 62)</td>
<td>7.01</td>
<td>6.26</td>
<td>[33]</td>
</tr>
<tr>
<td>Natural (Simms et al 61)</td>
<td>6.93</td>
<td>6.21</td>
<td>[2, 34]</td>
</tr>
<tr>
<td>Natural (Gruner and smith 55)</td>
<td>6.92</td>
<td>6.22</td>
<td>[2, 35]</td>
</tr>
<tr>
<td>Synthetic</td>
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<td>6.2669</td>
<td>[24]</td>
</tr>
<tr>
<td>Synthetic</td>
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<td>6.268</td>
<td>[36]</td>
</tr>
<tr>
<td>Synthetic</td>
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<td>6.263†</td>
<td>[21, 37]</td>
</tr>
<tr>
<td>Synthetic</td>
<td>6.979‡</td>
<td>6.253‡</td>
<td>[1]</td>
</tr>
<tr>
<td>Synthetic</td>
<td>6.991†*</td>
<td>6.320†*</td>
<td>[20]</td>
</tr>
</tbody>
</table>

† unit cell parameters have been convert from kX units to Å units using the conversion factor 1.00202 outline by Bragg and Armstrong Wood in 1947 [38].

‡ data referenced as coming from Fuchs and Gebert (1958), however the published paper by Fuchs and Gebert [21] originally quoted values in kX units, when converted using the factor published in 1947 [38] (values quoted in above table), they differ from the values quoted by Burns [5], it is therefore believed that these values have been erroneously transcribed or calculated.

* unit cell data based upon incomplete indexing.
1.2.1.2 Properties of Coffinite

The enthalpy of coffinite has been studied by a number of groups. The results from these studies however vary significantly. Mazeina et al. [39] suggest that that enthalpy of coffinite formation is similar to that of NpSiO$_4$. The Gibbs free energy of coffinite was first calculated by D. Langmuir in 1978 [40] based on the equilibrium with natural waters and was reported to be 1882.3 kJ/mol. In 2002 Fleche used ab initio calculations to give a $\Delta G^\circ_f$ of 2028 kJ/mol. Both Grambow and Giffaut [41] as well as Robit-Pointeau et al [42] state that the $\Delta G^\circ_f$ calculated back in 1978 may be inaccurate as Al-silicates, quartz and chalcedony control the concentration of H$_4$SiO$_4$ (aq) in groundwater.

The thermal stability of coffinite appears to differ and is dependent on the nature of coffinite and supposedly the conditions under which it was heated. Natural coffinite sourced by Fuchs and Hoekstra was found to be stable when ignited to 400 °C where the sample turned from black to a grey green colour [37]. The authors believed that at least in part the black colour was as a result of associated organic matter [37]. Upon heating this sample further to 500 °C in air, it gradually decomposed to U$_3$O$_8$ and SiO$_2$ [37]. Other samples of natural coffinite have been known to decompose to UO$_2$ and amorphous silica after heating beyond 400 °C, where another sample (from Jack Pile mine) was found to retain structural stability when heated to 500 °C [20]. Synthetic coffinite appears to be more stable than its natural counterpart. Hoekstra and Fuchs found their synthetic coffinite was stable in vacuum for at least 5 hours at 700 °C [20], whereas Fuchs and Hoeskstra found synthetic coffinite stable up to 1000 °C in vacuum and 500 °C in air [37]. Pointeau et al. found that over time their synthetic coffinite decomposed to form UO$_2$ and a silicon-rich amorphous phase (as was observed in one of the natural samples above), though they suggest that over extended periods of time decomposition could occur even at lower temperatures (250 °C) [24].
2.1.2 Gangue Mineralogy Associated with Coffinite

Before discussing the mineralogy of coffinite bearing ores it is important to state that as coffinite can be an alteration product of uraninite it is often found in deposits containing this mineral [4], [2, 8, 17].

Of all the minerals found to be associated with coffinite, the two most common are quartz and chlorite, although they may or may not be present in the same deposit. Galena, chalcopyrite and pyrite are also commonly associated with coffinite. As the mineralogy of ore deposits are unique the gangue mineralogy associated with coffinite differs from deposit to deposit. Table 2.9 lists some of the major mineral phases associated with coffinite, from various deposits around the world.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Deposit found</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Haematite</td>
<td>Olympic Dam, Nabarlek</td>
<td>[8, 9, 43]</td>
</tr>
<tr>
<td>Quartz</td>
<td>Olympic Dam, Nabarlek, Vaal River, Coutras Deposit, Mt Taylor Mine</td>
<td>[8, 9, 14, 19, 43, 44]</td>
</tr>
<tr>
<td>Sericite</td>
<td>Olympic Dam</td>
<td>[8, 43]</td>
</tr>
<tr>
<td>Chlorite</td>
<td>Olympic Dam, Nabarlek, Vaal River, Mt Taylor Mine, Gabon</td>
<td>[8, 9, 14, 19, 43, 45]</td>
</tr>
<tr>
<td>Baryte</td>
<td>Olympic Dam</td>
<td>[8, 43]</td>
</tr>
<tr>
<td>Florencite</td>
<td>Olympic Dam</td>
<td>[8, 43]</td>
</tr>
<tr>
<td>Bastnaesite</td>
<td>Olympic Dam</td>
<td>[8, 43]</td>
</tr>
<tr>
<td>Rutile (TiO₂)</td>
<td>Olympic Dam, Gabon</td>
<td>[8, 43, 45]</td>
</tr>
<tr>
<td>Apatite</td>
<td>Olympic Dam</td>
<td>[8]</td>
</tr>
<tr>
<td>Calcite</td>
<td>Olympic Dam</td>
<td>[8]</td>
</tr>
<tr>
<td>Zircon</td>
<td>Olympic Dam</td>
<td>[8]</td>
</tr>
<tr>
<td>Slag Glass</td>
<td>Olympic Dam</td>
<td>[8]</td>
</tr>
<tr>
<td>Galena</td>
<td>Olympic Dam, Gabon, Cigar Lake</td>
<td>[8, 15, 45, 46]</td>
</tr>
<tr>
<td>Chalcocite</td>
<td>Olympic Dam</td>
<td>[8, 43]</td>
</tr>
</tbody>
</table>
2.2 Experimental

2.2.1 Materials

2.2.1.1 Uranium bearing ore sample (Uranium leach feed)

The uranium bearing ore sample investigated was obtained from the Olympic Dam processing plant in South Australia. As it was a uranium leach feed sample it has undergone some processing (such as flotation) to remove valuable commodities (mostly copper). This sample is typical of what is presented to the uranium leach process at Olympic dam and was used as received.
2.2.1.2 Natural Sample Containing Coffinite

The natural sample containing coffinite used in this study was acquired from the Museum of Victoria geology collection. The sample originated from New Mexico, and upon acquisition of the sample, it was the authors understanding that the sample had been identified by geologists as containing coffinite (no characterisation data was available from the supplier of the sample).

2.2.2 Characterisation Techniques

2.2.2.1 Elemental Analysis

The methodology for the elemental analysis conducted on the uranium containing ore body is summarised in Table 2.10.
<table>
<thead>
<tr>
<th>Element for Analysis</th>
<th>Methodology Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>Samples were fused with sodium carbonate to bring elements into solution and result determined using a specific ion electrode</td>
</tr>
<tr>
<td>Cl</td>
<td>Samples were fused with sodium carbonate at 1000 °C, whereby the resultant melt was leached in deionised water and result determined colourimetrically</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;2+&lt;/sup&gt; and Fe&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>A sub sample was digested with sulphuric and hydrofluoric acids and result determined volumetrically</td>
</tr>
<tr>
<td>Fe, Mg, Si, Al, Ti, V, Cr, Ce, La, U (sample preparation)</td>
<td>The samples were fused with sodium peroxide and the subsequent melt was dissolved in dilute hydrochloric acid for analysis. Due to the high furnace temperatures used, volatile elements are lost. This procedure is particularly efficient for determination of major element composition (including silica) in the samples or for the determination of refractory mineral species</td>
</tr>
<tr>
<td>Fe, Mg, Si, Al, Ti, V, Cr, Mn, Cu, K, Ca, Zn, S, Co, P, Ba, Mo, S_IDE</td>
<td>Results determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)</td>
</tr>
<tr>
<td>Ce, La, U, Zr(MAD), Bi, As, Pb</td>
<td>Results determined by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)</td>
</tr>
<tr>
<td>Mn, Cu, K, Ca, Zn, S, Co, P, Ba, Mo, (sample preparation)</td>
<td>The sample was digested and refluxed with a mixture of acids (hydrofluoric, nitric, hydrochloric and perchloric acids). Though this multi acid digest approaches a total digest for many elements some refractory minerals are not completely attacked.</td>
</tr>
<tr>
<td>S_IDE, Tot C (sample Preparation)</td>
<td>The sample was leached with a sodium carbonate solution to dissolve sulphate and water soluble sulphur species. Sulphide species remain undissolved and hence the sulphide sulphur content is calculated as the difference between total and soluble sulphur</td>
</tr>
<tr>
<td>Tot Org C, CO&lt;sub&gt;2&lt;/sub&gt; (sample preparation)</td>
<td>The sample was acidified to remove carbonate and then residual carbon was determined using a total combustion analyser.</td>
</tr>
<tr>
<td>Tot C, Tot Org C, CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Result was determined by Total Combustion Analysis</td>
</tr>
</tbody>
</table>
2.2.2.2 X-Ray Diffraction (XRD)

Standard X-ray diffraction patterns were obtained on a Bruker D8 Advance fitted with a Copper tube (Cu Kα radiation), monochromator and scintillation detector. Diffraction patterns were run at an accelerating voltage of 40 kV and current of 35 mA using a 1 ° fixed divergence slit. Data was collected over a 2 theta range of 10-90 ° in increments 0.015 ° (total run time of 138 min). The instrument was calibrated with a silica calibration standard prior to use. For occupational health and safety reasons the samples was specially prepared in a sample holder that allows kapton film to be placed over the top of the powdered samples to reduced possible inhalations of radioactive dust particles.

In-situ High Temperature XRD (HT-XRD) analysis was conducted on the same instrument as above, coupled with a HTK 2000 high temperature attachment. All samples were mixed with ethanol and lacquer and placed on a platinum heating strip under vacuum (10-7 Torr) for analysis; the natural sample containing Coffinite was crushed to less than 75 µm before analysis.

The uranium containing ore body was analysed between the range 10-90 °2θ with a step size of 0.0200 °2θ and 1 second per step on a 1800 second delay. Patterns were acquired by HT-XRD at 50 °C, 100 °C and every 100 °C thereafter up to and including 1000 °C.

The data acquired for the natural sample containing Coffinite was done between the 2θ range 10-90 ° with a step size of 0.02 °2θ and 2.5 seconds per step. Six temperatures were analysed: 50 °C, 200 °C and every 200 °C thereafter up to and including 1 000 °C.
Synchrotron X-ray diffraction patterns were obtained on the uranium containing ore body (uranium containing ore body) using the powder diffraction beamline at the Australian Synchrotron using photon energy of 16.5 KeV and a beam current of 163 mA. A Mythen, microstrip detector was used and hence each pattern was taken in two parts where the 2θ start position was offset by 0.5 °2θ allowing the patterns to later be merged together creating one full pattern with no gaps. For each pattern an acquisition time of 480 seconds was used.

2.2.2.3 Thermal Gravimetric Analysis (TGA)

TGA experiments for the uranium containing ore body were conducted on a Perkin Elmer TGA 7, Thermogravimetric analyser attached to a Perkin Elmer thermal analysis controller TAC 7/DX with a Perkin Elmer gas selector. The analysis method used was as follows: held at 20 °C for 1 minute, heated from 20 °C to 1000 °C at 5 °Cmin⁻¹ and held at 1000 °C for 1 minute under an inert atmosphere of nitrogen gas.

Thermogravimetric Analysis (TGA) experiments for the natural sample containing Coffinite were conducted on the same instrument as above. The sample was analysed via the following method: held at 30 °C for 1 minute, heated from 30 °C to 750 °C at 1 °Cmin⁻¹ in air and from 750 °C to 1000 °C under an inert atmosphere of nitrogen gas.

2.2.2.4 Scanning Electron Microscopy / Energy Dispersive Spectroscopy

Scanning Electron Microscopy (SEM) images were obtained using a FEI Quanta 200 Environmental Scanning Electron Microscope; operating at 30 kV with 1 nm resolution at a working distance of 10 mm, and an EDAX Silicon (Lithium) X-ray detector, for Energy Dispersive Spectroscopy (EDS). Approximately 0.7-0.8 g of sample was mixed with epoxy resin and mounted in a 25 mm round mould for curing. After curing, the sample mounts were heated in a drying oven for 2-3 hours, allowed to cool and then the basal part of each sample mount was sectioned to expose a fresh cross-sectional surface.
The newly exposed surface was then polished using successively finer grades of emery paper followed by a final surface polishing using a sequence of 6, 3 and 1 \( \mu \)m diamond pastes. To prevent possible dissolution and/or contamination of water-sensitive phases in samples, all cutting and polishing was conducted in the absence of water.

2.2.2.5 X-Ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) analysis was conducted using a Thermo K-Alpha XPS instrument at a pressure of 1x10^-9 Torr or lower. The survey C1s and U 4f core level spectra were analysed with monochromatic Aluminium K alpha radiation (photon energy of 1486.6 eV) at a pass energy of 20 eV and an electron take off angle at 90°. The overall resolution was 0.1 eV for XPS measurements. The samples were prepared by pressing powdered samples in a die press at 8,000 Kg of pressure, and affixing the pressed sample to carbon tape on the sample plate. The Carbon 1s peak was used as the internal standard and defined as 285 eV.

2.2.2.6 Electron Probe Micro Analysis (EPMA)

EPMA of Uranium Bearing Ore Sample (ULF)

Samples were divided into two size fractions by dry sieving (>75\( \mu \)m and <75\( \mu \)m). These samples were supplied to CSIRO’s Minerals department for additional sample preparation (as polished cross-sections in epoxy resin) and analysis. For further information regarding the sample preparation, please refer to Appendix A.

Field Emission Gun (FEG)-EPMA mapping was conducted on the sample using a high resolution Field Emission Gun (FEG) equipped EPMA (JEOL 8500F Hyperprobe). High contrast back scattered electron (BSE) imaging was used to locate regions of high uranium content. These regions were then mapped using a combination of wavelength dispersive (WD) and energy dispersive (ED) spectroscopic techniques. Fe, Si, U Ti and Pb were mapped using WD (standards used for these elements can be found in Appendix A). Elements not measures by WD spectrometry were measured using two
energy-dispersive (ED) spectrometers operating in parallel. Operating conditions can be found in Table 2.11.

**Table 2.11: FEG-EPMA Hyperprobe operation conditions for mapping of uranium bearing ore sample**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acc. voltage (kV)</td>
<td>12</td>
</tr>
<tr>
<td>Beam current (nA)</td>
<td>50</td>
</tr>
<tr>
<td>Map area (μm)</td>
<td>160 × 120?</td>
</tr>
<tr>
<td>Matrix size (pixels)</td>
<td>800 × 600?</td>
</tr>
<tr>
<td>Step size (μm)</td>
<td>0.2-1.0</td>
</tr>
<tr>
<td>Dwell time (ms)</td>
<td>25</td>
</tr>
</tbody>
</table>

After mapping, the element distribution data were manipulated using the software package CHIMAGE (in-house proprietary software developed by CSIRO Process Science and Engineering – Harrowfield et al., 1993 [48]) allowing for individual elemental data or combined element maps (See Appendix A for more information).

The data was also analysed using an automated clustering algorithm which identifies chemical groupings. The clustering procedure is a multi-element approach with the groupings of elements that are identified via the clustering algorithm representing statistically different chemical phases [49]. The chemical phases identified by the clustering procedure can then be transferred back onto the mapped region to provide a “phase-patched” map showing the distribution of mineral phases within the mapped area.

**EPMA of Natural Sample Containing Coffinite**

Samples were prepared as polished cross-sections in epoxy resin at CSIRO (see Appendix A). Initially the sample was mapped and analysed in the same way as that of the above sample, where here WD spectrometry was used to map for Fe, Si, U and Pb and the operating conditions were as bellow (Table 2.12).
Table 2.12: FEG-EPMA Hyperprobe operating conditions for mapping of natural sample containing coffinite

<table>
<thead>
<tr>
<th>Map name</th>
<th>Coffinite (Natural) (map1)</th>
<th>Coffinite (Natural) (map2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acc. voltage (kV)</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Beam current (nA)</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Map area (μm)</td>
<td>160 × 120</td>
<td>800 × 600</td>
</tr>
<tr>
<td>Matrix size (pixels)</td>
<td>800 × 600</td>
<td>800 × 600</td>
</tr>
<tr>
<td>Step size (μm)</td>
<td>0.2</td>
<td>1.0</td>
</tr>
<tr>
<td>Dwell time (ms)</td>
<td>25</td>
<td>25</td>
</tr>
</tbody>
</table>

The chemical composition of coffinite was quantitatively determined using a JEOL 8900 Superprobe electron microprobe analyser (EMPA, JEOL 8900). The accelerating voltage and beam current were 20 kV and 20 nA, respectively, and the beam diameter was defocused to 5 μm.

A number of elements were analysed (Fe, Pb, Si, Ti, Th, Al, P, Ca, Y, S and O) and a separated energy-dispersive system was used during the analysis to check for the presence of other elements. The counting time for each element was 20 seconds on the peak and 10 seconds on each side of the peak (to measure background). (The standards used for calibration can be found in Appendix A)

All elemental analyses were corrected for atomic number (Z), absorption (A) and fluorescence (F) using the CITZAF Phi-Rho-Z matrix correction procedure ([50-52]) implemented on the JEOL 8900 EPMA. In order to determine the possible influence of different matrix correction procedures, the PAP procedure of Pouchou and Pichoir, [53-55] was also used to calculate the element abundances. There was no significant difference in results obtained from either matrix correction procedure.
2.3 Results and Discussion

2.3.1 Uranium Bearing Ore Sample (Uranium Leach Feed)

The uranium bearing ore sample was characterised using the following techniques: Elemental analysis, XRD (standard and synchrotron) and EPMA. As the sample was known to contain < 1000 ppm of coffinite (based on bulk analysis data provided by the supplier of the sample) the main focus of the studies on this sample were to characterise the gangue minerals present, as it was uncertain if a large enough coffinite grain could be located in a sub sample (in a reasonable time frame) for detailed studies.

2.3.1.1 Elemental Analysis

Elemental analysis was conducted initially to accurately determine the amount of uranium in the sample and hence if it could have possibly contained a significant amount of coffinite suitable for conducting detailed characterisation studies. The results of the elemental analysis are given in Table 2.13.

The sample contained 422 ppm of uranium, and though a relatively small amount it was reasonable to assume that there would be enough coffinite in the sample for characterisation studies to be conducted. The elemental analysis results also indicated that approximately half of the sample was made up of iron and silicon oxides as well as reasonable contributions from elements such as aluminium, fluorine, potassium, copper, calcium, cerium, lanthanum, phosphorus and barium. The elemental data is discussed further (in conjunction with the XRD results) in a later section.
Table 2.13: Uranium bearing ore sample (ULF) elemental analysis results

<table>
<thead>
<tr>
<th>Element for Analysis</th>
<th>Unit</th>
<th>Result</th>
<th>Element for Analysis</th>
<th>Unit</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>%</td>
<td>1.67</td>
<td>S_IDE</td>
<td>%</td>
<td>0.08</td>
</tr>
<tr>
<td>Cl</td>
<td>%</td>
<td>0.06</td>
<td>As</td>
<td>ppm</td>
<td>86</td>
</tr>
<tr>
<td>Fe^{2+}</td>
<td>%</td>
<td>1.29</td>
<td>Ce</td>
<td>ppm</td>
<td>2500</td>
</tr>
<tr>
<td>Fe^{3+}</td>
<td>%</td>
<td>31.1</td>
<td>Co</td>
<td>ppm</td>
<td>65</td>
</tr>
<tr>
<td>Fe</td>
<td>%</td>
<td>32.4</td>
<td>La</td>
<td>ppm</td>
<td>1610</td>
</tr>
<tr>
<td>Mg</td>
<td>%</td>
<td>0.17</td>
<td>P</td>
<td>ppm</td>
<td>1450</td>
</tr>
<tr>
<td>Si</td>
<td>%</td>
<td>18</td>
<td>Pb</td>
<td>ppm</td>
<td>57</td>
</tr>
<tr>
<td>Mn</td>
<td>ppm</td>
<td>138</td>
<td>Ba</td>
<td>ppm</td>
<td>7030</td>
</tr>
<tr>
<td>Al</td>
<td>%</td>
<td>4.31</td>
<td>Mo</td>
<td>ppm</td>
<td>65</td>
</tr>
<tr>
<td>Cu</td>
<td>ppm</td>
<td>1560</td>
<td>Ti</td>
<td>ppm</td>
<td>0.13</td>
</tr>
<tr>
<td>K</td>
<td>%</td>
<td>1.88</td>
<td>V</td>
<td>ppm</td>
<td>100</td>
</tr>
<tr>
<td>Na</td>
<td>%</td>
<td>0.12</td>
<td>U</td>
<td>ppm</td>
<td>422</td>
</tr>
<tr>
<td>Ca</td>
<td>%</td>
<td>2.01</td>
<td>Cr</td>
<td>ppm</td>
<td>50</td>
</tr>
<tr>
<td>Zn</td>
<td>ppm</td>
<td>54</td>
<td>Tot C</td>
<td>%</td>
<td>0.14</td>
</tr>
<tr>
<td>Zr(MAD)</td>
<td>ppm</td>
<td>111</td>
<td>Tot Org C</td>
<td>%</td>
<td>0.01</td>
</tr>
<tr>
<td>Bi</td>
<td>ppm</td>
<td>2.9</td>
<td>CO_{2}</td>
<td>%</td>
<td>0.5</td>
</tr>
<tr>
<td>S</td>
<td>ppm</td>
<td>3050</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.3.1.2 Uranium Mineralogy

As there was limited uranium in the sample identifying and studying the uranium mineralogy was difficult as it was below the detection limit for many analytical techniques such as XRD.

EPMA was conducted on five sections of uranium containing ore body samples of different size fractions. Uranium was found sparingly throughout the sample. Uraninite, the most abundant uranium mineral at Olympic Dam was located only in the smaller
size fraction (<75 µm) (Figure 2.6), although in the larger size fractions (refer to 2.3.1.3 Gangue Mineralogy Figure 2.18 to Figure 2.20) the presence of uranium in an iron oxygen matrix was observed. This phase is most probably uraninite within a hematite or another iron oxygen matrix, which was unable to be resolved by the software.

Coffinite as such was not identified as a mineral phase in any of the sections analysed, although uranium in a silicon oxygen matrix was observed in four of the five phase maps. This uranium in a silicon oxygen matrix was most likely non-stoichiometric coffinite. Hereafter in this section this non-stoichiometric coffinite will be referred to as coffinite.

The > 75 µm area 4 (Figure 2.7) was the informative map when trying to understand the coffinite mineralogy. The size of coffinite varies from 10 x 10 µm grains of an irregular shape to 3 µm more typically square or triangular (in cross-sectional shape) down to approximately 1 µm spherical type grains. Coffinite was found both at the edges of particles as well as completely encapsulated by various gangue minerals. Surrounding each encapsulated coffinite grain the phase map indicates a uranium edge phase, this phase has no mineral assigned as it will be the grain boundary and contain a mixture of both the coffinite and the gangue mineral. In this sample the coffinite was found to be encapsulated by a number of different minerals such as; hematite, quartz, sericite, Fe chlorite. When the coffinite is associated with hematite or Fe chlorite, a thin layer (0.5 µm) of uranium in an iron oxygen phase (possibly uraninite) was found between the defined coffinite and U-edge phases. The largest coffinite grain in Figure 2.7 also contains uranium in a calcium oxygen matrix.

Uranium was also found in other unnamed phases containing elements such as calcium, iron, aluminium, silicon and oxygen.
Figure 2.6: EPMA phase map of uranium bearing ore sample <75 µm area 1

Figure 2.7: EPMA phase map of uranium bearing ore sample >75 µm area 4
2.3.1.3 Gangue Mineralogy

**X-Ray Diffraction Techniques**

X-ray diffraction studies on the uranium containing ore body were conducted using two different energy sources, monochromatic copper radiation and a synchrotron light source. XRD was used to identify the major mineral phases present in the sample (that were in a crystalline form). Due to the detection limit of the instrument any phases that are below approximately 1 wt% would not be detected via this technique, and hence the technique was used almost exclusively to study the gangue mineralogy.

The XRD pattern obtained from XRD analysis conducted using Cu radiation is presented in Figure 2.8. The most significant peaks observed in the pattern are as a result of the minerals hematite (Fe₂O₃) and quartz (SiO₂), denoted by ^ and * respectively. On closer analysis a tentative identification of fluorite (CaF₂) was made; however around the most intense fluorite peak (approximately 28.25 °) uraninite and bornite peaks also occur (Figure 2.9) and may have contributed to the intensity of the major fluorite peak.
Figure 2.8: Standard X-ray diffraction pattern of uranium bearing ore sample (range of 10 - 80° 2θ)

Figure 2.9: Standard X-ray diffraction pattern of uranium bearing ore sample (range of 27 to 29° 2θ) showing library matches for fluorite, bornite and uraninite

(♦ Fluorite; ■ Bornite; ● Uraninite)
It was difficult to distinguish minor phases from the background interference. Background interference can come from various different effects, namely the iron fluorescence caused via using copper radiation as well as the in-homogeneity of the particle size of the samples. Though the kapton film used to cover samples for safety reasons should not produce significant background interference, the raised background (found at low angles) synonymous with X-ray amorphous material was found to be primarily due to this film.

The less intense peaks in the XRD pattern were almost indistinguishable from the background and hence no conclusive identification could be made. As the sample was a complex matrix of multiple minerals at varying amounts, many of the mineral species present in the sample were expected to be pushing the detection limits of the XRD technique, however the library matching software (Bruker AXS DIFFRAC.EVA) was used to assist in identifying plausible minerals which may be present in the sample

- sericite \((\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH,F})_2)\)
- florencite \((\text{CeAl}_3(\text{PO}_4)_2(\text{OH})_6)\)
- bornite \((\text{Cu}_5\text{FeS}_4)\)
- rutile \((\text{TiO}_2)\)
- spinel group minerals
- uraninite

These findings are consistent with previous work conducted on samples from the Olympic Dam deposit [8, 17, 43].

High temperature in-situ XRD analysis of the uranium containing ore body was conducted to investigate the minerals contained in the leach feed could be obtained. Upon annealing (or heat treatment) as many minerals undergo known transformations and or decomposition, allowing for changes in crystalline phases to be detected via XRD.

The results of the in-situ HT-XRD analysis are presented in Figure 2.10 - Figure 2.12. When the leach feed was heated to 800 °C under an inert atmosphere no significant changes were observed in the XRD patterns. When the sample was heated beyond 800
°C a number of significant changes were observed. Between 800 °C - 900 °C the peak at approximately 72 °20 disappeared and the appearance of a new peak at approximately 30 ° could be seen. At temperatures between 900 °C - 1000 °C a significant decrease in the peaks at approximately 33 ° and 41 ° were observed. The peaks located at approximately 33 °, 41 ° and 76 °20 are due to the presence of hematite, as these peaks decreased in intensity (or disappeared) it led to a closer inspection of the peak located at approximately 36 °20 (also due to the presence of hematite). It was not until a closer examination of this peak was conducted that it appeared this peak had actually shifted to a lower 20 value (35 °). When scrutinised even more closely this “shift” may be better explained by the formation of a new peak at approximately 35 °20 whereas the peak found at approximately 36 °20 has actually decreased in intensity significantly. Hematite is known to decompose at temperatures above 800 °C [56] and hence the decrease in the hematite peaks (~33 °, ~36 °, ~41 ° and ~76 °20) are consistent with those findings.

The formation of the two new peaks at approximately 30 ° and 35 °20 correspond with the two major peaks for cuprospinel and hence it is believed that upon heating the uranium feed leach above temperatures of 800 °C this mineral was formed. For the formation of cuprospinel to occur upon heating an appreciable quantity of copper would be required to be already present in the leach feed sample. From the observation of a shoulder present on the peak located at approximately 28 °20 and the tentative match for bornite already being suggested, it is considered the most likely source of copper. It has been reported that bornite decomposed at temperature in excess of 670 °C [56] and as there is no observable decrease in the peak at approximately 28 ° at temperatures above 700 °C, two conclusions can be made; 1) this peak is most likely not due to the presence of bornite in the sample or 2) another mineral(s) present in the leach feed sample such as fluorite or uraninite contributed significantly to the intensity of this peaks and hence masked any significant reduction which would be caused by the decomposition of bornite.

In order to further investigate if uraninite was one of the mineral species responsible for the peak located at approximately 28 °20 HT-XRD analysis of the leach feed sample
was conducted in air (as opposed to under vacuum as in the previous analysis above) because uraninite is known to readily converted to pitchblende (U₃O₈) upon heating in air. It was then expected that if uraninite was a significant contributor to the peak in question, this peak would decrease. The results of HT-XRD studies conducted in air are presented in Figure 2.13 where no significant decrease in the peak at approximately 28° occurred suggesting that this peak is either not due to the presence of uraninite and/or the contribution of this peak being caused by the presence of uraninite is not significant, resulting in the most likely conclusion that this peak is predominately caused by the presence of fluorite.

Figure 2.10: In-situ high temperature X-ray diffraction patterns of uranium bearing ore sample from room temperature to 1000 °C (range of 10 to 80 ° 2θ)
Figure 2.11: In-situ high temperature X-ray diffraction patterns of uranium bearing ore sample from 800 °C to 1000 °C (range of 60 ° to 80 ° 2θ)

Figure 2.12: In-situ high temperature X-ray diffraction patterns of uranium bearing ore sample from 800 °C to 1000 °C (range of 25 ° to 45 ° 2θ)
Synchrotron XRD

Due to the ambiguity surrounding the mineral phases present, XRD patterns of the uranium containing ore body were collected from the synchrotron light source, which has a much higher level of resolution when compared with those patterns collected on a laboratory based Copper source instrument.

The synchrotron data supported the identification of hematite, quartz and fluorite that were also identified using the standard XRD instrument / in-situ HT-XRD. There were a number of tentative gangue mineral identifications made when analysing the standard XRD patterns, these included sericite, rutile and spinel group minerals; none of these minerals were identified in the uranium containing ore body upon the analysis of Synchrotron data. The greater resolution and brilliance of the synchrotron beam allowed for the identification of a number of gangue minerals that were not identified using standard techniques (XRD and in-situ HT-XRD), these minerals are listed below;
- Florencite (CeAl₃(PO₄)₂(OH)₆)
- barite (BaSO₄)
- birnessite (K₀.₅Mn₂O₄.₃(H₂O)₀.₅)
- siderite (FeCO₃)
- chalcopyrite (CuFeS₂)
- cuprospinel (Cu₀.₈₆Fe₂.₁₄O₄)
- alurgite (K₀.₉₄Na₀.₀₆)(Mg₀.₉₈Al₁.₇₅Fe₀.₁₅Mn₀.₂)(Al₀.₉Si₃.₀₈)O₁₀(OH)₂)
- muscovite (K,Na) (Al,Mg,Fe)₂ (Al₀.₉Si₃.₀₈)O₁₀(OH)₂)
- calcite (CaCO₃)

Of these all except barite, birnessite, cuprospinel and alurgite are commonly found at the Olympic Dam deposit [8, 9, 43].

From Figure 2.16 it is visible that with the use of synchrotron light it was possible to eliminate the ambiguity which surrounded the peak at approximately 28° 2θ, as to establish that this peak is observed due to the presence of fluorite and not bornite, it may however have very minor contributions from the presence of uraninite.

Due to the nature of a natural sample such as these ore tailing, homogeneity is always of concern. In order to determine if any bias due to the heterogeneity of the sample was present and may have contributed to the identification of different minerals a number of different samples were collected and analysed. It was found that the patterns of each separate sample only varied in intensity and contained identical peaks, indicating that no significant bias was present in the XRD results.
Figure 2.14: Synchrotron vs Standard X-ray diffraction pattern of the uranium bearing ore sample

Figure 2.15: Synchrotron vs Standard X-ray diffraction pattern of the uranium bearing ore sample in the range of 37° to 45° 2θ
Figure 2.16: Synchrotron X-ray diffraction pattern of uranium bearing ore sample (range of $27.5^\circ$ to $29^\circ$ 2$	heta$) showing the peak at $\sim 28^\circ$ 2$	heta$ and library matches for fluorite, bornite and uraninite.

(♦ Fluorite; □ Bornite; ● Uraninite)

**Thermogravimetric Analysis**

Thermogravimetric Analysis (TGA) was conducted on the uranium leach feed to investigate if heating the sample resulted in any reactions and or processes that could cause a significant change in the mass of the uranium containing ore body. From the results obtained in the TGA experiment, a minor mass loss (approximately 2 %) was observed when the leach feed was heated to a temperature of approximately 700 °C. Upon further heating (to a temperature of 1000 °C) a more substantial mass loss of approximately 4 % was noted. For understanding this mass loss, information which was gathering from HT-XRD analysis (Figure 2.10) was required. It was discovered that the temperature range at which the most significant mass loss was observed corresponded closely with the range in which the formation of cuprospinel and hematite decomposition was observed. Hence this mass loss was most likely due to the aforementioned processes.
Figure 2.17: TGA output of uranium bearing ore sample
(indicating mass loss with respect to temperature)

Electron Probe Microanalysis

In all phase maps it is evident that the major gangue phases found in the uranium leach feed are hematite, quartz, sericite, fluorite, barite and Fe chlorite, which were present in all five phase maps (Figure 2.6, Figure 2.7, Figure 2.18-Figure 2.20). Dolomite and florencite appear in four of the five maps, Bastnaesite-La and Fe Mg aluminosilicate appear in three phase maps and in only the larger size fraction (>75 µm) an unidentified Ca/Fe/O mineral was also found in three of the maps however it was observed in both fractions. K-feldspar, chalcopyrite and rutile can be found in two of the maps and phases such as zircon and CuSx are found in just one phase map.
Figure 2.18: EPMA phase map of uranium bearing ore sample >75 µm area 1

Figure 2.19: EPMA phase map of uranium bearing ore sample >75 µm area 2
2.3.2 Natural Sample Containing Coffinite

As the uranium bearing ore sample contained limited coffinite, it was not possible to obtain quantitative chemical information on that sample. The natural sample containing coffinite is an example of a coffinite specimen from a geology collection, and though no data on the purity of the sample was given, it was believed that this sample was the best available source for attempting to analyse the composition of coffinite. Quantitative chemical information is important in order to be able to compare the composition of any synthetic coffinite with that which is found in nature.

2.3.2.1 Uranium Mineralogy

X-Ray Photoelectron Spectroscopy

The natural sample containing coffinite exhibited a single Uranium oxidation state. The U-4f7/2 core level was found to have a binding energy of 382.4 eV and the U-4f5/2 core level was fitted to 393.0 eV (not shown in the figure below). Though the U-4f7/2 peak position is indicative of the uranium oxidation state, the peak position for any given oxidation state may be shifted depending on the compound the uranium is a constituent
of; as a result of the influence of neighbouring ions dictated by the crystal structure [57]. In this case the best way to identify the oxidation state is through satellite (shake-up or shake-off) peaks. Due to the lack of a satellite peak at a higher binding energy of 6-6.8 eV it is believed that the oxidation state of uranium (at/near the surface) for this sample is primarily U (VI).

![Graph showing XPS data](image)

**Figure 2.21: Uranium U-4f7/2 -core XPS data of natural sample containing coffinite**

*Scanning Electron Microscopy / Energy Dispersive Spectroscopy*

SEM and EDAX spot analysis of the bulk sample (Figure 2.22) indicated a number of elements being present within the bulk of the sample. The most predominate element was silicon followed by oxygen, confirming the presence of a large quantity of quartz in the sample. Other elements present included, vanadium, aluminium, potassium and uranium. Within the bulk sample a grain of coffinite was located and EDAX analysis performed (Figure 2.23). The EDAX elemental plot indicated that silicon was the major element present, however unlike the bulk this grain contained a much higher percentage of uranium, indicated by the intensity of the U (M shell) line. A grain which contained high relative percentages of uranium, silicon and oxygen appears to be coffinite. This coffinite grain contained elemental impurities including vanadium, aluminium, potassium and sulphur. These impurities may be incorporated into the coffinite structure or may be closely associated, in mineral form, with the coffinite grain.
Elemental mapping of the coffinite grain featured in Figure 2.23 and Figure 2.24 was conducted, analysing for all elements seen in the spot analysis acquisition. EDAX elemental maps show areas with the highest concentration of the element of interest as more intense with colour, if the element is not present it will appear black in the elemental map. The main grain featured in the Back Scattered electron (BSE) image, believed to be coffinite, had a significant quantity of uranium. However the silicon and oxygen elemental map showed this grain to contain less of each element than the grain surrounding it. This was to be expected as the relevant percentage of silicon and oxygen in quartz (the bulk material and surrounding grains) are much higher than in coffinite. The elemental mapping also indicated that there were significant quantities of aluminium and sulphur within the same grain as coffinite.
Figure 2.22: EDAX spectra of natural sample containing coffinite
Insert: BSE image of sample

Figure 2.23: EDAX spectra of a coffinite grain found in the natural sample
Insert: BSE image of coffinite grain found in a natural sample (area of EDAX)
Figure 2.24: EDAX elemental mapping of a coffinite grain found in the natural sample
An observation from an initial backscattered electron (BSE) survey of the natural sample containing coffinite indicated that there was limited coffinite present in the sample. One substantial piece of coffinite was eventually located and mapped in detail (Figure 2.25). This large coffinite grain, 120-140 μm in size, consisted of patchy, polycrystalline aggregates with heterogeneous BSE contrast (Figure 2.25a).

Individual element maps for uranium (Figure 2.25b) and silicon (Figure 2.25c) indicate that the BSE data was strongly correlated with variations in both elements. Brighter regions in the BSE image corresponded to areas with greater amounts of uranium (as elements with high atomic numbers appear brighter in BSE images, while the slightly darker areas indicate regions of higher silicon content). The variation in uranium and silicon across the grain is better visualised when the elements Si, O and U are plotted together on the one map (Figure 2.25d). On this plot, areas of higher uranium appear slightly deeper reddish in colour whereas silicon-rich regions are more of a lighter red orange colour. Areas of the map that are light blue indicate silicon and oxygen rich regions (no uranium) representing either quartz (SiO₂) or aluminosilicates. Distinguishing between quartz and aluminosilicate can be achieved by comparing Figure 2.25d with Figure 2.25c. In Figure 2.25, the Si element distribution map, quartz appears red (i.e. maximum Si) while phases such as low-U coffinite and aluminosilicates appear various shades of yellow or green, depending on their silicon content. The variation of silicon and uranium within the grain is examined in more detail in Figure 2.26 where a line profile is taken across the central part of the grain. Individual profiles for silicon and uranium show a clear correlation with regions of high silicon having corresponding low uranium content and vice versa.
Figure 2.25: EPMA map results from the natural sample containing coffinite sample (Map 1).

Image a) the BSE image, b) the U distribution map, c) the Si distribution map, d) a Si/O/U three element map, and, e) the final phase patched map.

The colour scale bar in b) and c) both indicate relative concentration.
Figure 2.26: Silicon distribution map (a) and corresponding U and Si profile across the natural coffinite (b).

The position of the line profile across the grain is indicated by the red line in Figure 2.25.

The map data was analysed using the automated clustering algorithm in CHIMAGE to identify chemical groupings. Results of the cluster analysis are shown in Figure 2.25e. The main chemical phases identified by the clustering procedure were; coffinite (shown in red in Figure 2.25e), quartz (green), a low U (high Si) coffinite phase (blue) and minor
potassium-rich feldspar (orange). The unnamed purple phase in Figure 2.25e represents material that is intermediate in composition between coffinite and low-U coffinite and corresponds to the green coloured patches shown in the Si distribution map (Figure 2.25c). It has a higher silicon content than coffinite but a lower silicon content than the low-U coffinite phase. The slight variations in U:Si ratio in the central part of the grain were not separated into distinct phases by the clustering. It was only where there was an obviously large compositional difference that a separate phase was indicated. This highlights the difficulties in using chemistry-based classification schemes to separate different phases as there are potentially a large number of phases that could be identified, depending on the compositional boundaries set for each phase. Representative ED spectra showing the differences in chemistry between different crystallites within the coffinite are provided in Figure 2.27.
Figure 2.27: Representative ED spectra showing the differences in chemistry between different crystallites within the coffinite.

**Quantitative EPMA**

Quantitative EPMA results (Table 2.14) indicated that the major elemental impurities were phosphorus and sulphur, while other small amounts of impurities (Ti, Ca, Al and Y) were also seen, they were present at levels slightly below the 2σ detection limit for
each element and hence have not been included in Table 2.14. Analyses indicated that the weight percentages of U and Si vary over wide ranges from 57.48-62.22 wt% and from 10.99-13.27 wt%, respectively (Appendix B). The overall U:Si is very low, 0.62, compared with the expected U:Si of coffinite (i.e. 1.00). The low U:Si indicates excess silicon and depletion in U compared to ideal USiO₄ (72.1 wt% U; 8.5 wt% Si) and this was confirmed by recalculation of the formula (assuming ideal USiO₄) which comes out as U₀.₈Si₁.₂O₄ (neglecting the presence of P and S impurities).

Table 2.14: Quantitative EPMA results for the natural sample containing coffinite

<table>
<thead>
<tr>
<th>Element</th>
<th>Natural Sample Containing Coffinite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>n.d.</td>
</tr>
<tr>
<td>Pb</td>
<td>n.d.</td>
</tr>
<tr>
<td>Si</td>
<td>11.73</td>
</tr>
<tr>
<td>U</td>
<td>61.51</td>
</tr>
<tr>
<td>Ti</td>
<td>&lt;d.l.</td>
</tr>
<tr>
<td>Th</td>
<td>n.d.</td>
</tr>
<tr>
<td>Al</td>
<td>&lt;d.l.</td>
</tr>
<tr>
<td>P</td>
<td>0.018</td>
</tr>
<tr>
<td>Ca</td>
<td>m.d.</td>
</tr>
<tr>
<td>Y</td>
<td>&lt;d.l.</td>
</tr>
<tr>
<td>S</td>
<td>0.221</td>
</tr>
<tr>
<td>O</td>
<td>21.37</td>
</tr>
<tr>
<td>Total</td>
<td>94.85</td>
</tr>
<tr>
<td># analyses</td>
<td>5</td>
</tr>
<tr>
<td>U:Si atomic Ratio</td>
<td>0.62</td>
</tr>
</tbody>
</table>

n.d. = not detectable
<d.l. = below detection limit

The analytical totals for the natural coffinite vary widely from 91.4-98.2 wt% although the analysis with the highest total still only gives a U:Si of 0.72. It is noted however, the
low totals are consistent with other workers who have attempted to analyse naturally occurring coffinite [2, 15]. In general, the low analytical totals typical of microprobe analyses of coffinite may be attributed to a combination of the following factors: (1) substitution of hydroxyl for silica or absorption of non-structural hydroxyl during metamictisation; (2) the presence of U6+; (3) angstrom sized domains of amorphous silica; and (4) the additive effects of trace amounts of elements not in the analytical program, especially the REEs. These potential sources of errors are discussed below.

Hydroxyl was originally thought to be an essential component of coffinite, since then anhydrous coffinite has been synthesized [21, 37], and infrared and Differential Thermal Analysis (DTA) studies have shown that hydroxyl is not an essential constituent of coffinite. Nonetheless, \((\text{OH})_4^{4-}\) may substitute for \((\text{SiO}_4)^{2-}\), or non-structural hydroxyl may be absorbed during metamictisation due to radioactive decay. Partial metamictisation causes disordering of crystal domains and, finally, may lead to a complete breakdown of coffinite into amorphous silica and uraninite. However, the analyses of this study show excess P and Si, suggesting that \((\text{OH})\) has not substituted for silica. It is possible that the excess silica and deficiency in U may represent the presence of fine-grained silica and/or partial leaching of the uranium by hydrothermal fluids which, given that significant sulphur was measured in the coffinite, appear to have been S-rich (this may be important as uranium is soluble when present as a uranyl sulfate species).

The presence of U\(^{6+}\) has been confirmed in uraninite [58] and in coffinite by X-ray photoelectron spectroscopy [59]. The uranyl ion, therefore, may partly account for low analytical totals and for apparent under population of the uranium site, because the data reduction programs did not allow for the presence of U\(^{6+}\). If all the U were present as U\(^ {6+}\), the average total would increase to 99.61 %. It is not likely, however, that all of the uranium would be present as the hexavalent species. The natural coffinite was checked by ED examination for the possible presence of other elements not included in the quantitative data set. No other elements were identified to be present in the coffinite.
2.3.2.2 Gangue Mineralogy

X-Ray Diffraction / High Temperature X-Ray Diffraction

The standard XRD powder pattern of the natural sample containing coffinite indicated a clear presence of quartz; it showed no signs of uranium mineralogy, including coffinite. This was most likely caused by uranium being under the detection limit of the instrument or being amorphous. High temperature XRD was conducted to obtain more information about the mineralogy; upon heating various minerals may be altered, decompose and some may crystallise allowing for detection via X-ray methods such as XRD. Upon heating, only minimal changes in the XRD patterns were observed. These changes are attributed to known quartz phase changes. At 573 °C \( \alpha \) quartz converts to \( \beta \) quartz; at 867 °C, \( \beta \) quartz converts to \( \beta \) tridymite which is stable at temperatures below 1,737 °C [60].

![High Temperature X-Ray Diffraction Pattern]

Figure 2.28: HT-XRD pattern of the natural sample containing coffinite
Upon further examination of the natural sample containing coffinite, there were no other areas where coffinite was located. However, fine-grained uraninite was present in the sample in reasonable quantities. An 800 x 600 µm area was mapped, much larger than the coffinite grain map, allowing examination of surrounding phases in order to determine the dominant gangue mineralogy of the sample.

The main chemical phases identified by the clustering procedure (Figure 2.29) were; quartz (the dominant mineral in the sample) and potassium-rich feldspar. Minor phases included: albite (Na-rich feldspar), portlandite (a calcium hydroxide phase), kaolinite, and an unnamed KMgVFe aluminosilicate (coffinite was also present in the sample but was not identified within the area covered by Map Area 2). The main uranium-bearing phases located in the sample were uraninite and the unnamed KMgVFe aluminosilicate which typically contained low levels of uranium. Representative ED spectra for each of these U-bearing phases are shown in Figure 2.30.
Figure 2.29: EPMA clustered map result from the natural sample containing coffinite (Map 2) showing the dominate mineral phases present.
Figure 2.30 Representative ED spectra from the two U-bearing phases in map area 2. The top spectrum is for uraninite while the bottom spectrum is from the unnamed KMgVFe aluminosilicate phase.
2.3.2.3 Other Analysis

**Thermogravimetric Analysis**

The thermogravimetric analysis mass loss curve and its derivative (Figure 2.31), indicates three regions of mass loss. Theoretically if coffinite contains 2 moles of water, the mass loss of water would equate to 9.8%. The total mass loss of this natural sample is approximately 10%. As the true theoretical mass of the natural sample is not known, it would be difficult to say how much of this 10% is due to water. The main phase of this sample is quartz, which is known to be stable to high temperatures, hence it is believed that the first loss between 50-200 °C can be attributed to water loss and is typical of the loss associated with water from interlayer sites [61]. The second loss from 350-600 °C is the region at which natural coffinite is known to degrade [20, 37]. This loss can be attributed to this degradation process which also corresponds with the dehydroxylation of water [61], it is also within this region that any associated organics would be lost. The further mass loss when the temperature is raised above 600 °C is most probably the continual degradation of coffinite into UO₂ and SiO₂ [20, 37].

![Figure 2.31: Thermogravimetric analysis mass loss curve with the associated derivative curve of natural sample containing coffinite](image)
2.4 Chapter Summary

Elemental analysis of the uranium bearing ore sample was found to contain 422 ppm of uranium. These results also indicated the large presence of iron and silicon as well as reasonable contributions of elements such as Al, F, K, Cu, Ca, Ce, La, P and Ba. The uranium mineralogy was established via EPMA. Uraninite was identified only in the <75 µm fraction of the sample where fractions above this size indicated the presence of Uranium in a Fe-O matrix (presumably) uraninite. Although coffinite was not identified as a phase in any of the size fractions, a Uranium in a Si-O matrix was identified and believed to be non-stoichiometric coffinite. Coffinite was found to be located on the edge of large particles as well as being completely encapsulated by minerals such as, hematite, quartz, sericite and Fe chlorite. Each coffinite was surrounded by a phase labelled U-edge, which corresponds to the region where the grain boundaries of the two minerals meet. In cases where coffinite was adjoining minerals such as hematite or Fe chlorite a thin layer of uranium in a Fe-O matrix (uraninite) was found. The size of the coffinite grains varied from 10 x 10 µm (irregular in shape) to 1 µm (spherical grains). Other un-named uranium minerals were also found in the sample.

Gangue mineralogy was found to make up the bulk of the sample; this information was obtained through a variety of techniques. Standard XRD analysis allowed for confident identification of only hematite and quartz, where In-situ HT-XRD enabled the further confident identification of fluorite (using a process of elimination and the stability of bornite and uraninite at high temperatures). In-situ HT-XRD results also confirmed the presence of a significant quantity of a copper bearing mineral/compound due to the formation of cuprospinel that was observed at high temperatures. The improved spatial resolution and intensity of the synchrotron data allowed for superior phase identification of a variety of minerals where standard X-ray techniques gave inconclusive results. Synchrotron data allowed identification of minor phases including florencite, barite and birnessite with trace amounts of other minerals including rutile, siderite, chalcopyrite, cuprospinel, alurgite, muscovite and calcite. Due to the trace levels of various minerals and plausible elemental substitution of many minerals, X-ray
diffraction data alone was not able to be used to determine the complete mineralogy of such a complex assemblage. EPMA analysis highlighted just how variable the sample can be. The major gangue mineralogy identified included minerals such as; hematite, quartz, sericite, fluorite, barite and Fe chlorite. In addition EPMA also positively identified a number of other minerals throughout the sample (dolomite, florencite, bastnasite-La, Fe Mg aluminosilicate, unidentified Ca-Fe-O mineral, K-feldspar, Chalcopyrite, rutile, zircon and CuSx). TGA showed a total mass loss of approximately 6 wt%, with the most substantial loss (~ 4%) corresponding to the same temperature range at which the formation of cuprospinel and hematite decomposition occurred.

The natural sample containing coffinite was found to contain only limited coffinite with XRD patterns indicating that the primary phase is quartz. HT-XRD showed only minimal changes upon heating which was attributed to the phase transformation of quartz (α quartz to β quartz and then to β tridymite). EMPA located a significant coffinite grain (120 – 140 µm) which was a patchy, polycrystalline aggregate with heterogeneous BSE contrast. Analytical totals varied between, 91.4 % to 98.2 % with the weight per cent of Uranium and Silicon varied throughout the sample ranging from 57.48 % to 62.22 % and 10.99 % to 13.27 % respectively. The U:Si ratio also varied and was found to be low (over all U:Si 0.62) where the highest ratio was 0.72; with the edge of the coffinite grain containing greater silicon abundances. Through recalculating the formula (assuming the ideal USiO₄) the coffinite in the natural sample is non-stoichiometric (U₀.₈Si₁.₂O₄) when neglecting the presence of phosphorous and sulphur impurities. XPS analysis indicated that the detectable uranium in the sample is in the VI oxidation state. EDAX analysis indicated the predominance of Quartz (silicon and oxygen) in the bulk sample and trace amounts of vanadium, aluminium, potassium and uranium. When the sample was heated the only changes detectable by XRD were the known quartz phase transitions. TGA experiments indicated the loss of water upon heating and the possible degradation of the coffinite to UO₂ and SiO₂ as suggested by the literature.
2.5 References


3.1 Introduction

As mentioned in the previous chapter (Chapter 2) coffinite is typically found in nature as very fine grains usually occurring as microscopic inclusions and/or intergrowths with other minerals or organic matter [1-3]. As a consequence of its occurrence, isolating significant quantities of high purity samples of pure coffinite is extremely difficult. This has led to research being conducted on the preparation of “synthetic” forms of coffinite to enable detailed investigations to be conducted on various aspects of this important uranium bearing compound.

In 1955, Steiff et al. listed five groups that had worked on the synthesis of coffinite where all groups had been unsuccessful in their attempts [1]. The first method for the preparation of synthetic coffinite was reported by Hoekstra and Fuchs in 1956 [4], since then there have been a number of researchers that have used this method or amended forms of it to prepare synthetic coffinite [5-8]. The method for synthetic coffinite preparation described by Hoekstra and Fuchs [4] is a hydrothermal method involving uranium tetrachloride (UCl₄) and sodium metasilicate (Na₂SiO₃) as the key reactants.

The method for preparing synthetic coffinite that was reported by Hoekstra and Fuchs [4] was as follows:

“1 mmole each of uranium tetrachloride and sodium metasilicate are dissolved in 10 mL of water. Sodium hydroxide solution is added dropwise to the uranium silicate solution until a stiff gel forms near the neutral point. Enough additional base is added to make the mixture slightly alkaline (pH 8 to 10). The gelatinous precipitate is then centrifuged and transferred to a vitreous silica tube which is placed in an Inconel bomb tube. We carry out these operations in a nitrogen atmosphere to prevent oxidation of the
uranium. The sealed Inconel tube is heated for 4 to 5 days at 250 °C to crystallise the USiO₄.” [4]

Hoekstra and Fuchs [4] reported that the synthetic coffinite produced using this method was a bluish-green solid that appeared to be isotropic under a microscope and had a refractive index of 1.83 to 1.85. Characterisation of the synthetic material generated using varying conditions confirmed the presence of tetragonal crystals of coffinite through X-ray powder diffraction patterns. All samples however were found to be contaminated with quartz (SiO₂) or cristobalite (SiO₂).

In 1959 Fuchs and Hoekstra [5] published another paper on the preparation of synthetic coffinite. In this publication the method reported involved the same starting materials and quantities as described in the first paper, though this time distilled water was specified and they also specified the concentration of sodium hydroxide (NaOH) used as 1 M. As with the first brief method reported, the addition of base was required to make the solution slightly alkaline. In the revised method, the desired pH of solution was not described, though it would be reasonable to assume it was in the vicinity of 8 to 10 (the same pH described by Hoekstra and Fuchs [4] in the original brief method).

The gel was then broken by the addition of a few extra drops of base and shaking the mixture. The gel precipitate is centrifuged (as per the first method), and the supernate is decanted to a volume of 6 mL and “the preparation” buffered with sodium bicarbonate to make a 0.5 M solution and to achieve a pH of 8.3. Excess silica (0.25 g) was then added in the form of vitreous silica and the slurry poured into a platinum cup before being placed in an Inconel hydrothermal reaction vessel and heated to 250 °C for 24 Hr or 5 days at 200 °C. The synthetic coffinite formed via this method was a microcrystalline solid that required separation from the excess silica (quartz) - this was achieved by gravimetric separation techniques.
Although Fuchs and Hoekstra published a number of papers on the synthesis of coffinite, the conditions they used were not clear and open to interpretation \[8, 9\] and the coffinite produced clearly contained significant levels of impurities, they put forth a lot of research into the understanding of synthetic coffinite formation. Fuchs and Hoekstra believed that the depolymerisation of the polysilicate and the formation of USiO$_4$ occurs during the heating process and not the precipitation step. It was found that if uranium (IV) hydroxide and silica were mixed under the same experimental conditions the formation of uraninite and quartz were observed, leading to the understanding that co-precipitation of uranium and silica was required for the preparation of synthetic coffinite. They also outline the importance of the pH of solution and the use of a buffer; it was found that without the use of a buffer the synthesis could not be repeated effectively and that a pH of between 8 and 10.5 was required for the successful production of coffinite. Temperature was a further parameter tested in the Fuchs and Hoekstra \[5\] study and the lower limit studies where the formation of synthetic coffinite was prepared was found to be 200 °C. However, coffinite was also produced when the solution was heated to 120 °C for 120 Hr and then heated an additional 120 Hr at 225 °C. The authors at first believed this result to be conflicting, as uranium(IV) hydroxide was precipitated separately suggesting that uraninite, under appropriate conditions, can be converted to coffinite. The authors then suggest that the formation of coffinite at lower temperatures is purely a rate problem if the UO$_2$ crystallisation at lower temperatures occurs during the drying step \[5\].

In 1977 Mulak \[10\] published a new method of preparing synthetic coffinite, which was to be used in a study of crystal field parameters of USiO$_4$. This method was based upon the earlier work conducted by Fuchs and Hoekstra \[5\] and also on the studies conducted by Mumpton and Roy \[11\] on the hydrothermal stability of the zircon and thorite group. Mulak’s procedure was only briefly discussed. As in previous outlined methods Mulak used equimolar amounts of UCl$_4$ and Na$_2$SiO$_3$ dissolved in water; however this time the synthesis was up-scaled to the larger amounts of 5 mmole. As per previous methods, the solution was buffered with sodium bicarbonate to a pH of 8.3 (though more specific it is within the range stated in previous methods) and excess silica was added in the form of vitreous silica. The reaction was carried out in a glass
container inside in a Teflon lined stainless steel bomb and then heated for 200 °C – 250 °C for 24 Hr to 120 Hr. Besides the difference in the vessels used, the time and temperature was consistent with previous methods. Melak conducted this method in an argon atmosphere in order to prevent the U(IV) from oxidising, this was the first report of atmosphere of the reaction was controlled during the experiment.

In 1991 Farrokh Pishva completed a Master’s degree on the topic “Synthesis of uranium silicate by a hydrothermal method” [7]. Unlike every other method reported in literature this procedure claims to produce a uranium(IV) silicate under slightly acidic conditions. A solution of uranium tetrachloride was prepared by chemical methods from uranyl nitrate and to that; sodium metasilicate (1 mmol solutions) was added. A yellow precipitate was formed (this finding had not been previously reported). 2 M sodium hydroxide was then added to adjust the pH to 6. The precipitate was then placed in a sealed reactor and heated (hydrothermally reacted) for 24 Hr at 250 °C and 600 psi.

In 2009 the most recent and comprehensive paper was written on the synthesis and characterisation of coffinite by Pointeau et al. [8]. Although this method was based on the protocol outlined by Fuchs and Hoekstra [5], there were a number of differences. Firstly the reaction was carried out under reducing conditions (95 % N2/5 % H2) to prevent any oxidation of U(IV) to U(VI). Unlike all other methods, Pointeau et al. did not have silicon in excess, in fact one mmole of UCl4 and a slightly sub stoichiometric amount of Na2SiO3 were reported to have been utilised. Each reagent was dissolved separately in 5 mL of degassed water and UCl4(aq) was then added drop-wise to Na2SiO3(aq). The authors found it necessary for the additions to occur in this order (uranium added to metasilicate) for successful coffinite synthesis. The pH was then adjusted to about 8 using a 2 M sodium hydroxide solution and buffered with sodium bicarbonate to a pH close to 9 where the final concentration of carbonate ions was equal to 0.5 M. In this method the preliminary gel phase was directly used for the precipitation step. The hydrotethermal reaction took place in a Parr Instrument
Research surrounding the synthesis of coffinite has been conducted sporadically over many years, though with the publication of each new paper on synthetic coffinite comes a new or altered method. At the time the research in this chapter was conducted the most recent publication by Pointeau et al. [8] was not available and therefore the coffinite method outlined in the following sections of this chapter was based upon the earlier work of Hoekstra and Fuchs [4] and Fuchs and Hoekstra [5]. Many of the key issues and ambiguous sections from previous synthetic methods that were investigated in this study were also addressed in the Pointeau et al. publication, the method developed and presented in this thesis is very similar to that developed and published by Pointeau et al. (2009) [8]. A method(s) for producing high quality and reproducible synthetic coffinite is important for to a variety of research areas. Synthetic coffinite allows for the fundamental understanding of mineral processes such as dissolution, which are studied in this thesis. Synthetic coffinite may also be used in the study of nuclear waste management; as spent fuel is comprised of uraninite and coffinite is a known alteration product [3, 12-15], which may determine the amount of uranium leached from the spent fuel by natural ground water [16-19].

3.2 Experimental

3.2.1 Chemical Reagents

The following reagents used for the preparation of uranium dioxide (UO$_2$), uranium tetrachloride (UCl$_4$), and synthetic coffinite were of laboratory grade:

- Uranyl acetate (UO$_2$(CH$_3$COO)$_2$·2H$_2$O)
- Carbon tetrachloride (CCl$_4$)
- Sodium metasilicate (Na$_2$SiO$_3$)
• Sodium hydroxide (NaOH)
• Sodium bicarbonate (NaHCO₃)

3.2.2 Synthesis of UO₂

Uranium dioxide (UO₂) was synthesised via a heat treating method, whereby uranyl acetate was heated to 600 °C for 12 Hr in air, allowed to cool then heated further to 900 °C for 6 Hr under reducing conditions (95 % Ar₂ and 5 % H₂).

3.2.3 Synthesis of Uranium Tetrachloride

Uranium tetrachloride (UCl₄) was prepared using a custom made setup featured below in Figure 3.32, and based on the method outlined by Kahan et al. [20]. UO₂ was placed in a quartz boat and heated to 400 °C in an inert atmosphere of dry nitrogen gas. After reaching temperature, an excess of carbon tetrachloride (CCl₄) was added drop-wise at a rate of approximately 20 mL/Hr. UCl₄ is very hygroscopic and easily oxidised therefore much care was taken when transferring and weighing to ensure it did not come in contact with air. In order to remove the sample from the reaction tube, a positive flow of nitrogen gas was created, the flask in the ice bath and bubbler were disconnected and transfer tube connected. Once the quartz boat had been moved into the transfer tube the caps were then connected and the nitrogen turned off.
3.2.4 Analytical Techniques

A variety of analytical techniques were used in the characterisation of prepared synthetic coffinite. For methodology relating to X-Ray Diffraction / High Temperature X-Ray Diffraction, Scanning Electron Microscopy / Energy Dispersive Spectroscopy, X-Ray Photoelectron Spectroscopy and Thermogravimetric Analysis, please refer to Chapter 2.2.2 (Characterisation Techniques). Only additional characterisation techniques, not previously described or changes in instrumental conditions, are discussed below.

3.2.4.1 X-ray Diffraction

XRD patterns obtained were analysed with the Bruker Eva (Evaluation) software and used the JCP2.2CA database within the software to aid and confirm any particular phases present in the sample. The coffinite library match, used during the phase identification process, has the database identification number 01-072-0169 and ISCD collection code of 01548, the data for this library match was supplied by Fuchs and Gebert (1958) [6] and calculated from ICSD using POWD-12++(1997). The uraninite...
library match has the database identification number 00-041-1422 with the data being supplied by Fritsche and Sussiek-Fronefeld (1988).

### 3.2.4.2 Fourier Transform Infrared Analysis

Fourier Transform Infrared (FTIR) (mid IR) analysis was conducted on a Perkin Elmer spectrum 100 spectrometer within the mid infrared region of between 4000 cm\(^{-1}\) and 400 cm\(^{-1}\). Each spectrum was collected using a potassium bromide (KBr) disk sample preparation method for a total of 36 scans at a resolution of 4 cm\(^{-1}\).

The FAR-IR analysis was completed on a Perkin Elmer Spectrum 2000, between the Far IR region (660 cm\(^{-1}\) and 160 cm\(^{-1}\)). Each sampled was prepared as a polyethylene disc and spectrum collected with 48 scans at a resolution of 4 cm\(^{-1}\).

### 3.2.4.3 Electron Probe Microanalysis

Electron Probe Microanalysis (EPMA) was conducted on the prepared synthetic coffinite to understand the composition and homogeneity of the individual crystals. This technique also allowed for comparison with the natural sample containing coffinite to identify any variation in chemistry between natural and synthetic coffinites.

As with the natural sample containing coffinite, two types of EPMA information were obtained. Initially, the sample was mapped and then further examined by quantitative EPMA techniques to determine the chemistry of the coffinite. Please refer to Chapter 2.2.2.5 for preparation and FEG-EPMA methodology and Chapter 2.2.2.6, for the methodology for quantitative EPMA. The only variation in operating conditions for the analysis of synthetic coffinite (compared to the natural sample containing coffinite (Chapter 2) is to the Hyperprobe operating conditions, for each map of the synthetic coffinite the conditions can be found in Table 3.15.
Table 3.15: FEG-EPMA hyperprobe operating conditions for mapping of synthetic coffinite.

<table>
<thead>
<tr>
<th>Map Name</th>
<th>Synthetic Coffinite (map1)</th>
<th>Synthetic Coffinite (map1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acc. voltage (kV)</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Beam current (nA)</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Map area (μm)</td>
<td>$307.2 \times 307.2$</td>
<td>$180 \times 240$</td>
</tr>
<tr>
<td>Matrix size (pixels)</td>
<td>$1024 \times 1024$</td>
<td>$600 \times 800$</td>
</tr>
<tr>
<td>Step size (μm)</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Dwell time (ms)</td>
<td>25</td>
<td>25</td>
</tr>
</tbody>
</table>

3.2.4.4 Surface Area Analysis

Surface area analysis was carried out using an ASAP2010 instrument. The sample was degassed overnight at a temperature of 150 °C. Nitrogen was used as the analysis gas and the following parameters were measured: BET surface area, Langmuir surface area, micropore area, external surface area, BJH adsorption and desorption cumulative surface area of pores between 1.7 and 300 nm diameter, micropore volume, BJH adsorption and desorption cumulative pore volume of pores between 1.7 and 300 nm diameter, adsorption and desorption average pore diameter and BJH adsorption and desorption average pore diameter.

3.3 Results

3.3.1 Investigations on preparation of synthetic coffinite

As mentioned previously in the introduction to this chapter, there is much ambiguity surrounding some aspects of the methods that have been published for the preparation of synthetic coffinite. Initial preparations of synthetic coffinite conducted (that were based on the information provided in the aforementioned literature) did not result in
the successful preparation of coffinite. Hence it was decided to investigate the influence of altering some of the conditions that were deemed ambiguous.

The aspects of the method used which did not result in the formation of coffinite that were investigated included:

- What portion of the solution was used after centrifuging
- Treatment of UCl$_4$
- Presence of oxygen (degassing water and NaOH solution)
- U:Si ratio
- Breaking of gel

Investigations on the influence of the aforementioned aspects resulted in the production of synthetic coffinite. The method / conditions that resulted in the formation of the highest purity synthetic coffinite prepared are discussed in the proceeding paragraphs.

**Method for the Highest Purity Synthetic Coffinite Formation**

Synthetic coffinite prepared using the following reaction conditions (which based on X-ray diffraction analysis led to the highest purity synthetic coffinite), it was this coffinite which was used for all further characterisation and experiments.

In a glove bag under a dry and inert environment, . Equimolar (5mmol) of sodium metasilicate and UCl$_4$ were each dissolved in 25 mL of degassed water and 10 mL of 5mmol UCl$_4$(aq) was added drop-wise to the Na$_2$SiO$_3$(aq). The addition of 2 M sodium hydroxide solution was used to form a gel at an approximate pH of 8. The solution was then buffered to a pH of between 8.5 and 9 using the appropriate amount of NaHCO$_3$, for the solution to contain a concentration of 0.5 M carbonate ions. This buffered solution was placed sealed in a Teflon lined stainless steel autoclave vessel and heated to 250 °C.
in a carbolite muffle furnace for 24 Hr. After the vessel was allowed to cool the product was washed with water (and mild sulfuric acid) and allowed to air dry.

**Experimental/Methodology Progression**

Synthetic coffinite was produced via a developed method adapted from those previously described by Hoekstra and Fuchs [4] and Fuchs and Hoekstra [5]. Though many parameters were changed during the method development, there were some reaction conditions which were kept constant throughout all experiments; these are described in the following paragraph.

It was known that the atmosphere of which the reaction was carried out in was an important aspect of the reaction; hence the reaction was conducted in a glove bag under an inert environment of dry nitrogen. 2 M sodium hydroxide was used to form a gel at an approximate pH of 8-9 and the solution was then buffered to a pH of between 8.5 and 9 using an appropriate amount of sodium bicarbonate so the solution contains a concentration of 0.5 M carbonate ions. This buffered solution was then sealed in a Teflon lined stainless steel autoclave vessel and placed in a carbolite muffle furnace at 250 °C for 24 Hr. After the vessel was allowed to cool the product was washed with water and allowed to air dry.

Initial experiments were conducted by adding equimolar 5 mmol of Na$_2$SiO$_3$ and UCl$_4$ (weighed in the presence of oxygen) to 50 mL of water, with excess silica in the form of silica gel. After the addition of sodium hydroxide (NaOH) the solution was centrifuged and experiments were conducted with; 1) the supernate; 2) the precipitate (gel); 3) the entire solution, un-centrifuged, used for all subsequent steps. Excess silica was difficult to separate from the other synthesised material, so the above reactions were re-tested used a sub stoichiometric amount of UCl$_4$, to obtain excess silicon in the reaction. All
experiments conducted using the methods above resulted in the synthesis of unidentified phases with no sign of synthetic coffinite formation.

At this stage it was thought that the uranium in the UCl₄ may have oxidised to the U(VI) state resulting in the inability to form synthetic coffinite which has uranium in the U(IV) oxidation state. UCl₄ was then weighed in a glove bag under an inert atmosphere to prevent oxidation and adsorption of water from the environment. Upon this change, it was possible that trace amounts of coffinite were present in the product, though it was still dominated by the presence of unknown phases.

If the presence of oxygen (or lack of oxygen) was so critical in the formation of synthetic coffinite, it was decided to investigate if the removal of dissolved oxygen in the water would improve the reaction. Changing this aspect alone caused the most significant advance in the methodology of synthetic coffinite, as for the first time a positive identification of synthetic coffinite could be made from the XRD patterns of the product. The product still contained far more impurities, such as unidentified phases and uraninite, than coffinite. As the NaOH, used to raise the pH and form the gel, is an aqueous solution and hence could also contain dissolved oxygen, this solution was also degased and experiment re-tested. This resulted in a slightly better coffinite to impurity ratio, although coffinite was still only a minor phase in the product.

Though many of the previously published papers described a method using excess silica, none elaborated on the amount of excess silica required or the ratio of U:Si that were used. The investigation into the amount of uranium to silicon required for the successful preparation of synthetic coffinite was then investigated. Equimolar (5mmol) of sodium metasilicate and UCl₄ were each dissolved in 25 mL of degassed water. In order to obtain excess silicon in solution, the addition of 5, 10, 15, or 20 mL of UCl₄ (aq) was added drop-wise to the sodium metasilicate (aq). When 5 mL (U:Si 0.20:1) or 20 mL (U:Si 0.79:1) was used in the reaction the XRD patterns (Figure 3.33) indicated no formation of synthetic coffinite and only the formation of uraninite (00-041-1422
When 15 mL of $\text{UCl}_4$ (aq) was added to the aqueous sodium metasilicate (U:Si 0.59:1) the presence of coffinite was confirmed through library matching of the XRD pattern, though there was substantial contamination from the formation uraninite (Figure 3.33).

For the successful preparation of synthetic coffinite (with no or minimal contamination) 10 mL of $\text{UCl}_4$(aq), with a U:Si of 0.39 was required (See Figure 3.33 for XRD pattern). The formation of pure $\text{USiO}_4$ was confirmed through a library match of a known coffinite pattern (01-072-0169 coffinite, syn). The prepared coffinite appears to be pure, as possible impurities such as uranium dioxide (uraninite) and silica ($\text{SiO}_2$) were not apparent in the pattern. The lack of impurities does not suggest however that this sample is void of all trace impurities, as they could be present at levels beyond the detection limit of the XRD technique (≈1 weight %).

Experiments with the addition of 10 and 15 mL of $\text{UCl}_4$(aq) additions were also conducted to investigate if breaking of the gel (after NaOH addition) would alter the purity of the product. The results indicated that there was no difference to the purity of the synthetic coffinite formed, regardless of the gel being broken or not during the reaction.
Figure 3.33: XRD pattern of synthetic coffinite

Table 3.16: Summary of methods used for synthetic coffinite production and corresponding results based on XRD analysis

<table>
<thead>
<tr>
<th>Important Parameters</th>
<th>Result based on XRD Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equimolar (5 mmol) Na$_2$SiO$_3$ and UCl$_4$, added to water at the same time</td>
<td>No formation of coffinite. Formation of unidentified phase(s)</td>
</tr>
<tr>
<td>Excess silica (as silica gel)</td>
<td>No formation of coffinite. Formation of unidentified phase(s)</td>
</tr>
<tr>
<td>Supernate used</td>
<td>No formation of coffinite. Formation of unidentified phase(s)</td>
</tr>
<tr>
<td>Precipitate (gel) used</td>
<td>No formation of coffinite. Formation of unidentified phase(s)</td>
</tr>
<tr>
<td>Entire solution used</td>
<td>No formation of coffinite. Formation of unidentified phase(s)</td>
</tr>
<tr>
<td>5 mmol Na$_2$SiO$_3$ slightly sub stoichiometric amount of U as UCl$_4$, added to water at the same time</td>
<td>No formation of coffinite. Formation of unidentified phase(s)</td>
</tr>
<tr>
<td>Entire solution used</td>
<td>unidentified phase(s)</td>
</tr>
<tr>
<td>----------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td><strong>5 mmol Na$_2$SiO$_3$</strong>&lt;br&gt;slightly sub stoichiometric amount of U as UCl$_4$&lt;br&gt;added to water at the same time&lt;br&gt;Entire solution used</td>
<td>No formation of coffinite. Formation of unidentified phase(s)</td>
</tr>
<tr>
<td>UCl$_4$ weighed under inert atmosphere</td>
<td>Possibility of coffinite formation. Formation of unidentified phase(s)</td>
</tr>
<tr>
<td>UCl$_4$ weighed under inert atmosphere&lt;br&gt;Degased water used</td>
<td>Identification of coffinite (minor phase). Formation of unidentified phase(s) and uraninite</td>
</tr>
<tr>
<td>UCl$_4$ weighed under inert atmosphere&lt;br&gt;Degased water and NaOH used</td>
<td>Identification of coffinite (minor phase). Formation of unidentified phase(s) and uraninite. (Slightly more coffinite)</td>
</tr>
</tbody>
</table>

---

<table>
<thead>
<tr>
<th>5 mmol Na$_2$SiO$_3$ dissolved in 25 mL water&lt;br&gt;5 mmol UCl$_4$ dissolved in 25 mL water&lt;br&gt;Entire solution used&lt;br&gt;UCl$_4$ weighed under inert atmosphere&lt;br&gt;Degased water and NaOH used</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>5 mL of UCl$_4$(aq) used in reaction</td>
<td>No coffinite formation; possibly partially-amorphous uraninite</td>
</tr>
<tr>
<td>10 mL of UCl$_4$(aq) used in reaction</td>
<td>Formation of coffinite and substantial formation of uraninite</td>
</tr>
<tr>
<td>15 mL of UCl$_4$(aq) used in reaction</td>
<td>Formation of synthetic coffinite, with little to no impurities</td>
</tr>
<tr>
<td>20 mL of UCl$_4$(aq) used in reaction</td>
<td>No coffinite formation; possibly partially-amorphous uraninite</td>
</tr>
<tr>
<td>Breaking or not breaking gel</td>
<td>Did not alter the result</td>
</tr>
</tbody>
</table>
3.3.1.1 Fourier Transform Infrared Spectroscopy

Bulk analysis techniques such as FTIR are suitable for determining the existence of impurities (uraninite/UO$_2$). Both the mid and far FTIR spectra (Figure 3.34 and Figure 3.35) provided a positive match for coffinite. Within the mid-IR region, coffinite was confirmed by the sharp band found at 576.83 cm$^{-1}$ which is assigned as an internal mode of coffinite and the strong bands between the region 860 – 1000 cm$^{-1}$ indicative of SiO$_4^{4-}$ modes [21]. In the far-IR region, characteristic coffinite bands are also observed, by the second internal mode of coffinite at 443.1 cm$^{-1}$, the external mode of rotation (333.2 cm$^{-1}$) and the external mode of translation at 237 cm$^{-1}$. The latter is slightly shifted compared to what was published by Zhang et al. [21]. By comparing the coffinite FTIR spectra with that of pure uraninite, it is highly unlikely there is any uraninite present in the synthetic coffinite as the band at 520 cm$^{-1}$ in the mid-IR region and the most significant band in the far-IR region (486.4 cm$^{-1}$) typical of uraninite, are absent in the spectra of the synthetic coffinite, this is highlighted by the red oval in the spectra.

Figure 3.34: Mid FTIR spectra of synthetic coffinite and uraninite
a) uraninite b) coffinite
3.3.1.2 Unit cell determination

Based upon methods outlined by Holland and Redfern [22], the unit cell parameters for synthetic coffinite were refined and errors calculated using the refinement software program, UnitCell [23]. The unit cell parameters calculated for the synthetic coffinite were found to be within 1% of other reported values published (Table 3.17).

Table 3.17: Crystallographic unit cell data of synthetic coffinite compared to other published synthetic coffinite data

<table>
<thead>
<tr>
<th>Coffinite Sample</th>
<th>a=b (Å)</th>
<th>c (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>6.99795 ± 0.0002</td>
<td>6.27197 ± 0.0002</td>
<td>n/a</td>
</tr>
<tr>
<td>Pointeau et al</td>
<td>7.0135 ± 0.0004</td>
<td>6.2669 ± 0.0006</td>
<td>[8]</td>
</tr>
<tr>
<td>Dubinchuk et al (hypergenic)</td>
<td>6.98</td>
<td>6.30</td>
<td>[24, 25]</td>
</tr>
<tr>
<td>Dubinchuk et al (hydrothermal)</td>
<td>6.93</td>
<td>6.30</td>
<td>[24, 25]</td>
</tr>
</tbody>
</table>
† unit cell parameters have been converted from kX units to Å units using the conversion factor 1.00202 reported by Bragg and Armstrong Wood in 1947 [26].

‡ data referenced as coming from Fuchs and Gebert (1958) [6]; it is believed that the values quoted by Burns and Finch (1999) [2] have been erroneously transcribed or calculated as they differ from the values published by Fuchs and Gebert (1958) [6], the original data is quoted in kX units and then converted to Å using the factor published in 1947 [26], these values are also quoted in the table with references [5, 6].

* unit cell data based upon incomplete indexing

### 3.3.1.3 X-Ray Photoelectron Spectroscopy

XPS studies were conducted to establish the oxidation state of uranium in the synthetic coffinite. The results of this analysis (Figure 3.36) show that when the peaks of the uranium 4f-core levels are deconvoluted, mixed uranium oxidation states appear to be present. The major contributions are found at 381.1 ± 0.2 eV and 392.0 ± 0.2 eV for the U-4f7/2 and U-4f5/2 levels respectively, whereby the minor contribution of the U-4f7/2 peak appears at 382.5 ± 0.2 eV and satellite peak at 386.8 ± 0.2 eV. These results are in agreement with the findings proposed by Pointeau et al [8]. The predominant oxidation state present at the surface of the sample is uranium(IV), indicated not only by the binding energies but also confirmed by the position of the satellite peak at a higher binding energy of 6 eV. Because the samples used in this study were kept in air and no etching of the surface was completed during the analysis the presence of uranium(VI) was detected as a result of surface oxidation due to the samples exposure to oxygen, which is consistent with the findings of Pointeau et al [8]. It was found that approximately 40 % of the surface had oxidised to uranium(VI).
3.3.1.4 Scanning Electron Microscopy and Energy Dispersive Spectroscopy

Scanning Electron Microscopy (SEM) was used to investigate the microstructure of the synthetic coffinite. The morphology of the prepared coffinite is consistent with that observed by Pointeau et al. whereby they describe the synthetic coffinite as polycrystalline aggregates [8]. The synthetic coffinite here does however differ slightly from that prepared by Pointeau et al. with regards to the uniformity of the sample. Pointeau et al. presented “patchy” back scatter electron (BSE) images indicating a heterogeneous sample which was later confirmed by EPMA elemental mapping. Each coffinite grain prepared lacks the “patchy” appearance in the BSE images as reported by Pointeau et al. indicating a more homogenous sample. From the images in Figure 3.37, the synthetic coffinite sample appears quite dense and non-porous. Examination of the microstructural features at a higher magnification than shown in Figure 3.37 (up to 5000 x) did not reveal any additional structural details.
Figure 3.37: BSE images of coffinite at various magnifications
(a) magnification 400x (b) magnification 895x (c) magnification 2000x (d) magnification 2800x

EDAX analysis was conducted on four different sub-samples of the prepared coffinite to investigate its homogeneity and possible inclusions of impurities. The EDAX spectra of all sub-samples (Figure 3.38) exhibited similar uranium; silicon and oxygen distributions; suggesting a fairly consistent level of homogeneity within the bulk sample. EDAX analysis did not indicate any inclusions of pure uraninite.
Figure 3.38: EDAX spectra of synthetic coffinite sub-samples
(EDAX spectra correspond to the images above)
The carbon peaks seen in the spectra given in Figure 3.38 came from two sources; 1) the carbon tape which was used to adhere the sample to the sample stubs and 2) from the carbon coating which was used to prevent charging of the sample under the electron beam.

3.3.1.5 Electron Probe Microanalysis

EPMA Mapping
The BSE of individual pieces of coffinite indicated textural inhomogeneity within the pieces, where the central parts appeared to be coarsely crystalline and the edges of the particles exhibited a much finer-grained texture (see Figure 3.39a Figure 3.41). Elemental maps were collected over two texturally different particle types within the sample.

Map Area 1
The first map (Figure 3.39) was obtained over a large ~300 micron sized particle. The results are presented as a series of maps including BSE map, individual elemental maps showing the distribution of the elements (U, Si, S and O) as well as three element map overlaying the distributions of Si, S and U.

From initial observations the data indicated that the synthetic material has a remarkably similar texture to the analysed coffinite grain found in the natural sample (Chapter 2). The synthetic coffinite mapped in Area 1 consisted of patchy, polycrystalline aggregates with heterogeneous BSE contrast (Figure 3.39a). Individual element maps for uranium (Figure 3.39b) and silicon (Figure 3.39c) showed that the BSE correlated strongly with variations in both elements. The brighter areas in the BSE image corresponded to regions with greater amounts of uranium while the slightly darker regions indicated areas where there was higher silicon content. The edges of the coffinite grain appear to have a greater amount of silicon present (Figure 3.39c) with some internal crystallites also exhibiting variations in the uranium silicon ratio. This can be observed in the silicon distribution map (Figure 3.39c) where there are both
yellow and green patches present. The oxygen content was also highly correlated with 
the distribution of silicon (Figure 3.39e)

As the sample was washed with sulphuric acid prior to analysis to remove any 
impurities, the distribution of sulphur within the particle was also mapped (Figure 
3.39d). Sulphur was found to be distributed throughout the sample at very low levels 
though it was slightly depleted at the edges of the particle. While there was no clear 
correlation between sulphur and any other element, there was an apparent weak 
relationship between sulphur and silicon.

Using the automated clustering algorithm in CHIMAGE the map was analysed to identify 
chemical groupings, these results are presented in Figure 3.40. The main chemical 
phases identified by the clustering procedure were coffinite; shown in red, and a low 
uranium (high silicon) coffinite-like phase shown in blue (at the edges). Although it was 
recognised that there were variations in the uranium silicon ratio in the crystallites at 
the centre of the particle, the variation was not particularly large and hence this 
material has all be assigned the single phase of coffinite. In comparison, the change in 
the uranium silicon ration at the edge of the particle was more substantial and, 
therefore, this has been designated as a different phase (low-U coffinite) in Figure 3.40. 
To illustrate the differences in the uranium silicon ration representative ED spectra for 
the coffinite and low-U coffinite phases have been included in Figure 3.40.
Figure 3.39: EPMA map area 1 of synthetic coffinite.
a) BSE Image; b) U distribution map; c) Si distribution map; d) S distribution map e) O
distribution map; f) Si/S/U element map. *the colour scale bars in images b) to e) indicate relative concentrations.
Figure 3.40: Clustered EPMA map for synthetic coffinite map area 1; plus representative ED spectra from the two U/Si phases identified.

*The spectrum on the left (red) represents the phase designated as coffinite, whilst the spectra on the right (blue) represents the phase designated as coffinite (low U) which is present at the edges of the particle.
Map Area 2
The particle mapped in Area 2 was an elongated particle exhibiting a variety of textural features ranging from a coarse, crystalline texture along one side of the particles gradually grading to a finer crystallite size along the opposite crystal edge. The texture appears to be consistent with that of material settling in a reaction flask (the material is allowed to settle with finer material settling at the top). The sample then appears to have been dried, leading to fractures through the sample and then broken up into various sized pieces.

Similar chemical trends as to those observed in Map Area 1 were observed in this sample, as there were regions which containing high silicon, low uranium crystallites and the depletion of uranium appeared to increase with progression towards the edges of the particle (Figure 3.41). The most obvious difference between this particle and the one in Map Area 1 is in the distribution of sulphur. In the second particle, sulphur is concentrated along the fractures where it appears to still correspond to relatively high uranium values. This suggests that the sulphuric acid used to wash the sample may have reacted with the uranium to form a sulfate compound (possibly U(SO₄)₂).

The presence of a sulfate phase was confirmed through the cluster analysis which indicated the formation of this phase along the fractures and edges of the particle (Figure 3.42a). The presence of sulfate suggests that the sample was not washed effectively with the acid as the sulfate precipitated during drying. Washing the sample further with water may potentially remove this phase as (U[SO₄]₂) is known to be soluble in water. coffinite, low U coffinite as well as trace amounts of quartz and Fe-oxide were also identified as the other phases present in this particle.
Figure 3.41: EPMA map area 2 of synthetic coffinite
a) BSE Image; b) U distribution map; c) Si distribution map; d) S distribution map e) O distribution map; f) Si/S/U element map. *the colour scale bars in images b) to e) indicate relative concentrations.
Figure 3.42: Clustered EPMA map of synthetic coffinite area 2 with ED spectra of the U-bearing phases
a) Clustered EPMA map; b) ED spectra of phase designated coffinite; c) ED spectra of phase designated coffinite (S, low U); d) ED spectra of phase designated U sulphate.
The representative ED spectra (Figure 3.42b-d) have been included to illustrate the variation of the uranium silicon ratio between the coffinite, low-U coffinite and uranium sulfate phases. Note that the low levels of sulphur were also detected in both the coffinite and the low-U coffinite. It is not clear from the map data whether this represents sulfuret incorporated into the structure of the coffinite or it is the precipitation of ultra-fine-grained sulfuret on the coffinite (in micro and/or nano pores, the latter being most likely). The resolution of the mapping (300nm) is unable to separate the coffinite and sulphur into separate phases within it is finely intergrown.

**Quantitative EPMA Results**

Quantitative analysis indicated that the weight percentages of uranium and silicon varied over wide ranges from 62.72 to 65.44 wt% and 8.93 to 11.33 wt% respectively (Appendix B). This washed product also contained 0.124 to 0.494 wt% sulphur. The overall uranium silicon ratio is low, 0.73, when compared to the expected uranium to silicon ratio of 1.00 for coffinite, which indicates the presence of excess silicon and a depletion in uranium compared to “Stoichiometric” USiO$_4$ (72.1 wt% U and 8.5 wt% Si). Though this result may suggest that coffinite has not been formed during the synthesis experiments, it would be an erroneous assumption based on XRD measurements (Figure 3.33), as these results indicated coffinite is indeed present in substantial quantities within the sample. The EPMA results suggest that the Coffinite is likely to be extremely fine grained, below the analysis volume of the electron beam, and intimately mixed with a nanocrystalline silica-rich phase (as not significant excess quartz was identified during XRD analysis, it is suggested that the excess silica is of an amorphous nature). The presence of amorphous silica leads to higher than expected silicon levels and lower uranium contents when probed by the electron beam.

It is interesting to note that the recent attempts to synthesise coffinite by hydrothermal methods carried out by Pointeau et al [8] also led to the formation of patchy polycrystalline grains that exhibited uranium contents of ~ 63 wt% and silicon contents of ~ 13 wt%, similar to those reported in Table 3.18. These gave a corresponding low uranium silicon ratio of ~0.6. They attributed the low uranium silicon ratio resulting from the presence of a Si-rich phase in the sample, which was most prominent around
the edges of grains but was assumed to be present within the interior as amorphous, nanocrystalline material. In contrast to the current results however, Pointeau et al. [8] managed to synthesis coffinite that appeared to be stoichiometric (and water-free). They proposed that long synthesis times caused decomposition of coffinite over time to produce $\text{UO}_2$ and Si-rich amorphous material.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
<th>Synthetic Coffinite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>&lt;d.l.</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>&lt;d.l.</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>10.34</td>
<td></td>
</tr>
<tr>
<td>U</td>
<td>64.32</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>&lt;d.l.</td>
<td></td>
</tr>
<tr>
<td>Th</td>
<td>&lt;d.l.</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>&lt;d.l.</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>&lt;d.l.</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>&lt;d.l.</td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>&lt;d.l.</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.203</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>20.23</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>95.12</td>
<td></td>
</tr>
<tr>
<td># analyses</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>U:Si atomic Ratio</td>
<td>0.73</td>
<td></td>
</tr>
</tbody>
</table>
3.3.1.6 BET Analysis
A summary of the BET analyses data obtained for the prepared synthetic coffinite can be found in Table 3.19 - 3.7.

<table>
<thead>
<tr>
<th>Table 3.19: Area data of synthetic coffinite</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area</td>
</tr>
<tr>
<td>Langmuir surface area</td>
</tr>
<tr>
<td>Micropore area</td>
</tr>
<tr>
<td>External surface area</td>
</tr>
<tr>
<td>BJH adsorption cumulative surface area of pores between 1.7 and 300 nm diameter</td>
</tr>
<tr>
<td>BJH desorption cumulative surface area of pores between 1.7 and 300 nm diameter</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 3.20: Volume data of synthetic coffinite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micropore Volume</td>
</tr>
<tr>
<td>BJH adsorption cumulative pore volume of pores between 1.7 and 300 nm diameter</td>
</tr>
<tr>
<td>BJH desorption cumulative pore volume of pores between 1.7 and 300 nm diameter</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 3.21: Pore size data of synthetic coffinite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption average pore diameter</td>
</tr>
<tr>
<td>Desorption average pore diameter</td>
</tr>
<tr>
<td>BJH adsorption average pore diameter</td>
</tr>
<tr>
<td>BJH desorption average pore diameter</td>
</tr>
</tbody>
</table>
3.3.1.7 Thermogravimetric Analysis

The thermogravimetric analysis mass loss curve and its derivative (Figure 3.43), indicates three regions of mass loss, the same as seen in the natural sample containing coffinite. The first loss is between 50 and 250 °C can be attributed to water loss and is typical to the loss associated with water from interlayer sites [27]. The second region appears more significant than that seen in the natural sample and extends from 400 to 750 °C. In this region there also appears to be a couple of different losses as signified by the derivative of the mass loss curve. The various losses may be caused by a number of changes taking place in the sample. Firstly this is the temperature range at which dehydroxylation occurs [27] and considering there is some evidence to suggest that coffinite contains water in the form of attached OH- part of the mass loss during this temperature range is most probably due to this. Natural coffinite is known to degrade at 400 to 500 °C [4, 5] although synthetic coffinite is quite stable to much higher temperatures (pointeau); it is possible that synthetic coffinite experiences subtly mass losses over the temperature range 400 to 700 °C yet are able to retain the essential crystal structure causing the no change in the XRD pattern. During the EPMA analysis a uranium-sulfur phase was observed, this phase could be lost during this temperature. At temperatures above 800 °C there appears to be very little loss and may be attributed to strongly bound water, as dehydroxylation can occur to temperature up to 900 °C [27]. The total mass loss is about 7 weight % which equates to less than 2 moles of water. If the total mass loss is from water, this synthetic coffinite contains between 1 and 1.5 moles of water.
Chapter 3

3.4 Chapter Summary

Coffinite was successfully synthesised through the method outlined in this chapter when 10 mL of UCl$_4$(aq) was used. When the synthesis was conducted using 5 mL or 20 mL of UCl$_4$(aq) the resulting product was found to be uraninite with no coffinite detectable via XRD. The product synthesised using 15 mL of UCl$_4$(aq) was found to contain coffinite though had a substantial amount of uraninite as the impurity.

The unit cell parameters of the prepared synthetic coffinite were calculated to be (a=b 6.99795±0.0002 Å and c 6.27197±0.0002 Å). These were within 1 % of previously reported values. SEM analysis indicated a uniform appearance under the conditions studied. EDAX analysis showed that the uranium, silicon and oxygen abundances were relatively consistent throughout the sample though minor variations were noticed. This analysis did not indicate the presence of uraninite, which was supported through mid and FAR FTIR analysis, with the spectra being consistent with other published data for coffinite. XPS analysis found the major oxidation state of uranium to be in the IV state.
though approximately 40 % of the surface uranium had been oxidised to U(VI), again consistent with findings of others.

The synthetic coffinite was found to have a low surface area (78.44 m\(^2\)/g); micropore volume of 0.10579 cm\(^3\)/g; adsorption and desorption pore size of 15.4303 nm and 16.7207 nm respectively. The TGA data obtained supported the theory that coffinite contains water in a number of different varieties and the total water content is somewhere between 1 and 1.5 moles.

EPMA data was an extremely useful analysis tool as it was able to resolve features that could not be achieved by the SEM. Two pieces of coffinite were analysed that contained quite different textural features. The texture of coffinite in Map Area 1 was very similar to that of the coffinite found in the natural sample (patchy, polycrystalline aggregates with heterogeneous BSE contrast). The BSE contrast correlated strongly with uranium and silicon variated. The edge of the particle (darker contrast in BSE) contained greater amounts of Si, the centre of the particle also exhibited variation in the U:Si ratio (although minimal). The oxygen content was found to correlate with the silicon content. Sulfur was found to be distributed at low levels throughout the sample and a weak relationship between sulfur and silicon was established. The clustering program identified two coffinite phases, coffinite and coffinite low in uranium (high in silicon).

Map Area 2 exhibited a range of textural features with one edge being of a coarse, crystalline nature gradually changing to a finer crystalline size on the opposing edge. This is consistent with material that is allowed to settle in a reaction flask (as was done during synthesis method). This particle also contained fractures, consistent with the drying of the sample; this can cause particles of various sizes. Similar chemical trends were seen in this sample as compared to map area 1 with the exception of sulfur distribution. Sulfur was found to be concentrated along the fractures of the particle and was found to correspond with high uranium content. This was attributed to the sulphur reacting with the uranium which was confirmed by the identification of a sulfate phase. Trace amounts of quartz and Fe-oxide were also found in this sample. Quantitative analysis found that the weight percent of both uranium and silicon varied throughout the sample, 62.72 – 65.44 wt % and 8.93 – 11.33 wt % respectively. The overall uranium to silicon ratio was low (0.73) compared to the theoretical value of 1.0. Although in
saying this; the ratio found in this sample is higher than the ratio, of \(~0.6\), that was published by Pointeau et al [8]. The sample also contained between 0.124 and 0.494 wt % of sulfur.

By collating that EPMA and XRD data it is proposed that the coffinite synthesised is of an extremely fine grain (below the analysis volume of the electron beam for EPMA) and intimately missed with nano-crystalline silicon rich phase which is amorphous (and thus not observed in the XRD pattern).

3.5 References


CHAPTER 4

INVESTIGATIONS ON THE DISSOLUTION OF SYNTHETIC COFFINITE
4.1 Background

As discussed in a previous section (section 1.2.2) the dissolution (leaching) of uranium from uranium bearing minerals is a key step in the main processes used in the production of uranium oxide concentrate ($\text{U}_3\text{O}_8$) – the compound that is subsequently used to produce the form of uranium used as a nuclear fuel. Optimisation of the dissolution (leaching) sub-process is therefore of significant interest to uranium producers.

It is widely accepted that a number of factors influence the dissolution of uranium from uranium bearing minerals. The factors that have been reported to date to have the most influence on the extent and/or rate of dissolution include [1, 2]:

- Type of lixiviant
- Concentration of lixiviant
- Temperature
- Oxidation-reduction potential (ORP) of leach solution

It is important to note however, that the aforementioned is based mostly on studies conducted using synthetic uraninite and/or ores that predominantly contain uraninite. Very few studies have been reported in the open literature on the dissolution of uranium from coffinite. The lack of studies on uranium dissolution from coffinite is most likely due to a combination of (1) difficulty in isolating the pure mineral/obtaining high purity samples of the mineral and (2) coffinite has not been present/or not present in significant quantities in ore bodies that have been selected for mining to date. Although there have been very few studies on the dissolution of uranium from coffinite reported in the open literature, multiple researchers have stated that coffinite dissolution is slower in sulphuric acid when compared to uraninite dissolution [3-5].

The majority of papers written on the subject of uranium dissolution mostly focus on “bulk” uranium dissolution from uranium bearing ores and do not discuss the results
with specificity to uranium minerals such as coffinite. Though coffinite may be a common uranium mineral at many deposits \([4, 6-15]\) it often only comprises as a small percentage of the uranium, i.e 1.7-2.7\% \([4]\), making assumptions based upon the general findings for uranium dissolution from these studies for the dissolution of coffinite may or may not be correct. General findings of studies conducted where coffinite is specifically mentioned in the sample include:

- Acid has significant impact on uranium extraction \([3, 8, 16]\)
- Temperature can have an effect on uranium extraction, results varied dependent on the temperatures and ranges tested. \([3, 8, 16]\)
- Ferric (Fe\(^{3+}\)) in solution appears to have the most influence on uranium extraction, this parameter also plays a critical role in the solution ORP. \([3, 8, 16-19]\)

The most recent and comprehensive study on the dissolution of uranium from coffinite was published in 2010 by Maley et al \([20]\). This study was conducted using a sample mixture containing natural coffinite. The exact amount of coffinite in the sample was not reported, however it was reported that the sample contained \(\approx 1500\) ppm of uranium (measured as U\(_3\)O\(_8\)), and almost 100\% of the uranium present in the sample was identified as coffinite. The dissolution studies conducted by Maley et al \([20]\) on the sample mixture containing coffinite were conducted at 30 °C, with sulphuric acid lixiviant at a pH of 1.7; ferric sulphate was added at varying amounts to study the effect of iron. The authors found a strong relationship between ferric concentration and uranium dissolution. At a solution ORP of 475 mV (versus a Ag/AgCl reference electrode) and [Fe]\(_{\text{Total}}\) between 15 mg/L and 1500 mg/L, uranium dissolution above 80\% was achieved after 6 hours. The main findings reported in this paper with respect to the effect of Fe were as follows \([20]\):

- The extent of uranium leached from coffinite rose 3\% over 24 hours when the [Fe]\(_{\text{Total}}\) was increased from 15 mg/L to 1000 mg/L.
  - the authors also noted that “this effect was greatest at the shorter leach times” (6 Hours).
• The greatest single increase in uranium dissolution (between concentrations) was found when \([\text{Fe}]_{\text{Total}}\) was increased from 15 mg/L to 300 mg/L for dissolution times greater than 12 hours.

• There was no significant increase in uranium extraction when total \([\text{Fe}]\) was increased from 1000 mg/L to 1500 mg/L.

The authors also studied the effect of solution ORP and found this parameter had a greater effect on uranium extraction than \([\text{Fe}^{3+}]\) based on the three ORP values tested (425, 475 and 525 mV). When the ORP was raised from 425 to 475 mV using an \([\text{Fe}^{3+}]\) of 0.2 and 0.5 g/L, the most significant increase in uranium dissolution was observed. The authors concluded that coffinite, unlike uraninite, is driven not only by the solution ORP but also the \([\text{Fe}^{3+}]\) [20].

The dissolution of coffinite from two South African ores was reported on in two recent publications by Lottering and Lorensen [16] and Lottering et al [4]. The first of these publications involved studies on a natural low grade ore sample containing very small amounts of coffinite (initial coffinite ranged from 4.7-17.5 ppm in sub-samples). When this ore was leached for 24 hours at 60 °C with sulphuric acid (16.3 kg/t) and at an ORP between 380-450 mV (without the addition of an oxidant), 76 % of the coffinite was leached. At elevated ORP values (500 mV and 700 mV) complete coffinite dissolution was observed. Any ore residue remaining was then subjected to leaching under aggressive conditions (24 hours, 16.3 kg/t sulphuric acid, 4 kg/t MnO2 oxidant at 60 °C), where complete dissolution was achieved. [16]. In the latter of the two aforementioned studies, which also involved a natural ore sample from the Witwatersrand region (again only containing trace amounts of coffinite (1.7-2.7 % of uranium as coffinite)) between 0.5 and 4.8 % of the residue was found to contain coffinite after 24 hours of leaching under aggressive conditions (16.3 kg/L H₂SO₄, 60 °C and 4 kg/L of oxidant MnO₂.) [4].
In the study conducted by Macnaughton et al. on uranium dissolution from an Australian natural ore containing coffinite [3, 9], the major findings pertaining specifically to coffinite are summarised below:

- "Coffinite can be leached in ferric sulphate solutions, however the rate is generally slower than either U\textsuperscript{6+} or the U\textsuperscript{4+} forms of uraninite". (A similar statement can be found in [4])
- Block leaching studies showed very slow continuous dissolution.
- Dissolution was increased as the pH decreased although still slow.
- During conventional studies it was reported that the slow leaching rate observed above 80 % uranium dissolution was most probably due to the leaching of coffinite as well as any poorly liberated uraninite.

The chemistry of coffinite dissolution has received very little attention to date. To the authors’ best knowledge the only chemical equation that has been used to represent the dissolution of uranium from coffinite in sulfuric acid (Equation 4.1), appeared in a technical report published by researchers from the Lomonosov Moscow State University, Chemistry Department (radiochemistry division) [21]. This report titled “Review of technologies used for uranium and other metals (copper and gold) leaching” and the equation of interest is featured in a section describing the experience Rosatom (the regulatory body of the Russian nuclear complex) has in uranium leaching. The equation as it appeared in this publication was not balanced.

\[
\text{USiO}_4 + 2\text{SO}_4^{2-} + 2\text{H}^+ + \text{O}_2 + \text{H}_2\text{O} \leftrightarrow \text{UO}_2\text{SO}_4_{(\text{soln.})} + \text{H}_4\text{SiO}_4_{(\text{soln./gel})} \quad \text{Equation 4.11}
\]

Solution ORP is known to be an important factor in determining the feasibility of uranium dissolution as well as defining the uranium dissolution kinetics. This parameter is used to control and maintain the uranium dissolution/leaching as it can be analysed on-line with an ORP-probe. As minerals in uranium ores may contain both Fe\textsuperscript{3+} and Fe\textsuperscript{2+} mineral species, which can influence the solution ORP, the ratio of Fe\textsuperscript{3+}:Fe\textsuperscript{2+} in the system is critical for the both the rate and extent of uranium dissolution [21]. On
account of the intimate relationship exhibited between iron and the oxidation reduction potential (ORP), numerous studies were conducted to ascertain the effect of ferric ion concentration ([Fe$^{3+}$]), ferrous ion concentration ([Fe$^{2+}$]), total iron concentration ([Fe]$_{\text{Total}}$) and Fe$^{3+}$: Fe$^{2+}$ ratio (ORP). The ORP of the solution used to dissolve uranium(IV) minerals has been identified to have a significant effect on the rate and / or extent of dissolution of uranium(IV) minerals. The main oxidant used in uranium minerals processing leachate solutions is typically ferric ion (which is generated via dissolution of iron bearing gangue minerals in the uranium bearing ore and / or added in the form of an oxide). The ratio of ferric to ferrous ions in leachate solutions typically has the most significant influence on leachate solution ORP. Though ORP is possibly the most important parameter from a processing point of view, as it is used to monitor and control the dissolution/leach process, there is a need to understand other parameters which many influence uranium dissolution from coffinite in order to gain a holistic understanding of the dissolution process.

The main aims of the studies reported in this chapter were to investigate the influence of the following parameters on the dissolution of uranium from synthetic coffinite;

- Temperature
- Sulfuric acid concentration
- Total Iron at Constant ORP (Fe$^{3+}$:Fe$^{2+}$ ratio)
- Effect of Solution ORP
- Influence of [Fe$^{2+}$] at constant [Fe$^{3+}$]

Dissolution experiments were designed specifically to investigate coffinite dissolution in isolation from other influencing uranium and gangue minerals. The decision to use synthetic coffinite was based on the following reasons:

- Finding enough natural coffinite with the absence of other impurities to conduct all the necessary experiments was not possible
- Relatively large quantities of synthetic coffinite can be prepared
• Synthetic coffinite is representative of the coffinite found in nature (refer to Chapters 3 and 4)

• The uniformity of synthetic coffinite allows for better comparison between dissolution results. Natural coffinite varies significantly with respect to the inseparable gangue mineralogy and elemental substitutions.

The residues produced from dissolution tests were also collected and analysed to investigate possible changes in composition, as a result of dissolution of uranium from synthetic coffinite.

To the author’s best knowledge there have been very few detailed studies on the influence of the aforementioned parameters on the dissolution of uranium from coffinite, whilst no studies on the dissolution of uranium from synthetic coffinite under the conditions studied in this work.

Improving the understanding of the rate and/or extent of uranium dissolution from coffinite will aid in improving the efficiency of uranium dissolution from coffinite bearing ores.

### 4.2 Experimental

#### 4.2.1 Materials

The following chemicals were used (as received) in the experimental work discussed in this chapter: Sulphuric acid (H₂SO₄), ferric sulphate (Fe₂O₁₂S₃·xH₂O), Ferrous Sulphate (Fe₂SO₄·7H₂O), Sodium Chlorate (NaClO₃), Nitric Acid (HNO₃), elemental uranium reference standard and terbium nitrate (N₃O₉Tb·6H₂O),
The synthetic coffinite used in dissolution experiments was prepared as described in Chapter 3.3.1.

4.2.2 Methods

4.2.2.1 Dissolution experiments

Dissolution experiments were conducted in a 1 L round bottom glass reaction vessel which was sealed with a six port Perspex lid. The ports allowed for the inclusion of a condenser tube, ORP probe (standard platinum electrode with Ag/AgCl reference electrode), thermocouple for temperature control, overhead mechanical stirrer, additions port and sample port. The reaction vessel was heated via an electronic temperature controlled heating mantle.

The procedure for all dissolution experiments was as follows:

1. An aqueous solution of appropriate concentration of ferric and / or ferrous sulphate was added to the reaction vessel.
2. Mechanical stirrer started (stirring rate of 426 RPM)
3. Reaction vessel heated to desired temperature
4. Once at temperature the appropriate amount of acid was added.
5. After an equilibration time of 10 minutes, the required amount of synthetic coffinite was added (this was designated time zero)
6. Samples were collected at pre-determined intervals.

Samples collected from the reaction vessel were allowed to settle in the pipette used for collection for approximately 5-10 seconds to allow for inspection of any visible solids in collected samples. If any visible solids were present the sample was immediately placed back into the reaction vessel. If no visible solids were present samples were filtered through a 0.45 μm nylon syringe filter. 0.5 mL of the filtered sample was then added to
a volumetric flask containing 5 % nitric acid and 25 ppb terbium internal standard (as terbium nitrate) (required for ICP-MS analysis).

The following experimental conditions (Table 4.22) were used for all dissolutions experiments except where otherwise specified. These conditions are hereafter referred to as standard conditions. Solution ORP was maintained constant throughout each experiment using sodium chlorate (NaClO₃).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>50 °C</td>
</tr>
<tr>
<td>[Sulfuric Acid]</td>
<td>15 g/L (0.15 M)</td>
</tr>
<tr>
<td>Initial [U]</td>
<td>100 ppm (4.20x10⁻⁴ M)</td>
</tr>
<tr>
<td>[Fe³⁺]:[Fe²⁺]</td>
<td>25:75 (ORP ≅ 460 mV)</td>
</tr>
<tr>
<td>[Fe³⁺]</td>
<td>1.0 g/L (0.018 M)</td>
</tr>
</tbody>
</table>

4.2.2.2 Analytical / Characterisation methods

Characterisation of synthetic coffinite
The analytical / characterisation techniques used to characterise the synthetic coffinite used in the research presented in this chapter were given in previous chapters.

Calibration of ORP probe
According to manufacturer's guidelines, the ORP probe does not require calibrating as such. Before use the ORP probe is conditioned with a 470 mV solution used as received from the manufacturer, by allowing the ORP probe to be immersed in solution for 15 mins. The ORP value displayed on the controller unit is noted, if the ORP has a divergence greater than 20 mV the ORP probe is replaced. If the value displayed is within this limit and not 470 mV the difference is noted and the output of all further analysis is adjusted by this difference.
Determination of Dissolved Uranium

The concentration of uranium dissolved during dissolution studies was determined through ICP-MS. The samples were prepared as described previously in this chapter (4.2.2.1). All analysis was conducted in Full Quant mode on an Agilent Technologies 7700X ICP-MS attached to a ASX-520 ICP-MS Auto Sampler. Refer to Table 4.23 for operating parameters.

Table 4.23: Agilent 7700X ICP-MS operating conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma Power</td>
<td>4550 W</td>
</tr>
<tr>
<td>Plasma Gas Flow</td>
<td>15 L/min</td>
</tr>
<tr>
<td>Carrier Gas Flow</td>
<td>1.05 L/min</td>
</tr>
<tr>
<td>Sample Depth</td>
<td>8 mm</td>
</tr>
<tr>
<td>Spray Chamber Temperature</td>
<td>2 °C</td>
</tr>
<tr>
<td>KED</td>
<td>3 V</td>
</tr>
<tr>
<td>Helium Gas Flow Rate</td>
<td>4.3 mL/min</td>
</tr>
</tbody>
</table>

Uranium standards were prepared to 1000, 100, 10, 1 and 0 ppb and all samples contained 25 ppb internal standard of terbium.

Characterisation of residue samples from dissolution tests

The analysis and characterisation of residue samples from the dissolution experiments were conducted via, SEM, EDS, Quantitative EPMA, and TGA. The methods for analysis using these techniques have been previously described. For information regarding SEM/EDS refer to 2.2.2.4, EPMA refer to 3.2.4.3 and TGA refer to 2.2.2.3.
4.3 Results and Discussion

4.3.1 Studies on the effect of multiple parameters on uranium dissolution from synthetic coffinite.

The influence of the following four parameters on the dissolution of uranium from synthetic coffinite were investigated

- Temperature
- Concentration of sulfuric acid
- Total iron concentration ([Fe]_{Total}) at constant ORP (constant [Fe^{3+}]:[Fe^{2+}] ratio)
- Solution ORP ([Fe^{3+}]:[Fe^{2+}] ratio)

4.3.1.1 Effect of Temperature

The effect of temperature on the dissolution of uranium from synthetic coffinite was investigated at four temperatures (50 °C, 60 °C, 80 °C and 95 °C). The conditions used for these experiments are outlined in Table 4.24. The following parameters were constant in all tests; initial coffinite (uranium) concentration, initial ferric and ferrous concentrations and sulphuric acid concentration. The initial solution ORP for the tests conducted varied (due to the relationship between temperature and ORP (see Nernst equation (Equation 4.2)). The initial ORPs obtained at the different temperatures investigated were maintained throughout the duration of experiments via the addition of sodium chlorate.

\[ E_{cell} = E_{cell}^\circ - \frac{RT}{zF} \ln Q \]  

Equation 4.12

E_{cell}: Cell potential
E_{cell}^\circ: Standard cell potential
F: Faraday’s constant (9.6485339924)x10^{4} C mol^{-1}
z: number of electrons transferred in the cell reaction
Q: reaction quotient
Table 4.24: Test conditions for tests conducted on the effect of temperature.

<table>
<thead>
<tr>
<th>Initial Uranium Concentration</th>
<th>100 ppm (4.20x10^{-4} M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Ferric (Fe^{3+}) Concentration</td>
<td>1 g/L (0.02 M)</td>
</tr>
<tr>
<td>Initial Ferrous (Fe^{2+}) Concentration</td>
<td>3 g/L (0.05 M)</td>
</tr>
<tr>
<td>Initial Ferric : Ferrous Ratio</td>
<td>25:75</td>
</tr>
<tr>
<td>Initial Sulfuric Acid Concentration</td>
<td>15 g/L (0.15 M)</td>
</tr>
<tr>
<td>Temperature</td>
<td>50 °C, 60 °C, 80 °C and 95 °C</td>
</tr>
</tbody>
</table>

The results obtained from the tests investigating the effect of temperature on uranium dissolution from coffinite are presented in Figure 4.1. From the results presented in Figure 4.1 it can be seen that very rapid dissolution occurred within the first minute at each of the temperatures tested, with the rate of this rapid dissolution being very similar regardless of reaction temperature. After this initial ≈ 1 minute period reaction temperature however clearly had a significant influence on the rate of dissolution observed. The differences in dissolution before and after the 1 min sampling time was most likely due to the samples either containing another uranium compound (impurity) that dissolved rapidly under all of the conditions tested and / or the prepared coffinite was not homogenous and may have contained regions susceptible to rapid leaching. (Based on XRD analysis coffinite was however clearly the main component in the samples tested (refer to section 3.31), NOTE: The majority of dissolution tests were conducted prior to obtaining EPMA data on synthetic coffinite which confirmed the presence of the impurity uranyl sulphate as mentioned in section 3.3.1.5). As the rates of dissolution observed after ≈ 1 minute were therefore most likely due to the dissolution of bulk coffinite, the focus of this chapter, only the trends observed from ≈ 1 minute onwards are discussed in this and subsequent sections. The rapid dissolution (or more accurately rapid increase in soluble uranium) observed in the first minute of testing was investigated prior to the obtaining of EPMA data which indicated that this was most likely due to samples containing the soluble impurity uranyl sulphate). The results of these investigations, conducted prior to knowing the coffinite samples contained low levels of uranyl sulphate, are given in Appendix C.
The results obtained on the effect of temperature on the dissolution of uranium from coffinite can be summarised as follows:

- Minimal change in rate and extent of uranium dissolution was observed when the temperature was increased from 50 °C to 60 °C.
- Increasing the temperature to 80 °C (from 60 °C) substantially increased both the rate and extent of uranium dissolution.
- A further increase in temperature to 95 °C saw the rate of uranium dissolution increase substantially in the first 30 mins, however there was little improvement in the extent of uranium dissolved from synthetic coffinite after 90 minutes.

From the results obtained it appears that the only temperature at which equilibrium solubility may have been attained (within the time frame tested) was for the 95 °C test as the dissolution curve began to plateau (after ≅ 40 mins) in this test. For all of the other temperatures tested however it was clear that equilibrium solubility was not reached at any of these temperatures within the time frame tested. The extent of uranium dissolution at 90 mins in the 95 °C test was ≅ 80%, hence if this system was at equilibrium complete uranium dissolution from synthetic coffinite could not be obtained at 95 °C under the conditions used ([U] 100 ppm; [Fe³⁺] 1 g/L; [Fe²⁺] 3 g/L; [H₂SO₄] 15 g/L; ORP 500 mV).
Figure 4.1: Uranium dissolution of synthetic coffinite at various temperatures
Conditions: \([\text{U}]_{\text{initial}} = 100 \text{ ppm (}4.20 \times 10^{-4}\text{ M); [Fe}^{3+}]_{\text{initial}} = 1 \text{ g/L; [Fe]}_{\text{Total}} = 4 \text{ g/L; Fe}^{3+}:\text{Fe}^{2+} = 25:75; \text{Initial U}:\text{Fe}^{3+} = 1:4.2; [\text{H}_2\text{SO}_4]_{\text{initial}} = 15 \text{ g/L (}\approx 0.15\text{ M).}}

The activation energy and Arrhenius parameter for uranium dissolution from synthetic coffinite under the conditions studied were also determined. The activation energy for this reaction was calculated to be 64.6 kJ/mol with an Arrhenius parameter of 220. These values are much larger when compared with uranium dissolution from synthetic uraninite under similar conditions (Temperature = 35, 50, 65, 80, 95 °C, \([\text{H}_2\text{SO}_4] = 15 \text{ g/L, Initial [Uranium]} = 100 \text{ ppm, [Fe]}_{\text{Total}} = 3 \text{ g/L, Fe}^{3+}:\text{Fe}^{2+} = 25:75, \text{ORP 460.2 mV, Fe}^{3+}:\text{U}^{4+} = 2:1), where the activation energy reported was 2.51 kJ/mol and the Arrhenius parameter, 24.182 [22]. These findings are consistent with statements in the literature comparing the dissolution of uraninite and coffinite, where uraninite is quoted as being more readily dissolved in dilute acid compared to coffinite [4].

4.3.1.2 Effect of Sulfuric Acid

To study the effect of sulphuric acid on the dissolution of uranium from synthetic coffinite four different acid concentrations were initially investigated under the
conditions given in Table 4.25. Solution ORP was maintained throughout all tests as discussed in section 4.3.1.1.

Table 4.25: Experimental conditions for tests conducted on the effect of sulphuric acid concentration

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Uranium Concentration</td>
<td>100 ppm</td>
</tr>
<tr>
<td>Ferric (Fe³⁺) Concentration</td>
<td>1 g/L</td>
</tr>
<tr>
<td>Ferric:Ferrous Ratio (ORP)</td>
<td>25:75 (440-463mV)</td>
</tr>
<tr>
<td>Temperature</td>
<td>50 °C</td>
</tr>
<tr>
<td>Sulfuric Acid Concentration</td>
<td>1.5, 15, 30 and 70 g/L</td>
</tr>
</tbody>
</table>

The results from the tests on the effect of sulphuric acid concentration are presented in Figure 4.2. The results from these tests showed that as the acid concentration was increased the rate of uranium dissolution decreased (over the acid concentration range tested, 1.5-70 g/L) (Figure 4.2).
Figure 4.2: Dissolution of synthetic coffinite at various \([\text{H}_2\text{SO}_4]\) (1.5, 15, 30 and 70 g/L)

Conditions: Temperature = 50 °C; \([\text{U}]_{\text{initial}} = 100 \text{ ppm (}4.20 \times 10^{-4} \text{ M)}\); \([\text{Fe}^{3+}]_{\text{initial}} = 1 \text{ g/L}; \text{Fe}^{3+}:\text{Fe}^{2+} = 25:75; \text{ORP (}440-463 \text{ mV)}\); Initial \text{U}:\text{Fe}^{3+} = 1:4.2; [\text{H}_2\text{SO}_4]_{\text{initial}} = 1.5, 15, 30, 70 \text{ g/L.}

The effect of acid concentration was investigated further by studying the effect of acid concentration over a larger sulphuric acid concentration range (0.5 g/L to 300 g/L). The experimental conditions for these experiments are given in Table 4.26.

Table 4.26: Experimental conditions for additional tests conducted on the effect of sulphuric acid concentration

<table>
<thead>
<tr>
<th>Initial Uranium Concentration</th>
<th>100 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferric (Fe(^{3+})) Concentration</td>
<td>1 g/L</td>
</tr>
<tr>
<td>Ferric : Ferrous Ratio (ORP)</td>
<td>25:75 (440-463 mV)</td>
</tr>
<tr>
<td>Uranium : Ferric Molar Ratio</td>
<td>1:4.2</td>
</tr>
<tr>
<td>Temperature</td>
<td>50 °C</td>
</tr>
<tr>
<td>Sulfuric Acid Concentration</td>
<td>0.5, 15, 100 and 300 g/L</td>
</tr>
</tbody>
</table>
The results obtained from the additional experiments on the effect of sulphuric acid concentration are presented in Figure 4.3. The results obtained in these tests showed a similar trend for increasing acid concentration from 0.5 g/L to 100 g/L (i.e. a decrease in rate of uranium dissolution). The result obtained for the test conducted using a sulphuric acid concentration of 300 g/L however showed a similar overall rate for uranium dissolution as that obtained using a sulphuric acid concentration of 0.5 g/L, whilst the initial rate of uranium dissolution for the 300 g/L system was slightly lower than that observed for the 0.5 g/L system.

![Figure 4.3: Dissolution of synthetic coffinite at various \([\text{H}_2\text{SO}_4]\) (0.5, 15, 100 and 300 g/L)](image)

**Conditions:** Temperature = 50 °C; \([\text{U}]_{\text{initial}} = 100 \text{ ppm (}4.20 \times 10^{-4}\text{ M)};} \ [\text{Fe}^{3+}]_{\text{initial}} = 1 \text{ g/L;} \ \text{Fe}^{3+}:\text{Fe}^{2+} = 25:75; \ \text{ORP (}437-474 \text{ mV)}; \ \text{Initial U:Fe}^{3+} = 1:4.2; \ [\text{H}_2\text{SO}_4]_{\text{initial}} = 0.5, 15, 100, 300 \text{ g/L.}

The combined results from the two sets of experiments conducted on the effect of acid are shown in Figure 4.6. The trends observed for uranium dissolution from coffinite at several different acid concentrations (0.5, 1.5, 15, 30, 70, 100 and 300 g/L) include;
• Maximum uranium dissolution from synthetic coffinite, after 90 min, occurred at a sulphuric acid concentration of 1.5 g/L

• Uranium dissolution from synthetic coffinite increases (by ≈ 4 %) when the sulphuric acid concentration increases from 0.5 g/L to 1.5 g/L

• A decrease in the extent of uranium dissolution is observed when the sulphuric acid concentration is increased from 1.5 g/L to 100 g/L, with the most significant decrease in the extent of uranium dissolution from 1.5 g/L to 15 g/L

• At very high sulphuric acid concentrations (300 g/L) the second largest amount of uranium was leached from synthetic coffinite (out of the seven acid concentrations tested).

Figure 4.4: \([H_2SO_4]\) Vs % uranium dissolved in 90 mins

The trends observed for the effect of acid concentration on uranium dissolution from coffinite may have been due to one or more of the following phenomena:

• Silicate gelling

• Variation in Fe species

• Change in the potential difference between the \(U^{4+}\) to \(UO_2^{2+}\) reaction and ferrous to ferric reaction (see equations 4.3 and 4.4)
$U^{4+} + 2H_2O \rightarrow UO_2^{2+} + 4H^+ + 2e^-$ \hspace{1cm} \textbf{Equation 4.13}

$Fe^{2+} \rightarrow Fe^{3+} + e^-$ \hspace{1cm} \textbf{Equation 4.14}

Silicate gelling is a process that has been previously reported to suppress the dissolution of zinc silicate. As the structure of zinc silicate and coffinite are similar, this explanation may also aid in the understanding of the interesting effect of acid concentration in uranium dissolution from synthetic coffinite. In the case of zinc silicate, the “silicate portion” of the zinc silicate hydrolyses forming a gel at the surface of the zinc silicate which hinders further dissolution [23]. This silica gel can be formed by Equation 4.5, when the water content is increased or when water is in excess [23]. The formation of this same gel has also been proposed for coffinite (Equation 4.1) and was reported in a technical report published by researchers from the Lomonosov Moscow State University, Chemistry Department (radiochemistry division) [21]. Water would be in excess for all experiments conducted in this study. Increasing the acid concentration may also cause stronger acids to be converted into weaker acids as dehydrated SiO$_2$ is transformed into silicic acid [23]. An increase of silica gel in solution may cause coffinite to be encapsulated in the forming silica gel, inhibiting the ability to be attacked by the acid, resulting in a lowering of the extent of uranium leaching.

$Zn_2SiO_4 + 2H_2SO_4 + \infty H_2O \rightarrow 2Zn^{2+} + 2SO_4^{2-} + \infty H_2O + H_4SiO_4(\text{gel})$ \hspace{1cm} \textbf{Equation 4.15}

The second possible reason for the interesting effect of acid concentration on the dissolution of uranium from coffinite, involved the likely reliance of dissolution of uranium from coffinite on the types and amounts of iron species present in solution. As discussed earlier tetravalent uranium (observed in uraninite and coffinite) is required to be oxidised to the more soluble form (U$^{6+}$), (Equation 4.6) which is achieved using ferric ion.
If iron plays a pivotal role in the dissolution of uranium from coffinite, the speciation of the added iron in these experiments must be investigated. Free iron ions and iron complexes are known to be highly dependent on both the temperature and solution composition. At 50 °C (the temperature of these experiments), the stability of HSO₄⁻ and Fe(SO₄)²⁻ is increased (when compared to 25 °C), this stability causes a decrease in the amount of free ions in solution [24]. The most dominate species in solution at high sulphuric acid concentrations (200 g/L), containing Fe²⁺ and Fe³⁺ was reported by Casas et al and reported to be HSO₄⁻ (70.2-72.2 % of sulphate species), H⁺, Fe²⁺ (78-83 % of ferrous species) and FeH(SO₄)₂ (96.6-93.9 % of ferric species) [24]. Under these conditions there is not a significant amount of free ferrous in solution, almost all of the ferric species is complexed, either as one of the dominant species (FeH(SO₄)₂) or as Fe(SO₄)²⁻ (2.1-5.9 %) and FeSO₄⁺ (1.3-0.2 %) [24], this would result in the availability of the iron for participation in the oxidation of uranium to be greatly diminished hence lowering the uranium dissolution (as per the mechanism in Equation 4.6). The paper by Lee and Tavlaride, 1985 [25] does not take into consideration the formation of the neutral species FeH(SO₄)₂ (which was later proven to be present through Raman Spectroscopy and theoretical/experimental agreement [24]) found the major ferric species across all acid concentrations was FeSO₄⁻; At high acid concentrations Fe(SO₄)²⁻ was found to be more abundant than free Fe³⁺ ions, where at low acid concentrations the reverse was found [25].

Similarly another possible factor which may describe the observed effect of acid concentration on the dissolution of uranium from synthetic coffinite, involves the difference between the potentials of the U⁴⁺ to UO₂²⁺ reaction and ferrous to ferric reaction. Merrit [2] noted that increasing the acid concentration from approximately 3 to 20 g/L increased the percentage of uranium extraction from uraninite greatly. It was found the maximum dissolution was observed at concentrations between 20 to 30 g/L.

\[ \text{UO}_2 + \text{Fe}^{3+} \rightarrow \text{UO}_2^{2+} + 2\text{Fe}^{2+} \]

Equation 4.16
and beyond this point a steady decrease in uranium extraction was observed. It was reported that the decrease in the rate of U⁴⁺ from UO₂ at high acid concentrations was a result of the increasing acid concentration reducing the potential difference between equations 4.3 and 4.4. The maximum uranium dissolution for uraninite was observed at concentrations of 20 to 30 g/L H₂SO₄.

Research on the influence of acid concentration on uraninite dissolution has resulted in two main general findings: Firstly the uraninite dissolution rate increases with increasing acid concentration and secondly at higher concentrations acid has been found to have no significant effect [2]. The latter has resulted in several researchers reporting that the solution pH has a more significant effect compared to acid concentration [10, 22, 26]. The influence of acid concentration of the dissolution of coffinite exhibited similar trends to those observed for the dissolution of zinc silicates [23] as well as a definitive acid concentration at which optimum dissolution (extraction) occurred, as was previously reported by T. V. Arden in Merrit [2]. The uranium dissolution from coffinite, though similar to that of uraninite appears to respond differently to acid concentration as made most apparent by the difference in the acid concentration at which optimum dissolution (extraction) occurred. The findings obtained on the influence of acid concentration on coffinite dissolution show that acid concentration has a complex influence on the dissolution of this mineral.

**4.3.1.3 Effect of Total Iron ([Fe]_{Total}) at Constant ORP (constant Fe³⁺: Fe²⁺ ratio)**

The effect of [Fe]_{Total} on uranium dissolution from synthetic coffinite was investigated under some conditions similar to those used in uranium minerals processing (Table 4.27). The initial solution ORPs that were obtained for the tests conducted using different [Fe]_{Total} are given in Table 4.28. Initial solution ORPs were maintained throughout tests by adding 4 % (w/w) sodium chlorate solution.
Table 4.27: Experimental parameters for tests investigating effect of $[\text{Fe}]_{\text{Total}}$ on uranium dissolution from synthetic coffinite

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Uranium Concentration</td>
<td>100 ppm</td>
</tr>
<tr>
<td>Sulfuric Acid Concentration</td>
<td>15 g/L</td>
</tr>
<tr>
<td>Temperature</td>
<td>50 °C</td>
</tr>
<tr>
<td>Ferric : Ferrous Ratio</td>
<td>25:75</td>
</tr>
<tr>
<td>$[\text{Fe}]_{\text{Total}}$</td>
<td>0.38, 4.00, 8.00, 14.00 g/L</td>
</tr>
<tr>
<td>Ferric ($\text{Fe}^{3+}$) Concentration</td>
<td>0.01, 1, 2, 3.5 g/L</td>
</tr>
<tr>
<td>Uranium : Ferric Molar Ratio</td>
<td>1:0.4, 1:4.2, 1:8.5, 1:14.9</td>
</tr>
</tbody>
</table>

Table 4.28: Corresponding $[\text{Fe}]_{\text{Total}}$, ORP, $[\text{Fe}^{3+}]$ and $\text{U:Fe}^{3+}$ ratio, values

<table>
<thead>
<tr>
<th>$[\text{Fe}]_{\text{Total}}$ (g/L)</th>
<th>ORP</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.38</td>
<td>468</td>
</tr>
<tr>
<td>4.00</td>
<td>462</td>
</tr>
<tr>
<td>8.00</td>
<td>451</td>
</tr>
<tr>
<td>14.00</td>
<td>437</td>
</tr>
</tbody>
</table>

The results obtained from the tests on the influence of $[\text{Fe}]_{\text{Total}}$ are presented in Figure 4.5. Increasing the $[\text{Fe}]_{\text{Total}}$ appeared to have no significant effect on the extent or rate of uranium dissolution from coffinite when the $\text{Fe}^{3+}:\text{Fe}^{2+}$ ratio is maintained. Ram et al. found that $[\text{Fe}]_{\text{Total}}$ had a significant effect on the rate of uranium dissolution from synthetic uraninite, where small increases in the $[\text{Fe}]_{\text{Total}}$ resulted in large increases in the dissolution rate. The dependence between the rate of uranium dissolution from synthetic uraninite and $[\text{Fe}]_{\text{Total}}$ was found to be at a maximum when the solution ORP was ≥460 mV [19].
Figure 4.5: Uranium dissolution from synthetic coffinite at various \([\text{Fe}]_{\text{Total}}\) at an ORP of 452 ± 16 mV

Conditions: Temperature = 50 °C; \([\text{U}]_{\text{initial}} = 100 \text{ ppm} (4.20 \times 10^{-4} \text{ M}); \text{Fe}^{3+}:\text{Fe}^{2+} = 25:75;\)

~ constant ORP (452±16 mV); \([\text{H}_2\text{SO}_4]_{\text{initial}} = 15 \text{ g/L} (0.15 \text{ M}) .

The effect of \([\text{Fe}]_{\text{Total}}\) on uranium dissolution from synthetic coffinite was investigated further by studying the influence of \([\text{Fe}]_{\text{Total}}\) using solutions at four different ORP values (660, 565, 512, 490 and 410 mV) (Figure 4.6 to Figure 4.10). The results of these tests are summarised in Table 4.29.

Figure 4.6: Uranium dissolution from synthetic coffinite at various \([\text{Fe}]_{\text{Total}}\) at an ORP of 410 ± 20 mV
Figure 4.7: Uranium dissolution from synthetic coffinite at various $[\text{Fe}]_{\text{Total}}$ at an ORP of 490 ± 16 mV

Figure 4.8: Uranium dissolution from synthetic coffinite at various $[\text{Fe}]_{\text{Total}}$ at an ORP of 512 ± 3 mV
Figure 4.9: Uranium dissolution from synthetic coffinite at various $[\text{Fe}]_{\text{Total}}$ at an ORP of 565 ± 5 mV

Figure 4.10: Uranium dissolution from synthetic coffinite at various $[\text{Fe}]_{\text{Total}}$ at an ORP of 660 ± 30 mV
Table 4.29: Summary of Results obtained on the dissolution of coffinite in solution of varying ORP

<table>
<thead>
<tr>
<th>ORP (mV)</th>
<th>Fe³⁺:Fe²⁺</th>
<th>Observations / Trends in dissolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>410</td>
<td>5:95</td>
<td>Significant decrease in rate when [Fe]_{Total} increased from 0.38 g/L to 4 g/L; no change when increased further to 14 g/L</td>
</tr>
<tr>
<td>452</td>
<td>25:75</td>
<td>No change in rate or extent when [Fe]_{Total} increased from 0.38 g/L to 14 g/L</td>
</tr>
<tr>
<td>490</td>
<td>50:50</td>
<td>Minimal decrease to no change in rate and extent when [Fe]_{Total} increased from 0.38 g/L to 4 g/L and from 4 g/L to 14 g/L</td>
</tr>
<tr>
<td>521</td>
<td>75:25</td>
<td>Significant decrease in rate and extent when [Fe]_{Total} increased from 0.38 g/L to 4 g/L and from 4 g/L to 14 g/L</td>
</tr>
<tr>
<td>555</td>
<td>90:10</td>
<td>Significant decrease in rate and extent when [Fe]_{Total} increased from 0.38 g/L to 4 g/L and from 4 g/L to 14 g/L</td>
</tr>
<tr>
<td>660</td>
<td>100:0</td>
<td>Significant increase in extent and rate when [Fe]_{Total} increased from 0.38 g/L to 4 g/L; no change when further increased to 14 g/L</td>
</tr>
</tbody>
</table>

Based on the trends discussed in Table 4.29 the following conclusions on the influence of [Fe]_{Total} on the dissolution of uranium from synthetic coffinite can be made:

- The influence of [Fe]_{Total} on the dissolution of uranium from synthetic coffinite is highly dependent on solution ORP.
- At low solution ORP (410 mV) increasing [Fe]_{Total} resulted in a significant decrease to dissolution rates (for [Fe]_{Total} ranging from 0.38 – 4.0 g/L), and no change was observed when [Fe]_{Total} was increased beyond this point.
- At moderate ORPs (452 – 490 mV) minimal decrease to no change was observed as [Fe]_{Total} was increased over the range tested (0.38 – 14 g/L).
- At high ORPs (512 – 565 mV) increasing [Fe]_{Total} causes a significant decrease in the dissolution rate (when [Fe]_{Total} is increased from 0.38 – 14.0 g/L),
• At very high ORP (660 mV) increasing \([\text{Fe}]_{\text{Total}}\) causes a significant increase in the dissolution rate (when \([\text{Fe}]_{\text{Total}}\) is increased from 0.38 – 4.0 g/L), whilst no change in the dissolution rate occurred when \([\text{Fe}]_{\text{Total}}\) was increased from 4.0 - 14.0 g/L.

At high the ORP value (660±30 mV) the most significant difference (increase) in the extent of uranium dissolution from synthetic coffinite was observed (≅ 15 % of the total uranium). Generally it was found that as the \([\text{Fe}]_{\text{Total}}\) was increased the extent of uranium dissolution from synthetic coffinite decreased, however under solution ORP conditions similar to those used in uranium minerals processing (452 mV), no change was observed.

The results / trends on the effect of total iron at constant ORP (constant \(\text{Fe}^{3+}:\text{Fe}^{2+}\) ratio) on coffinite dissolution discussed in the previous paragraphs are not consistent with those obtained from similar studies conducted on uraninite dissolution. Analysis of the complex trends observed on the effect of \([\text{Fe}]_{\text{Total}}\) at solution ORPs of 410 – 565 mV on coffinite dissolution indicated that these trends may have involved a specific contribution from \(\text{Fe}^{2+}\) (or species’ that require \(\text{Fe}^{2+}\) for formation). This is based on the fact that the complex trends observed with increasing \([\text{Fe}]_{\text{Total}}\) were only observed in systems where \(\text{Fe}^{2+}\) was present initially in solution (for example no \(\text{Fe}^{2+}\) was present initially in the tests conducted at ≅ 660 mV (refer to Table 4.30) and the trend observed here was not complex – dissolution increased with increasing \([\text{Fe}]_{\text{Total}}\) over the \([\text{Fe}]_{\text{Total}}\) range studied. Studies conducted on uraninite have also shown that \(\text{Fe}^{2+}\) can have a detrimental effect on the rate of dissolution of this mineral [18, 19]. The actual mechanism by which \(\text{Fe}^{2+}\) (or species’ that require \(\text{Fe}^{2+}\) for formation) may have influenced the dissolution of coffinite was not investigated in detail as no methodology was available for conducting such an investigation (in-situ). \(\text{Fe}^{2+}\) may have contributed to the observed trends by contributing to the formation of a passivating compound layer which hindered dissolution of coffinite. Further studies are however needed to confirm or deny such a role.

4.3.1.4 Effect of Solution Oxidation Reduction Potential (ORP)
Although solution ORP was discussed in the previous section the influence of this parameter was not investigated and discussed in detail (as the main focus was the influence of $[\text{Fe}]_{\text{Total}}$). It was therefore decided to investigate the influence of ORP at constant $[\text{Fe}]_{\text{Total}}$ (influence of $\text{Fe}^{3+}:\text{Fe}^{2+}$).

The effect of the $[\text{Fe}^{3+}]$ to $[\text{Fe}^{2+}]$ ratio (ORP) on dissolution of coffinite was investigated by changing the $[\text{Fe}^{3+}]$ to $[\text{Fe}^{2+}]$ ratio whilst holding $[\text{Fe}]_{\text{Total}}$ constant. Six $[\text{Fe}^{3+}]$ to $[\text{Fe}^{2+}]$ ratio's (using three different $[\text{Fe}]_{\text{Total}}$) were investigated (refer to Table 4.30). All experiments were conducted at 50 °C with an initial uranium slurry concentration of 100 ppm ($4.20\times10^{-4}$ M) and 15 g/L of sulfuric acid.

| Table 4.30: Fe$^{3+}$ to Fe$^{2+}$ ratio, ORP and [Fe]$^{\text{Total}}$ conditions |
|---------------------------------|-----------------|-----------------|-----------------|
| 0.38 g/L[Fe]$^{\text{Total}}$ | 4.00 g/L[Fe]$^{\text{Total}}$ | 14.00 g/L[Fe]$^{\text{Total}}$ |
| ORP (mV) | Fe$^{3+}$:Fe$^{2+}$ ratio | ORP (mV) | Fe$^{3+}$:Fe$^{2+}$ ratio | ORP (mV) | Fe$^{3+}$:Fe$^{2+}$ ratio |
| 630 | 100:0 | 640 | 100:0 | 690 | 100:0 |
| 570 | 90:10 | 560 | 90:10 | 560 | 90:10 |
| 515 | 75:25 | 510 | 75:25 | 510 | 75:25 |
| 500 | 50:50 | 490 | 50:50 | 480 | 50:50 |
| 470 | 25:75 | 460 | 25:75 | 450 | 25:75 |
| 430 | 5:95 | 400 | 5:95 | 390 | 5:95 |

The results of the tests on the effect of solution ORP using [Fe]$^{\text{Total}}$s of 0.38, 4 and 14 g/L respectively are presented in Figure 4.54 to Figure 4.56. The results of these tests are summarised in Table 4.31.
Figure 4.11: Uranium dissolution of synthetic coffinite at various ORP values with a constant \([\text{Fe}]_{\text{Total}}\) of 0.38 g/L
Conditions: Temperature = 50 °C; \([\text{U}]_{\text{initial}}\) = 100 ppm (4.20x10^{-4} M); \([\text{H}_2\text{SO}_4]_{\text{initial}}\) = 15 g/L (0.15 M), \([\text{Fe}]_{\text{Total}}\) of 0.38 g/L.

Figure 4.12: Uranium dissolution of synthetic coffinite at various ORP values with a constant \([\text{Fe}]_{\text{Total}}\) of 4 g/L
Conditions: Temperature = 50 °C; \([\text{U}]_{\text{initial}}\) = 100 ppm (4.20x10^{-4} M); \([\text{H}_2\text{SO}_4]_{\text{initial}}\) = 15 g/L (0.15 M), \([\text{Fe}]_{\text{Total}}\) of 4 g/L.
Figure 4.13: Uranium dissolution of synthetic coffinite at various ORP values with a constant [Fe]$_{\text{Total}}$ of 14 g/L.
Conditions: Temperature = 50 °C; [U]$_{\text{initial}}$ = 100 ppm (4.20x10$^{-4}$ M); [H$_2$SO$_4$]$_{\text{initial}}$ = 15 g/L (0.15 M), [Fe]$_{\text{Total}}$ of 14 g/L.

<table>
<thead>
<tr>
<th>[Fe]$_{\text{Total}}$</th>
<th>Observations / Trends</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.38 g/L</td>
<td>The rate of dissolution increased with increasing ORP. Increasing the ORP from 570 mV to 630 mV led to a significant increase in the rate and extent of uranium dissolution.</td>
</tr>
<tr>
<td>4.00 g/L</td>
<td>The rate of dissolution increased with increasing ORP. Increasing the ORP from 560 mV to 640 mV led to a significant increase in the rate and extent of uranium dissolution.</td>
</tr>
<tr>
<td>14.0 g/L</td>
<td>The rate of dissolution increased with increasing ORP. Increasing the ORP from 565 mV to 690 mV led to a significant increase in the rate and extent of uranium dissolution.</td>
</tr>
</tbody>
</table>

From the results presented in Figure 4.54 -Figure 4.56 and discussed in Table 4.32 it can be seen that for all [Fe]$_{\text{Total}}$ tested, the trends with respect to solution ORP were the same, coffinite dissolution increased with increasing solution ORP. These trends were
observed in all solutions over the entire solution ORP ranges studied (390 – 660 mV). The other significant trend observed in all tests was the significant increase in coffinite dissolution rate when the solution ORP went from 560 – 690 mV, corresponded to a change in the Fe$^{3+}$: Fe$^{2+}$ from 90:10 to 100: 0 (i.e no Fe$^{2+}$ present).

Ram et al. found (under similar reaction conditions) that the rate and extent of uranium dissolution from UO$_2$ was significantly increased once the ORP was elevated to 460 mV and above; with 460 mV being the optimal ORP for the most effective dissolution with respect to the dependency on [Fe]$^{\text{Total}}$ [19]. Both of these results highlight the importance of ORP on the reaction and suggest that for each reaction there is a quite dramatic effect once the ORP reaches a specific value. A distinct increase in dissolution once a certain potential is achieved is indicative of a rate determining step in the dissolution mechanism being controlled by an electrochemical reaction.

### 4.3.1.5 Influence of [Fe$^{2+}$] at constant [Fe$^{3+}$]

The effect of [Fe$^{2+}$] was investigated by changing the [Fe$^{3+}$] to [Fe$^{2+}$] ratio, whilst holding [Fe$^{3+}$] constant, in order to obtain a clearer understanding of the influence of Fe$^{2+}$. The influence of Fe$^{2+}$ when Fe$^{3+}$ was held constant was investigated at three different [Fe$^{3+}$] (0.1, 1 and 3.5 g/L). All experiments were conducted under standard temperature, acid and initial uranium concentration experimental conditions (refer to Table 4.22). The [Fe$^{3+}$]: [Fe$^{2+}$] ratios that were used in the tests conducted at constant [Fe$^{3+}$] are given in Table 4.32.

<table>
<thead>
<tr>
<th>Fe$^{3+}$ to Fe$^{2+}$ Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 to 0</td>
</tr>
<tr>
<td>90 to 10</td>
</tr>
<tr>
<td>75 to 25</td>
</tr>
<tr>
<td>50 to 50</td>
</tr>
<tr>
<td>25 to 75</td>
</tr>
</tbody>
</table>

Table 4.32: Fe$^{3+}$ to Fe$^{2+}$ ratios used for tests on effect of ORP at constant [Fe$^{3+}$]
The influence of [Fe$^{2+}$] on the dissolution of uranium from synthetic coffinite whilst maintaining the same amount of Fe$^{3+}$, is presented in Figure 4.14. From the data presented in Figure 4.14 it can be seen that [Fe$^{2+}$] had a significant effect on the amount of uranium dissolved, where the addition of only a small quantity of Fe$^{2+}$ to each of the systems studied caused a significant reduction in the amount of uranium dissolved after 90 minutes. For all systems it was found that increasing [Fe$^{2+}$] led to a decrease in the uranium dissolution.
Figure 4.14: Uranium Dissolution after 90 mins vs $[Fe^{2+}]$ at various $[Fe^{3+}]$
The degree to which the $[\text{Fe}^{2+}]$ influenced the dissolution, in the systems containing different amounts of $\text{Fe}^{3+}$, did however vary. Firstly increasing $[\text{Fe}^{2+}]$ had a greater effect (in terms of percentage decrease in dissolution) for the system containing the lowest amount of $\text{Fe}^{3+}$ (0.1 g/L) (see inset Figure 14.4). There was very little difference in the effect of $[\text{Fe}^{2+}]$ for the 1.0 and 3.5 g/L $\text{Fe}^{3+}$ systems over the $[\text{Fe}^{2+}]$ range studied. The significant depression of uranium dissolution observed as soon as trace amounts of $\text{Fe}^{2+}$ are present is in contrast to the effect low concentrations of $[\text{Fe}^{2+}]$ were reported to have on uraninite dissolution [18]. For example Nicol et al. (1975) reported in their study (using three different $[\text{Fe}^{3+}]$), a region at very low $[\text{Fe}^{2+}]$ where the dissolution of $\text{UO}_2$ was completely independent of $[\text{Fe}^{2+}]$ and hence depended exclusively on $[\text{Fe}^{3+}]$. Clearly no similar region was observed in this study for the dissolution of synthetic coffinite, hence indicating that there is a significant difference in the influence of $\text{Fe}^{2+}$ on coffinite dissolution compared to uraninite dissolution.

Figure 4.15 shows the extent of uranium dissolution after 90 minutes versus solution ORP for each of the three $[\text{Fe}^{3+}]$ tested. This graph again emphasises the significant impact any $\text{Fe}^{2+}$ in the system has on the amount of uranium dissolved (as the data collected at solution ORPs > 575 mV were for systems where no $\text{Fe}^{2+}$ was present). It is interesting to note, that the trend line connecting the data points from 550 mV ($\text{Fe}^{3+}:\text{Fe}^{2+} = 90:10$) to 580 mV ($\text{Fe}^{3+}:\text{Fe}^{2+} = 100:0$) for the $[\text{Fe}^{3+}]$ 0.1 g/L test intersects the trend line connecting data points from 560 mV ($\text{Fe}^{3+}:\text{Fe}^{2+} = 90:10$) to 660 mV ($\text{Fe}^{3+}:\text{Fe}^{2+} = 100:0$) for the $[\text{Fe}^{3+}]$ 1.0 g/L tests. It is also interesting to note that based on the data presented in Figure 4.15 at a solution ORP of $\approx 585$ mV a higher degree of leaching would be obtained using a $[\text{Fe}^{3+}]$ of 0.1 g/L compared to $[\text{Fe}^{3+}]$ of 1.0 g/L or 3.5 g/L (the aforementioned being based on data extrapolation at $\approx 585$ mV using the trend lines – see Figure 4.15).
With the current data it is only possible to hypothesise, however it is plausible that this reaction is not purely electrochemical and that the presence of Fe\(^{2+}\) in solution may have a physical affect which supresses the dissolution of uranium from coffinite. Despite the variation in ORP, each system containing an initial Fe\(^{3+}\):Fe\(^{2+}\) ratio of 5:95, 25:75 or 100:0 resulted in a very similar amount of uranium being dissolved after 90 mins, when compared to other systems containing the same Fe\(^{3+}\):Fe\(^{2+}\) ratios.

### 4.3.1.6 Influence of Residence Time

The influence of residence time on uranium dissolution from coffinite was investigated under standard dissolution test conditions (refer to Table 4.22). This was conducted to investigate the equilibrium solubility of coffinite under these conditions – an aspect which is of significant interest to the uranium minerals processing industry. The
results of the test investigating the influence of residence time on uranium dissolution from coffinite are shown in Figure 4.16. It was found that under standard dissolution experimental conditions (Table 4.22) complete dissolution of uranium from coffinite was obtained between 36 and 48 hours (which corresponded to a final uranium concentration of \( \cong 4.2 \times 10^{-4} \) M (100 mg/L).

![Graph showing uranium dissolution over time](image)

**Figure 4.16: Uranium dissolution of synthetic coffinite 72 hour leach under standard conditions**

### 4.3.2 Characterisation of Dissolution Residue

Visually the leach residue analysed did not appear to differ significantly from the original synthesised coffinite. SEM/EDS images can be found in Figure 4.17 to Figure 4.19. From mapping analysis there appeared to be regions of high silicon and low uranium and EDS analysis indicated a change in the uranium silicon ratio of the sample was observed compared to the synthetic coffinite prior to leaching.
Figure 4.17: BSE Images of Leach Residue

Figure 4.18: EDS of Leach Residue Corresponding to Points (I-IV) from Figure 4.17
Three different leach residues were analysed using EPMA, these samples were found to be extremely difficult to analyse due to their instability under the electron beam. In order to generate the data shown in Table 4.33; the beam current was reduced to only 1.5 nA, the accelerating voltage reduced to 15 kV and the beam de-focused to 20 microns. When analysed at the same conditions as for the synthetic coffinite (i.e. 30 nA, 20 kV and 5 micron defocus) the residue tended to volatilise and disappear leaving holes in the sample.

Under the less energetic operating conditions, the sample remained stable throughout the analysis, without any evidence of beam damage although analysis totals for all residue samples were extremely low (60-62 wt%). It is unclear why the analysis totals were so low – possibilities include; significant nano-porosity and/or the presence of water (or hydrous species). Quantitative EPMA analysis conducted on leached residue
material indicate a U:Si of 0.43-0.48, a significant decrease when compared with the synthetic coffinite prior to leaching. The comparison of the Si contents between the starting material and residue remained relatively constant. This means that the decrease in the U:Si appears to be caused by the removal of uranium which has decreased from 64.32 wt% in the starting material to between 34-37 wt% in the residues (≅ 45% decrease). The result suggests that uranium is selectively dissolved from the coffinite.

Table 4.33: Quantitative EPMA Results of Coffinite Leach Residue

<table>
<thead>
<tr>
<th>Element (wt%)</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>n.d.</td>
<td>0.111</td>
<td>0.94</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt;d.l.</td>
<td>&lt;d.l.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Si</td>
<td>9.59</td>
<td>9.12</td>
<td>9.01</td>
</tr>
<tr>
<td>U</td>
<td>34.90</td>
<td>34.69</td>
<td>36.97</td>
</tr>
<tr>
<td>Ti</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Th</td>
<td>0.016</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Al</td>
<td>0.013</td>
<td>&lt;d.l.</td>
<td>&lt;d.l.</td>
</tr>
<tr>
<td>P</td>
<td>0.022</td>
<td>0.023</td>
<td>n.d.</td>
</tr>
<tr>
<td>Ca</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Y</td>
<td>0.031</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>S</td>
<td>0.472</td>
<td>0.557</td>
<td>0.235</td>
</tr>
<tr>
<td>O</td>
<td>16.47</td>
<td>16.40</td>
<td>16.44</td>
</tr>
<tr>
<td>Total</td>
<td>61.31</td>
<td>60.84</td>
<td>62.58</td>
</tr>
<tr>
<td># analyses</td>
<td>7</td>
<td>24</td>
<td>29</td>
</tr>
</tbody>
</table>

U:Si Ratio

n.d. = not detected
<d.l. = below detection limit
Further characterisation was conducted to establish differences between the synthetic coffinite samples before and after leaching. The thermogravimetric analysis mass loss curve and its derivative (Figure 4.63) of the synthetic coffinite post leaching, indicates three regions of mass loss, the same as seen in the natural sample containing coffinite. The total mass loss of the synthetic coffinite sample after leaching, when heated to 1000 °C, is about 5 weight % (compared to 7 weight % prior to leaching).

![TGA of Coffinite Leach Residue](image)

Figure 4.20: TGA of Coffinite Leach Residue

The first loss between 50 and 250 °C can be attributed to water loss and is typical to the loss associated with water from interlayer sites Cejka, J., 1999 [27]. The mass loss during this temperature region appears similar to the synthetic coffinite prior to leaching (results can be found in Chapter 33.1.7). The second mass loss region extends from approximately 400 to 750 °C, with the majority of the mass loss peaking at approximately 500 °C, and a shoulder appearing at just above 600 °C. Though the overall mass loss during this region is very similar to the synthetic coffinite prepared prior to leaching the profile of the derivative curve is very different and indicates that there has been a change in the sample during leaching. At temperatures above 800 °C there appears to be very little loss, even less than the sample prior to leaching, this loss may be attributed to strongly bound water, as dehydroxylation can occur to temperature up to 900 °C Cejka, J., 1999 [27].

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One of the explanations considered for the instability of the sample under the electron beam during EPMA and very low analysis totals during quantitative experiments, was the suggestion of excessive amounts of water being present in the sample after leaching. The TGA results indicated no excessive amounts of water or hydrolysis species to be present in the sample, and therefore it is highly likely that the low analysis totals observed in the quantitative EPMA was as a result of the presence of significant quantities of nano-porous material.

### 4.4 Chapter Summary

The results of uranium dissolution from synthetic coffinite have been summarised below.

**Effect of Temperature**

- Minimal change in rate and extent of uranium dissolution was observed when the temperature was increased from 50 °C to 60 °C
- Increasing the temperature to 80 °C (from 60 °C) substantially increased both the rate and extent of uranium dissolution.
- A further increase in temperature to 95 °C saw the rate of uranium dissolution increase substantially in the first 30 mins, however there was little improvement in the extent of uranium dissolved from synthetic coffinite after 90 minutes.
- The activation energy was calculated to be 64.6 kJ/mol
- Arrhenius parameter of 220
- Equilibrium solubility may have been obtained after ≅ 40 mins at 95 °C as the dissolution curve began to plateau at this point (and 100% uranium dissolution was not achieved).

**Effect of Sulfuric Acid**

- Maximum uranium dissolution from synthetic coffinite, after 90 min, occurred at a sulphuric acid concentration of 1.5 g/L.
• Uranium dissolution from synthetic coffinite increases (by \(\cong 4\%\)) when the sulphuric acid concentration increases from 0.5 g/L to 1.5 g/L.

• A decrease in the extent of uranium dissolution is observed when the sulphuric acid concentration is increased from 1.5 g/L to 100 g/L, with the most significant decrease in the extent of uranium dissolution from 1.5 g/L to 15 g/L.

• At very high sulphuric acid concentrations (300 g/L) the second largest amount of uranium was leached from synthetic coffinite.

• The unusual increase and subsequent decrease in the extent of uranium dissolution with increasing acid concentration (over the range tested) may have been caused by one or more of the following phenomena:
  o Silicate gelling
  o Variation in Fe species
  o Change in the potential difference between the \(\text{U}^{4+}\) to \(\text{UO}_2^{2+}\) reaction and ferrous to ferric reaction.

Effect of Total Iron ([Fe]_{Total}) at Constant ORP (constant \(\text{Fe}^{3+:}\text{Fe}^{2+}\) ratio)

• Increasing the \([\text{Fe}]_{\text{Total}}\) appeared to have little effect on the extent or rate of uranium dissolution from coffinite when the \(\text{Fe}^{3+:}\text{Fe}^{2+}\) ratio is maintained.

• The influence of \([\text{Fe}]_{\text{Total}}\) on the dissolution of uranium from synthetic coffinite is highly dependent on solution ORP.
  o At low to moderate/high ORPs (410 – 555 mV) lower \([\text{Fe}]_{\text{Total}}\) results in slightly increased dissolution rates (for \([\text{Fe}]_{\text{Total}}\) ranging from 0.38 – 8.0 g/L).
  o At very high ORP (660 mV) increasing \([\text{Fe}]_{\text{Total}}\) causes a significant increase in the dissolution rate (when \([\text{Fe}]_{\text{Total}}\) is increased from 0.38 – 4.0 g/L), whilst no change in the dissolution rate occurred when \([\text{Fe}]_{\text{Total}}\) was increased from 4.0 - 8.0 g/L.
  o At high ORP values (660±30 mV) the most significant difference in the extent of uranium dissolution from synthetic coffinite was observed (\(\cong 15\%\) of the total uranium). Generally it was found that as the \([\text{Fe}]_{\text{Total}}\) was increased the extent of uranium dissolution from synthetic coffinite
decreased, however under solution ORP conditions similar to those used in uranium minerals processing (452 mV), no changed was observed.

- Trends may have involved a specific contribution from Fe$^{2+}$ (or species’ that require Fe$^{2+}$ for formation)
- Complex trends observed with increasing [Fe]$^\text{Total}$ were only observed in systems where Fe$^{2+}$ was present initially in solution.

**Effect of Solution Oxidation Reduction Potential (ORP)**

- coffinite dissolution increased with increasing solution ORP. These trends were observed in all solutions over the entire solution ORP ranges studied (390 – 660 mV).
- An increase in coffinite dissolution rate when the solution ORP went from 560 – 690 mV, corresponded to a change in the Fe$^{3+}$: Fe$^{2+}$ from 90:10 to 100: 0 (i.e no Fe$^{2+}$ present).

**Influence of [Fe$^{2+}$] at constant [Fe$^{3+}$]**

- [Fe$^{2+}$] had a significant effect on the amount of uranium dissolved
- A significant depression of uranium dissolution was observed as soon as trace amounts of Fe$^{2+}$ were present in the system.
- For all systems it was found that increasing [Fe$^{2+}$] led to a decrease in the uranium dissolution.
- [Fe$^{2+}$] had a greater effect (in terms of percentage decrease in dissolution) for the system containing the lowest amount of Fe$^{3+}$ (0.1 g/L)
- There was very little difference in the effect of [Fe$^{2+}$] for the 1.0 and 3.5 g/L Fe$^{3+}$ systems over the [Fe$^{2+}$] range studied.
Influence of Residence Time

- Under standard dissolution experimental conditions complete dissolution of uranium from coffinite was obtained between 36 and 48 hours (which corresponded to a final uranium concentration of $\approx 4.2 \times 10^{-4}$ M (100 mg/L).

Characterisation of Dissolution Residue

- Visually the leach residue analysed did not appear to differ significantly from the original synthesised coffinite.
- EPMA analysis was extremely difficult and analysis totals for were extremely low (60-62 wt%).
- Quantitative EPMA analysis conducted on leached residue material indicate a U:Si of 0.43-0.48 (a significant decrease when compared with the starting synthetic coffinite).
- The Si content of the sample pre and post leach remained relatively constant.
- The U content of the sample decrease $\approx 45\%$ after leaching
- Thermogravimetric analysis curve is similar to that of naturally occurring coffinite and exhibits a total mass loss $\approx 5$ wt % (compared to the $\approx 7$ wt% observed for synthetic coffinite prior to leaching) and did not indicated excessive inclusion of water.
- The TGA derivative curve indicates the sample has undergone some alteration during leaching.

4.5 References


17. Laxen, P.A., A fundamental study of the dissolution in acid solutions or uranium minerals from South African ores, in Faculty of Engineering. 1973, University of Witwatersrand: Johannesburg.


CHAPTER 5

CONCLUSION AND FUTURE WORK
5.1 Conclusions

5.1.1 Characterisation of a Uranium Bearing Ore and a Natural Coffinite Sample

The Uranium bearing ore and natural sample containing coffinite were highly complex and required the use of multiple characterisation techniques, including synchrotron XRD and EPMA, was necessary to gain a detailed understanding of the sample mineralogy.

Based on the detailed characterisation studies that were conducted on the uranium bearing ore sample used in this study the following conclusions were made regarding the uranium and gangue mineralogy of this sample.

Uranium mineralogy – Based on EPMA analysis the following results were observed:

- Uraninite was identified only in the <75 µm fraction of the sample where fractions above this size indicated the presence of Uranium in a Fe-O matrix (presumably) uraninite
- Uranium in a Si-O matrix was identified and believed to be non-stoichiometric coffinite.
- Coffinite was found to be located on the edge of large particles as well as being completely encapsulated by minerals such as, hematite, quartz, sericite and Fe chlorite
- Coffinite was surrounded by a phase labelled U-edge, which corresponds to the region where the grain boundaries of the two minerals meet.
- In cases where coffinite was adjoining minerals such as hematite or Fe chlorite a thin layer of uranium in a Fe-O matrix (uraninite) was found.
- The size of the coffinite grains varied from 10 x 10 µm (irregular in shape) to 1 µm (spherical grains).
- Other un-named uranium minerals were also found in the sample.

Gangue mineralogy – Based on XRD and EPMA analysis the following gangue minerals were identified
• Hematite (identified as a major constituent by XRD and EPMA)
• Quartz (identified as a major constituent by XRD and EPMA)
• Fluorite (identified as a major constituent by EPMA and in-situ HT-XRD)
• Sericite (identified as a major constituent by EPMA)
• Fe Chlorite (identified as a major constituent by EPMA)
• Barite (identified as a major constituent by EPMA and minor phase by Synchrotron XRD)
• Florencite (identified as a minor phase synchrotron XRD by EPMA)
• Birnessite (identified as a minor phase synchrotron XRD)
• Rutile (identified in trace amounts by synchrotron XRD and EPMA)
• Siderite (identified in trace amounts by synchrotron XRD)
• Chalcopyrite (identified in trace amounts by synchrotron XRD and EP=A)
• Cuprospinel (identified in trace amounts by synchrotron XRD)
• Alurgite (identified in trace amounts by synchrotron XRD)
• Muscivite (identified in trace amounts by synchrotron XRD)
• Calcite (identified in trace amounts by synchrotron XRD)
• Other minerals only identified by EPMA include:
  o Dolomite
  o Bastbasite-La
  o Fe-Mg aluminosilicate
  o Unidentified Ca-Fe-O mineral
  o K-feldspar
  o Zircon
  o CuSx

Based on the detailed characterisation studies that were conducted on the natural sample containing coffinite, the following conclusions were made regarding the mineralogy of this sample.

• Primary mineral phase identified as quartz by XRD, EPMA, EDAX
• Limited coffinite was identified by XRD and EPMA
EPMA analysis of coffinite identified in the natural sample was found to have the following characteristics

- 120 – 140 µm in size
- Visual appearance was patchy, polycrystalline aggregate with heterogeneous BSE contrast
- Quantitative analytical totals varied between, 91.4 % to 98.2 %
- Uranium content varied throughout the sample (57.48 wt% to 62.22 wt%)
- Silicon content varied throughout the sample (10.99 wt% to 13.27 wt%)
- U:Si ratio varied and was found to be low (over all U:Si 0.62) where the highest ratio was 0.72
- The edge of the coffinite grain containing greater silicon abundances
- non-stoichiometric \((U_{0.8}Si_{1.2}O_4)\) when neglecting the presence of phosphorous and sulphur impurities

Other characterisation results of the natural sample containing coffinite included that the detectable uranium in the sample was in the VI oxidation state, trace amounts of vanadium, aluminium and potassium were found. TGA experiments also indicated that upon heating to 1000 °C degradation of coffinite to \(UO_2\) and \(SiO_2\).

### 5.1.2 Preparation and Characterisation of Synthetic Coffinite

Based on the research conducted on the preparation of synthetic coffinite via a hydrothermal method it can be concluded that the following steps / conditions are critical to the preparation of this mineral via this method

- The ratio of \(UCl_4\) to Sodium metasilicate used
- The removal of residual oxygen from all solutions

Coffinite was successfully synthesised via the method outlined in chapter 3 when all solutions and water used in the reaction had the residual oxygen removed and 10 mL of \(UCl_4(aq)\) was used (resulting in a U:Si ratio of 0.39). When the synthesis was conducted using 5 mL or 20 mL of \(UCl_4(aq)\) the resulting product was found to be uraninite with no
coffinite detectable via XRD. The product synthesised using 15 mL of UCl₄(aq) was found to contain coffinite though had a substantial amount of uraninite as the impurity.

From the characterisation results obtained for prepared synthetic coffinite the following properties of this mineral were determined

- The coffinite synthesised is of an extremely fine grain and intimately mixed with a nano-crystalline silicon rich amorphous phase.
- Unit cell parameters calculated as, a=b 6.99795±0.0002 Å and c 6.27197±0.0002 Å
- The major oxidation state of uranium to be in the IV state though approximately 40 % of the surface uranium had been oxidised to U(VI)
- BET analysis resulted in the following findings:
  - The synthetic coffinite had a low surface area (78.44 m²/g)
  - Micropore volume of 0.10579 cm³/g
  - Adsorption pore size of 15.4303 nm
  - Desorption pore size of 16.7207 nm
- The total water content of synthetic coffinite was calculated between 1 and 1.5 moles.
- EPMA found two distinctively different types of coffinite, with respect to textural features.

The majority of the synthetic coffinite sample was found to exhibit the following characteristics.

- Texture was similar to the coffinite found in the natural sample (patchy, polycrystalline aggregates with heterogeneous BSE contrast).
- The edge of the particle contained greater amounts of silicon.
- The centre of the particle also exhibited variation in the U:Si ratio (although minimal).
- Sulfur was found to be distributed at low levels throughout the sample.
- The clustering program identified two coffinite phases, coffinite and coffinite low in uranium (high in silicon).

Quantitative EPMA analysis of the synthetic coffinite found the following:
• Uranium content varied throughout the sample (62.72 – 65.44 wt %)
• Silicon content varied throughout the sample (8.93 – 11.33 wt %)
• The overall uranium to silicon ratio was low (0.73) compared to the theoretical value of 1.0.
• The sample also contained between 0.124 and 0.494 wt % of sulfur.

A second type of coffinite was also identified by EPMA, which was consistent with material that is allowed to settle in a reaction flask (as was done during synthesis method). This type of coffinite was found to contain fractures where sulphur and uranium was concentration. Trace amounts of quartz and Fe-oxide were also found in this sample.

### 5.1.3 Dissolution of Synthetic Coffinite

From the results obtained from the studies conducted on the influence of various parameters on uranium dissolution from synthetic coffinite the following conclusions were reached:

Temperature has a significant influence on the dissolution of synthetic coffinite. The dissolution of synthetic coffinite increases with increasing temperature between 50 and 90 °C. The aforementioned influence of temperature is most pronounced when the temperature is increased from 60 to 80 °C.

The activation energy for synthetic coffinite dissolution (under the conditions used in this study Initial [U] 4.20x10^-4 M (100 ppm); Initial [Fe^{3+}] 0.02 M (1 g/L), Initial [Fe^{2+}] 0.05 M (3 g/L), Initial [H_2SO_4] 0.15 M (15 g/L)) is 64.6 kJ/mol. The equilibrium solubility of uranium (coffinite) under the conditions studied is most likely 83 mg/L may have been obtained after ≅ 40 mins at 95 °C as the dissolution curve began to plateau at this point (and 100% uranium dissolution was not achieved).

The concentration of sulphuric acid had an interesting effect on the extent of uranium dissolution from synthetic coffinite. The trends observed that increased acid resulted in an increased in dissolution until the optimum acidic concentration was reached (1.5 g/L). At this point the extent of uranium dissolution continued to decrease with...
increasing acid concentration until excessive acid concentrations were used and even then only a small increase in the dissolved uranium was observed when compared to the large amount of acid used. This trend may have been caused by one or more of the following:

- Silicate gelling
- Variation in Fe species
- Change in the potential difference between the $U^{4+}$ to $UO_2^{2+}$ reaction and ferrous to ferric reaction.

Increasing the $[\text{Fe}]_{\text{Total}}$ appeared to have some effect on the extent or rate of uranium dissolution from coffinite when the $\text{Fe}^{3+}$:$\text{Fe}^{2+}$ ratio is maintained, though was found to be highly dependent on solution ORP. Generally it was found that as the $[\text{Fe}]_{\text{Total}}$ was increased the extent of uranium dissolution from synthetic coffinite decreased. However under solution ORP conditions similar to those used in uranium minerals processing (452 mV), no change was observed and at the very high ORP value (660±30 mV) the most significant difference (an increase) in the extent of uranium dissolution from synthetic coffinite was observed ($\cong$ 15 % of the total uranium).

At low solution ORP (410 mV) increasing $[\text{Fe}]_{\text{Total}}$ resulted in a significant decrease to dissolution rates (for $[\text{Fe}]_{\text{Total}}$ ranging from 0.38 – 4.0 g/L), and no change was observed when $[\text{Fe}]_{\text{Total}}$ was increased beyond this point. At moderate ORPs (452 – 490 mV) minimal decrease to no change was observed as $[\text{Fe}]_{\text{Total}}$ was increased over the range tested (0.38 – 14 g/L). At high ORPs (512 – 565 mV) increasing $[\text{Fe}]_{\text{Total}}$ causes a significant decrease in the dissolution rate (when $[\text{Fe}]_{\text{Total}}$ is increased from 0.38 – 14.0 g/L). At very high ORP (660 mV) increasing $[\text{Fe}]_{\text{Total}}$ causes a significant increase in the dissolution rate (when $[\text{Fe}]_{\text{Total}}$ is increased from 0.38 – 4.0 g/L), whilst no change in the dissolution rate occurred when $[\text{Fe}]_{\text{Total}}$ was increased from 4.0 - 14.0 g/L. The complex trends observed with increasing $[\text{Fe}]_{\text{Total}}$ were only observed in systems where $\text{Fe}^{2+}$ was present initially in solution.

As the solution ORP increased (390 – 660 mV) so did the extent of uranium leach from synthetic coffinite.
The ferric (Fe$^{2+}$) concentration had a significant effect on the amount of uranium dissolved, where a significant depression in uranium dissolution was observed as soon as trace amounts of Fe$^{2+}$ were present in the system. It was found that increasing [Fe$^{2+}$] led to a decrease in the uranium dissolution in all systems studied (Fe$^{3+}$:Fe$^{2+}$ 100:0, 90:10, 75:25, 50:50, 25:75, 5:95 at [Fe$^{3+}$] of 0.1 g/L, 1 g/L and 3.5 g/L) with the greatest effect begun observed in those systems contain the lowest amount of Fe$^{3+}$ (0.1 g/L).

Under standard dissolution experimental conditions complete dissolution of uranium from coffinite was obtained between 36 and 48 hours (which corresponded to a final uranium concentration of $\approx 4.2 \times 10^{-4}$ M (100 mg/L).

### 5.1.4 Characterisation of Dissolution Residue

After dissolution the residue was collected and analysed, visually the leach residue analysed did not appear to differ significantly from the original synthesised coffinite. A significant decrease in the U:Si (0.433-0.48) was observed when compare to the preleached samples, where the silicon content remained constant before and after leach and the uranium content of the sample decreased approximately 45% after leaching. Thermogravimetric analysis curve did not indicate the presence of the inclusion of excessive water, though did suggest that the sample has undergone some alteration during leaching.

### 5.2 Future Work

The following aspects of coffinite dissolution are recommended for future work:

#### Detailed studies on the influence of Fe$^{2+}$

The unexpected finding where as soon as Fe$^{2+}$ was introduced into the system caused a significant decrease in the extent of uranium dissolution, indicted that future studies are required to understand this process. It is possible that Fe$^{2+}$ contributes or facilitate in
the passivation of the sample resulting in a reduced amount of uranium available for leaching.

**Studies on the influence of dopants on coffinite dissolution**

As coffinite is never found in nature as USiO$_4$ preparing a synthetic coffinite that contains various amounts of water and/or hydroxyl substitutions and various dopants such as REE and P, would be beneficial for future dissolution studies to investigate the influence these known substitutions have on uranium dissolution. A study such as this would assist in the understanding of the dissolution properties of the various forms of natural coffinite.

**Studies on the influence of structure (crystalline vs amorphous)**

As coffinite itself contains uranium and is found in close proximity to the radioactive minerals, in nature the mineral is often found in state where its crystal structure has been damaged by radiation over time. Trying to replicate the distorted and damaged crystal structure through the use of irradiation techniques may useful for studying how the degree of crystalinity of a coffinite sample influences uranium dissolution.

**Research on the influence of foreign species that are commonly found in uranium minerals processing leach slurries**

During the industrial leaching process, many other foreign species are present, which may or may not influence uranium dissolution from coffinite. The influence of gangue mineralogy is a very important factor that should be included in any future dissolution studies. These experiments can be structured in a way to fundamentally study foreign ions (anions and cations) which are present in common gangue minerals (i.e. cations – Na, Mg, K, and Ca; anions - F, Cl, Br and I). Dissolution experiments can also be conducted where known amounts of common gangue minerals (synthetic and/or natural) are added to synthetic coffinite dissolution studies. Known quantities of synthetic coffinite can also be added to dissolution studies of uranium bearing ores, future studying the influence of gangue mineralogy in complex system. Some foreign species may have a positive effect on uranium leaching from coffinite, as has been observed for uraninite. This could assist industries in better understanding how
coffinite may behave during leaching or even suggest plausible additives that may be used to extract uranium from difficult to process coffinite

**Electrochemical studies**

Future studies into the potentials associated with coffinite dissolution can be conducted through electrochemical experimentation methods. These experiments may be useful for understanding the mechanism by which uranium is dissolved from coffinite.

**Studies on the influence of coffinite pre-treatment on dissolution**

There are a number of pre-treatment methods which may also be investigated as to their influence on uranium dissolution from coffinite, these include processes such as roasting or fusing the silicate portion of coffinite.
CHAPTER 6

COMPLETE LIST OF REFERENCES
Chapter 6


KALMYKOV, S.N., Technical Report 1 : Review of the Technologies Used for Uranium and Other Metals (Copper and Gold) Leaching. 2010, Lomonsov Moscow State University; Chemistry department; Radiochemistry division: Moscow.


APPENDIX A

ELECTRON PROBE MICROANALYSIS (EPMA)

- Sample Preparation
- Standards for WD Spectrometer Calibration
- RGB Colour Mixing
Sample Preparation

All samples were prepared in an ARPANSA certified laboratory with appropriate measures taken to minimise exposure to the radiation source.

A small amount (<1 gm) of natural coffinite from New Mexico, synthetic coffinite and each of the three leached residues were supplied for analysis while up to 10 gm of the museum sample coffinite was made available. Approximately 0.7-0.8 gm from the first five samples was mixed with a small amount of epoxy resin and poured into 5 mm diameter x 0.1 mm deep holes that had been pre-drilled in a 25 mm round plastic resin holder, and allowed to cure overnight. For the much larger volume natural sample, approximately 3-5 gm of material was mixed with epoxy resin and mounted in a separate 25 mm round mould for curing. After curing, the sample mounts were heated in a drying oven for 2-3 hours, allowed to cool and then the basal part of each sample mount was sectioned to expose a fresh cross-sectional surface. The newly exposed surface was then polished flat using successively finer grades of emery paper followed by a final surface polishing using a sequence of 6, 3 and 1 µm diamond pastes. To prevent possible dissolution and/or contamination of water-sensitive phases in samples, all cutting and polishing was conducted under water absent conditions.

The sample mounts were finally coated with a 15 nm film of carbon immediately prior to analysis in the electron microprobe. The carbon film was necessary to prevent charge build-up on the surface of the sample when probed by the electron microprobe beam.

Standards used for calibrating the EPMA WD Spectrometers

Prior to mapping the WD spectrometers were calibrated for the bolded elements using the following standards:

- hematite ($\text{Fe}_2\text{O}_3$)
- wollastone ($\text{CaSiO}_3$)
- uranium oxide ($\text{UO}_2$)
- rutile ($\text{TiO}_2$)
- anglesite ($\text{PbSO}_4$)
Appendix A

Element Distribution Data – RGB Colour Mixing
As mentioned previously in Chapter 2 (2.2.2.6), after mapping, the element distribution data were manipulated using the software package CHIMAGE (in-house proprietary software developed by CSIRO Process Science and Engineering – Harrowfield et al., 1993). CHIMAGE allows the individual element data to be displayed either as single element distribution scatter plots or as combined element maps (where data for three elements are combined on the one mapped region using a red/blue/green palette – see below for a description).

Mixing of colours has important bearing on the interpretation of FEG-EPMA maps. The three basic colours, R red, G green and B blue are used to designate the distribution of a particular element. Depending on the composition of the mineral or phase being examined overlaps in the element distribution will lead to mixing of the colours. The resulting colours and their interpretation are determined by examination of a colour mixing chart as shown in the figure below. For example, if the distribution of elements Si (blue), O(green) and U (red) are plotted on a map, grains that represent quartz (Si+O) would appear light blue i.e. the mixture of green and blue basic colours will give a light blue colour. Similarly, oxides or Al-rich aluminosilicates would appear green (not much Si and no or U) and U-rich oxides (no Si) may appear red or yellow/orange (depending on oxygen content). Note that black is obtained when there is an absence of the three primary colours (indicating areas on the map where there is no Si, O or U).

![Colour mixing chart](image)

Figure A.1 Colour mixing chart for interpreting FEG-EPMA element distribution map data.
Figure A.2 Three element map showing the distribution of Si, O and U within a mapped region.
APPENDIX B

QUANTITATIVE ELECTRON PROBE MICROANALYSIS (EPMA) TABULATED RESULTS
### Quantitative Electron Probe Microanalysis (EPMA) Results

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**Synthetic Coffinite Leach Residue Sample Under Standard Conditions (Sample A)**

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**Synthetic Coffinite Leach Residue Sample Under Standard Conditions (Sample B)**
| 170 | 16.88 | 0.245 | 0.026 | 8.33  | 0.029 | 0.000 | -0.025 | -0.006 | 0.189 | 0.000 | 0.024 | 40.90 | 66.59 |
| 171 | 16.46 | 0.000 | 0.044 | 8.06  | -0.047 | -0.307 | -0.038 | 0.009 | 0.301 | -0.065 | -0.145 | 41.11 | 65.38 |
| 172 | 17.61 | 0.147 | 0.036 | 8.35  | 0.006 | -0.103 | 0.032 | -0.004 | 0.281 | -0.357 | -0.061 | 40.64 | 66.58 |
| 173 | 17.51 | 0.148 | -0.009 | 8.75  | 0.053 | 0.103 | -0.029 | -0.008 | 0.130 | -0.098 | -0.012 | 40.02 | 66.55 |
| 174 | 15.51 | 0.146 | 0.003 | 8.90  | 0.053 | -0.204 | 0.016 | 0.023 | 0.377 | -0.421 | 0.036 | 41.37 | 65.81 |
| 175 | 16.22 | -0.343 | 0.258 | 8.67  | -0.059 | -0.512 | 0.003 | 0.007 | 0.528 | 0.194 | 0.006 | 40.72 | 65.69 |
| 176 | 15.79 | 0.554 | -0.073 | 9.66  | 0.018 | -0.208 | -0.038 | 0.026 | 0.139 | 0.034 | -0.025 | 30.14 | 56.02 |
| 177 | 16.21 | -0.201 | 0.111 | 9.58  | -0.030 | 0.000 | 0.048 | 0.029 | 0.106 | 0.334 | -0.006 | 30.39 | 56.57 |
| 178 | 16.78 | 0.741 | -0.232 | 9.63  | -0.042 | -0.617 | -0.054 | 0.007 | 0.109 | -0.131 | -0.067 | 38.34 | 64.47 |
| 179 | 16.37 | 0.247 | -0.006 | 9.82  | 0.048 | -0.309 | -0.035 | -0.001 | 0.077 | -0.23 | 0.037 | 37.41 | 63.43 |
| 180 | 13.50 | 0.146 | 0.018 | 7.43  | 0.006 | 0.204 | -0.025 | -0.01 | 0.161 | -0.291 | 0.036 | 35.68 | 56.86 |
| 181 | 12.89 | 0.049 | 0.082 | 7.64  | 0.000 | 0.103 | -0.038 | 0.000 | 0.202 | -0.033 | -0.043 | 30.64 | 51.49 |
| 182 | 19.58 | 0.254 | -0.143 | 13.73 | 0.080 | 0.105 | 0.019 | -0.011 | 0.373 | -0.135 | 0.032 | 35.82 | 69.71 |
| 183 | 15.72 | 0.345 | 0.128 | 7.90  | -0.012 | 0.412 | -0.019 | -0.016 | 0.120 | 0.065 | -0.116 | 35.26 | 59.79 |
| 184 | 20.44 | -0.200 | 0.016 | 11.72 | -0.03 | -0.624 | 0.042 | 0.019 | 0.166 | 0.000 | 0.000 | 40.91 | 72.45 |
| 185 | 15.01 | 0.100 | 0.126 | 8.47  | 0.024 | 0.934 | -0.026 | 0.002 | 0.331 | 0.033 | -0.056 | 30.04 | 54.99 |
| 186 | 17.03 | -0.147 | -0.197 | 8.97  | -0.065 | 0.308 | -0.016 | 0.024 | 0.271 | 0.26 | -0.061 | 40.87 | 67.25 |
| 187 | 15.83 | 0.150 | 0.021 | 9.12  | -0.060 | -0.624 | -0.035 | 0.022 | 0.260 | -0.033 | -0.093 | 31.56 | 56.11 |
| 188 | 15.91 | -0.198 | 0.284 | 9.23  | -0.018 | -0.103 | -0.064 | 0.019 | 0.291 | -0.033 | 0.148 | 34.45 | 59.92 |
| 189 | 16.04 | 0.248 | -0.106 | 8.96  | 0.054 | -0.31 | -0.08 | -0.011 | 0.247 | -0.066 | 0.037 | 34.60 | 59.61 |
| 190 | 15.20 | -0.396 | 0.018 | 9.13  | 0.042 | -0.103 | 0.010 | -0.018 | 0.225 | 0.46 | 0.018 | 34.65 | 59.24 |

Appendix B
<table>
<thead>
<tr>
<th>Point</th>
<th>O</th>
<th>Fe</th>
<th>Th</th>
<th>Si</th>
<th>P</th>
<th>Ti</th>
<th>Ca</th>
<th>Al</th>
<th>S</th>
<th>Pb</th>
<th>Y</th>
<th>U</th>
<th>Total</th>
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<td>0.099</td>
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<td>0.09</td>
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<td>9.01</td>
<td>0.00</td>
<td>-0.11</td>
<td>-0.02</td>
<td>0.00</td>
<td>0.23</td>
<td>-0.01</td>
<td>-0.02</td>
<td>36.97</td>
<td>62.58</td>
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Synthetic Coffinite Leach Residue Sample with No Ferrous (Fe$^{3+}$: Fe$^{2+}$ 100:0)

<table>
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<tr>
<th>Point</th>
<th>O</th>
<th>Fe</th>
<th>Th</th>
<th>Si</th>
<th>P</th>
<th>Ti</th>
<th>Ca</th>
<th>Al</th>
<th>S</th>
<th>Pb</th>
<th>Y</th>
<th>U</th>
<th>Total</th>
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<td>0.400</td>
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<td>9.03</td>
<td>0.024</td>
<td>-0.205</td>
<td>-0.032</td>
<td>0.019</td>
<td>0.321</td>
<td>0.033</td>
<td>0.110</td>
<td>38.06</td>
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<tr>
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<td>0.024</td>
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<td>-0.054</td>
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<td>0.092</td>
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<td>-0.094</td>
<td>9.18</td>
<td>0.042</td>
<td>-0.207</td>
<td>-0.016</td>
<td>0.030</td>
<td>0.470</td>
<td>-0.197</td>
<td>-0.006</td>
<td>37.60</td>
<td>64.67</td>
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<tr>
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<td>15.63</td>
<td>-0.099</td>
<td>-0.142</td>
<td>9.48</td>
<td>0.054</td>
<td>0.310</td>
<td>-0.022</td>
<td>0.023</td>
<td>0.362</td>
<td>0.033</td>
<td>-0.056</td>
<td>36.08</td>
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<td>200</td>
<td>16.04</td>
<td>0.050</td>
<td>0.094</td>
<td>9.72</td>
<td>-0.018</td>
<td>0.000</td>
<td>-0.055</td>
<td>0.005</td>
<td>0.441</td>
<td>0.201</td>
<td>0.031</td>
<td>30.12</td>
<td>56.63</td>
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<td>17.86</td>
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<td>-0.141</td>
<td>11.40</td>
<td>0.025</td>
<td>-0.421</td>
<td>0.006</td>
<td>0.005</td>
<td>0.924</td>
<td>0.034</td>
<td>0.038</td>
<td>28.42</td>
<td>57.63</td>
</tr>
<tr>
<td>Ave</td>
<td>16.47</td>
<td>-0.01</td>
<td>0.02</td>
<td>9.59</td>
<td>0.02</td>
<td>-0.19</td>
<td>-0.03</td>
<td>0.01</td>
<td>0.47</td>
<td>0.03</td>
<td>0.03</td>
<td>34.90</td>
<td></td>
</tr>
</tbody>
</table>

Appendix B
APPENDIX C

INVESTIGATION OF
OBSERVED INITIAL RAPID
RATE OF URANIUM
DISSOLUTION
Investigation of initial rapid rate of uranium dissolution observed in a number dissolution tests

As mentioned previously in the body of this thesis (4.3.1.1) very rapid dissolution was observed in the first few minutes of almost all dissolution tests which were independent of the reaction conditions used. This observation was noted prior to the EPMA results and any knowledge of the presence of soluble uranium and hence it was decided to investigate possible reason(s) for this very rapid dissolution in the initial few minutes.

The first possible reason investigated involved the possibility that the prepared coffinite contained surface uranium in the highly soluble oxidised form (6+ oxidation state). This hypothesis was investigated by pre-treating the coffinite under reducing conditions (pre-treatment conditions) to try and reduce any surface oxidised uranium that may have been present. The results are presented in Figure C.3 where it was found that both the initial quantity of uranium dissolved and the extent of uranium dissolved after 90 minutes were lower than that in the test using coffinite that had not been pre-treated under reducing conditions.

![Figure C.3: Synthetic coffinite pre-treated under reducing conditions dissolution experimental conditions](image-url)
As the presence of oxidised uranium at the surface of coffinite was considered most likely not responsible for the majority of the uranium dissolved in the first few minutes it was decided to further investigate this phenomenon by determining if it still occurred in the absence of ferric ions. This was based on the assumption that the synthetic coffinite samples used may have contained surface U(IV) species that were more readily oxidised / dissolved than U in the bulk of the sample (and hence if this was the case dissolution of such a species would not occur in the absence of Fe(III)). In the first experiment conducted in the absence of iron (experimental conditions can be found in Table C.1), results are presented in Figure C.4.

Table C.1: Dissolution conditions for standard, no iron and water only experiments

<table>
<thead>
<tr>
<th></th>
<th>Standard</th>
<th>No Iron</th>
<th>Water Only</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Uranium Concentration</td>
<td>100 ppm</td>
<td>100 ppm</td>
<td>100 ppm</td>
</tr>
<tr>
<td></td>
<td>(4.20x10^-4 M)</td>
<td>(4.20x10^-4 M)</td>
<td>(4.20x10^-4 M)</td>
</tr>
<tr>
<td>Temperature</td>
<td>50 °C</td>
<td>50 °C</td>
<td>50 °C</td>
</tr>
<tr>
<td>Initial Sulfuric Acid Concentration</td>
<td>15 g/L (0.15M)</td>
<td>15 g/L (0.15M)</td>
<td>0 g/L</td>
</tr>
<tr>
<td>Initial Ferric (Fe^{3+}) Concentration</td>
<td>1 g/L</td>
<td>0 g/L</td>
<td>0 g/L</td>
</tr>
<tr>
<td>Initial Ferric : Ferrous Ratio</td>
<td>25:75</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Initial Uranium : Ferric Molar Ratio</td>
<td>1:4.2</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Figure C.4: Dissolution of uranium from synthetic coffinite; comparison of standard conditions and no iron experiments
The ORP of the experiment shown in Figure C.4 was 410 mV and though there was no iron in this system a similar amount of uranium was found to dissolve within the first few minutes and over the entire 90 minute period when compared to previous experiments containing iron (ORP values 390-570 mV). This result suggested that the mechanism which controlled the dissolution of uranium under the aforementioned conditions (ORP values < 570 mV) did not rely significantly on the presence of iron.

Based on the results observed that indicated iron did not have a significant influence on the rapid dissolution observed in the first few minutes of tests it was decided to remove another oxidising agent (though very mild), sulphuric acid. This test studied the dissolution of uranium from synthetic coffinite in water; results are given in Figure C.5.

![Graph showing uranium dissolution](image)

Figure C.5: Dissolution of uranium from synthetic coffinite; comparison of standard conditions, no iron and water only experiments

It was found that only 3 % of the uranium was dissolved within the first few minutes of the reaction, a significant drop from the 15 % (approximately) observed in all other experiments. Even in water, uranium continued to dissolve from the synthetic coffinite for the entire 90 minute period, though the extent of uranium dissolution at 90 minutes
was much lower than any other experiment. This result suggested that only approximately 3% of the initial uranium dissolution is as a result from surface uranium in a 6+ oxidation state.

One hypothesis, that during the dissolution studies the readily soluble U$^{6+}$ contained within the synthetic sample would readily dissolve and hence leave only uranium in the 4+ oxidation state. This was investigated by collecting the synthetic coffinite which remained after leaching. This residue was then washed, dried and subjected to another dissolution experiment under conditions similar to what is used in the uranium minerals processing industry (Figure C.6). A second re-leaching experiment was also conducted as drying the alterations in the sample may occur during the washing and drying process. For this experiment synthetic coffinite was leached (under conditions similar to those used in the uranium minerals processing industry) and after 10 mins the experiment was stopped solid residue collected washed and added in slurry form to a new leach solution(Figure C.7).

When the coffinite was wash dried and re-leached the initial dissolution decreased to about half and then subsequent dissolution proceeded at a similar rate to that previously seen in the original leach. When the coffinite was not allowed to dry there was a significant decrease in the initial amount of uranium dissolved and though the uranium continued to dissolve it did so very slowly.

This finding suggests that as the Coffinite is exposed to the atmosphere the surface Coffinite may be able to be oxidised allowing the oxidised Coffinite to leach readily, as well as during the drying process the Coffinite may experience site defects, such as cracking increasing the surface area and allowing the sulfuric acid a chance to attack the portions of Coffinite that were inaccessible during the first leaching process.
Figure C.6: Uranium dissolution of synthetic coffinite under standard conditions previously leached and dried

Figure C.7: Uranium dissolution of synthetic coffinite under standard conditions slurry was re-leached after the initial 10 min
Anybody who has been seriously engaged in scientific work of any kind realizes that over the entrance to the gates of the temple of science are written the words:—“Ye must have faith”

Max Plank
~ THE END ~