Radionuclide interactions with materials relevant to a geological disposal facility

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Metadata Record: [https://dspace.lboro.ac.uk/2134/25231](https://dspace.lboro.ac.uk/2134/25231)

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Radionuclide Interactions with Materials Relevant to a Geological Disposal Facility

By

Oliver Preedy

A doctoral thesis submitted in partial fulfilment of the requirements for the award of

Doctor of Philosophy

Loughborough University

September 2016

Research Supervisor: Dr George Weaver & Professor Peter Warwick
Abstract

Materials representative of those found in a Geological Disposal Facility (GDF) for the long-term storage of nuclear waste have been investigated for their ability to retard the movement of ionic species found in nuclear waste. Fe$_{1-x}$O, Fe$_2$O$_3$, Fe$_3$O$_4$ (from steel corrosion) and sandstone (bedrock) used as physical barriers in the GDF have been treated using solutions of pH 7-13 which are representative of the leachate expected from concrete encapsulation of waste in contact with groundwater. A mimic of portlandite cement, Ca(OH)$_2$ was also prepared carbonate-free via a saccharate method for use in these leachate experiments. Materials have been characterised using a mixture of techniques such as Powder X-ray Diffraction (PXRD) and Infra-red Spectroscopy which focus on the bulk, short range techniques such as Extended X-ray Absorption Fine Structure (EXAFS), Scanning Electron Microscopy(SEM) and Nuclear Magnetic Resonance(NMR) and physical measurements such as diffusion experiments and fluorescence spectroscopy.

Characterisation of the bulk materials before and after treatment using PXRD and SEM indicates that high purity iron oxides are affected differently by the solutions of varying pH. While not detectable by bulk techniques, SEM analysis evidence of the surface of the materials showed that Fe$_{1-x}$O was deleteriously affected by solutions with pH > 7 more than the more oxidised materials. Initially needle-like crystals formed on the surface of Fe$_{1-x}$O that are characteristic of goethite which at long aging times up to 168 h, showed transformation to crystal morphologies characteristic of Fe$_2$O$_3$. As the alkalinity increased, the transformation of Fe$_{1-x}$O to Fe$_2$O$_3$ slowed. Dissolution of the iron surfaces in the solutions of pH 7-13 were determined by measuring the concentration of dissolved iron using ICPMS. While Fe$_{1-x}$O and Fe$_3$O$_4$ followed first order kinetics, the dissolution kinetics for Fe$_2$O$_3$ appeared more complex. As the alkalinity increased, the rate constant for dissolution decreased in all cases indicating that higher pH is better for containment due to the formation of a passivated surface layer evidenced by SEM.

The sorption of uranium to the iron oxide surfaces was investigated as a function of pH (7-13). In all cases, there was evidence of uranium sorption. The greatest sorption was evidenced when Ca(OH)$_2$ was present which is most likely due to the precipitation of the known phase, calcium uranate. In the absence of calcium hydroxide, the sorption of uranium to the iron oxide surfaces decreased as the pH increased, reflecting the increase in formation of the anionic uranium species. In the presence of carbonate, the sorption of uranium onto the surfaces also decreases reflecting the formation of the soluble uranyl carbonate species. NMR spectroscopy of uranyl species in solution indicates that the chemical shift is strongly affected by pH shifting from 163 ppm to 175 ppm as the pH changes from 7 to 13 and allowing the uranium speciation to be used as a pH probe. A much
smaller shift in respect of temperature of less than 0.5 ppm was observed in the temperature range studied between 25 and 50°C. The quality of fluorescence spectra has been shown to be strongly affected by complexing species present in solution, the best spectra achieved with non-complexing species such as perchlorate.

Migration experiments of the radionuclides uranium, thorium and technetium has been investigated by placing sandstone cores in alkaline solution and analysing both the water itself and the core to examine retention and transport. The results determined that the technetium diffused readily through the sandstone matrix. The uranium and thorium did not achieve breakthrough. This was attributed to the low solubility’s and the formation of stable precipitates.
Acknowledgements

So many people have provided me with help and support over the duration of my studies; I hope that I am able to acknowledge all of them here.

Firstly, I would like to thank the EPSRC/NDA and Dr Nick Evans for providing me with the opportunities that have arisen from this PhD project and allowing me to work as part of the AMASS consortium. Professor Mary Ryan and Dr Jiahui Qi have been a great source of encouragement, ideas and interesting discussions.

I would like thank Dr Sandie Dann, Professor Peter Warwick and Dr George Weaver. Without their support this thesis would not be in the state it is today. A special mention must go to Sandie and Peter for their outstanding support and advice without their involvement this would have not been possible.

I have been fortunate enough to become familiar with a wide range of both analytical and materials techniques, but that would not have been possible if it had not been for the patience and expertise of the people running them I would like to thank them now. Mrs Pauline King for her help running the CHN samples as well as always managing to fix the diffractometer when it decided not to like me. For all the help with the NMR analysis and letting me put uranium in the Magnet Dr Mark Edgar. For his help with the SEM images Dr Keith Yendall. Finally, Professor Fred Moss lemans for all the insults while at the beamline and your help teaching me how to understand the wiggles in k-space. Stuart Pinkney your help with all the IT issues has been a great support, and always nice to catch up and see your friendly face.

I have had a lot of support from the Chemistry department throughout both my undergraduate and PhD studies. I would like to thank Dr Dave Worrall for all his help surrounding the submission of this thesis as well as his knowledge surrounding the photochemistry in this thesis. For her support throughout this PhD; and useful discussions thanks go to Dr Caroline Kirk. For all the interesting discussions and for making me look at things in a different light Professor Stephen Fletcher.

Although I think that it is fair to say that the radiochemistry group has had some challenges over the course of my PhD, it has been a great group to work in. I never though it possible for so much information and support have been given. I would like to thank both past and present members, Dr Sneh Jain, Dr Ricky Hallam, Dr Stephen Pendleton, Dr Larry Anjolaiya, Mr Matt Issacs, Mr Joel Garner,
Miss Joanna Kulaszewska, Mr Dimitris Kosmidis and Mr Matt Druce I think a special mention has to go to Dr John Hinchliff for helping me get into the lab, Ms Joan Sutherland for looking out for all of us (and her medical help), Ms Julie Turner for her help and advice which has enabled me to do the most scary chemistry I have ever done and finally Dr James Holt for his constant nagging to ensure I submitted this thesis.

Throughout my 10 years at Loughborough I have made some fantastic friends who have made the experience and even the science enjoyable. I would like to thank Dr Iain Kirpatrick, Mr Craig Buck, Mr John Hodgson, Miss Sally O’Hara, Dr Jagdeep Sagu and a special mention to Dr Alex Hill for always reminding me when it was lunchtime.

This almost goes without saying but my family have been an inexhaustible source of help and support. I will never be able to thank my Mum and Dad enough had it not been for their encouragement and guidance I would not have been able to peruse the opportunities I have. To my brothers, Nicholas, Richard and Simon thank you for always being there. I can’t really write this and not acknowledge my grandparents who are sadly not here to see the completion of this thesis, but who helped shape me into the person I am today and I am eternally in their debt. I would also like to thank my extended family Susan, Steve, Claire, Lauren, Carol, Dave and of course Dylan and Lola for their encouragement and believing in me.

Finally, to Hayley, who has been here for me throughout and has had to put up with the PhD ups and downs, while completing her PhD. It has made for some challenging times with lots of late nights and early starts and I could not have done it without you.
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Chapter One: Introduction
1.0 Introduction

1.1 Background

The safe management and disposal of nuclear waste is one of the largest technological challenges of the twenty-first century. This is a challenge that all countries that rely on nuclear power for energy generation face, however this thesis focuses specifically on the waste legacy of the United Kingdom (UK).

The birth of the UK’s nuclear industry was in the late 1940s, shortly after the use of atomic weapons by the United States of America in 1945. This led to a rapid development of the UK’s nuclear weapons program which was launched in 1947 at the Sellafield site. In addition to weapons development, this was also a period of great scientific and engineering accomplishments in the area and saw the UK’s first nuclear reactor, Windscale Pile Number One, becoming operational in 1950.

It was soon realised that the nuclear fission reactor technology used to generate plutonium for weapons, could also be used for domestic purposes in the form of energy generation. This was to become a reality in 1956, when the UK’s first nuclear power plant Calder Hall was opened. Due to the emphasis on establishing a nuclear industry, and the speed at which the UK went from having no nuclear industry to having both a weapons program and a power station for civilian use, it could be argued that the long-term consequences were not fully considered at the outset. As a result, this has left the UK with a large nuclear waste legacy.

Currently over 14% of the electricity generated globally arises from nuclear power stations, that figure rises to about a third in the European Union. With the diminishing resources of fossil fuels coupled with the stigmatism surrounding fracking and geothermal energy, a need for low carbon energy production is being sought after.

Despite the bad publicity that the nuclear industry has attracted over the past 70 years, i.e. the Windscale fire, Chernobyl and most recently the Fukushima disaster of 2011, energy companies have still been pursuing the commissioning of new nuclear power stations. For nuclear power to be a viable option, the waste needs to be considered during the planning stages and the large existing nuclear waste inventory that has been generated though previous social, military and medical activity must be addressed.
1.2 UK nuclear waste problem

1.2.1 Waste classification and volume

Material that has no further use, and is contaminated by, or incorporates, radioactivity above certain levels defined in UK legislation, is known as radioactive waste. Radioactive wastes range from those that contain high concentrations of radioactivity to general industrial and medical wastes that are only lightly contaminated with radioactivity.

In the UK, radioactive wastes are classified in terms of the nature and quantity of radioactivity they contain and their heat-generating capacity, as High Level Wastes, Intermediate Level Wastes or Low Level Wastes.

1.2.1.1 High Level Wastes (HLW)

Waste in which the temperature may rise significantly as a result of their radioactivity is defined as High Level Waste (HLW). The fact that the waste will change temperature during aging and storage must therefore be taken into account in the design of storage and/or disposal facilities.

1.2.1.2 Intermediate Level Wastes (ILW)

Waste exceeding the upper boundaries for LLW, but which do not require heating to be taken into account in the design of storage or disposal facilities is Intermediate Level Waste (ILW).

1.2.1.3 Low Level Wastes (LLW)

Waste having a radioactive content not exceeding 4 GBq per tonne of α activity, or 12 GBq per tonne of β/γ activity is termed Low Level Waste (LLW). The majority of the waste by volume falls into the low level waste category, where it comprises 93.9 % of the waste inventory, as shown in Figure 1.1 below.
Although by volume a large percentage of the waste is low level waste, the majority of the activity arises from the high level waste, resulting in a relatively small volume where the majority of the activity is concentrated as shown in Table 1.1.

**Table 1.1 Activity and Predicted Activity as a Function of Waste Type and Year.**

<table>
<thead>
<tr>
<th>Waste Type</th>
<th>Total activity / TBq</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>01/04/2010</td>
</tr>
<tr>
<td>HLW</td>
<td>80,000,000</td>
</tr>
<tr>
<td>ILW</td>
<td>3,900,000</td>
</tr>
<tr>
<td>LLW</td>
<td>40</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>83,900,040</td>
</tr>
</tbody>
</table>

This waste is comprised of a whole range of different materials including organic and inorganic materials and metals as shown in Table 1.2.
Table 1.2 Summary of Waste Legacy by Material Type and Waste Level

<table>
<thead>
<tr>
<th>Materials</th>
<th>Mass / Tonnes</th>
<th>HLW</th>
<th>ILW</th>
<th>LLW</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Metals</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stainless steel</td>
<td>1</td>
<td>40,000</td>
<td>120,000</td>
<td></td>
</tr>
<tr>
<td>Other steel</td>
<td>1</td>
<td>49,000</td>
<td>430,000</td>
<td></td>
</tr>
<tr>
<td>Magnox</td>
<td>0</td>
<td>7,300</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>Aluminium</td>
<td>0</td>
<td>1,200</td>
<td>17,000</td>
<td></td>
</tr>
<tr>
<td>Zircaloy</td>
<td>0</td>
<td>1,400</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Other metals</td>
<td>21</td>
<td>3,100</td>
<td>210,000</td>
<td></td>
</tr>
<tr>
<td><strong>Organics</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cellulosic</td>
<td>0</td>
<td>2,000</td>
<td>100,000</td>
<td></td>
</tr>
<tr>
<td>Plastics</td>
<td>0</td>
<td>6,900</td>
<td>48,000</td>
<td></td>
</tr>
<tr>
<td>Rubbers</td>
<td>0</td>
<td>1,700</td>
<td>13,000</td>
<td></td>
</tr>
<tr>
<td>Other organics</td>
<td>0</td>
<td>1,200</td>
<td>35,000</td>
<td></td>
</tr>
<tr>
<td><strong>Inorganics</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Concrete, cement &amp; sand</td>
<td>0</td>
<td>59,000</td>
<td>2,700,000</td>
<td></td>
</tr>
<tr>
<td>Graphite</td>
<td>0</td>
<td>81,000</td>
<td>15,000</td>
<td></td>
</tr>
<tr>
<td>Glass &amp; ceramics</td>
<td>2,000</td>
<td>610</td>
<td>9,700</td>
<td></td>
</tr>
<tr>
<td>Sludge’s, flocs &amp; liquids</td>
<td>0</td>
<td>31,000</td>
<td>11,000</td>
<td></td>
</tr>
<tr>
<td>Other inorganics</td>
<td>640</td>
<td>2,000</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td><strong>Soil &amp; rubble</strong></td>
<td>0</td>
<td>1,500</td>
<td>790,000</td>
<td></td>
</tr>
<tr>
<td><strong>Unspecified</strong></td>
<td>0</td>
<td>16,000</td>
<td>160,000</td>
<td></td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td>2,663</td>
<td>304,910</td>
<td>4,658,885</td>
<td></td>
</tr>
</tbody>
</table>

1.2.2 Radionuclides of interest

The importance of a radionuclide in nuclear wastes is assessed by considering:

(i) the quantity of the radionuclide present in the waste;
(ii) how solubility and sorption effect transport of the radionuclide and
(iii) the physical and chemical forms of the radionuclide in the waste forms.

Of interest are uranium, thorium and technetium and some aspects of their properties and aqueous chemistry are reported below.
1.2.2.1 Uranium and its aqueous chemistry

Uranium, as it occurs in nature, consists of a mixture of the three isotopes $^{238}\text{U}$, $^{235}\text{U}$, and $^{234}\text{U}$. The relative abundances of $^{238}\text{U}$, $^{235}\text{U}$, and $^{234}\text{U}$ have been measured by various investigators and best value for the $^{238}\text{U}$, $^{235}\text{U}$, and $^{234}\text{U}$ relative abundances are listed in Table 1.3.

Table 1.3: Relative Abundance of Natural Uranium Isotopes$^{10}$.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Mole fraction</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}\text{U}$</td>
<td>99.27%</td>
<td>0.0650%</td>
</tr>
<tr>
<td>$^{235}\text{U}$</td>
<td>0.72%</td>
<td>0.0004%</td>
</tr>
<tr>
<td>$^{234}\text{U}$</td>
<td>0.01%</td>
<td>0.0005%</td>
</tr>
</tbody>
</table>

The variation of isotopic ratio of the uranium isotopes in nature may vary by as much as 0.1%. By utilizing mass spectrometric and nuclear disintegration data, the (chemical) atomic weight of natural uranium is calculated to be (238.0289 +/- 0.0001). The isotope $^{238}\text{U}$ is the parent of the natural $4n + 2$ radioactive series, and the isotope $^{235}\text{U}$ is the parent of the natural $4n + 3$ radioactive series. $^{234}\text{U}$ arises from $^{238}\text{U}$ by radioactive decay and these two isotopes are thus linked to each other, but $^{235}\text{U}$ appears to be of independent origin. The isotope $^{235}\text{U}$, which exists in nature to the extent of 0.72%, was identified by Dempster using mass spectrometry in 1935$^{11}$. This isotope is of special importance since it undergoes fission with slow neutrons. Complete fission of $^{235}\text{U}$ gives rise to an energy equivalent of about 2107 kWh kg$^{-1}$ which corresponds to approximately 200 MeV per fission. Advantage can be taken of the fissionability of $^{235}\text{U}$, not only to generate large amounts of power, but also to synthesise other important actinide elements. Uranium, with its natural isotopic composition, can be used in nuclear reactors to generate neutrons.

The chain reaction is sustained by the excess neutrons produced by the fission of $^{235}\text{U}$, while neutrons in excess of those required to propagate the chain reaction can be captured by the other natural isotope to produce plutonium$^{12}$.

\[
^{238}\text{U} + n \rightarrow ^{239}\text{U}
\]

Equation 1.1

\[
^{239}\text{U} \rightarrow ^{239}\text{Np} \rightarrow ^{239}\text{Pu}
\]

Equation 1.2
Aqueous uranium chemistry is dominated by hexavalent species due to the low solubility of uranium (IV) species. Uranium (V) species are transient unless stabilised by coordination and hence are rarely observed in solution.

The only known uranium (V) ion is the linear dioxouranium ion UO$_2^+$ and uranium (IV) species are only stable under anoxic conditions. The other known uranium oxidation state is trivalent, however this is extremely uncommon and is not generally observed, unless under electrochemical control in synthetic conditions$^{13-16}$.

The rate of redox transformations between the oxidation states is rapid when there is no change in chemical environment between the oxidised and reduced forms. This means the reactions shown in equation 1.3 and 1.4 are facile, but the reaction in 1.5 is slow.

$$UO_2^{2+} + e^- \rightleftharpoons UO_2^+$$  \hspace{1cm} \text{Equation 1.3}$$

$$U^{4+} + e^- \rightleftharpoons U^{3+}$$  \hspace{1cm} \text{Equation 1.4}$$

$$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + H_2O$$  \hspace{1cm} \text{Equation 1.5}$$

The un-complexed uranium (VI) ion normally exists in solution as uranyl ion species, UO$_2^{2+}$. By changing the pH, a range of uranium hydroxyl species can also be formed and these are shown in the Porbaix diagram (Figure 1.2) together with reduced species of uranium$^{17}$.

![Figure 1.2 Porbaix diagram of Uranium Speciation as Function of pH$^{18}$]
The hydrolysis of uranium is well documented in the literature\textsuperscript{19}, the general mechanism for the hydration of the uranyl ion is shown in Equation 1.6.

\[
x UO_2^{2+} + yH_2O = (UO_2)_{x}(OH)_{y}^{2x-y} + yH^+
\]

\textbf{Equation 1.6}

At lower pH values and uranium concentration the formation of monomeric uranium hydroxide species is typical, as shown in the Figure 1.2. This shows that as the pH increases more hydroxyl species are added and anionic species are favoured. If the uranium concentration is sufficiently increased then polymeric uranium species are formed, the structures of which are shown in Figure 1.3\textsuperscript{19}.

\textbf{Figure 1.3: Polymeric Uranium Species formed at Low pH.}

The solubility of uranium species decreases as the solution becomes more basic, however there has been some uncertainty surrounding the solubility and speciation under hyperalkaline conditions.
A possible explanation for this is colloid formation; a study has confirmed the presence of stable uranium colloidal nanoparticles of the order or 20 nm which form at relatively low concentrations of uranium of $2.5 \times 10^{-5}$ mol dm$^{-3}$.\textsuperscript{9, 20} The UO$_2$$^{2+}$ ion has been shown to readily complex with organic and inorganic ligands\textsuperscript{21–26}. However only the uranium carbonate system will be discussed in this thesis as it is most relevant to the work associated with movement of species in a nuclear waste repository.

Under neutral conditions it has been shown that the dominant uranium carbonate species is the trimeric [UO$_2$(CO$_3$)$_3$]$^3-$ ion, however as the alkalinity is increased other anionic species have been shown to be present for instance the [(UO$_2$)$_3$(CO$_3$)$_6$]$^{16-}$ ion. The complexation with carbonate at high pH has been shown to result in increased solubility relative to the uranium hydroxyl species\textsuperscript{15, 19, 22, 27–35}.

1.2.2.2 Thorium and its aqueous chemistry

Thorium is an element of interest as it can be used in order to produce energy similar to uranium, and is also a daughter product in the uranium decay series as is shown in figure 1.4. Currently the UK has approximately 60 tonnes of uranium designated as waste and that number is expected to increase\textsuperscript{9, 36}.

The aqueous chemistry of thorium is dominated by the tetravalent thorium (Th$^{4+}$) cation\textsuperscript{12}. As the pH increases, the solubility decreases and insoluble thorium dioxide dominates as shown in Figure 1.5. The hydrolysis behaviour of the aqueous thorium IV ion has to be investigated by potentiometric titration between pH values of 2.5 and 4, as above pH 5 thorium is largely insoluble\textsuperscript{37}. It has been shown that at thorium concentrations between $10^{-2}$ and $10^{-4}$ mol dm$^{-3}$, the aqueous chemistry is dominated by the polymeric thorium hydroxyl species. However the polymeric species that have been suggested which are similar to the uranium species discussed previously are not supported by spectroscopic measurements\textsuperscript{17, 19, 38–44}. Studies under similar conditions have shown the formation of colloidal thorium species resulting in a range of stability constants for thorium in the literature\textsuperscript{42}. 
Thorium is known to complex with both inorganic and organic ligands with some of the most strongly complexing anions being the halides with the stability constants decreasing from F\(^-\) to Br\(^-\). Thorium has also been shown to complex with oxygen donor ligands such as nitrate; however this will not be discussed in this thesis.
1.2.2.3 Technetium and its Aqueous Chemistry

As discussed previously, when the uranium fission reaction is initialised by bombardment with thermal neutrons, fission products are produced. One of the highest yielding fission products is $^{99}\text{Tc}$ with a yield of approximately 6%\(^{45}\). Aqueous technetium chemistry is dominated by the pertechnetate anion (TcO$_4^-$) where the technetium is in the VII oxidation state\(^ {19}\). It is possible to reduce the technetium to Tc(IV) however these results in the precipitation of TcO$_2$, Tc$_4$O$_7$ or Tc$_3$O$_4$ as illustrated below in Figure 1.6.
The solubility of the pertechnetate ion has been shown to be high over all pH ranges, and work to limit its mobility has been discussed extensively using iron oxides as a natural reductant as well as microbial induced reduction\textsuperscript{46–49}. However it has also been shown that the reduced technetium species increase in solubility as the pH increases which is of relevance when evaluating the mobility of technetium under repository conditions. It has been suggested that the solubility of TcO\textsubscript{2} increases by approximately one order of magnitude for ever pH unit past values of 8.5.

1.3 Proposed Methods of Disposal

There have been a number of methods proposed for dealing with the UK’s nuclear waste legacy and these are summarised in a report by Nirex\textsuperscript{50}. Various options suggested include:

- Long term storage above ground;
- Near surface disposal;
- Deep geological disposal;
- Deep borehole disposal;
- Rock melting;
- Direct injection;
Disposal at sea;
Sub-seabed disposal;
Disposal in subduction zones;
Disposal in ice sheets;
Disposal in outer space.

Although all of these methods have been discussed at some point, only a few have been seriously considered.

1.3.1 Deep Geological Disposal

Since 2008, the preferred option, in the UK, for waste management is geological disposal in a deep (300–1,000 m) underground repository. The repository is known as a Geological Disposal Facility (GDF) and is a concept that was developed by Nirex and is now being managed by Radioactive Waste Management Ltd.

Radionuclides may escape from the repository by dissolution into the surrounding groundwater or, by the production of gases. The equation for linear transport of a radionuclide in an aqueous system is described in the following transport equation.

\[
\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} - \frac{B_d C^*}{\theta \cdot \partial t}
\]

Equation 1.7

Where
- $\delta C/\delta t =$ change in concentration over time, mol s$^{-1}$
- $D_L =$ diffusion coefficient of longitudinal hydrodynamic dispersion, m$^2$ s$^{-1}$
- $C =$ solute concentration of liquid phase, mol dm$^{-3}$
- $v_x =$ average linear groundwater velocity, m s$^{-1}$
- $t =$ time, s
- $B_d =$ bulk density of aquifer, kg dm$^{-3}$
- $\theta =$ porosity of saturated aquifer, %
- $C^* =$ amount of solute sorbed per unit weight of solid, mol kg$^{-1}$
- $x =$ distance at which to compute $C$, m
is a partial differential equation, referred to as the “advective-dispersive solute-transport equation”.

This equation describes quantitatively the three major processes of (1) advection, which describes the transport of solutes by the bulk motion of flowing ground water$^{55,56}$, and (2) hydrodynamic dispersion, which describes the spread of solutes along and transverse to the direction of flow resulting from both mechanical mixing and molecular diffusion$^{57}$. These are the two physical processes that govern the movement of ground-water solutes. In addition to these two processes, a third process, that of chemical reactions, including those mediated by microorganisms or caused by interaction with aquifer material or other solutes, may also affect the concentration of a solute in the groundwater.

In the equation above, the retardation process known as the chemical sink, referred to generally as sorption, is one of the key areas within performance assessment where chemists can contribute to solute transport calculations. The effect of e.g complexing ligands (or colloids) on contaminant transport is to reduce the effectiveness of this chemical sink.

Apart from the choice of the geological environment, dispersion and advection are beyond the control of the GDF designers. However, the third term in the equation – the sorption term can be manipulated and depends on radionuclide speciation, solubility and sorption.

To contain the radioactivity as much as is possible, the proposed safety strategy of the GDF relies on a multi-barrier concept to radionuclide dissolution and transport. A barrier may be in the near-field i.e. in the engineered part of the repository or in the far-field i.e. the surrounding geological environment of the GDF. These barriers include

- **Physical containment** - achieved by immobilisation and packaging of wastes in steel containers;
- **Geological isolation** - achieved by emplacement of the waste packages in vaults excavated deep underground within a suitable geological environment;
- **Chemical conditioning** - achieved by backfilling the vaults with a cement-based material (the Nirex Reference Vault Backfill – NRVB) at a time determined by future generations;
- **Geological containment** - achieved by emplacement in a suitable geological environment, after final closure of the repository at a time determined by future generations.$^{50,58}$

The concept is detailed in six Generic Documents that set out the system specification, the designs for the transport system and the repository, and three supporting generic safety assessments$^{35,59–64}$. The concept for multi barrier containment is shown diagrammatically in Figure 1.7.
The safety requirement is for the GDF to remain stable until the levels of radioactivity have decayed to those of background radiation (ca 1,000,000 years).

The current concept is generic and hypothetical due to the siting process requiring the host community to volunteer for the facility. Although several communities have expressed an interest, a site has not yet been selected.

1.3.1.1 The Near Field

On closure of the GDF, groundwater will ingress into the repository and the porewater in the near field will be of high pH, due to cement dissolution, and low Eh (i.e. reducing) due to canister corrosion and possible microbial action. High pH and low Eh porewater conditions will act as a chemical barrier to the movement of key radionuclides such as actinides, which are generally least soluble in their lowest oxidation states, e.g. U(IV). In addition, the presence of iron corrosion products and cement surfaces will also reduce the transport of some radionuclides by presenting surfaces which will interact with radionuclides thereby removing them from the porewater. The mobility of radionuclides transferred from the near-field into the far-field will be further retarded by sorption onto the geological material hosting the repository. Clearly, the repository host rock will be chosen to have a combination of low water flow and physical stability.
As stated previously, the chemical conditions of the porewater in the near field of the GDF will be highly alkaline, due to cement dissolution, and reducing conditions, due to the rusting of iron. Alkaline conditions develop because of the presence of the cementitious backfill material which will buffer the initial pH of the pore water to approximately 13.4. As time passes, the pH of the pore water will fall as the highly soluble potassium and sodium hydroxides are dissolved by ground water flow. Eventually as the potassium and sodium hydroxides are removed by the groundwater, the chemistry of the repository will be dominated by calcium hydroxide and calcium silicate hydrate which are the less soluble phases in the cement. These largely insoluble phases will be washed out much slower than the potassium and sodium hydroxides, until the repository conditions finally return to that of typical groundwater timescales. A theoretical trajectory of a repository pH as a function of time is shown in Figure 1.9.
1.3.1.2 Corrosion of Stainless Steel Canisters

Over their lifetime, the waste packages will be exposed to a range of different chemical environments, with varying concentrations of chloride, pO₂ and degrees of moisture content and humidity\textsuperscript{69–75}. Over time, the stainless steel packages will corrode and eventually fail, although the rate of corrosion will depend on the local environment.

Iron containing phases will be therefore be present throughout the engineered GDF environment primarily from the corrosion of the steel canisters in the near field, as well as iron minerals in the far field. Corrosion of iron will lead to the formation of iron-oxides and oxyhydroxides, and as the GDF becomes de-oxygenated iron (II) oxide phases will be stabilised. Fe(II)-phases have already been demonstrated to be significant in controlling radionuclide solubility\textsuperscript{33,67,76–94}.

The corrosion processes can be separated into two main areas; general corrosion and local corrosion. General corrosion refers to the uniform dissolution of metal species over time. Localised corrosion or pitting corrosion is a localized form of corrosion by which cavities or "holes" are produced in a material. Pitting is considered to be more dangerous than uniform corrosion damage because it is...
more difficult to detect, predict and design against. Corrosion products often cover the pits. A small, narrow pit with minimal overall metal loss can lead to the failure of an entire engineering system. Pitting corrosion, which, for example, is almost a common denominator of all types of localized corrosion attack, may assume different shapes. 

Pitting corrosion can produce pits with their mouth open (uncovered) or covered with a semi-permeable membrane of corrosion products. Pits can be either hemispherical or cup-shaped. Pitting can be initiated by three mechanisms, firstly localized chemical or mechanical damage to the protective oxide film; water chemistry factors which can cause breakdown of a passive film are acidity, low dissolved oxygen concentrations and high concentrations of chloride. Pitting can also be initiated by localized damage to, or poor application of, a protective coating or the presence of non-uniformities in the metal structure of the component. Apart from the localized loss of thickness, corrosion pits can also be harmful by acting as stress risers. Fatigue and stress corrosion cracking may initiate at the base of corrosion pits.

As currently in the UK there is no selected site for a GDF, a wide range of geology is being considered. The geology of the surrounding environment will affect the chemistry and the corrosion products formed. The effect of these different geological phases has been studied widely and the results are discussed in the literature\textsuperscript{66} a schematic is shown below in figure 1.10.

Iron minerals are ubiquitous in the environment and will play a key role in the far field. The minerals present will almost certainly be iron oxides and oxyhydroxides such as magnetite, haematite and goethite. On the event of the containers and other barriers failing, this may result in some
radionuclides being mobilised and these iron phases may play an important role in retarding migration

The corrosion of stainless steel has been widely studied and the corrosion products formed are well understood for many aqueous conditions\textsuperscript{66,71}. It has been shown that where oxic aqueous corrosion is the main failure mechanism, the expected corrosion products are magnetite [Fe\textsubscript{3}O\textsubscript{4}], haematite [\textalpha-Fe\textsubscript{2}O\textsubscript{3}], goethite [\textalpha-FeO\textsubscript{OH}] and lepidocrocite [\textgamma-FeO\textsubscript{OH}] and wüstite [Fe\textsubscript{1-x}O].

Under repository conditions, the canisters will be exposed to hyper-alkaline conditions associated with cementitious materials (grout, engineering cement, backfill) where the pH is likely to be > 12. The steel is protected from corrosion by a thin passive film, which over time may lose its protective properties by the presence of ions which enhance the rate of corrosion such as chloride. However, over time the GDF will also become deoxygenated. Due to the strongly reducing geochemical conditions associated with the GDF environment minerals are likely to be part of the long term stable solid phase assemblage.

\textbf{1.3.1.3 The Far Field}

The Far Field is the zone beyond the alkaline disturbed zone which is within the theoretical range of potential impact of migration from the repository; however, the normal environmental conditions are expected to be sufficient to prevent significant radionuclide migration.

\textbf{1.3.1.4 Host rock}

The host rock is of importance as it is the last barrier before any radioactivity reaches the geosphere. Extensive research has been conducted over the past three decades to determine whether the geology in the UK that is suitable to host a geological disposal facility. Due to currently no site being chosen for such a repository the generic safety case for a geological disposal facility has considered three broad (generic) host-rock types.

These rock types are:

\textbf{Higher strength rocks}: These rocks, for example granite, themselves generally have a very low permeability to water flow so that any water flow that does occur is in open cracks, or fractures, that have formed in the rock mass. This type of rock is planned to be used in Finland and Sweden at the sites chosen for their geological disposal facilities for spent nuclear fuel.

\textbf{Lower strength sedimentary rocks}: These rocks are generally physically uniform and any flow of water occurs through the overall rock mass. The Swiss Opalinus Clay geological
disposal concept is designed for this type of rock.

**Evaporites:** These rocks, for example rock salt, may contain water that has been trapped within them ever since they were formed, but they are isolated from water flow that could dissolve them. In the USA this type of rock is used for the Waste Isolation Pilot Plant, where waste has been disposed of for more than a decade, in New Mexico; Germany has also developed a concept for this type of rock.

1.4 Aims and objectives

The work that comprises this thesis arises from two research projects.

**Atomic and Macro-Scale Studies of Surface Processes: Towards a Mechanistic Understanding of Surface Reactivity and Radionuclide Binding Mechanisms (EP/I036389/1)***

And:

**Biogeochemical Gradients and Radionuclide transport (NE/H007768/1)**

Both projects are concerned with providing underpinning science to be used in a geological disposal facility safety case. The bulk of the work arose from the AMASS project, the main aim of which was to develop a mechanistic understanding of radionuclide interactions with iron oxide surfaces, under conditions likely to exist in a geological disposal facility (GDF).

This project was designed to link experimental and multi-scale modelling studies on selected key surfaces which are designed to address fundamental questions on:

(i) How the surfaces of candidate materials in an engineered barrier system (EBS) behave in a typical disposal environment and,

(ii) The effect of any alteration processes on radionuclide/surface interactions.
Figure 1.11 Schematic Diagram of the Components of the AMASS project

Due to the complexity of the chemistry associated with a GDF, this project utilises model systems to simplify the problem, and allow an experimental approach to be established that is able to be transferred to more complex systems. Some of the processes outlined in the schematic are shown in figure 1.11, where surface interactions such as surface adsorption or incorporation into the mineral phases are not easily differentiated by some analysis techniques.

The need for a better understanding of the processes whereby radionuclides are retained by the barriers in a geological disposal facility was highlighted in 1996 in the assessors report denying planning permission for a rock characterisation facility. This PhD thesis is largely concerned with macroscale experiments and solution chemistry of the uranium/iron oxide systems in the presence of solutions representative of cementitious pore fluids.

1.4.1 Material selection

To allow the mechanistic approaches of the effect on material ageing in the presence of cementitious fluids to be elucidated it was decided to use model systems representative of corrosion products that might be formed in the environment associated with a geological disposal facility.

1.4.1.2 Iron oxides

As previously discussed, key phases of interest include those containing iron which will originate from the stainless steel containers used to encapsulate the waste matrix. It is expected that the iron
canisters will corrode over time ensuring that the aqueous chemistry is reducing. Therefore, a range of simple iron oxides that are common corrosion products were selected for this study.

1.4.1.2.1 Fe$_{1-x}$O

The work arising from the AMASS project was funded by the EPSRC and the NDA and the case for support is given in section 7.1. Due to the aqueous chemistry being reducing, it is expected that iron (II) species will be stabilised, one of the phases expected to be formed is wüstite (Fe$_{1-x}$O)$^{66}$. FeO was also chosen in this study as part of the collaborator work involved a modelling component and as FeO crystallises with the simple sodium chloride structure (space group Fm-3m) shown below in figure 1.12, this should simplify the modelling approach.

![Crystal structure of FeO](image)

*Figure 1.12: Crystal structure of FeO; larger gold spheres represent the iron(II) ions and the smaller gold spheres the oxide anions*
1.4.1.2.2 Fe$_2$O$_3$

Initially the corrosion products formed through the corrosion of the stainless steel canisters will be iron (III) species, the most common is haematite $\alpha$-Fe$_2$O$_3$. The structure is more complicated than that of the FeO as it crystallises with a trigonal structure in the space group R-3c shown below in figure 1.13.

![Crystal structure of Fe$_2$O$_3$](image)

Figure 1.13: Crystal structure of Fe$_2$O$_3$; the larger gold spheres represent the iron(III) ions and the smaller red spheres the oxide anions
1.4.1.2.3 \( \text{Fe}_3\text{O}_4 \)

The other common iron oxide that may be formed upon the corrosion of stainless steel is magnetite \( \text{Fe}_3\text{O}_4 \). The mineral crystallises with the spinel structure \((\text{AB}_2\text{O}_4)\) and belongs to the Fd-3m space group. The A and B sites are made up of iron (II) and iron (III) species shown below in figure 1.14 where the iron (III) sites are shown in purple and the iron (II) in gold.

![Figure 1.14: Crystal structure of \( \text{Fe}_3\text{O}_4 \); the larger gold and purple spheres represent the iron(II) and iron(III) ions respectively and the smaller red spheres the oxide anions](image-url)
1.4.1.3 Calcium hydroxide

As one of the primary physical barriers is cement, a cementitious analogue was needed. The bulk of cement phases is dominated by the calcium silicate hydrate gel phase, however this is a phase that is able to readily change its composition and is challenging to synthesise repeatedly, therefore is not a good candidate to be used as a model system. It was therefore decided that calcium hydroxide would be investigated. It also will buffer the pH of a geological disposal facility due to the low solubility. Calcium hydroxide forms in a trigonal unit cell and is part of the P3m space group, the structure of which is shown below in figure 1.15.

![Figure 1.15: Crystal structure of Ca(OH)$_2$; large blue spheres represent the calcium cations and the red spheres the oxygen ions. The smaller white spheres are the hydrogen ions.](image)

1.4.1.4 Sandstone

Unlike the simple materials described as the other model compounds, sandstone is not a simple single phase material but a natural material comprised of several phases. Sandstone is comprised predominately of α-quartz which consists of corner sharing SiO$_4$ tetrahedra that form in space group P3$_2$1 and can be seen below in figure 1.16. However, there are also several other minor phases including iron oxides that give sandstone a red/brown colouration.
Figure 1.16: Crystal structure of SiO$_2$; larger blue spheres are silicon cations and the smaller red spheres the oxides anions.
Chapter Two: Experimental
2.0 Experimental

2.1 Analytical Techniques

The following sections describe analytical techniques used in this project. In summary, the techniques used are shown in the following table:

<table>
<thead>
<tr>
<th>Technique</th>
<th>Reason for use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid Scintillation Counting</td>
<td>Measurement of radioactivity</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Metal analysis ppb (w.v) level</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Metal analysis ppm (w.v) level</td>
</tr>
<tr>
<td>Powder X-ray Diffraction</td>
<td>Phase Identification</td>
</tr>
<tr>
<td>Fluorescence spectroscopy</td>
<td>Uranium speciation</td>
</tr>
<tr>
<td>SEM</td>
<td>Surface morphology</td>
</tr>
<tr>
<td>Infra-red spectroscopy</td>
<td>Determination of functional groups</td>
</tr>
<tr>
<td>Ion chromatography</td>
<td>Quantification of aqueous carbonate</td>
</tr>
<tr>
<td>X-Ray absorption spectroscopy</td>
<td>Phase identification</td>
</tr>
<tr>
<td>Optical spectroscopy</td>
<td>Determination of functional groups/speciation</td>
</tr>
<tr>
<td>Nuclear magnetic resonance spectroscopy</td>
<td>Determination of functional groups/speciation</td>
</tr>
</tbody>
</table>

2.1.1 Liquid scintillation counting

Liquid scintillation counting (LSC) is an analytical technique which allows the quantitative measurement of an alpha, beta or gamma emitting radionuclides. LSC is more commonly used for the measurement of alpha and beta emitters and was developed in the 1950s to increase the counting efficiency the low energy beta emitters $^{14}\text{C}$ and $^3\text{H}$. A schematic diagram of the instrumentation is shown in Figure 2.1.

![Schematic Diagram of a Scintillation Counter Measurement](image)
Figure 2.2 provides a graphic illustration of how the radiation emitted from radioactive materials interacts with the mixture of solvent and solute and leads to a count being recorded by the scintillation counter.

![Figure 2.2 Schematic Illustration of Scintillation Process](image)

Although LSC may be used for measuring alpha, beta or gamma radiation, for simplicity, only beta interactions will be described here. LSC relies on the production of pulses of light emitted from a liquid scintillation cocktail when a beta particle loses its energy in the cocktail. A suitable solution of beta radiation is added to the cocktail, a beta particle mainly interacts with the solvent molecules producing electronically excited solvent molecules. Rather than returning to their ground states, the excited solvent molecules pass on their excitation energy to the scintillant molecules which return to their ground states by emitting photons of light.

Two major principles govern the mechanism of LSC:

i) No electrical pulses/unit time $\alpha$ No light flashes/unit time $\alpha$ No $\beta$ particles emitted/unit time

**This gives radioactivity measurement**

ii) Pulse Height (nA or mV) $\alpha$ Intensity of light flash (No of photons) $\alpha$ $\beta$ particle energy

**This gives a pulse height spectrum**
Photomultipliers acquire light through a glass or quartz window that covers a photosensitive surface, called a photocathode. Light flashes hit the photocathode of the photo multiplier tube (PMT) which then releases electrons that are multiplied by electrodes in the photomultiplier tube which are known as metal channel dynodes. At the end of the dynode chain is an anode or collection electrode. Over a very large range, the current flowing from the anode to ground is directly proportional to the photoelectron flux generated by the photocathode. A LSC normally has two PMTs. The amplitude of the PMT pulse depends on the location of the event with respect to the PMT. An event producing 100 photons will be represented by a larger pulse if the event is closer to the PMT than if the event is more remote. The signal from each PMT is fed into a circuit which produces an output only if the 2 signals occur together, that is within the resolving time of the circuit, approximately 20 nanoseconds (coincidence circuit). By summing the amplitude of the pulses from each PMT, an output is obtained which is proportional to the total intensity of the scintillation. This analogue pulse rises to its maximum amplitude and falls to zero. The amplitude of the electrical pulse is converted into a digital value and the digital value, which represents the beta particle energy, passes into the analyser where it is compared to digital values for each of the LSC’s channels. Each channel is the address of a memory slot in a multi-channel analyser which consists of many storage slots or channels concerting the energy range from 0-2000 keV.

The number of pulses in each channel is displayed. In this manner, the sample is analysed and the spectrum can be plotted to provide information about the energy of the radiation or the amount of radioactive material dissolved in the cocktail. A schematic diagram of a photomultiplier tube is shown in Figure 2.3

![Figure 2.3: Schematic Diagram of a Photomultiplier Tube](image)

The spectral response, quantum efficiency, sensitivity, and dark current of a photomultiplier tube are determined by the composition of the photocathode. The best photocathodes capable of responding to visible light are less than 30 percent quantum efficient, meaning that 70 percent of
the photons impacting on the photocathode do not produce a photoelectron and are therefore not detected. Photocathode thickness is an important variable that must be monitored to ensure the proper response from absorbed photons. If the photocathode is too thick, more photons will be absorbed, but fewer electrons will be emitted from the back surface, but if it is too thin, too many photons will pass through without being absorbed. The photomultiplier tube used in this thesis is a side-on design, which uses an opaque and relatively thick photocathode. Photoelectrons are ejected from the front face of the photocathode and angled toward the first dynode. Electrons emitted by the photocathode are accelerated toward the dynode chain, which may contain up to 14 elements. Focusing electrodes are usually present to ensure that photoelectrons emitted near the edges of the photocathode will be likely to land on the first dynode. Upon impacting the first dynode, a photoelectron will invoke the release of an additional electron that is accelerated towards the next dynode, and so on. The surface composition and geometry of the dynodes determines their ability to serve as electron multipliers. Because gain varies with the voltage across the dynodes and the total number of dynodes, electron gains of 10 million are possible if 12-14 dynode stages are employed. Photomultipliers produce a signal even in the absence of light due to dark current arising from thermal emissions of electrons from the photocathode, leakage current between dynodes, as well as stray high-energy radiation. Electronic noise also contributes to the dark current and is often included in the dark-current value.

2.1.2 Inductively coupled plasma – mass spectrometry / optical emission spectrometry (ICP-MS / ICP OES)

Both ICP-MS and ICP-OES are destructive spectroscopic methods used to determine the concentration of species in solution. Both techniques use inductively coupled plasma to fully ionise the sample. The main difference between the two methods is detection; ICP-MS uses mass spectrometry as a detection mechanism whereas ICP-OES uses the characteristic optical emission resulting from the ionisation of the species in question. Typically, ICP-MS is more sensitive than ICP-OES making it more suitable for trace metal analysis.98

2.1.2.1 Inductively coupled plasma

The plasma is an extremely efficient ionisation source allowing molecules to be broken down to ions. The plasma is generated by introducing free electrons into the plasma gas usually argon. The
electrons are generated by a spark, which are then accelerated by an electric field to the ionisation potential of the gas. This initiates an avalanche breakdown allowing the formation of steady state plasma. A schematic of a typical ICP torch is shown in Figure 2.4.

The generated plasma is the ionisation source, capable of ionising most molecules to ions due to the extreme heat generated by the plasma. A schematic of the characteristic shape of the plasma, with the approximate temperatures associated with each zone is shown in Figure 2.5.

Once lit, the plasma has an annular shape which allows efficient entry of gases and liquids, and operates at a temperature between six and seven thousand Kelvin.
2.1.2.2 ICP-MS

Inductively coupled plasma mass spectrometry (ICP-MS) is a type of mass spectrometry which can detect metals and several non-metals at concentrations of the order of parts per trillion. This is achieved by passing the sample through the inductively coupled plasma, resulting in the sample being ionized. The ions are then focussed by the ion lenses where the ions are separated by mass using a mass filter. Depending on the instrument, the ions will then be passed through a quadrupole, some devices have two quadrupole devices where one is used as a collision reaction cell. The selected ion is then transferred to the detector and the information reported to the work station controlling the instrument, a schematic diagram of the experimental technique is shown in Figure 2.6.

![Figure 2.6 Schematic Diagrams of the ICP-MS](image)

2.1.2.2.1 The Quadrupole

A quadrupole is a collection of four rods which have a potential voltage applied across them, which results in each rod being an electrode. The electrodes are oriented such that the electrodes of the same charge are opposed as depicted in Figure 2.7.
Each pair of rods is connected and both have a direct voltage along with a superimposed alternating current as well. The voltages on each pair of rods can be expressed as:

\[ +V_{DC} + V_{AC} \cos(\omega t) \]

Equation 2.1

\[ -V_{DC} - V_{AC} \cos(\omega t) \]

Equation 2.2

The minus sign on the alternating current applied to the negatively charge rods denotes that the two pairs of rods are 180° degrees out of phase with the positively charge rods. By varying the voltages on the rods it is possible to use the quadrupole as a mass filter, whereby only ions of a specific mass to charge ratio usually denoted m/z are stable through the centre of the 4 rods and are hence detected by the detector shown in figure 2.8.
interfering species: argon from the plasma, component gases of air as well as contamination from glassware and the cones.

The variety of applications exceeds that of inductively coupled plasma atomic emission spectroscopy and includes isotopic speciation\textsuperscript{100,101}. Due to possible applications in nuclear technologies, ICP-MS hardware is a subject for special exporting regulations.

The advantages of ICP-MS are the ability to perform multi elemental analysis in one run, the large linear dynamic range and low limits of detection allow a wide variety of sample types to be analysed. The disadvantages are that high matrix samples lower the sensitivity, as well as lengthy sample preparation is required.

\textbf{2.1.2.3 ICP-OES}

Inductively coupled plasma optical emission spectrometry (ICP-OES), and is an analytical technique used for the detection of trace metals. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited ions and ions that emit electromagnetic radiation at wavelengths characteristic of an element. The intensity of this emission is indicative of the concentration of the element within the sample. The ICP-OES is composed of two parts: the ICP and the optical spectrometer\textsuperscript{102}.

An aqueous sample is introduced into the nebulizer where it is aerosolised and introduced directly into the plasma. The sample immediately collides with the electrons and charged ions in the plasma and is broken down into charged ions. The various molecules break up into their respective ions which then become ionised, giving off radiation at the characteristic wavelengths of the elements involved. The emitted light is separated into its different wavelengths. The light intensity is measured with a photomultiplier tube (or tubes) physically positioned to view the specific wavelengths for each element line involved. In more modern units, the separated wavelengths fall upon an array of semiconductor photodetectors such as charge coupled devices (CCDs). In units using these detector arrays, the intensities of all wavelengths within the system's range can be measured simultaneously, allowing the instrument to analyse for every element to which the unit is sensitive all at once. Thus, samples can be analysed very quickly.

The intensity of each line is then compared to previously measured intensities of known concentrations of the elements, and their concentrations are then computed by interpolation along the calibration lines. In addition, special software generally corrects for interferences caused by the presence of different elements within a given sample matrix\textsuperscript{103,104}. A schematic of a typical ICP-OES system is shown in Figure 2.9.
2.1.3 Powder X-Ray diffraction

Powder X-ray diffraction is a solid state characterisation technique which was used in this thesis to identify the different phases present in the test materials. Reflections are observed from powdered samples containing a large number of small crystallites typically between $10^{-4}-10^{-7}$ m in size. Each powder diffraction pattern exists as a sequence of reflections which can be matched against the ICDD database to determine the presence of known phases within the sample. Crystal system, space group and elements all affect a diffraction pattern in such a way that each pure phase has a unique pattern which can be matched like a fingerprint.

When a sample is irradiated with X-rays the incident X-rays interact with the electrons present in the material which result in scattering of the X-rays as they interact with the electron clouds of the atoms present in the sample\textsuperscript{105}.

2.1.3.1 Generation of X-Rays

X-rays are generated by striking a metal target for example copper or cobalt, with a stream of electrons. The electron bombardment ejects core electrons from the metal (providing the beam is higher in energy than that of the core electrons). This process creates an electron vacancy, which is filled by a higher energy electron, and the excess energy is emitted as an X-ray with a precise energy.
\[ \Delta E = h\nu \]

Equation 2.3

Where:

\( \Delta E \) = Energy difference

\( h \) = Planck’s constant

\( \nu \) = frequency of the emitted radiation

2.1.3.2 The X-ray tube

A schematic of a typical X-ray tube is shown below in figure 2.10. The beam of electrons is created by heating a tungsten filament in a vacuum. The resulting electrons are then accelerated towards the metal target by applying a potential difference usually between 20,000-50,000 V. This results in the emission of X-rays of characteristic energy. The X-rays exit the tube through a beryllium window. Beryllium is chosen for the window material as due to its low molecular weight the material is transparent to X-rays.

![Figure 2.10 Schematic Diagram of an X-ray Tube](image)

-44-
2.1.3.3 Scattering of X-rays by Crystalline Solids

When an X-ray interacts with a crystalline material, it is subsequently scattered by a set of planes which are defined by the Miller Indices h,k,l as shown in figure 2.11.

![Interaction of X-rays with a lattice planes separated by d-spacing, dhkl.](image)

In order for usable data to be produced from the X-ray measurement, the scattered X-ray beam from the points X and Z must produce diffracted beams which are in phase. This is only achieved if the extra distance travelled from W to X and X to Y is an integral number of wavelengths. The difference is usually referred to as the path difference and is dependent on the lattice spacing and angle of the incident X-ray as described below in equation 2.4.

\[
\text{Path difference} = WX + XY = 2d_{hkl} \sin \theta = n\lambda
\]

**Equation 2.4**

Where:

- \( n \) = An integer (typically taken as 1)
- \( \lambda \) = X-Ray wavelength
- \( \theta \) = diffraction angle

The above equation is known as the Bragg equation and is generally written in the form

\[
n\lambda = 2dsin\theta
\]

**Equation 2.5**

In any crystalline material, there are an infinite number of planes with different Miller indices where each set of planes has a particular separation. For any given set of planes, there will be a diffraction maximum at a particular value of \( \theta \). The relationship between the diffraction angle and the lattice parameter can be defined by combining the Bragg and lattice parameter equations, an example for a cubic system is shown below:
Given the lattice parameter equation

\[
\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}
\]

Equation 2.6

And the Bragg equation

\[n\lambda = 2dsin\theta\]

Equation 2.7

By setting \(n\) equal to 1 the equation can be rewritten as

\[
\frac{1}{d} = \frac{2sin\theta}{\lambda}
\]

Equation 2.8

Which means that \(\frac{1}{d^2}\) is equal to

\[
\frac{1}{d^2} = \frac{4sin^2\theta}{\lambda^2}
\]

Equation 2.9

Equating the \(\frac{1}{d^2}\) for the value in the lattice parameter equation gives

\[
\frac{h^2 + k^2 + l^2}{a^2} = \frac{4sin^2\theta}{\lambda^2}
\]

Equation 2.10

Rearranging to make \(sin^2\theta\) the subject results in

\[
sin^2\theta = \frac{\lambda^2 (h^2 + k^2 + l^2)}{4a^2}
\]

Equation 2.11

2.1.3.4 Powder diffraction measurements

Due to the large number of crystallites in a powdered sample, all possible orientations are present in the sample at once and as the incident radiation contacts the sample it is diffracted in all possible directions simultaneously. Each lattice spacing gives rise to a cone of diffraction, where each cone is a set of closely spaced dots, and where each dot is representative of diffraction from a single crystallite. Due to the large number of crystallites, a continuous cone is formed. The position of these cones is then measured using a diffractometer.
A schematic of a powder XRD diffractometer is shown in figure 2.13. The figure shows two types of Bragg-Brentano geometry; reflectance and transmission.

Since powder diffraction data are affected by several factors including crystal system, nearly all crystalline solids have a characteristic and unique diffraction pattern. This arises due to each crystalline solid having characteristic reflections and intensities allowing phase identification to be made by comparing diffraction patterns with a library. This technique allows characterisation of materials with multiple phases, and is commonly used for clay mineral identification, quality control and a wide range of other applications.
Figure 2.13 Schematic Diagram of a Powder Diffractometer upper reflectance, lower transmission
2.4 Infra-red spectroscopy

Infra-red radiation is the term used to describe electromagnetic radiation with frequencies and hence energies lower than those associated with visible light. When a beam of infra-red radiation is incident upon a collection of certain molecules, absorption of discrete frequencies by the molecule occurs, which in turn correspond to well defined energies. It is the absorption at discrete energies that makes infra-red spectroscopy a useful analytical technique, allowing molecular functional groups to be determined as well as in certain cases allowing structural information such as bond lengths to be determined\(^{106}\).

2.4.1 Infra-red spectrometer

In a typical infra-red spectrometer, the radiation is emitted from a heated filament as a continuous range of frequencies which correspond to discrete wavelengths. This radiation is then passed through the sample, as the radiation is passed through the sample a percentage of it will be absorbed at discrete frequencies corresponding to specific functional groups associated with the molecule. The resulting radiation is then passed through a system of slits and mirrors resulting in a collimated beam. The collimated beam is then dispersed by either a prism or a grating, allowing the radiation to be separated and then detected. The detector is typically a thermocouple and is capable of monitoring the radiation emitted at different wavelengths allowing a spectrum to be collected. A

![Diagram of an infra-red spectrometer](image-url)

schematic of a typical infra-red spectrometer is shown below in figure 2.14.
To explain the nature of the infra-red absorption spectrum, this section will discuss using a model for diatomic molecules. Although the same process is true for polyatomic molecules, they have more degrees of freedom making the illustration more difficult. The vibration of a diatomic molecule can be approximated to two masses attached by a spring and can be treated as a simple harmonic oscillator obeying Hooke’s law.

\[ F = kX \]

**Equation 2.12**

Where:

- \( F \) = Force
- \( k \) = force constant of the spring
- \( X \) = spring displacement from relaxed position

Hooke’s law shown above states that the force exerted by a spring is directly proportional to the spring constant multiplied by the displacement of the spring from its resting position. It can be shown that the resultant simple harmonic motion of the spring can be shown that:

\[ \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \]

**Equation 2.13**

Where:

- \( \nu \) = Frequency of oscillation
- \( K \) = force constant of the spring
- \( \mu \) = Reduced mass (defined by equation (4))

Reduced mass defined by the equation:

\[ \mu = \frac{m_1 m_2}{(m_1 + m_2)} \]

**Equation 2.14**

Where:

- \( m_1 \) = Mass of atom 1
- \( m_2 \) = Mass of atom 2
The above equation can hence be used to describe chemical bonds in terms of fundamental frequency, where $K$ becomes the force constant of the bond. The stretching frequency can be shown pictorially, for a diatomic molecule the bond oscillates linearly when the bond is compressed the forces are opposed to the compression of the bond, the opposite is true when the bond is stretched. This is shown diagrammatically in figure 2.15.\textsuperscript{107,108}

![Schematic diagram of stretching vibrations in compressed and stretched positions](image)

**Figure 2.15: Schematic diagram of stretching vibrations in compressed and stretched positions**

### 2.5 Ion Chromatography

Chromatography uses the principle that an analyte in solution interact with solid phases at varying rates allowing them to be readily separated. A basic schematic of the chromatography process is shown in Figure 2.16.

Ion-exchange chromatography retains analyte molecules on the column based on columbic (ionic) interactions. The stationary phase surface displays ionic functional groups (R-X) that interact with analyte ions of opposite charge. This type of chromatography is further subdivided into cation
exchange chromatography and anion exchange chromatography. The ionic compound consisting of
the cationic species and the anionic species can be retained by the stationary phase.
Anion exchange chromatography retains anions using positively charged functional groups of the
column; the inverse is true for cation exchange chromatography.

Figure 2.16 Schematic Diagram of Chromatography Experiment

A sample is introduced into a sample loop of known volume. A buffered aqueous solution known as
the mobile phase carries the sample from the loop onto a column that contains some form of
stationary phase material. This is typically a resin or gel matrix consisting of agarose or cellulose
beads with covalently bonded charged functional groups. The target analytes (anions or cations) are
retained on the stationary phase but can be eluted by increasing the concentration of a similarly
charged species that will displace the analyte ions from the stationary phase. For example, in cation
exchange chromatography, the positively charged analyte could be displaced by the addition of positively charged sodium ions. The analytes of interest must then be detected by some means, typically by conductivity or UV/Visible light absorbance. A schematic of a typical ion chromatography setup is shown in Figure 2.17.\textsuperscript{109,110}
2.6 X-ray absorption spectroscopy

XAS spectroscopy utilises X-rays to gain information about the subject being analysed. X-rays are quanta of light in the energy range 500 eV to 500 keV. At these energy ranges light is absorbed by all matter through the photoelectric effect.

Figure 2.18 XAS Spectroscopy Schematic

This involves a core electron absorbing the energy from a suitable X-ray and being ejected from the atom, emitting a photo electron, the energy of which is governed by the energy of the incident x-ray and the electron binding energy.

\[ KE_{Photo e^{-}} = E_{X-ray} - E_{BE} \]

Equation 2.15

If the energy of the incident X-ray is lower than that of the electron binding energy, the X-ray will be absorbed. After the core electron is ejected, electrons from higher energy shells rearrange filling the vacancy, the difference in energy is compensated by emission of an X-ray of precise energy.

XAS is primarily concerned with the linear absorption coefficient commonly given the symbol \( \mu \), the absorption coefficient is a measure of the likelihood that x-rays will be absorbed according to the Beer-Lambert law.

\[ I = I_{0}e^{-\mu t} \]

Equation 2.16

Where:

\( I \) = Intensity of transmitted radiation
For the majority of X-ray energies the absorption coefficient is a smooth function of energy, the value is dependent on the density of the sample, the atomic mass, atomic number and X-ray energy. The relationship can be described by the equation below:

\[ \mu = \frac{\rho Z^4}{AE^3} \]

Equation 2.17

Where:
\[ \mu = \text{Linear adsorption coefficient} \]
\[ \rho = \text{density} \]
\[ Z = \text{atomic number} \]
\[ A = \text{Atomic mass} \]
\[ E = \text{energy of incident x-ray} \]

The strong dependence on the atomic number and X-ray energy is a fundamental property of X-rays and as a result leads to elemental selectivity.

When the incident X-ray has energy equal to that of the binding energy of a core level electron, there is a sharp rise in adsorption. This is the adsorption edge and corresponds to core electron being ejected from the atom. EXAFS analysis is concerned with the intensity of the adsorption coefficient as a function of energy both near (XANES) and at energies past the edge (EXAFS), the resulting plot of \( \mu \) against \( E \) is an XAS spectrum\textsuperscript{111–113}.

The resulting spectrum can then be analysed to determine the oxidation state and the co-ordination of the sample by solving the equation below.
\[
\chi(k) = \frac{N S O^2 F_k}{2 k R} \sin(2kR + \delta k) e^{-2\sigma^2 k^2}
\]

Equation 2.17

Where:

- \( N \) = co-ordination number
- \( SO^2 \) = amplitude of oscillation
- \( F_k \) = amplitude of scatter
- \( R \) = scattered distance
- \( \delta k \) = phase shift
- \( \sigma^2 \) = Debye waller factor

In practice the equation is solved by fitting a model to the experimental spectra. The modal is produced using fitting software. The fitting process usually begins with using known crystallographic information file (CIF) representative of the analysed sample. This allows atom positions and hence bond lengths and co-ordination numbers to be estimated. This information can then be used to run a FEFF calculation which generates a list of scattering paths associated with the structure from the CIF file. A selection of the generated scattering paths which accurately describe the system can then be used to generate the model. The model can further be refined by estimating the difference in energy shift between the model and the data and the amplitude of the oscillations.

2.9 Optical spectroscopy

2.9.1 UV-Vis

Absorbance spectroscopy is an optical technique that characterises compounds by the colour of light that they absorbed and at what wavelengths are absorbed. The technique measures the light that is transmitted and converts it to absorbance using the Beer-Lambert Law.

\[
A = \varepsilon b c = -\log T = \log \frac{I_0}{I}
\]

Equation 2.18

Where \( A \) is the absorbance, \( \varepsilon \) is the molar extinction coefficient, \( b \) is the path length (1 cm in the case of most uv-vis spectrometers), \( c \) is the concentration of the absorbing material, \( T \) is the transmittance and \( I_0 \) and \( I \) are the intensities of incident and transmitted light.
Due to the logarithmic relationship between absorbance and transmittance, there are limitations to the concentrations that can be measured accurately. The absorbance value should not be allowed to greatly exceed 1 absorbance unit. Beyond this range deviations from linearity occur.\textsuperscript{114}

2.9.2 Fluorescence spectroscopy

Photochemistry involves processes in which light and matter interact. In several cases the light is used as an excitation source to promote low energy systems to more energetic ones. Fluorescence is a photochemical phenomenon that can be utilised as a detection technique.

\textit{2.9.2.1 Fluorescence}

An electron in the outer shell may be promoted to a higher electronic energy level. When in this higher electronic level, the system is unstable and the promoted electron must return to the ground state, and a photon may be released. The ejection of photons from this transition is named fluorescence if the initial and final states have the same spin multiplicity.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fluorescence_diagram.png}
\caption{A diagram to demonstrate fluorescence, highlighting the absorption (1) and emission (2).}
\end{figure}
Fluorescence is a photo-initiated process; an electron is promoted by the absorption of light. The emitted photon is normally of lower energy than the incident photon, as some energy is lost to the system as heat (vibrational energy). This causes the colour of the emitted radiation to shift towards red. This shift is from ultraviolet into the blue end of the visible spectrum (ca. 400 nm), through the visible colours and from the red end of the visible spectrum (ca. 700 nm), and into the infrared. This phenomenon is known as Stokes fluorescence. For the opposite to occur (a higher energy photon being released than the absorbed photon), a second source of energy is required (e.g. thermal energy). This is known as anti-Stokes fluorescence.\[^{115}\]

Stokes shift is depicted in Figure 2.20

![Stokes' shift diagram](image)

**Figure 1.20:** A diagram to demonstrate the relationship between absorption and emission spectra, with relation to Stoke’s shift.

Planck’s equations characterise the relationship between the components that make up light (energy, \(E\); frequency, \(\nu\); and wavelength, \(\lambda\)) and describes their proportionality with respect to the speed of light in a vacuum \((c = 2.99792458 \times 10^8 \text{ ms}^{-1})\) and the Planck’s constant \((h = 6.6260755 \times 10^{-34} \text{ Js})\).

\[
E = h\nu = \frac{hc}{\lambda}
\]
This demonstrates the inverse proportionality between energy and wavelength, and highlights Stokes fluorescence is the energetically preferred transition. that

**Figure 2.21: A Depiction of the Electromagnetic Spectrum.**

Fluorescence is a very fast process. The time from absorption of the incident photon to ejection of the emitted photon (the fluorescence lifetime) is normally in the order of a few nanoseconds. Phosphorescence is a much longer process as it requires a spin forbidden intersystem-crossing transition (from singlet to triplet or vice versa) to occur before the photon may be ejected. This can take hours, but usually occurs in the order of seconds or less\(^\text{107}\).

Due to differences in the relative stabilities of excited states (post excitation but prior to de-excitation and photon ejection) fluorescent materials have fluorescence lifetime signatures. A more stable excited state will take longer to return to the ground state than a less stable state and will therefore have a longer fluorescence lifetime. Excited triplet states generally take a lot longer to return to the ground state due to the need for intersystem crossing to occur (phosphorescence). There are three main types of fluorescence lifetime spectroscopy: time-correlated single photon counting, phase-shift and stroboscopic techniques.

By using a pulsed source, such as a laser it is possible to use the previously mentioned techniques to determine the fluorescence lifetime of a material. Where the minimum detectable life-time is directly related to the perturbation period. As both the spectral and temporal measurements are orthogonal to each other they allow more information to be gained about the sample studied, and allow discrimination between samples with similar spectra. This in turn allows co-ordination and aqueous speciation to be determined.
2.10 Nuclear magnetic resonance spectroscopy (NMR)

NMR spectroscopy is based on the fact that atoms which contain an odd number of protons, an odd number of neutrons or both can be shown to have a magnetic moment. It is this magnetic property that NMR spectroscopy exploits. The hydrogen nucleus consisting of one proton, and hence has a magnetic moment. When an external magnetic field is applied the hydrogen nucleus can either align itself parallel or opposed to the direction of the magnetic field, shown pictorially in figure 2.22

![Figure 2.22 Magnetic Field Direction](image)

The two possible arrangements differ in energy; a discrete energy is required to change from one position to the other. These two orientations comprise the magnetic moment of the nucleus denoted by the symbol \( \mu \). This can be further broken down depending on the direction of the applied field \( +\mu \) (designated \( \alpha \)) or \( -\mu \) (designated \( \beta \)), depending on whether it is parallel or anti-parallel to the field. The energies of the two arrangements of the magnet are \( -\mu B_0 \) (aligned) and \( +\mu B_0 \) (opposed), where \( B_0 \) is the magnetic flux density of the applied field. The energy difference between the two arrangements can be shown to be \( 2\mu B_0 \), which is equal to the amount of energy required to invert the protons magnetic moment from the position of lower energy to the position of higher energy, shown in the equation below.

\[
\Delta E = h\nu = 2\mu B_0
\]

Equation 2.20

Where:

\( \Delta E \) = Change in energy

\( h \) = Planck constant

\( \nu \) = frequency

\( \mu \) = Magnetic moment
From the equation, it is important to realise that the energy gap between the two states is directly proportional to the applied field shown below.

This leads to a lack in sensitivity as the population of the excited state is directly proportional to the magnetic field applied, making the technique less sensitive than spectroscopic methods that rely on electronic or vibrational transitions\textsuperscript{116}.

2.10.1 Schematic of an NMR spectrometer

There are several different types of NMR instrumentation. This section will discuss pulsed NMR spectrometers which are used in this thesis. As previously discussed, since the population differences are small which results in low sensitivity, pulsed NMR spectrometers a schematic of which is given in figure 2.24
Pulsed NMR spectrometers work by supplying a range of different frequencies instantaneously to the sample which is located in a constant magnetic field. This is achieved by irradiating the sample with a short pulse of electromagnetic radiation, such that the applied frequencies are in the region expected to contain the resonances associated with the analyte.

2.11 Scanning electron microscopy

Scanning electron microscopy (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that are derived from electron-sample interactions reveal information about the sample including external morphology, chemical composition and crystalline structure. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques. SEM is capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions (using EDS), crystalline structure, and crystal orientations (using EBSD).
2.11.1 Fundamental Principles of Scanning Electron Microscopy (SEM)

Accelerated electrons in an SEM carry significant amounts of kinetic energy and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathodoluminescence—CL), and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination). X-ray generation is produced by inelastic collisions of the incident electrons with electrons in discrete orbitals (shells) of atoms in the sample. As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength (that is related to the difference in energy levels of electrons in different shells for a given element). Thus, characteristic X-rays are produced for each element in a material that is "excited" by the electron beam. SEM analysis is considered to be "non-destructive"; that is, X-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyse the same materials repeatedly.

2.11.2 Scanning Electron Microscopy (SEM) Instrumentation

Essential components of all SEMs include the following:

- Electron Source ("Gun")
- Electron Lenses
- Sample Stage
- Detectors for all signals of interest
- Display / Data output devices
- Infrastructure Requirements:
  - Power Supply
  - Vacuum System
  - Cooling system
  - Vibration-free floor
  - Room free of ambient magnetic and electric fields
SEMs always have at least one detector (usually a secondary electron detector), and most have additional detectors. The specific capabilities of a particular instrument are critically dependent on which detectors it accommodates.

There is arguably no other instrument with the breadth of applications in the study of solid materials that compares with the SEM. The SEM is critical in all fields that require characterization of solid materials. While this contribution is most concerned with geological applications, it is important to note that these applications are a very small subset of the scientific and industrial applications that exist for this instrumentation. Most SEM’s are comparatively easy to operate, with user-friendly "intuitive" interfaces. Many applications require minimal sample preparation. For many applications, data acquisition is rapid (less than 5 minutes/image for SEI, BSE, spot EDS analyses.) Modern SEMs generate data in digital formats, which are highly portable.

Samples must be solid and they must fit into the microscope chamber. Maximum size in horizontal dimensions is usually on the order of 10 cm, vertical dimensions are generally much more limited and rarely exceed 40 mm. For most instruments samples must be stable in a vacuum on the order of 10^-5 - 10^-6 torr. Samples likely to outgas at low pressures (rocks saturated with hydrocarbons, "wet" samples such as coal, organic materials or swelling clays, and samples likely to decrepitate at low pressure) are unsuitable for examination in conventional SEM’s. However, "low vacuum" and "environmental" SEMs also exist, and many of these types of samples can be successfully examined in these specialized instruments. EDS detectors on SEM’s cannot detect very light elements (H, He, and Li), and many instruments cannot detect elements with atomic numbers less than 11 (Na). Most SEMs use a solid state X-ray detector (EDS), and while these detectors are very fast and easy to utilize, they have relatively poor energy resolution and sensitivity to elements present in low abundances when compared to wavelength dispersive x-ray detectors (WDS) on most electron probe microanalyses (EPMA). An electrically conductive coating must be applied to electrically insulating samples for study in conventional SEM’s, unless the instrument is capable of operation in a low vacuum mode.
2.2 Experimental methodology

2.2.1 Solid Characterisation

2.2.1.1 Powder characterisation by X-Ray diffraction and Infra-Red spectroscopy

The iron compounds and the calcium hydroxide shown in Table 2.2 were used in sorption studies. Sandstone was used in diffusion experiments.
All solids were analysed by powder X-ray diffraction (PXRD) and Fourier Transform Infra-Red spectroscopy (FT-IR) to ensure that the reagents were of high purity and to identify any impurity phases that may be present.

<table>
<thead>
<tr>
<th>Material</th>
<th>Supplier</th>
<th>Purity / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO (wustite)</td>
<td>Sigma Aldrich</td>
<td>99.70</td>
</tr>
<tr>
<td>Fe₂O₃ (haematite)</td>
<td>Sigma Aldrich</td>
<td>99.99</td>
</tr>
<tr>
<td>Fe₃O₄ (magnetite)</td>
<td>Sigma Aldrich</td>
<td>99.99</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium hydroxide</td>
<td>Sigma Aldrich</td>
<td>97.00</td>
</tr>
<tr>
<td>Sandstone</td>
<td>Hollington quarry</td>
<td>N/A</td>
</tr>
</tbody>
</table>

For the PXRD analyses, samples were ground using an agate pestle and mortar and either placed into a flat plate Perspex sample holder for reflectance measurements or between two strips of magic tape ™ for transmission experiments. The Perspex holder was then transferred to a Bruker D8 advance diffractometer configured in reflectance geometry and operating with monochromated copper Kα₁. Powder diffraction data were collected between 5 and 80 degrees (2θ) using a 0.0147 2θ step. The collected diffraction patterns were analysed using the Bruker Eva software with the PDFMaintEX library version 9.0.133 to determine the phases present in each sample. For the transmission experiments samples were mounted on the Bruker D8 discover diffractometer operating with monochromated cobalt Kα₂ radiation and collected between 5 and 80 degrees using a 0.0147 step. Transmission experiments were required for all iron-containing samples due to the absorption/fluorescene issues caused by using copper radiation on the reflection instrument.
All FT-IR measurements were carried out using a Shimazdu 8400s FT-IR spectrometer, fitted with a golden gate attachment. The powdered sample was placed into the spectrometer and clamped.
between the diamond and ruby plates. Measurements were completed between 400-4000 cm\(^{-1}\) and averaged over 16 scans to identify any functional groups of interest.

2.2.1.2 Elemental analysis of disaggregated Hollington sandstone

The elemental composition of the sandstone used in the diffusion experiments was determined by complete acid digestion of the sample. Approximately 0.3 g of disaggregated sandstone was accurately measured and placed into a PTFE digestion autoclave. 10 cm\(^3\) of acid was then added to the insert (acid composition was 5 cm\(^3\) trace metal analysis HF 48 wt%, 3.25 cm\(^3\) trace metal analysis HCl and 1.75 cm\(^3\) trace metal analysis HNO\(_3\)). The acid solution was prepared to have a concentration of 1 ppm (w.v) \(^{115}\)In to account for any volatile losses during digestion. The samples were then placed into the sample carousel shown below, and transferred to a Mars microwave digestion system fitted with an acid vapour scrubber, a three stage process where the volatiles are drawn through a 1 mol dm\(^{-3}\) boric acid solution, followed by 1 mol dm\(^{-3}\) sodium hydroxide and finally deionised water. The loaded carousel was placed into the digestion system and ramped to 180 \(^\circ\)C over a period of 30 min, the samples were then held at temperature for a further 10 min.

![Figure 2.25 Disaggregation Digestion Apparatus](image)

The samples were allowed to cool and then removed from the microwave. The vessels were opened to reveal a small amount of undigested solid present at the bottom of the digester. The PTFE digestion vessel was rinsed with 20% trace metal analysis HNO\(_3\) (sigma Aldrich) and diluted to 5 cm\(^3\). The sample was then diluted 10 fold by removing 1 cm\(^3\) using a syringe fitted with a 0.22 \(\mu\)m PTFE syringe filter and diluting to a final volume of 10 cm\(^3\) to give a final acid concentration of 2%, the
samples were then analysed for uranium, thorium and indium, as well as full quantitative analysis by ICP-MS. Calibration standards ranging from 0.1-100 ppb were prepared by diluting the 1000 ppm (w.v) uranium, thorium and indium standards (sigma Aldrich) with 2% nitric acid. Full quantitative analysis was carried out using an Agilent 7700 ICP-MS analysing for $^{238}$U, $^{232}$Th and $^{115}$In. Instrumental drift was accounted for using a 1 ppb $^{209}$Bi standard, using the analyte:Bi ratio to accurately determine the analyte concentrations.

2.2.1.3 Calcium hydroxide synthesis

Calcium hydroxide was used in sorption experiments and to ensure that the calcium hydroxide used throughout the project was pure, calcium hydroxide was prepared as and when required. Two methods of preparation were investigated and these are described below.

i) Preparation under atmospheric conditions

$$CaCl_2(aq) + 2NaOH(aq) \rightarrow Ca(OH)_2(S)$$

Equation 2.21

A solution of calcium chloride with a concentration equal to 1 mol dm$^{-3}$ was prepared by dissolving 11.0014 g of calcium chloride (Sigma Aldrich) in 100 cm$^3$ of deionised water which had previously been boiled and simultaneously purged with nitrogen. A second solution of 2 mol dm$^{-3}$ sodium hydroxide (Fischer scientific) was prepared in a similar manner by dissolving 8.0015 g of sodium hydroxide in 100 cm$^3$ of deionised water. Both solutions were then sealed and stored under a nitrogen atmosphere in a Braun glove box. The sodium hydroxide was added to the calcium chloride solution dropwise resulting in colourless precipitate. The mixture was then removed from the nitrogen atmosphere and the precipitate separated by vacuum filtration. The precipitate was washed 2 x 100 cm$^3$ of cold deionised water to remove any sodium chloride impurities and finally washed with 100 cm$^3$ of cold ethanol. The washed precipitate was then allowed to air dry and analysed using powder X-ray diffraction. Diffraction patterns were collected for 2θ values between 5 and 80 using a Bruker D8 advance diffractometer in reflectance geometry and fitted with a Cu kα₁ X-ray tube. The collected diffraction patterns were analysed using the Bruker Eva software with the PDFMaintEX library version 9.0.133 to determine the phases present.

ii) Calcium hydroxide synthesis under nitrogen atmosphere

A solution of calcium chloride with a concentration equal to 1 mol dm$^{-3}$ was prepared by dissolving 11.01 g of calcium chloride (Sigma Aldrich) in 100 cm$^3$ of deionised water which had previously been boiled and simultaneously purged with nitrogen. A second solution of 2 mol dm$^{-3}$ sodium hydroxide (Fischer scientific) was prepared in a similar manner by dissolving 7.99 g of sodium hydroxide in 100
cm$^3$ of deionised water. The weighing and solution preparation was carried out under a positive pressure of nitrogen using a Braun glove box. The sodium hydroxide was added to the calcium chloride solution dropwise resulting in a colourless precipitate. The mixture was then removed from the nitrogen atmosphere and the precipitate separated by vacuum filtration. The precipitate was washed 2 x 100 cm$^3$ of cold deionised water to remove any sodium chloride impurities and finally washed with 100 cm$^3$ of cold ethanol. The washed precipitate was then allowed to air dry and analysed using powder X-ray diffraction. Powder diffraction data were collected on the product using the standard parameters given in section 2.2.1.3 and phase identification performed using the EVA programme and phase identification software by matching against the International Centre for Diffraction Data (ICDD) database. To determine the effect of age of NaOH on the preparation, a solution of calcium chloride with a concentration equal to 1 mol dm$^{-3}$ was prepared by dissolving 11.00 g of calcium chloride (Sigma Aldrich) in 100 cm$^3$ of deionised water which had previously been boiled and simultaneously purged with nitrogen. A second solution of 2 mol dm$^{-3}$ sodium hydroxide was prepared in a similar manner by dissolving 7.91 g of fresh sodium hydroxide (Fischer scientific) in 100 cm$^3$ of deionised water. The weighing and solution preparation was carried out under a positive pressure of nitrogen using a Braun glove box. The sodium hydroxide was added to the calcium chloride solution dropwise resulting in a colourless precipitate. The mixture was then removed from the nitrogen atmosphere and the precipitate separated by vacuum filtration. The precipitate was washed 2 x 100 cm$^3$ of cold deionised water to remove any sodium chloride impurities and finally washed with 100 cm$^3$ of cold ethanol. The washed precipitate was then allowed to air dry and analysed using powder X-ray diffraction. Powder diffraction data were collected on the product using the standard parameters given in section 2.2.1.3 and phase identification performed using the EVA programme and phase identification software by matching against the ICDD database.

iii) Calcium hydroxide synthesis using the saccharate method

A solution of calcium chloride with a concentration equal to 1 mol dm$^{-2}$ was prepared by dissolving 11.0014 g of calcium chloride (Sigma Aldrich) in 100 cm$^3$ 10% sucrose solution (Tate&Lyle) under ambient conditions. A second solution of 2 mol dm$^{-3}$ sodium hydroxide was prepared in a similar manner by dissolving 7.9994 g of sodium hydroxide (Fischer scientific) in 100 cm$^3$ of 10% sucrose solution. The sodium hydroxide was added to the calcium chloride solution dropwise resulting in colourless precipitate. The mixture was separated by vacuum filtration. The precipitate was washed 2 x 100 cm$^3$ of cold deionised water to remove any sodium chloride impurities and finally washed with 100 cm$^3$ of cold ethanol. The washed precipitate was then allowed to air dry and analysed using powder X-ray diffraction. Powder diffraction data were collected on the product using the standard
parameters given in section 2.2.1.1 and phase identification performed using the EVA programme and phase identification software by matching against the ICDD database.

2.2.1.4 Iron oxide ageing experiments

Experiments to determine how the bulk and surface properties of the iron oxide phases used in the sorption experiments may alter as a function of time were carried out. The three most common iron oxides, as shown in Table 2.3 and found in natural environments, were investigated using the batch method as described below.

<table>
<thead>
<tr>
<th>Material</th>
<th>Supplier</th>
<th>Purity / %</th>
</tr>
</thead>
<tbody>
<tr>
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<td>99.70</td>
</tr>
<tr>
<td>Fe₂O₃ (haematite)</td>
<td>Sigma Aldrich</td>
<td>99.99</td>
</tr>
<tr>
<td>Fe₃O₄ (magnetite)</td>
<td>Sigma Aldrich</td>
<td>99.99</td>
</tr>
</tbody>
</table>

Experiments were carried out in 50 cm³ plastic centrifuge tubes containing approximately 0.5 g of the solid material of interest followed by 50 cm³ of liquid with the solution pH ranging from 7 to 13.3. The pH was adjusted using either sodium hydroxide to achieve the pH values greater than 7, and 95% saturated calcium hydroxide was used to achieve the 12.3 pH value.

The contact time was varied between 8 and 720 h at room temperature after which the samples were centrifuged at 6000 rpm using a Hermle Z 200 A centrifuge. The supernatant liquid was then decanted and filtered through a 0.22 μm PTFE syringe filter to remove any colloidal iron that was present. The filtered solid samples were then transferred to a nitrogen atmosphere and allowed to dry.

Solid samples were analysed using FT-IR, PXRD and SEM. Functional groups were identified by IR spectroscopy using the parameters described in section 2.2.1.1 Powder diffraction data were collected on the product using the standard parameters given in section 2.2.1.1 and phase identification performed using the EVA programme and phase identification software by matching against the ICDD database. Scanning electron microscope images were collected using a Jeol 7100f,
samples were mounted onto aluminium stubs using carbon pads. The samples were then sputter coated with a gold palladium target (80:20) for a period of 90 seconds at 25 mA.

Solution analysis consisted of ICP-MS and pH measurements. Samples were prepared for ICP-MS by passing approximately 2 cm$^3$ of the supernatant liquid through a 0.22µm PTFE syringe filter with the addition of 2 cm$^3$ of 4% trace metal analysis nitric acid (sigma Aldrich) to give a final acid concentration of 2%. Calibration standards ranging from 0.1-100 ppb were prepared by diluting the 1000 ppm (w.v) iron standard (sigma Aldrich) with 2% nitric acid. Full quantitative analysis was carried out using an Agilent 7700 ICP-MS analysing for $^{56}$Fe. Instrumental drift was accounted for using a 1 ppb $^{115}$In standard, using the Fe:In ratio to accurately determine the iron concentration.

All pH measurements were completed using a Jenway pH meter fitted with an alkaline resistant probe to allow the alkaline solutions to be accurately determined. The pH meter was calibrated using 3 known pH buffers 7,10,13 (Sigma Aldrich).

### 2.2.1.5 Further Iron Oxide Ageing Experiments

Surface alteration experiments were conducted using a batch method: 0.5 g of isopropyl alcohol washed Fe$_{1-x}$O was placed into a 50 cm$^3$ Perspex centrifuge tube. All solutions were prepared with deionised water that had been boiled and degassed. Solutions were prepared to give pH values of 7 and 12 respectively, using NaOH to adjust the pH. Solutions were then divided into two batches and 0.1 mol dm$^{-3}$ anhydrous Na$_2$CO$_3$ added to half of the solutions. 50 cm$^3$ of the relevant solution was added to the tube experiments. Alteration was conducted under either atmospheric conditions or within a nitrogen atmosphere using a Braun glove box. Following 5 days incubation the supernatant was then separated by removing the majority with a syringe and passing the solution through a 0.22 μm filter to remove any particulate material.

**Table 2.4 Conditions for the Aging Experiments**

<table>
<thead>
<tr>
<th>Set of Conditions</th>
<th>$p$CO$_2$ / kPa</th>
<th>pH</th>
<th>Concentration of NaHCO$_3$ / mol dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.040</td>
<td>7</td>
<td>0.1</td>
</tr>
<tr>
<td>2</td>
<td>0.040</td>
<td>7</td>
<td>N/A</td>
</tr>
<tr>
<td>3</td>
<td>0.040</td>
<td>12</td>
<td>0.1</td>
</tr>
<tr>
<td>4</td>
<td>0.040</td>
<td>12</td>
<td>N/A</td>
</tr>
<tr>
<td>5</td>
<td>0.005</td>
<td>7</td>
<td>0.1</td>
</tr>
<tr>
<td>6</td>
<td>0.005</td>
<td>7</td>
<td>N/A</td>
</tr>
<tr>
<td>7</td>
<td>0.005</td>
<td>12</td>
<td>0.1</td>
</tr>
<tr>
<td>8</td>
<td>0.005</td>
<td>12</td>
<td>N/A</td>
</tr>
</tbody>
</table>

The supernatant liquid was analysed by ion chromatography and ICP-MS. The Fe$_{1-x}$O powders were analysed by XRD, High resolution X-ray Powder Diffraction (HR-XRPD), Field Emision Scanning
Electron Microscopy (FESEM) and elemental analysis. In addition, the surface area was measured before reaction via BET analysis using a Gemini 2360 V5.00.

A method for determining the concentration of aqueous carbonate and bicarbonate by ion chromatography was established, several literature references suggest that this is carried out routinely in water analysis\textsuperscript{118,119}. The setup consists of a Dionex DX100 ion chromatography system fitted with an AS15 column and a conductivity detector, using a 1.7mM/1.6mM carbonate/bicarbonate buffer.

A solution of 0.1 mol dm\textsuperscript{-3} NaHCO\textsubscript{3} was passed through the column with the 7 anion standard, two additional peaks were observed at 0.9 and 1.4 minutes respectively. When the solution was run through the column with the absence of the anion standard, the two peaks remained. This is shown below in figure 2.26.

![Figure 2.26 Counts against Retention Time](image)

To determine whether the counts scaled linearly with concentration for bicarbonate and carbonate, a set of standards from 0.002 – 0.01 mol dm\textsuperscript{-3} were made up and passed through the instrument to examine whether a good correlation was achieved. The correlation graph is shown in Figure 2.27a and Figure 2.27b for carbonate and bicarbonate respectively.

The effect of the surface treatment was analysed using a Jeol JSM-6010La Field Emission Scanning Electron Microscope (FESEM). Imaging was performed at 5 KeV with a working distance varying from 4.5-8.5mm.
Figure 2.27a Carbonate calibration graph of concentration against counts.

\[ y = 372608x - 621.96 \]
\[ R^2 = 0.9951 \]

Figure 2.27b Bicarbonate calibration graph of concentration against counts.

\[ y = 57616x - 93.439 \]
\[ R^2 = 0.9973 \]
Powder diffraction measurements were performed in $\theta$ - $2\theta$ geometry ($\lambda = 1.5406$ Å) on starting materials and products using a Bruker D8 Advance diffractometer in reflection geometry. An internal standard of silicon was used for calibration in order to allow for the detection of minor peak shifts. A Bruker D8 Discover diffractometer in transmission geometry operating with a cobalt radiation ($\lambda = 1.7890$ Å) was used to collect diffraction data on the samples containing iron. High Resolution synchrotron X-ray Powder Diffraction (HR-XRPD) measurements were performed at beamline I-11 at the Diamond Light Source. Measurements were conducted with monochromatic X-rays using a beam energy set at 15 keV ($\lambda = 0.827$ Å). Spectra were collected from 0 - 150° $2\theta$ with a 0.005° step-size. The multipoint N$_2$-BET method was used to measure the surface area of the starting materials. Samples were dried overnight under helium at room temperature and the surface area was then determined using the BET N$_2$ gas adsorption technique with a Micromeritics Gemini 2360 gas adsorption BET analyser adapted for low surface area materials. Reference material (carbon black) was also analysed.

2.2.2 Uranium solution studies

A number of preliminary measurements on uranium solutions were made and these are reported below.

2.2.2.1 Uranium absorption measurements by UV-Vis spectroscopy

The UV/Vis absorption spectrum of uranyl nitrate was investigated by preparing a stock solution of 0.1 mol dm$^{-3}$ by dissolving 1.2550 g of UO$_2$(NO$_3$)$_2$·6H$_2$O in 25 cm$^3$ of deionised water. From this stock solution a series of concentrations was prepared by taking the appropriate volume of the stock solution and making up to a total volume of 10 cm$^3$. These are summarised in Table 2.5. ICP-OES was used to measure the uranium concentration in solution. All ICP-OES measurements were completed using a Thermo scientific ICap 6000 spectrometer. Samples were prepared for ICP-OES by passing approximately 2 cm$^3$ of the supernatant through a 0.22µm PTFE syringe filter with the addition of 2 cm$^3$ of 4% trace metal analysis nitric acid (sigma Aldrich) to give a final acid concentration of 2%.
Table 2.5 Concentration of Uranium Standards

<table>
<thead>
<tr>
<th>Sample</th>
<th>Volume added to 10 cm³ / cm³</th>
<th>Concentration / ppm (w.v)</th>
<th>Concentration /mol DM-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.100</td>
<td>N/A</td>
<td>22610</td>
<td>0.095</td>
</tr>
<tr>
<td>0.075</td>
<td>7.5</td>
<td>18088</td>
<td>0.076</td>
</tr>
<tr>
<td>0.050</td>
<td>5.0</td>
<td>12376</td>
<td>0.052</td>
</tr>
<tr>
<td>0.025</td>
<td>2.5</td>
<td>5474</td>
<td>0.023</td>
</tr>
<tr>
<td>0.010</td>
<td>1.0</td>
<td>2380</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Calibration standards ranging from 0.1-100 ppm (w.v) were prepared by diluting the 1000 (w.v) ppm uranium standard (sigma Aldrich) with 2% nitric acid. The concentration of uranium in the each sample was determined from a calibration graph.

The absorbance spectra of the uranyl nitrate solutions were collected using a Cary 500s UV-Visible spectrophotometer. The instrument was set to baseline by recording a blank using deionised water before any measurements were taken. Absorbance spectra were collected between 190 and 800 nm using a 4 cm³ quartz fluorescence cuvette with a path length of 1 cm (Aireka cells). The cuvette was washed out 3 times with the solution of interest, and the exterior sides of the cuvette were dried with paper tissue (kimtech) before measurements were taken. The measurements were collected starting with the lowest concentration to the highest to minimise the effect of transfer from sample to sample. The collected data were analysed using origin and calibration graphs plotted using both the maximum peak absorbance and the area under the curve.

### 2.2.2.2 Uranium fluorescence measurements

A series of uranyl nitrate solutions were prepared with different concentrations by serial dilution of a 0.1 mol dm⁻³ uranyl nitrate solution. The 0.1 mol dm⁻³ solution was prepared by dissolving 0.5018 g of UO₂(NO₃)₂·6H₂O in 10 cm³ of deionised water. The range of uranium concentrations investigated was between 1x10⁻¹ and 1x10⁻⁴ mol dm⁻³, the solutions were prepared by pipetting 1 cm³ of the previous concentration and diluting to a total volume of 10 cm³. Fluorescence spectra were collected between 450 and 650 nm using a 4 cm³ quartz fluorescence cuvette with a path length of 1 cm (Aireka cells). The cuvette was washed out 3 times with the solution of interest, and the exterior sides of the cuvette were dried with paper tissue (Kimtech) before measurements were taken. The measurements were collected starting with the lowest concentration to the highest to minimise the effect of transfer from sample to sample. The collected data were analysed using origin and
calibration graphs plotted using both the maximum peak absorbance and the area under the curve. All measurements were made using the Edinburgh instruments FLS900 using a picosecond pulsed diode laser emitting at 375 nm as the excitation source.

2.2.2.3 Investigation of effect of bandwidth on uranium fluorescence spectrum

The 0.1 mol dm\(^{-3}\) \(\text{UO}_2(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}\) solution was prepared by dissolving 0.5012 g of \(\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}\) in 10 cm\(^3\) of deionised water. Fluorescence spectra were collected between 450 and 650 nm using a 4 cm\(^3\) quartz fluorescence cuvette with a path length of 1 cm (Aireka cells). The cuvette was washed out 3 times with the solution of interest, and the exterior sides of the cuvette were dried with paper tissue (kimtech) before measurements were taken. The bandwidth of both the entrance and exit slits were varied between 1 and 7 nm. All measurements were made using the Edinburgh instruments FLS900 using a xenon arc lamp operating at 375 nm as the excitation source to allow the data to be compared with the results collected using the diode laser.

2.2.2.4 Sodium diuranate synthesis

The problem of using uranyl nitrate solutions is that the fluorescence spectra have an increased background because of the presence of nitrate. To overcome this problem, the proposal was to use uranium perchlorate. To prepare a solution of uranium perchlorate, solid sodium diuranate was prepared and then dissolved in perchloric acid.

A stock solution of 0.5 mol dm\(^{-3}\) uranyl nitrate was prepared by dissolving 2.5107 g of \(\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}\) in 10 cm\(^3\) of deionised water, and placed into a 50 cm\(^3\) centrifuge tube and transferred to a fume cupboard. A second solution of approximately 16 mol dm\(^{-3}\) sodium hydroxide was prepared by dissolving 6.46 g of NaOH in 10 cm\(^3\) of deionised water; the concentrated sodium hydroxide solution was allowed to cool before use. The concentrated sodium hydroxide solution was added dropwise to the uranyl nitrate solution, until the solution was yellow/orange and opaque. The pH of the sample was checked for alkalinity using litmus paper. Once the pH was determined to be basic and there was evidence of precipitation the centrifuge tube was transferred to the a Hermle Z 200 A centrifuge and centrifuged at 6000 rpm for 20 min, resulting in a yellow/orange precipitate at the bottom of the centrifuge tube and a layer of clear liquid. The supernatant liquid was decanted, and the precipitate re-dissolved using 2 mol dm\(^{-3}\) perchloric acid, the precipitation procedure was repeated for a further two repetitions. The precipitate was then transferred to a watch glass and placed in an oven at 70°C for a period of 12 h. The precipitate was then prepared for powder X-ray diffraction by grinding the sample using an agate pestle and mortar in an inert atmosphere to
prevent inhalation of air born dust. A small amount of sample was then placed onto the adhesive side of a piece of magic tape™ tape and folded over to seal the powder between the tape. Powder diffraction data were collected on the product using the standard parameters given in section 2.2.1.1 and phase identification performed using the EVA programme and phase identification software by matching against the ICDD database.

A 1x10^{-2} mol dm^{-3} solution of uranyl perchlorate was prepared by dissolving 0.0632 g of Na₂U₂O₇ in 10 cm³ of 2 mol dm⁻³ HClO₄. All solutions were prepared under a positive pressure of nitrogen using a Braun glove box, and using boiled degassed water in an attempt to eliminate the presence of carbon dioxide. The concentration range was between 1x10⁻² and 1x10⁻⁴ mol dm⁻³. The samples were then placed into 4 cm³ plastic cuvettes fitted with stoppers and the lids sealed with parafilm. Fluorescence spectra were collected between 450 and 650 nm using the Edinburgh instruments FLS 900, using the 375 nm picosecond pulsed diode laser as the excitation source and with the bandwidth set to 1 nm.

2.2.2.5 Fluorescence lifetime measurements of uranyl nitrate

To determine whether measurements of the fluorescence lifetimes, of excited uranium, could be used to determine whether the uranium was complexed or not, fluorescence lifetimes were measured using an Edinburgh instruments FLS900 using a 375 nm picosecond pulsed diode laser as the excitation source. Typically, a stroboscopic technique has been reported in the literature due to the uranyl species typically being long lived. However, the FLS900 resolves excited state lifetimes by time-correlated single-photon counting (TCSPC) which usually yields greater counting statistics. TCSPC works by measuring the probability of a single photon being emitted after a specified time after the perturbation period. This in turn allows a histogram to be plotted of photon emission probability against time, which allows a statistical representation of the decay profile of the excited state.

Due to the statistical approach, TCSPC allows complex data sets to be analysed, and can separate bi and tri exponents allowing systems with multiple excited states to be measured simultaneously. However, with the increase in statistical rigour this does correspond to data collection periods being longer than those for other techniques.

In this experiment a 0.1 mol dm⁻³ uranyl nitrate solution was prepared by dissolving 0.5016 g of UO₂(NO₃)₂.6H₂O in 10 cm³ of 2 mol dm⁻³ nitric acid and made up to final volume with boiled degassed deionised water under a nitrogen atmosphere. The solution was placed into a sealed quartz fluorescence cuvette and sealed with a PTFE stopper and the top wrapped with parafilm. The sample
was excited at the 510 nm peak using a 375 nm diode laser operating at 50 MHz repetition rate. The decay of the excited uranyl species was observed by TCSPC with a time base of 20 microseconds.

2.2.2.6 Effect of carbonate on uranium fluorescence spectrum

Carbonate plays an important role in complexation of uranium in the near field water, therefore the effect of carbonate on uranium was investigated by using fluorescence spectroscopy. Samples were prepared from a 0.1 mol dm$^{-3}$ uranyl perchlorate stock made by dissolving 0.0632 g of sodium diuranate in dilute perchloric acid. A series of uranyl carbonate solution were prepared where the uranyl concentration was fixed at 1x10$^{-3}$ mol dm$^{-3}$ and the carbonate concentration varied to give ratios from 0 to 10. The concentration was fixed at pH 7 by the addition of NaOH or HClO$_4$ as necessary. All samples were prepared in a nitrogen atmosphere using boiled and degassed deionised water. Samples were transferred to 4 cm$^3$ plastic cuvettes sealed with parafilm. Absorbance spectra were collected between 190 and 800 nm using a 4 cm$^3$ quartz fluorescence cuvette with a path length of 1 cm (Aireka cells). The cuvette was washed out 3 times with the solution of interest, and the exterior sides of the cuvette were dried with paper tissue (Kimtech) before measurements were taken. The measurements were collected starting with the lowest concentration to the highest to minimise the effect of transfer from sample to sample. Fluorescence spectra were collected between 450 and 650 nm using an Edinburgh instruments FLS900 using a pico second pulsed diode laser at 375 nm as an excitation source. All ICP-OES measurements were completed using a Thermo scientific ICap 6000 spectrometer. Samples were prepared for ICP-MS by passing approximately 2 cm$^3$ of the supernatant through a 0.22 µm PTFE syringe filter with the addition of 2 cm$^3$ of 4% trace metal analysis nitric acid (sigma Aldrich) to give a final acid concentration of 2%. Calibration standards ranging from 0.1-100 ppm (w.v) were prepared by diluting the 1000 ppm (w.v) uranium standard (sigma Aldrich) with 2% nitric acid. The concentration of uranium in the samples was determined from the calibration graph and the values obtained are shown in Table 2.6
### Table 2.6 Concentration of Uranium determining by ICPMS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration / ppm</th>
<th>Concentration / mol dm(^{-3})</th>
<th>error (10^{-6})</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>186.35</td>
<td>7.83E-04</td>
<td>7.11E-06</td>
<td>6.81</td>
</tr>
<tr>
<td>0.10</td>
<td>183.60</td>
<td>7.71E-04</td>
<td>1.15E-05</td>
<td>6.97</td>
</tr>
<tr>
<td>0.20</td>
<td>190.44</td>
<td>8.00E-04</td>
<td>5.68E-06</td>
<td>6.81</td>
</tr>
<tr>
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<td>6.44E-06</td>
<td>7.03</td>
</tr>
<tr>
<td>0.40</td>
<td>172.73</td>
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<td>2.81E-06</td>
<td>7.23</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>7.73E-04</td>
<td>5.89E-06</td>
<td>6.91</td>
</tr>
<tr>
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<td>185.91</td>
<td>7.81E-04</td>
<td>2.62E-07</td>
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<tr>
<td>0.90</td>
<td>176.10</td>
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</tr>
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<tr>
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<td>179.21</td>
<td>7.53E-04</td>
<td>1.14E-05</td>
<td>7.43</td>
</tr>
<tr>
<td>10.00</td>
<td>176.27</td>
<td>7.41E-04</td>
<td>8.50E-06</td>
<td>7.37</td>
</tr>
</tbody>
</table>

#### 2.2.3.1 Magnetic susceptibility measurements

In order to complete the NMR requirements, the magnetic susceptibility of solid uranyl nitrate and aqueous uranyl carbonate (1x10\(^{-3}\) mol dm\(^{-3}\)) were measured using an Evans balance. The instrument was calibrated before measurements were taken using a barium chloride standard of known conductivity.

The magnetic susceptibility was calculated using the following two equations:

\[
\chi_M = \frac{C L (R - R_0) M}{10^3 m} \times 10^{-6 \text{ in cgs units}}
\]

**Equation 2.22**

Where:

- \(\chi\) = molar magnetic susceptibility
- C = constant derived from standard
- L = length of sample in cm
- R = balance reading of sample
- R\(_0\) = balance reading empty
- M = molar mass of sample
- m = mass of sample in grams
\[ \mu_{\text{eff}} = 2.83 \sqrt{\chi'_M \times T} \]

Equation 2.23

Where:
\[ \chi'_M = \text{corrected molar magnetic susceptibility} \]
\[ T = \text{temperature in K} \]
\[ \mu_{\text{eff}} = \text{magnetic moment in Bohr magnetons} \]

The corrected magnetic susceptibility was determined by applying a diamagnetic correction on all values taken from the literature\(^{120}\).

### 2.2.3.2 Effect of FEP insert of sodium carbonate NMR spectrum

Due to the hazardous nature of uranium, and the possibility at looking at hyper alkaline solutions and the effect that may have on the glass NMR tube, it was necessary for the sample to be double contained. This was achieved by using a fluorinated ethylene propylene insert (sigma Aldrich) that was designed to fit inside a standard NMR tube. However the precautionary act of adding an insert reduced the volume of the tube and therefore the volume of solution which could be placed inside the measuring tube. Therefore the effect of the reduced volume on signal to noise had to be investigated before the NMR spectra were measured.

In order to identify the likely need for longer running times with the FEP in place based on loss of signal to noise, a 0.03 mol dm\(^{-3}\) solution of sucrose (Tate & Lyle) was prepared by dissolving 0.1027 g in 10 cm\(^{3}\) of D\(_2\)O (sigma Aldrich). An aliquot of the sucrose solution was then placed into a standard glass NMR tube (Amphos) as well as into the FEP insert. Both samples were filled to the specified height optimised for the spectrometer. The \(^{13}\)C spectrum for the solution was collected using a Bruker 500 MHz NMR spectrometer.

### 2.2.3.3 Sodium carbonate limit of detection

Due to the low population of the excited state of carbon-13 within carbonate, NMR is not one of the most sensitive spectroscopic techniques, and therefore the limit of detection for the carbonate/bicarbonate system was investigated.

A series of sodium carbonate samples decreasing in concentration were prepared by initially preparing a stock solution of 0.1 mol dm\(^{-3}\)by dissolving 0.1070 g of Na\(_2^{13}\)CO\(_3\) (isotech) in 10 cm\(^{3}\) of D\(_2\)O (sigma Aldrich), subsequent samples were prepared by removing an aliquot from the stock solution and diluting with appropriate volume of D\(_2\)O to yield the desired concentration. The
samples were then placed inside the FEP insert and transferred to a glass NMR tube and the spectrum collected. In all cases the samples were prepared under a nitrogen atmosphere to prevent absorption of atmospheric CO$_2$ which could affect the spectrum obtained. The $^{13}$C spectrum for the solutions was collected using a Bruker 500 MHz NMR spectrometer. The concentrations of the samples are given in table 2.7

### Table 2.7 Concentration of Carbonate Stock Solution

<table>
<thead>
<tr>
<th>Desired Concentration / mol dm$^{-3}$</th>
<th>Volume / µl</th>
<th>Volume of 0.1 M Stock / µl</th>
<th>Actual concentration / mol dm$^{-3}$</th>
<th>Mass in NMR tube / µg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00E-01</td>
<td>2000</td>
<td>2000</td>
<td>1.02E-01</td>
<td>7609</td>
</tr>
<tr>
<td>1.00E-02</td>
<td>2000</td>
<td>200</td>
<td>1.02E-02</td>
<td>760.9</td>
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<td>2000</td>
<td>20</td>
<td>1.02E-03</td>
<td>76.09</td>
</tr>
<tr>
<td>7.50E-04</td>
<td>2000</td>
<td>15</td>
<td>7.62E-04</td>
<td>57.07</td>
</tr>
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<td>5.08E-04</td>
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<td>2000</td>
<td>5</td>
<td>2.54E-04</td>
<td>19.02</td>
</tr>
<tr>
<td>1.00E-04</td>
<td>2000</td>
<td>2</td>
<td>1.02E-04</td>
<td>7.61</td>
</tr>
</tbody>
</table>

#### 2.2.3.4 Effect of pH on sodium carbonate NMR spectrum

The effect of adjusting the pH on the chemical shift of sodium carbonate was investigated. A series of samples ranging from pH 7 to 13 were prepared where the concentration was fixed at 0.1 mol dm$^{-3}$ to allow signal to noise to be achieved in a reasonable number of scans. Samples were prepared from an initial sodium carbonate solution with a concentration of 1 mol dm$^{-3}$ this was achieved by dissolving 0.5345 g of Na$_2^{13}$CO$_3$ (isotech) in 5 cm$^3$ of D$_2$O (sigma Aldrich). The final concentration was achieved by adding 0.2 cm$^3$ of the stock solution to a plastic liquid scintillation vial and diluting to a final volume of 2 cm$^3$ with D$_2$O. The pH of the samples was controlled by the addition of NaOD (sigma Aldrich) and trace metal analysis HNO$_3$ (sigma Aldrich) before the final dilution. To eliminate the presence of any additional CO$_2$ all samples were prepared under a positive pressure of nitrogen using a Braun glove box. The pH was measured using a Hanna instruments piccolo plus portable pH meter that was calibrated using 7 and 10 pH buffers (sigma Aldrich). The solution compositions are
shown in table 2.8 The $^{13}$C spectrum for the solutions was collected using a Bruker 500 MHz NMR spectrometer.

<table>
<thead>
<tr>
<th>pH</th>
<th>$H^+$ added / mol dm$^{-3}$</th>
<th>$OH^-$ added / mol dm$^{-3}$</th>
<th>Measured pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.00</td>
<td>1.16E-02</td>
<td>N/A</td>
<td>7.04</td>
</tr>
<tr>
<td>7.50</td>
<td>1.05E-02</td>
<td>N/A</td>
<td>7.54</td>
</tr>
<tr>
<td>8.00</td>
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<td>8.00</td>
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<tr>
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<td>8.55</td>
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<td>N/A</td>
<td>1.50E-02</td>
<td>13.09</td>
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</tbody>
</table>

### 2.2.3.5 Effect of temperature on sodium carbonate NMR spectrum

To conclude this section on characterising the carbonate system in the absence of any uranyl species the effect of temperature was investigated because it has been reported in the literature that temperature has an effect on the carbonate chemical shift. Two variables were investigated i) the effect of temperature and ii) the effect of concentration. Three samples were prepared from a 0.1 mol dm$^{-3}$ stock solution prepared by dissolving 0.0215 g of Na$_2^{13}$CO$_3$ (Isotech) in 2 cm$^3$ of D$_2$O. To achieve the other two concentrations, 0.01 and 0.001 mol dm$^{-3}$ stock solutions were placed into a plastic liquid scintillation vial and diluted to a final volume of 2 cm$^3$ Samples were prepared under a positive pressure of nitrogen using a Braun glove box, and placed into an FEP insert before being placed into a glass NMR tube. The samples were placed into the NMR spectrometer and allowed to reach thermal equilibrium before the measurements were completed. $^{13}$C Spectra were recorded at temperatures between 25 and 50 °C with 5°C intervals, using a Bruker 500 MHz NMR spectrometer.
2.2.3.6 Effect of uranium on sodium carbonate NMR spectrum

The effect of uranium on the $^{13}$C-carbonate NMR spectrum was studied by preparing a range of samples of varying carbonate concentration with the uranium concentration fixed at $1 \times 10^{-3}$ mol dm$^{-3}$ and the carbonate concentration varied between $1 \times 10^{-3}$ mol dm$^{-3}$ and 0.1 mol dm$^{-3}$. Samples were prepared from a stock solution of 0.1 mol dm$^{-3}$ solution of Na$_2^{13}$CO$_3$ and the correct volume of 1000 ppm (w.v) ICP standard uranium in 2% HNO$_3$. All samples were fixed to pH 7 by the addition of deuterated sodium hydroxide in order for the data to be comparable with the fluorescence measurements discussed previously. All samples were prepared under a nitrogen atmosphere, samples were transferred to a FEP NMR tube insert and then placed into a glass NMR tube and the data collected using a Bruker 500 MHz NMR spectrometer.

2.2.4 Uranium sorption studies

2.2.4.1 Preliminary uranium sorption studies to surfaces relevant to geological disposal

The effect of pH on the sorption of uranium to a range of iron oxides, as shown in Table 2.8, and calcium hydroxide solid was investigated.

To investigate the effect of pH on sorption four solutions were used, deionised water, $1 \times 10^{-4}$ mol dm$^{-3}$ NaOH, 0.3 mol dm$^{-3}$ NaOH and 95% saturated Ca(OH)$_2$. The NaOH solutions were prepared by dissolving 0.0012 g, and 3.0152 g respectively, in a minimum volume of deionised water. The sodium hydroxide solution was then transferred to a plastic 250 cm$^3$ volumetric flask and diluted to 250 cm$^3$ using distilled water. The calcium hydroxide solution was prepared by adding 2.0562 g of calcium hydroxide to 1 dm$^3$ of deionised water, and stirred for approximately 1 d. The solution was then filtered under vacuum to remove any undissolved calcium hydroxide. After filtration 237.5 cm$^3$ of the filtered solution was placed into a plastic volumetric flask, and deionised water added to achieve the final volume. In addition to the 25 µl of a 0.01 mol dm$^{-3}$ UO$_2$(NO$_3$)$_2$.6H$_2$O solution was added to the stock solutions to give a final uranium concentration $1 \times 10^{-6}$ mol dm$^{-3}$. The 0.01 mol dm$^{-3}$ UO$_2$(NO$_3$)$_2$.6H$_2$O solution was prepared by dissolving 0.5021 g of UO$_2$(NO$_3$)$_2$.6H$_2$O in 100 cm$^3$ of deionised water. The samples were prepared by placing approximately 0.1 g of solid into a 50 cm$^3$ centrifuge tube, followed by 20 cm$^3$ of the relevant uranium solution. The mixture was then allowed to equilibrate; this was achieved by agitating these solutions for the duration of the experiment at room temperature in 50 cm$^3$ plastic vials on a flatbed shaker for one week to allow equilibrium to be reached. After this time period, the samples were centrifuged at 6000 rpm using a Hermle Z 200 A centrifuge and the supernatant liquid decanted. Then a 2 cm$^3$ aliquot of the supernatant liquid was removed using a plastic syringe with a 0.22µm filter and analysed by ICP-MS.
Samples were prepared for ICP-MS by passing approximately 2 cm³ of the supernatant through a 0.22µm PTFE syringe filter with the addition of 2 cm³ of 4% trace metal analysis nitric acid (sigma Aldrich) to give a final acid concentration of 2%. Calibration standards ranging from 0.1-100 ppb were prepared by diluting the 1000 ppm (w.v) uranium standard (sigma Aldrich) with 2% nitric acid. Full quantitative analysis was carried out using an Agilent 7700 ICP-MS analysing for ²³⁸U. Instrumental drift was accounted for using a 1 ppb ²⁰⁹Bi standard, using the U:Bi ratio to accurately determine the uranium concentration. The amount of metal adsorbed was calculated by comparing concentrations of the solution before and after adsorption. All sorption experiments were carried out in triplicate under ambient conditions.

2.2.4.2 Effect of pH on uranium sorption to iron oxides

To further investigate uranium sorption to iron, additional experiments were conducted using the three iron oxides used in 2.2.4. NaOH solutions with a pH ranging from 7 to 13 (as a result of varying NaOH concentration) were used in these experiments. The NaOH solutions were prepared by dissolving the appropriate amount of sodium hydroxide in a minimum volume of deionised water. The sodium hydroxide solution was then transferred to a plastic 250 cm³ volumetric flask and diluted to 250 cm³. In addition to the 25 µl of a 0.01 mol dm⁻³ UO₂(NO₃)₂ solution was added to the stock solutions to give a final uranium concentration 1x10⁻⁶ mol dm⁻³. The 0.01 mol dm⁻³ uranyl nitrate solution was prepared by dissolving 0.50212 g of UO₂(NO₃)₂.6H₂O in 100 cm³ of deionised water. The samples were prepared by placing approximately 0.1 g of solid into a 50 cm³ centrifuge tube, followed by 20 cm³ of the relevant uranyl solution. The mixture was then allowed to equilibrate; this was achieved by agitating these solutions for the duration of the experiment at room temperature in 50 cm³ plastic vials on a flatbed shaker for one week to allow equilibrium to be. After this the samples were centrifuged at 6000 rpm using a Hermle Z 200 A centrifuge and the supernatant decanted. Then a 2 cm³ aliquot of the supernatant was removed using a plastic syringe with a 0.22µm filter and analysed by ICP-MS. Samples were prepared for ICP-MS by passing approximately 2 cm³ of the supernatant through a 0.22µm PTFE syringe filter with the addition of 2 cm³ of 4% trace metal analysis nitric acid (sigma Aldrich) to give a final acid concentration of 2%. Calibration standards ranging from 0.1-100 ppb were prepared by diluting the 1000 ppm (w.v) uranium standard (sigma Aldrich) with 2% nitric acid. Full quantitative analysis was carried out using an Agilent 7700 ICP-MS analysing for ²³⁸U. Instrumental drift was accounted for using a 1 ppb ²⁰⁹Bi standard, using the U:Bi ratio to accurately determine the uranium concentration. All experiments were conducted in triplicate and carried out under both atmospheric and anaerobic conditions.
2.2.4.3 Effect of carbonate concentration on uranium sorption to iron oxides

To investigate the effect of pH and carbonate concentration on the sorption of uranium to the iron oxides, a series of solutions were used with carbonate concentrations ranging from $1 \times 10^{-2}$ to $1 \times 10^{-10}$ mol dm$^{-3}$ as well as carbonate solutions of pH 7 and 13. The solutions were prepared by serial dilution. A 0.01 mol dm$^{-3}$ solution of sodium carbonate was prepared by dissolving 0.2649 g anhydrous sodium carbonate (Fischer Scientific) in the minimum amount of deionised water, the solution was then transferred to a plastic 250 cm$^3$ volumetric flask. The pH was adjusted to the desired value by addition of sodium hydroxide before diluting to 250 cm$^3$. In addition to the 25 µl of a 0.01 mol dm$^{-3}$UO$_2$(NO$_3$)$_2$ solution was added to the stock solutions to give a final uranium concentration $1 \times 10^{-6}$ mol dm$^{-3}$. The 0.01 mol dm$^{-3}$ uranyl nitrate solution was prepared by dissolving 0.5022 g of UO$_2$(NO$_3$)$_2$.6H$_2$O in 100 cm$^3$ of deionised water. The samples were prepared by placing approximately 0.1 g of solid into a 50 cm$^3$ centrifuge tube, followed by 20 cm$^3$ of the relevant uranyl solution. The mixture was then allowed to equilibrate; this was achieved by agitating these solutions for the duration of the experiment at room temperature in 50 cm$^3$ plastic vials on a flatbed shaker for one week to allow equilibrium to be achieved. The samples were centrifuged at 6000 rpm using a Hermle Z 200 A centrifuge and the supernatant decanted. Then a 2 cm$^3$ aliquot of the supernatant was subjected to a 0.22µm filter and analysed by ICP-MS. Samples were prepared for ICP-MS by passing approximately 2 cm$^3$ of the supernatant through a 0.22µm PTFE syringe filter with the addition of 2 cm$^3$ of 4% trace metal analysis nitric acid (sigma Aldrich) to give a final acid concentration of 2%. Calibration standards ranging from 0.1-100 ppb were prepared by diluting the 1000 ppm (w.v) uranium standard (sigma Aldrich) with 2% nitric acid. Full quantitative analysis was carried out using an Agilent 7700 ICP-MS analysing for $^{238}$U. Instrumental drift was accounted for using a 1 ppb $^{209}$Bi standard, using the U:Bi ratio to accurately determine the uranium concentration. All experiments were conducted in triplicate and carried out under both atmospheric and anaerobic conditions.

2.2.4.4 X-Ray absorption measurements on sorbed uranium species to iron oxides

The EXAFS measurements were performed at the B18 experimental station at the Diamond Light Source, UK. This beamline is designed to collect bulk EXAFS analyses rapidly, by using the Quick EXAFS mode. The energy of the beam was calibrated against the first derivative of a Y foil, defined at 17,038 eV. The measurements were then conducted at the U LIII-edge in fluorescence mode using a 9 element Ge detector mounted perpendicular to the incoming beam. The double containment sealed samples were placed into a clamp in such way that each sample was positioned at 45° relative to the incoming X-ray beam. A schematic is shown below in figure 2.28.
Fe bulk EXAFS were collected at the Fe K-edge. An unreacted Fe_{1-x}O pellet was prepared and measured in transmission mode. Unfortunately, the design of the sample holders and density of the reacted substrate precluded data collection for the product solids in transmission-mode. Therefore, these measurements were completed in fluorescence mode similar to that described above, except that the surface of the sample holder was positioned nearly normal to the incident beam. This resulted in a glancing exit angle which decreases the impact of self-adsorption on the measured intensity. The EXAFS spectra were further corrected for remaining self-absorption using the Fluo algorithm in (d)Athena 0.9.18. The EXAFS, $\chi(k)$, were refined from the raw data by standard procedures, including background subtraction, normalization of absorption, conversion to momentum and k space. For each sample ca. 34 spectra were averaged to improve signal to noise ratio. The spectra were then analysed with (d)Artemis 0.9.18 and the phase/amplitude functions were calculated by FEFF6L. The theoretical fits were performed in R-space.
2.2.5 Sandstone Diffusion Experiments

2.2.5.1 Introduction

In this set of experiments, the diffusion of key radionuclides was investigated adapting a method previously used for determining radionuclide migration through cement cores\textsuperscript{123–125}. Sandstone cores were prepared so that they had a central cavity where the distance from the central cavity to the external face of the core was kept constant. The core was then sealed top and bottom by coating the surface with paraffin wax. The cores were then placed into a 250 cm\textsuperscript{3} pot (Nalgene) along with 200 cm\textsuperscript{3} of the liquid phases and allowed to equilibrate for a period of 48 hours. The core was then removed from the solution and any liquid in the central cavity removed using a Pasteur pipette. The radionuclide of interest in then added to the central core and a plastic lid wrapped in parafilm used to seal the cavity. The sealed core was then placed back into the 250 cm\textsuperscript{3} pot and sealed an example of the setup is shown below.

![Sandstone Core Experiments](image)

**Figure 2.29 Sandstone Core Experiments**

The external fluid was sampled periodically and analysed for increased concentration of the measured radionuclide allowing the diffusion rate to be determined.
2.2.5.2 Sandstone block porosity measurements using tritiated water

Tritiated water (HTO) was used to determine the porosity of the sandstone cores, as well as to determine the viability of the method. The sandstone cores were prepared by drilling a concentric hole in the core so that the diffusive length was from the bottom of the void was equal to that of the sides shown below in figure 2.30.

![Figure 2.30 Photograph of Sandstone Core](image)

The core was then placed into a 250 cm$^3$ pot (Nalgene) followed by 200 cm$^3$ of Young’s Cement Leachate (YCL) and allowed to equilibrate with the YCL for a period of 48 h. The core was then removed from the solution and any liquid in the central cavity removed with a Pasteur pipette. The central cavity of the core was the spiked with 1.5 cm$^3$ of HTO with a total activity of 3 kBq. The core was then sealed using a plastic stopper wrapped in parafilm to create a sufficient seal. The core was then placed back in to the solution and sealed; the external fluid was sampled at relevant time points. At each sampling point 1 cm$^3$ of the external fluid was removed and placed into a 20 cm$^3$ liquid scintillation vial, 10 cm$^3$ of liquid scintillation cocktail (meridian, goldstar) was added to the scintillation vial. The solution and scintillation cocktail were then fully mixed using a vortex mixer and placed into the liquid scintillation counter (Perkin Elemer Tricarb 2100 TR), the samples were allowed to settle and light adjust for 1 h. Samples were counted for tritium using a counting window between 2 and 18 KeV. All experimental procedures were completed under a positive pressure of nitrogen using a Braun glove box. Experiments were carried out in triplicate.
2.2.5.3 Uranium diffusion through intact sandstone block

Uranium and thorium are both important to the nuclear fuel cycle and form a proportion of the nuclear waste legacy. Experiments were conducted to determine the rate of migration of both ions through sandstone cores under cementitious conditions. This study considers four different solutions young cement leachate (YCL), intermediate cement leachate (ICL), old cement leachate (OCL) and a synthetic ground water (GW). The composition of the four solutions is shown below in table 2.9.

<table>
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<tr>
<th>Chemical</th>
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<th>ICL</th>
<th>OCL</th>
<th>GW</th>
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<td>10.0</td>
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<tr>
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The sandstone cores were prepared by drilling a concentric hole in the core so that the diffusive length was from the bottom of the void was equal to that of the sides. The core was then placed into a 250 cm³ pot (Nalgene) followed by 200 cm³ of YCL an allowed to equilibrate with the YCL for a period of 48 h.

The core was then removed from the solution and any liquid in the central cavity removed with a Pasteur pipette. The central cavity of the core was the spiked with 1.5 cm³ of slurry containing either uranium or thorium precipitates with a total activity of 3 kBq. The core was then sealed using a plastic stopper wrapped in parafilm to create a sufficient seal. The core was then placed back in to the solution and sealed; the external fluid was sampled at relevant time points this was carried out for 8 cores for each element. Concentrations of the elements in question were determined by ICP-MS. A 2 cm³ aliquot of the supernatant liquid was removed using a plastic syringe with a 0.22 μm filter and analysed by ICP-MS. Samples were prepared for ICP-MS by passing approximately 2 cm³ of the supernatant liquid through a 0.22 μm PTFE syringe filter with the addition of 2 cm³ of 4% trace
metal analysis nitric acid (Sigma Aldrich) to give a final acid concentration of 2%. Calibration standards ranging from 0.1-100 ppb were prepared by diluting the 1000 ppm (w.v) uranium or thorium standard (Sigma Aldrich) with 2% nitric acid. Full quantitative analysis was carried out using an Agilent 7700 ICP-MS analysing for $^{232}\text{Th}$. Instrumental drift was accounted for using a 1 ppb $^{209}\text{Bi}$ standard, using the Th or U:Bi ratio to accurately determine the concentration. After 6 months the core was removed from the YCL solution and 6 of the cores placed into 200 cm$^3$ of intermediate cement leachate. This process occurred a further 2 times until the solution was in a synthetic ground water, shown schematically in Figure 2.31.

![Figure 2.31 Production of Synthetic Ground Water](image)

At each solution change, two of the cement cores were sacrificed. The sacrificed cores had any remaining precipitate removed and were cut in half longitudinally using a Dewalt diamond saw cabinet. The solid was analysed by PXRD and solid cores analysed by autoradiography. All experimental procedures were completed under a positive pressure of nitrogen using a Braun glove box.

2.2.5.3.1 Uranium precipitation in young cement leachate

Uranium precipitates were prepared to a total of activity of 3 KBq; this was achieved by dissolving 0.2418 g of $\text{UO}_2(\text{NO}_3)_2\cdot6\text{H}_2\text{O}$ in 5 cm$^3$ of deionised water and placed into a 10 cm$^3$ centrifuge tube. 5 cm$^3$ of young cement leachate was added to dropwise to the uranyl nitrate solution upon addition of the cement leachate a yellow solid was observed, the pH of the solution was checked to ensure the solution was basic using litmus paper (Fischer scientific). The solutions were allowed at equilibrate for a period of two weeks before being used in any experiments, all samples were prepared under a positive pressure of nitrogen using a Braun glove box. After the equilibration period 8.5 cm$^3$ of the supernatant liquid was removed and uranium concentration determined by ICP-MS. A 2 cm$^3$ aliquot of the supernatant liquid was removed using a plastic syringe with a 0.22μm filter and analysed by...
ICP-MS. Samples were prepared for ICP-MS by passing approximately 2 cm$^3$ of the supernatant through a 0.22 µm PTFE syringe filter with the addition of 2 cm$^3$ of 4% trace metal analysis nitric acid (Sigma Aldrich) to give a final acid concentration of 2%. Calibration standards ranging from 0.1-100 ppb were prepared by diluting the 1000 ppm (w.v) uranium standard (Sigma Aldrich) with 2% nitric acid. Full quantitative analysis was carried out using an Agilent 7700 ICP-MS analysing for $^{238}$U. Instrumental drift was accounted for using a 1 ppb $^{209}$Bi standard, using the U:Bi ratio to accurately determine the uranium concentration. This process was performed for a total of 8 samples.

2.2.5.3.2 X-ray absorption measurements on uranium precipitates in a cementitious fluid

A similar set of experiments were conducted on cement cores that were not directly related to the work in this thesis. The project was fortunate to gain some beam time to identify the non-crystalline phases at the centre of the cement core, and so the analysis of these precipitates will be mentioned as there are similarities between the cement cores and that of the sandstone system studied in this thesis. The paper the data are associated with is currently in press and a copy is attached in supplementary data 2.

Samples were ground for EXAFS analysis using an agate pestle and mortar before mixing with cellulose to yield a concentration of approximately 2000 ppm (w.v). A 40 mg sample was placed into a Perspex sample holder, sealed with three layers of Kapton® tape and then heat sealed under nitrogen atmosphere. The EXAFS measurements were performed at the B18 experimental station at the Diamond Light Source. This beamline is designed to collect bulk EXAFS analyses rapidly by using the Quick EXAFS mode. The energy of the beam was calibrated against the K-edge first derivative of a Y foil, defined at 17,038 eV. Measurements were conducted at the U LIII-edge in fluorescence mode using a nine element Ge detector mounted perpendicular to the incoming beam. The sealed samples were placed into a clamp so that each sample was positioned at 45º relative to the incoming X-ray beam. The EXAFS spectra were further corrected for remaining self-absorption using the Fluo algorithm in Athena 0.9.18. EXAFS w(k) values were refined from the raw data by standard procedures, including background subtraction, normalization of absorption and conversion to momentum and k space. For each sample ~34 spectra were averaged to improve the signal-to-noise ratio. The spectra were then analysed with Artemis 0.9.18 and the phase/amplitude functions were calculated by FEFF6L. The theoretical fits were performed in R-space.

2.2.5.4 Thorium diffusion through intact sandstone block

The sandstone cores were prepared by drilling a concentric hole in the core so that the diffusive length was from the bottom of the void was equal to that of the sides. The core was then placed into
a 250 cm$^3$ pot (Nalgene) followed by 200 cm$^3$ of YCL an allowed to equilibrate with the YCL for a period of 48 h.

The core was then removed from the solution and any liquid in the central cavity removed with a Pasteur pipette. The central cavity of the core was then spiked with 1.5 cm$^3$ of slurry containing either uranium or thorium precipitates with a total activity of 3 kBq. The core was then sealed using a plastic stopper wrapped in parafilm to create a sufficient seal. The core was then placed back in to the solution and sealed; the external fluid was sampled at relevant time points this was carried out for 8 cores for each element. Concentrations of the elements in question were determined by ICP-MS. A 2 cm$^3$ aliquot of the supernatant liquid was removed using a plastic syringe with a 0.22 μm filter and analysed by ICP-MS. Samples were prepared for ICP-MS by passing approximately 2 cm$^3$ of the supernatant liquid through a 0.22 μm PTFE syringe filter with the addition of 2 cm$^3$ of 4% trace metal analysis nitric acid (Sigma Aldrich) to give a final acid concentration of 2%. Calibration standards ranging from 0.1-100 ppb were prepared by diluting the 1000 ppm (w.v) uranium or thorium standard (sigma Aldrich) with 2% nitric acid. Full quantitative analysis was carried out using an Agilent 7700 ICP-MS analysing for $^{232}$Th. Instrumental drift was accounted for using a 1 ppb $^{209}$Bi standard, using the Th or U:Bi ratio to accurately determine the concentration. After 6 months the core was removed from the YCL solution and 6 of the cores placed into 200 cm$^3$ of intermediate cement leachate. This process occurred a further 2 times until the solution was in a synthetic ground water (Figure 2.31).

At each solution change, two of the cement cores were sacrificed. The sacrificed cores had any remaining precipitate removed and were cut in half longitudinally using a Dewalt diamond saw cabinet. The solid was analysed by PXRD and solid cores analysed by autoradiography. All experimental procedures were completed under a positive pressure of nitrogen using a Braun glove box.

2.2.5.4.1 Thorium precipitation in young cement leachate

Thorium precipitates were prepared to a total of activity of 3 KBq; this was achieved by dissolving 0.4178 g of Th(NO$_3$)$_4$.5H$_2$O in 5 cm$^3$ of deionised water and placed into a 10 cm$^3$ centrifuge tube. 5 cm$^3$ of young cement leachate was added dropwise to the thorium nitrate solution upon addition of the cement leachate a white solid was observed. The pH of the solution was checked to ensure the solution was basic using litmus paper (Fischer Scientific). The solutions were allowed to equilibrate for a period of two weeks before being used in any experiments, all samples were prepared under a positive pressure of nitrogen using a Braun glove box. After the equilibration period, 8.5 cm$^3$ of the supernatant was removed and uranium concentration determined by ICP-MS. A 2 cm$^3$ aliquot of the supernatant liquid was removed using a plastic syringe with a 0.22 μm filter and analysed by ICP-MS.
Samples were prepared for ICP-MS by passing approximately 2 cm³ of the supernatant liquid through a 0.22 µm PTFE syringe filter with the addition of 2 cm³ of 4% trace metal analysis nitric acid (Sigma Aldrich) to give a final acid concentration of 2%. Calibration standards ranging from 0.1-100 ppb were prepared by diluting the 1000 ppm (w.v) thorium standard (Sigma Aldrich) with 2% nitric acid. Full quantitative analysis was carried out using an Agilent 7700 ICP-MS analysing for $^{232}$Th. Instrumental drift was accounted for using a 1 ppb $^{209}$Bi standard, using the Th:Bi ratio to accurately determine the uranium concentration. This process was performed for a total of 8 samples.

2.2.5.5 Technetium diffusion measurements through sandstone

2.2.5.5.1 Diffusion through intact sandstone block

The sandstone cores were prepared by drilling a concentric hole in the core so that the diffusive length was from the bottom of the void was equal to that of the sides. The core was then placed into a 250 cm³ pot (Nalgene) followed by 200 cm³ of YCL and allowed to equilibrate with the YCL for a period of 48 h.

The core was then removed from the solution and any liquid in the central cavity removed with a Pasteur pipette. The central cavity of the core was the spiked with technetium with a total activity of 3 kBq. The core was then sealed using a plastic stopper wrapped in parafilm to create a sufficient seal. The core was then placed back in to the solution and sealed; the external fluid was sampled at relevant time points this was carried out for 8 cores for each element. Concentrations of the elements in question were determined by ICP-MS. A 2 cm³ aliquot of the supernatant liquid was removed using a plastic syringe with a 0.22 µm filter and analysed liquid scintillation counting. After 6 months the core was removed from the YCL solution and 6 of the cores placed into 200 cm³ of intermediate cement leachate. This process occurred a further 2 times until the solution was in a synthetic ground water (Figure 2.31).

At each solution change, two of the cement cores were sacrificed. The sacrificed cores had any remaining precipitate removed and were cut in half longitudinally using a Dewalt diamond saw cabinet.

2.2.5.5.2 Diffusion through disaggregated sandstone cell

The diffusion of technetium through disaggregated sandstone was investigated using a diffusion cell setup. The setup consists of a cylindrical cell with screw cap ends with a path length of 10 cm and a diameter of 3.8 cm a schematic and actual representation are depicted below in figure 2.32.
2.2.5.5.3 Method optimisation

The method was optimised using tritiated water (HTO) as a conservative tracer. This enabled variables such as the volume of spike added and solid/liquid ratio to be optimised. The optimum conditions were determined to be:

- Dry mass of sandstone 380 g
• 20% w/w liquid to form slurry
• 50 μl tracer
• 3 KBq tracer added

2.2.5.5.4 Experimental

The diffusion cell was sealed at one end and orientated vertically. The cell was then half filled with
the sandstone cement leachate slurry (20% w/w cement leachate). This step was conducted in
stages and compacted using a syringe plunger from a 100 cm$^3$ syringe. The 3 KBq spike was then
added 50 μl of NH$_4$TcO$_4$ was placed in the centre if a filter paper this was then placed into the
diffusion cell, the cell was then packed and sealed.
The cell was then extracted using the extraction device depicted in figure 2.33.

![Figure 2.33 Diffusion cell extraction apparatus](image)

This involves removing one of the screw caps and mounting the cell vertically in the extraction tool.
A jack with a plunger the diameter of cell attached is then used to extract the fractions of the
sandstone from the cell. The fractions were then placed into a 50 cm$^3$ centrifuge tube along with 10
cm$^3$ of deionised water and placed onto a flatbed shaker for a period of 24 h. After the agitation, a 2
cm$^3$ aliquot was taken and transferred to a liquid scintillation vial and 10 cm$^3$ of scintillation cocktail
added.

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Chapter Three: Results and Discussion
3.0 Results and Discussion

3.1 Characterisation of Materials

The aim of this thesis is to understand how radionuclides interact with the materials found inside a nuclear waste repository in order to identify which phases are likely to enable or retard the movement of the ions in the environment. For this reason, it is important that the materials used to mimic the repository environment are as pure as possible and well-characterised to ensure that the interactions observed are unequivocally a result of the material of interest and the radionuclide rather than any impurity phase. Therefore the materials used in this study were characterised by using both XRD and IR techniques to determine the purity of the phases under investigation.

3.1.1 Analysis of Ca(OH)$_2$ from Sigma Aldrich

XRD analysis of the calcium hydroxide purchased from Sigma Aldrich identified an impurity which was determined to be calcite (calcium carbonate). The powder XRD pattern is shown below in Figure 4.1 with the reflections associated with the calcium hydroxide (reference pattern 00-044-1481) shown in green and the calcium carbonate impurity (reference pattern 00-05-0586) shown in blue.

![Reflectance XRD pattern of calcium hydroxide from Sigma-Aldrich with calcium hydroxide reference pattern 00-044-1481 shown in green and calcium carbonate reference pattern 00-05-0586 shown in blue](image-url)
The infra-red spectrum of the material also identifies the presence of carbonate with the stretch being observed at 1442 cm$^{-1}$ in a good agreement with the literature$^{126}$. The IR also identifies the presence of the hydroxyl groups with a stretch at 3642 cm$^{-1}$ and a stretch at 592 cm$^{-1}$ determined to be the calcium oxygen bond vibration by reference to the literature$^{127}$. Unfortunately, due to the calcium carbonate impurity, the Sigma Aldrich calcium hydroxide was therefore not suitable as a mimic repository material so calcium hydroxide with significantly higher purity was prepared.

3.1.2 Synthesis of High Purity Calcium Hydroxide

Ca(OH)$_2$ was precipitated from a solution of CaCl$_2$ and NaOH to attempt to produce a carbonate-free sample of Ca(OH)$_2$ for this study. The reaction scheme for the reaction is shown in equation 3.1.

$$\text{CaCl}_2 (aq) + 2\text{NaOH}(aq) \rightarrow \text{Ca(OH)}_2(S) + 2\text{NaCl}(aq)$$

Equation 3.1

3.1.2.1 Precipitation of Calcium Hydroxide under Ambient Conditions

The initial attempt to synthesise a high purity calcium hydroxide under these conditions was unsuccessful and the calcium carbonate impurity was still present as is shown below in figure 3.2. This can be attributed to the high alkalinity of the solution resulting in carbon dioxide from the air being absorbed by the solution on standing in air before the calcium chloride was added or possibly carbon dioxide being absorbed onto the surface of the sodium hydroxide pellets in the jar as the lid had been opened and closed.
3.1.2.2 Precipitation of calcium hydroxide from a mixture of calcium chloride and sodium hydroxide under anaerobic conditions

To limit the formation of calcite, the experiment was repeated under anaerobic conditions using degassed water to limit the possible ingress of atmospheric CO₂ into the system. The initial attempt at synthesising pure Ca(OH)₂ was relatively successful; the calcite phase was still present but the XRD pattern shows the signal is significantly reduced relative to the calcium hydroxide phase (Figure 3.3).
3.1.2.3 Precipitation of calcium hydroxide under anaerobic conditions with new sodium hydroxide

The method used for precipitating the Ca(OH)₂ used a 2:1 mixture of sodium hydroxide and calcium chloride. Both materials are hydroscopic, especially in the case of the sodium hydroxide. It is possible that as the sodium hydroxide was being measured that the surface of the pellets hydrated, forming a very concentrated sodium hydroxide solution on the pellet surface. Due to the high pH of the solution atmospheric CO₂ may have been absorbed later forming the calcite phase. The experiment was repeated ensuring that all measurements were carried out under a nitrogen atmosphere.

The XRD pattern for the synthesised calcium hydroxide under ambient conditions using reagents which had been opened and stored under a nitrogen atmosphere is shown below in figure 3.4.
Figure 3.4: Reflectance XRD pattern of glove box synthesised calcium hydroxide before washing step with NaCl impurity with calcium hydroxide reference pattern 00-044-1481 shown in green and calcium carbonate reference pattern 00-05-0586 shown in blue and sodium chloride pattern 00-005-0628 shown in red

XRD analysis of the product formed determined the absence of calcite in the unwashed sample, however there was a new unidentified secondary phase. This was determined to be excess sodium chloride, the by-product formed in the synthesis step. The sample was then washed with cold deionised and degassed water.
After the washing step the XRD pattern indicated that the sodium chloride phase had been removed, however the calcite phase was again present. This can be attributed to the washing being done under atmospheric conditions, allowing the formation of a calcium hydroxide solution which in turn can remove atmospheric carbon dioxide allowing calcite formation. The experiment was repeated with an attempt to limit exposure to carbon dioxide in the washing step; this was done by using a dry solvent such as ethanol in the washing step, as well as performing the filtration under a nitrogen atmosphere. The XRD pattern shown below shows that only calcium hydroxide is observed.
3.1.2.4 Precipitation of calcium hydroxide under anaerobic conditions with new sodium hydroxide and washings carried out under a nitrogen atmosphere

The XRD pattern for the synthesised calcium hydroxide under ambient conditions with washings carried out under a nitrogen atmosphere is shown in Figure 3.6.

![XRD pattern](image)

**Figure 3.6:** Reflectance XRD pattern synthesised calcium hydroxide in glove box with filtration step performed under nitrogen with calcium hydroxide reference pattern 00-044-1481 shown in green

The XRD pattern shown in figure 3.6 only has peaks present corresponding to calcium hydroxide, this is attributed to using a previously unopened bottle of NaOH and keeping the reaction in low partial pressure of CO₂. This prevents the concentrated NaOH solution forming on the surface of the pellets, and hence prevents carbonation and calcite formation.

3.1.2.5 Precipitation of calcium hydroxide under ambient conditions using the sacharate method

The pattern from the sacharate method mentioned in section 2.2.1.3 also only has the single calcium hydroxide phase present. The advantage of this method is that it can be performed quickly and on
the bench. There have been references in the literature that show this method is successful for formation of cement phases, such as ettringite without producing impurity phases\textsuperscript{128} as shown in figure 3.7.

![Figure 3.7 Reflectance Powder Diffraction Pattern of Ca(OH)\textsubscript{2} formed by the Sacharate Method with calcium hydroxide reference pattern 00-044-1481 shown in green](image)

3.1.3 Analysis of Fe\textsubscript{1-x}O from Sigma Aldrich

Fe\textsubscript{1-x}O is a simple iron oxide system which crystallises with the cubic halite structure in the space group Fm-3m with cell parameter 4.311 Å. This material was chosen as a surrogate for the mineral wüstit because the natural material does not typically crystallise phase pure and often contains several divalent ions substituted for the cation depending on the geological location. The mineral is uncommon due to the 2+ oxidation state, however it is expected that under conditions relevant to a geological disposal facility, high pH and low Eh iron species will be reduced and as a result low oxidation state iron oxides will be stabilised.

The XRD pattern of the powdered Fe\textsubscript{1-x}O is a good match to the database (reference pattern 074-1885) with no additional reflections as shown in figure 3.8. However, due to the air sensitivity of the
material as a result of oxidation of the iron by atmospheric oxygen, care was taken when handling the material.

![XRD Pattern]

**Figure 3.8: Transmission XRD Pattern of FeO from Sigma-Aldrich with the FeO reference pattern 00-06-0615 given in blue, the magnetite impurity reference pattern 00-19-0629 given in green and the residual elemental iron reference pattern 00-65-4899 in orange**

The infra-red spectrum collected on this material did not show any clear vibrational bands that could be associated with Fe$_{1-x}$O, this is to be expected as the IR stretching frequency associated with the iron oxide bond is low in wavenumber. There was no sign of any additional bands which could indicate the presence of impurities such as iron carbonates or iron oxyhydroxides in agreement with the XRD pattern that indicated that the material is of good purity within the limits of detection of the XRD technique showing trace amounts of magnetite and residual elemental iron left over from synthesis.

### 3.1.4 Analysis of Fe$_2$O$_3$ from Sigma Aldrich

Fe$_2$O$_3$ is a common iron oxide often found after steel corrosion, analogous to the mineral haematite. Under ambient and oxic conditions, it has been shown that Fe$_2$O$_3$ is one of the most stable iron oxides. As initially the conditions in a geological disposal facility are oxic, it is likely any iron species
formed from corrosion will be in the 3+ oxidation state, at least in the first instance. The XRD pattern of the powdered Fe$_2$O$_3$ indicates that the sample is largely haematite (reference pattern 00-33-0664) pattern as shown below in figure 3.9 with one anomalous reflection at 35 degrees which is consistent with Fe$_3$O$_4$.

![Figure 3.9 Transmission Powder X-ray Diffraction Pattern of Fe$_2$O$_3$ with the reference pattern 00-33-0664 given in pink](image)

3.1.5 Analysis of Fe$_3$O$_4$ from Sigma Aldrich

Fe$_3$O$_4$ is a mixed valence state iron oxide with iron oxidation states of 2+ and 3+. The iron oxide is synthetic analogue of the naturally occurring mineral, magnetite. Similar to Fe$_2$O$_3$ it is a commonly formed corrosion product when conditions are mildly reducing and so has similar importance to the Fe$_2$O$_3$. The XRD pattern of the magnetite sample purchased from Sigma-Aldrich is indicative of magnetite, with no observable impurities (reference pattern 00-19-0629).
3.1.6 Analysis of Sherwood sandstone from the Hollington quarry

Sandstone is a naturally occurring sedimentary rock with no clearly defined composition other than predominance of α-quartz. In addition to the quartz, a variety of minerals are found in sandstone depending on the geology of its location including iron oxides which give it its red/brown colouration. It is of importance to this thesis as 90% of the UK’s overburden rock is sandstone and so it is likely to be in the far-field of any geological disposal facility.

The powder X-ray diffraction pattern of the sandstone shows two clearly dominant silicate phases, predominantly α-quartz (reference pattern 00-46-1045) and microcline (KAlSi₃O₈) (reference pattern 00-19-0932).
Figure 3.11 Reflectance XRD pattern of sandstone from Hollington quarry. ICDD patterns for quartz (00-46-1045, blue) and microcline (00-19-0932, green) overlaid.

3.1.7 Summary of preparation and characterisation

A selection of starting materials were analysed by powder X-ray diffraction and infra-red spectroscopy to access the purity and composition of each material. Except for the calcium hydroxide, all materials appeared to be pure within the detection limits of the technique with no evidence of additional phases in either XRD pattern or infra-red spectrum of each material. Several attempts were made to synthesise a high purity calcium hydroxide phase from precipitation of calcium chloride and sodium hydroxide. Initial attempts in air resulted in the formation of calcium hydroxide (major phase) with calcium carbonate (minor phase) as an impurity. However, it was determined that by both working in carbon dioxide free conditions and storing starting reagents under anaerobic conditions that it was possible to form calcium hydroxide with no evidence of the calcium carbonate phase in the XRD pattern. A method for forming carbonate-free cement phases using a 10% sucrose solution was adapted to prepare pure calcium hydroxide in air. This resulted in a quick and simple method for synthesising approximately 97% pure Ca(OH)$_2$ without the need to
work extensively in anaerobic conditions (percentage purity approximated using error in analysis techniques).

3.2 Ageing of iron oxides Fe$_{1-x}$O, Fe$_2$O$_3$ and Fe$_3$O$_4$ under geological disposal facility conditions

Iron oxides are of significance in this study, due to the large amount of iron that is likely to be present in the repository both in stainless steel containers which are used in waste storage, and the surrounding rock itself (as iron oxides/hydroxides). Due to the highly alkaline and reducing geochemical conditions (high pH, low Eh) that are likely to be encountered within a deep cementitious Geological Disposal Facility, an array of corrosion products will be produced and these solids will evolve over the lifetime of the repository. A detailed understanding of the interactions between soluble radionuclides and the complex inventory of product surfaces is required for a detailed post closure safety case.

This section investigates the alteration of a selection of iron oxides under different sets of experimental conditions that are relevant to deep geological disposal. This information will be essential to understanding radionuclide sorption at both batch and synchrotron based sorption experiments.

This set of experiments focusses on three iron oxides Fe$_{1-x}$O (majority iron(II)), Fe$_2$O$_3$ (iron(III)) and Fe$_3$O$_4$ (mixed valence iron(II)/iron(III)).

Fe$_{1-x}$O, the iron(II) example has been selected as it is analogous to the iron mineral wüstite. As previously discussed, iron phases will be abundant in a GDF, when the repository is deoxygenated Fe(II) species will be stabilised and Fe$_{1-x}$O is one such example.

Fe$_2$O$_3$ and Fe$_3$O$_4$, synthetic analogues of the minerals haematite and magnetite, are examples of Fe(III) and Fe(II)/Fe(II) iron phases, it has been shown that corrosion of stainless steel such as the ILW canisters under GDF conditions generate both of the phases.

The experimental conditions were varied to take into account different pH range 7-13.3 including the use of a 95% saturated Ca(OH)$_2$ solution to mimic the effect of the concrete used to encapsulate nuclear waste in the stainless steel drums. The reason for using this wide pH span was to represent different stages of life in a repository accelerated by varying the conditions including pO$_2$/pCO$_2$ levels to mimic atmospheric to anaerobic conditions. Time intervals in contact with the different pH solutions were also varied to give an insight into the kinetics of the material transformation over
time. Although the corrosion of stainless steel under alkaline conditions has been studied, the effect on the corrosion products has not been covered in the literature and so the results in the section are necessary to allow the project to progress.

3.2.1 Iron oxide change in morphology determination by XRD

In all cases, there was no discernible change in the XRD patterns for any of the iron oxides under any of the exposure conditions. This was expected for the more stable iron oxides magnetite and haematite as they are both found commonly in nature over a wide range of conditions, however it was surprising that the FeO remained apparently unaltered as wüstite is sensitive to oxygen concentration. Since XRD is a bulk technique, the lack of major change in the XRD patterns can be explained by the reaction of the solution with the solids only taking place on the surface of the material; due to the penetrating nature of X-rays the bulk is being probed, and any surface transformations will be a low percentage of the volume of the solid in the beam and so any transformation at the surface is unlikely to be detected by XRD comparison of initial and final XRD patterns for the three iron oxides can been seen in figures 3.12-3.14. To examine more closely what was happening at the surface, a technique more sensitive to surface changes was required and SEM was chosen to visualise this behaviour.

Figure 3.12: Transmission X-Ray diffraction pattern of FeO before and after 720 hours exposure to pH7 solution unreacted shown in black reacted shown in red
Figure 3.13: Transmission X-Ray diffraction pattern of Fe$_2$O$_3$ before and after 720 hours exposure to pH7 solution unreacted shown in black reacted shown in red

Figure 3.14: Transmission X-Ray diffraction pattern of Fe$_3$O$_4$ before and after 720 hours exposure to pH7 solution unreacted shown in black reacted shown in red
3.2.2 Surface morphology by SEM

3.2.2.1 Fe$_{1-x}$O SEM images as a function of time and pH

The SEM images indicate that the surface of the Fe$_{1-x}$O was altered during the reaction with the selected solutions. The sample set that shows the most surface alteration is at pH 7 and a selection of images at varying time intervals is shown in figure 3.15. After eight hours, the surface has already changed significantly where needle like crystals are visible, this is presumed to be formation of goethite or a similar iron oxyhydroxides. The formation of these phases is seen until the 168 hour time frame, when the formation of spherical particles is observed. These spherical particles are likely to be the formation of haematite, or another more stable iron 3+ oxide. This would suggest that the reaction has reached equilibrium with the surface forming a protective coating of iron 3+ oxide which will block any further reaction of the bulk Fe$_{1-x}$O by passivation.

![Figure 3.15 SEM images of Fe$_{1-x}$O after treatment at pH 7 all images taken at the same magnification](image)

A similar reaction pathway is observed for the pH 10 data set; however, the reaction is considerably slower than that of the pH 7. Where the needle shaped crystals are not observed until after the 72 h time frame. Another indication that the process has happened slower is the size of the crystallites formed. The needle shaped crystals in the pH 10 samples are larger than those at pH 7 as they formed slower and hence initial nucleation acted as a seed crystal. A selection of time lapsed SEM images is shown in figure 3.16.
This trend continues in the data collected at pH 13, however in this case little or no formation of the needle shaped crystals is observed. In contrast to the crystal formation on the surface observed at lower pH, at pH 13 there is evidence of surface dissolution. After 8 h the surface is covered in corrosion pits that appear to be hemispherical in nature. As time progresses the particle size decreases. This dissolution can be attributed to the ferrous iron being more soluble than ferric iron, and hence some of the surface will dissolve until the solubility limit is reached\(^\text{130}\). This trend for the surface alteration being inhibited by the increase in alkalinity can be attributed to the formation of a passive iron oxide layer over the surface of the iron oxide and hence prevention of the formation of oxyhydroxides and stable iron(III) oxides. The images are shown below in Figure 3.17.
Figure 3.17: Pitting of the surface at pH 13 of the Fe$_{1-x}$O samples all images taken at the same magnification.

The samples exposed to 95% saturated calcium hydroxide solution shows similar SEM images to those of the hyper alkaline data set at pH 13. However, there is evidence of some smaller crystallites present on the surface; the clearest image of this in the 72 h image. This is almost certainly due to solid calcium hydroxide precipitating on the surface of the parent material.

Figure 3.18 Surface of Fe$_{1-x}$O treated with saturated Ca(OH)$_2$ solution all images taken at the same magnification.
3.2.2.2 Fe₂O₃ SEM images as a function of time and pH

The series of SEM images for the evolution of the Fe₂O₃ surface under pH 7 conditions is shown in figure 3.19. The images do not indicate that there is any significant change in morphology with only crystals with spherical morphology being evident over the time period.

![Figure 3.19](image)

**Figure 3.19 Surface of Fe₂O₃ after treatment at pH7 at varying time intervals all images taken at the same magnification.**

Initially it appears as if the particle size is decreasing as a function of time, which could be attributed to the dissolution of the surface. However, in the final image after 720 h of exposure there appears to be a collection of larger particles suggesting that some form of equilibrium has been reached and the smaller particles aggregated. This could be explained by dissolution of the solid phase, and the remaining crystals acting as a nucleation site which eventually leads to larger particle formation and reduced surface area. This process is known as Ostwald ripening where smaller particles dissolve into the solution more readily than the larger ones.

A similar phenomenon is seen in the time lapse of images for the pH 10 samples, however this process appears to be slower. This could be due to the pH being above the point of zero charge of the material and due to the alkalinity, a passive layer will be formed, this in turn prevents the dissolution of the surface and slows down the process.
Figure 3.20 SEM images of Fe₂O₃ samples aged at pH 10 all images taken at the same magnification.

At pH 13, the particle size is significantly smaller, and agglomeration of the particles is evident in the longest time frame image.

Figure 3.21 SEM images of Fe₂O₃ treated at pH 13 as a function of time all images taken at the same magnification.
The samples that were subject to 95% calcium hydroxide vary significantly from the rest of the Fe$_2$O$_3$ samples images are shown below. There appears to be no significant change in morphology of the surface particles throughout the 0-160 h exposure time, and the Fe$_2$O$_3$ sample varies from the Fe$_{1-x}$O samples with no evidence for surface precipitates of calcium hydroxide. The image of the sample with 720 h exposure time shows a significant change in morphology, where the particles have aggregated to form rods.
3.2.2.3 Fe₃O₄ SEM images as a function of time and pH

An analogous set of experiments to those performed on Fe₂O₃ and Fe₁₋ₓO were then performed on magnetite.

![SEM images of Fe₃O₄ particles exposed to pH 7 solution as a function of time](image)

The images do not appear to show any sign of morphology change, with the cuboidal crystals observable throughout. The same is seen in the pH 10 samples shown below in Figure 3.24. No sign of morphology changes or dissolution of the iron oxide, with the particle size remaining consistent throughout.

**Figure 3.23 SEM images of the Fe₃O₄ particles exposed to the pH 7 solution as a function of time**

*all images taken at the same magnification.*
Figure 3.24 SEM images as a function of time for magnetite at pH 10 all images taken at the same magnification.

A similar set of images were observed for the samples subjected to the pH 13 solution shown below in figure 3.25. The effect is even less evident where the initial and final images are very similar.

Figure 3.25 SEM images of Fe₃O₄ after treatment at pH 13 all images taken at the same magnification
One possible explanation for this is that the point of zero charge for Fe$_3$O$_4$ is significantly lower than that of the other two iron oxides and hence all measurements are above the point of zero charge resulting in a passive layer being formed and protecting the surface under all conditions.$^{132}$

The samples exposed to the 95% calcium hydroxide solution further back up these findings where there is no significant change in morphology as shown in figure 3.26.

![Figure 3.26 SEM micrograph of Fe$_3$O$_4$ after treatment with calcium hydroxide solution.](image)

### 3.2.3 Dissolution kinetics of Fe$_{1-x}$O, Fe$_2$O$_3$ and Fe$_3$O$_4$

The dissolution rates of Fe$_{1-x}$O, Fe$_2$O$_3$ and Fe$_3$O$_4$ were investigated by measuring the iron concentration in the supernatant liquid by ICP-MS after exposure of the iron oxides to deionised water solutions at pH 7, 10 and 13. A similar procedure was also used to determine the dissolution rate for calcium hydroxide solution. The objective of this group of experiments was to determine whether there are significant differences in the rate and quantity of dissolution of the three iron oxides with the pH of the added solution.
The rate of dissolution can be represented by the following equation:

\[
Rate = - \frac{d[A]}{dt} = k[A]^n
\]

Equation 3.2

Where:

\begin{align*}
A & = \text{Concentration of analyte} \\
k & = \text{rate constant} \\
n & = \text{reaction order}
\end{align*}

Assuming that the dissolution of the iron oxide phases is first order the equation can be represented as:

\[
Rate = - \frac{d[A]}{dt} = k[A]^1 = k[A]
\]

Equation 3.3

This can be rearranged to give the following equation:

\[
\frac{d[A]}{[A]} = -kdt
\]

Equation 3.4

Integrating both sides gives the following:

\[
\int_{[A]_0}^{[A]} \frac{1}{[A]} d[A] = -\int_{t_0}^{t} kdt
\]
Equation 3.5

Integration of equation 3.5 gives:

\[ \ln[A] - \ln[A]_0 = -kt \]

Equation 3.6

This can be rearranged to give:

\[ \ln \left( \frac{[A_t]}{[A_0]} \right) = -kt \]

Equation 3.7

By plotting the natural log of the analyte concentration against time, the slope of the line of the graph is equal to the rate constant since the equation is in the form \( y=mx \). The rate constant of the dissolution of iron oxides and of calcium hydroxide can be determined provided the dissolution follows first order kinetics.

3.2.3.1 Dissolution of the \( \text{Fe}_{1-x}\text{O} \) surface as a result of exposure to solutions of varying pH

The plot shown in Figure 3.27 gives the results obtained for the increase in iron concentration as a function of time for \( \text{Fe}_{1-x}\text{O} \) when exposed to the pH 7 solution. The plot appears to be near linear, however on close inspection it suggests that the rate of dissolution appears to be increasing. This can be explained by the apparent increase in surface area observed in the SEM images as the time in contact with the solution increased and the surface is eroded by the solution.
As stated, the rate constant for the dissolution of iron can be obtained by plotting the natural log of the decrease in iron as a function of time, the slope of the graph will determine the dissolution rate constant. The plot for Fe$_{3+x}$O when exposed to the pH 7 solutions is shown in Figure 3.28.
Using the slope of the graph the rate constant for the dissolution of Fe$_{1.3}$O when exposed to a pH 7 solution was determined to be $3 \times 10^{-11}$ seconds$^{-1}$. This suggests that when exposed to a pH 7 solution the dissolution kinetics are first order.

This process was repeated for the solutions at pH 10 and 13. In Figure 3.29 the increase in iron concentration in the solution is depicted as a function of time for the pH 10 solution.
The plot differs from the analogous plot for the pH 7 solution, where it is clearly apparent that the rate of dissolution is dropping off. This is consistent with the SEM images, as they showed the transformations happening on a slower time scale. This is likely to be due to the increased pH causing the formation of a protective passive layer which hinders further dissolution of the bulk material.

The results do not fully fit a linear regression; this could be due to the rate not being first order. On closer inspection of the results it could also be viewed that one of the points is an outlier and so the same principle as for the pH 7 examples can be followed. In this instance it would lead to a dissolution rate constant for the pH 10 samples of $1 \times 10^{-11}$ seconds$^{-1}$.

This value is three times smaller than that of the pH 7 sample. This value is consistent with the SEM results which indicate that the dissolution process is occurring at a noticeably slower rate than at pH 7 with less damage to the surface.
The same analysis was repeated for the pH 13 samples, shown in figure 3.31.

The results from the plot of iron concentration in the solution as a function of time are similar to the
results obtained from the pH 10 samples where the rate of dissolution rate appears to drop off and be approaching a saturation point, which is consistent with the hypothesis that at high pH a protecting passive layer is formed preventing the dissolution of the iron oxide surface, and these results are again in agreement with the SEM images.

The samples exposed to the 95% saturated calcium hydroxide solution show considerably different results to those seen previously. The concentration of iron in the solution initially increases rapidly, and then seems to reach equilibrium and the rate of dissolution slows. This can be seen in figure 3.33. To eliminate any colloidal particles of iron/calcium oxide/hydroxide which could produce false positives, the solutions were analysed using dynamic light scattering to check for any colloidal particles. The samples were also measured relative to a control standard to account for the difference in matrix, the results from these test samples were determined to be negative and so the results are a true depiction of the system studied.
Figure 3.33 Concentration of iron against time for Ca(OH)$_2$ solution

Figure 3.34 Natural logarithm of iron concentration against time for Ca(OH)$_2$ solution

$Y = -3 \times 10^{-11}X + 12.848$

$R^2 = 0.8222$
The plot used to determine the rate constant for the dissolution of the iron oxide surface clearly shows that the reaction is not first order as can be seen in Figure 3.34. One reason for this is due to evidence of precipitates that are likely to be Ca(OH)$_2$. The presence of the precipitates could begin to reduce the surface area in contact with the solution and as a result cause the dissolution of iron to slow.

3.2.3.2 Dissolution of the Fe$_2$O$_3$ surface as a result of exposure to solutions of different pH.

The results for the dissolution kinetic experiments for the Fe$_2$O$_3$ powders when exposed to the solutions varying in alkalinity and solution composition were treated in the same way as the Fe$_{1-x}$O samples. The plot for the Fe$_2$O$_3$ exposed to a pH 7 solution is given in Figure 3.35. The plot is different to that of the Fe$_{1-x}$O where the concentration of iron increases and then appears to plateau.

![Figure 3.35 Concentration of Iron against Time at pH 7 for Fe$_2$O$_3$](image-url)
The results plotted to determine the rate constant for the dissolution are shown in figure 3.36. As the results are non-linear, it would suggest that the process is not first order. On closer inspection of the results it could be that there are two separate first order processes occurring, one with a significantly faster rate constant than the latter.

Figure 3.36 Plot of Natural Logarithm against Time for Fe$_2$O$_3$ at pH 7

A similar trend is observed for the powder exposed to the pH 10 solution, where the iron concentration in solution increases rapidly at first and then begins to slow down. Compared to the previous Fe$_2$O$_3$ sample at pH 7 the increase in iron concentration in the solution increases notably faster as shown in Figure 3.37.
Figure 3.37: Iron Concentration as a Function of Time for Fe$_2$O$_3$ at pH 10.

Figure 3.38: Plot of Natural Logarithm of the Iron Concentration against Time for Fe$_2$O$_3$ at pH 10.

$$Y = -7 \times 10^{-12} X + 12.766$$

$$R^2 = 0.7279$$
This is also observed in the plot to determine the rate constant for the rate of iron dissolution shown in figure 3.38.

The graph is non-linear and the regression analysis suggests that the degree of linearity is less than that shown for the pH 7 results. This appears to be due to the points that correspond to the second process suggesting that as the pH is increased, the rate slows down; this is seen in the values of the rate constants obtained with the pH 10 being $7 \times 10^{-12}$ seconds$^{-1}$ vs $1 \times 10^{-11}$ for the pH 7.

The same trend is observed for the samples exposed to solutions with a pH value of 13, the results obtained are comparable with those seen for the pH 10 samples where there is a sharp increase in iron concentration followed by a plateau shown below in figure 3.39.
The values of the rate constants at pH 10 and pH 13 obtained are similar which would suggest that any effect that may be attributed to the pH seems to be redundant above values of 10. This is shown in figure 3.40 and with the pH 10 rate constant value being $7 \times 10^{-12}$ seconds$^{-1}$ vs $6 \times 10^{-12}$ for the pH 13.

The results for the samples exposed to the 95% saturated calcium hydroxide solution were similar to those obtained for the other samples in the Fe$_2$O$_3$ data set, as well as the Fe$_{1-x}$O samples exposed to 95% saturated calcium hydroxide solution, shown in figure 3.41.
The regression analysis of the kinetic plot shows the greatest divergence from non-linearity shown below in figure 3.42.
Figure 3.42 Plot of Natural Logarithm of the Iron Concentration against Time for the Fe$_2$O$_3$ sample in Ca(OH)$_2$ solution.

3.2.3.3 Dissolution of the Fe$_3$O$_4$ surface as a result of exposure to varying pH

The results for the dissolution kinetic experiments for the Fe$_3$O$_4$ powders when exposed to the solutions varying in alkalinity and solution composition were treated in the same way as the Fe$_{1-x}$O and Fe$_2$O$_3$ samples.

The plot for the Fe$_3$O$_4$ exposed to a pH 7 solution is shown in figure 3.43. The plot is similar to the plot for the Fe$_{1-x}$O, where the increase in iron in solution follows the same profile; the graph appears to be largely linear, however there is some evidence of the rate being faster at the beginning.
The kinetic plot is consistent with first order kinetics as outlined previously, giving a rate constant for dissolution of $2 \times 10^{-11}$ seconds$^{-1}$ shown in figure 3.44.

Figure 3.43 Plot of Iron Concentration against Time for the Fe$_3$O$_4$ sample at pH 7.

$$Y = -2 \times 10^{-11} X + 12.794$$

$R^2 = 0.9798$

Figure 3.44 Plot of Natural Logarithm of Iron Concentration against Time at pH 7 for Fe$_3$O$_4$. 

-135-
The results for the Fe$_3$O$_4$ solid in the pH 10 solutions are similar to those at pH 7.

The kinetic plot again shows good agreement with first order kinetics and has a rate constant similar to the pH 7 samples with a value of $2 \times 10^{-11}$ seconds$^{-1}$.

The kinetic plot does show some evidence that there is some divergence from linear as seen in the case of the Fe$_2$O$_3$ which seems to increase with the alkalinity, however not significant enough to affect the linearity. The plot of the natural logarithm of iron concentration against time is shown in Figure 3.46.
The results for the samples exposed to pH 13 solutions are in agreement with those obtained for the subsequent pH values are shown in Figure 3.47 and 3.48.
The kinetic plot is similar to the previous magnetite samples at lower pH and the value for the dissolution is the same as determined in the previous samples.

The plot of increase in iron concentration as a function of time for the Fe$_3$O$_4$ powder (figure 3.48) when exposed to the 95% saturated calcium hydroxide solution is similar to the previous results obtained. This is different to the previous two examples as the calcium hydroxide appeared to affect the dissolution kinetics.
This is further shown in the kinetic plot (figure 3.46) where the plot is linear, which is not observed in the Fe_{1-x}O samples. There appears to be a slight enhancement in the dissolution with a dissolution rate constant of 5 x 10^{-11} seconds\(^{-1}\).
3.2.3.4 Summary of iron oxide ageing experiments

The effect of solution composition and pH on three iron oxides relevant to geological disposal Fe$_{1-x}$O, Fe$_2$O$_3$ and Fe$_3$O$_4$ was investigated. The investigations were of the solid and liquid phases and looked for evidence to support the formation of secondary iron phases and dissolution of the iron minerals.

X-ray diffraction and FT-IR analysis did not determine the formation of any new crystalline phases or evidence for new functional groups being present. This can be attributed to the fact that the X-rays penetrate the surface into the majority bulk and so any phases formed on the surface of the crystals will not be observed using a conventional X-ray diffraction setup.

Evidence for the formation of phases formed on the surface of the powders was observed only for the Fe$_{1-x}$O powders. In this case formation of a needle like phase most likely an iron oxy-hydroxide is evident, later these crystals eventually look similar to those of the more stable Fe$_2$O$_3$. This phenomenon was observed for Fe$_{1-x}$O under all conditions, however as the alkalinity increased the transformation appeared to slow.

The dissolution rate of the iron surfaces was determined by analysis of the solution by ICP-MS, the dissolution rate constants were determined from graphical plots assuming that the dissolution would follow first order kinetics.

This was determined to be an approximation for the Fe$_{1-x}$O and Fe$_3$O$_4$ systems, however the Fe$_2$O$_3$ system clearly shows the kinetics is more complicated than first order. The introduction of the calcium hydroxide solutions also appears to alter the kinetics. In all cases the rate constant for dissolution decreases as the alkalinity increases which can attributed to the passive layer formation and is in agreement with the SEM images.
3.2.4 Further ageing experiments of the Fe$_{1-x}$O surface

3.2.4.1 Fe$_{1-x}$O Surface Alteration Experiments

3.2.4.1.1 X-ray diffraction study to determine crystalline phases present

In the iron oxide ageing experiments in section 3.2, the powders exposed to varying solutions of varying pH were analysed using laboratory based powder X-ray diffraction equipment shown in figure 3.51.

However, the standard laboratory apparatus was unable to determine any new phases after reaction since the bulk material was in vast excess compared to any material changes happening at the surface; the penetrating nature of the X-rays generating a signal relative to the majority bulk phase. These results are shown in the diffraction pattern figure 3.52. The bulk of the material is predominantly Fe$_{1-x}$O with much weaker reflections corresponding to iron metal and magnetite. An expansion of a single pattern is shown in Figure 3.52.
Figure 3.52 High resolution X-Ray diffraction pattern of FeO under varying solution conditions FeO reference pattern shown in pink with iron impurity shown in red

To determine the origin of the anomaly, as well as an attempt to observe any phases that may not have been observed under laboratory conditions, high-resolution synchrotron powder diffraction (HR-PXPD) analysis was carried out. The measurements using the HR-PXRD on both the reacted and unreacted samples agreed with the findings from the laboratory based study where no additional phases are determined to be present. The reflection barely observable in the laboratory based experiments was determined to be trace amounts of elemental iron. The presence of trace quantities of α-iron \([Fe^0]\) impurities could arise from two possible sources. Firstly, an excess of iron during the synthesis of starting material step which persist after reaction per the equation.

\[
Fe + Fe_2O_3 \rightleftharpoons 3FeO
\]

\textit{Equation 3.8}
The second alternative is related to the normal general formula of Fe$_{1-x}$O. This non-stoichiometric formula reflects the fact that the crystal structure of the material can accommodate a significant proportion of defects and iron can exist as both iron(II) and iron(III) in this lattice. Disproportionation reaction of the iron from divalent to trivalent occurs over a significant range allowing x to reach 0.14 easily. As a result, the excess material is ejected from the lattice as iron metal. The formation of defects in lattice systems is entropically favoured despite the loss in enthalpy associated with bond breaking as shown in Figure 3.53.

![Figure 3.53: Change in energy terms with an increasing number of defects](image)

The samples examined in these experiments were those of near neutral pH both in the presence and absence of sodium carbonate, as well as the hyper alkaline equivalent. The surface area is shown to increase in all cases, apart from the high pH where sodium carbonate was absent. This can be explained by the apparent dissolution of the iron oxide surface under all conditions apart from the hyper alkaline example, as the pH 12 sample with carbonate added buffered the pH to
approximately pH 9. Therefore as the other samples remained under alkaline conditions they do have a protective passive layer and so are affected less by the solution. This can be seen in table 3.1 showing the associated surface area with each sample.

Table 3.1 BET measurements to determine the change in surface area as a function of pH treatment.

<table>
<thead>
<tr>
<th>Na₂CO₃ NaOH (mol dm⁻³)</th>
<th>Surface area /m² g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₁₋ₓO unreacted</td>
<td>–</td>
</tr>
<tr>
<td>Fe₁₋ₓO pH 7</td>
<td>0</td>
</tr>
<tr>
<td>Fe₁₋ₓO pH 7 + C</td>
<td>0.1</td>
</tr>
<tr>
<td>Fe₁₋ₓO pH 12</td>
<td>0.01</td>
</tr>
<tr>
<td>Fe₁₋ₓO pH 12 + C</td>
<td>0.1</td>
</tr>
</tbody>
</table>

3.2.1.1.2 Changes in Fe₁₋ₓO morphology observed by SEM

FESEM results show that all reacted materials display surface alteration compared to the unreacted starting material. The systems that show the most significant alteration are those containing high concentrations of dissolved carbonate. Differences in alteration for anaerobic vs. atmospheric samples without NaHCO₃ are especially pronounced under hyper alkaline conditions and most likely can be attributed to the lack of an oxidized surface layer; under atmospheric conditions at High pH, surface iron(II) will rapidly oxidize to insoluble Fe(III) and passivate the surface.

Under anaerobic conditions however, the much more soluble Fe(II) will be released without impediment and the starting material may more easily be broken down into finer particle sizes. Diffraction did not show secondary phase precipitation in any of the experiments, and therefore the fine-grained materials in Figure 3.53 must represent an extremely small volume of non-Fe₁₋ₓO precipitates and most likely include fine-grained fragments and re-precipitates of Fe₁₋ₓO.
Figure 3.54 SEM Images as a Function of Sodium Carbonate and Sodium Hydroxide Concentration
3.3 Batch sorption experiments of uranyl species to materials relevant to geological disposal

The results in this section are from the interactions of aqueous uranium species with three iron oxides Fe$_{1-x}$O, Fe$_2$O$_3$ and Fe$_3$O$_4$ and calcium hydroxide which represents cement. Part of this section deals with the effect of pH on the extent of sorption of uranium to the solid iron oxides. As the pH is altered so too is the dominant uranium species in solution and this is shown by the plot of predicted uranium species in solution as a function of pH shown in figure 3.54. The figure was generated using the speciation software JCHESS$^{133}$, where the database had been modified to contain stability constants from the Hatches 20 database.

![Figure 3.55 Speciation Plot for Uranium as a Function of pH](image)

*Figure 3.55 Speciation Plot for Uranium as a Function of pH*

The effect of pH is important as the aqueous speciation of uranium varies considerably as the pH is altered as is shown in Figure 3.54. In addition to this, the surface will change with pH, if the surface is predominantly hydroxide terminated; the surface can vary from positive to neutral and finally negative.
3.3.1 Methodology

The sorption of radionuclides from solution onto a solid surface is usually investigated using the batch sorption method. The method allows the quantification of the extent of sorption to be calculated. The method followed is to add a certain volume of a known concentration of radionuclide solution to a known mass of solid. After equilibration, the radionuclide concentration remaining in solution is then measured. The concentration of radionuclide sorbed to the solid can then be calculated as the difference between the two concentrations. The distribution ratio, \( R_d \), can then be calculated. \( R_d \) is the distribution ratio for a given set of reaction conditions, for example temperature or pH. \( R_d \) is normally measured whereas \( K_d \) is the thermodynamic distribution ratio which is independent of reaction conditions apart from temperature and pressure.

The distribution ratio \( R_d \) is calculated as follows:

\[
R_d = \frac{A_i - A_f}{A_f} \times \frac{V}{M} \text{ cm}^3 \text{ g}^{-1}
\]

Equation 3.9

Where \( A_i \) and \( A_f \) are the initial and final concentrations respectively (mol dm\(^{-3}\)), \( V \) is the volume of the solution (L) and \( M \) is the mass of solid (g)

The batch method can be used to show how sorption alters when variables such as pH, ionic strength and complexing agents are changed or added to the system. This makes the batch method a powerful technique. However, there are some potential problems with the method e.g \( R_d \) can vary with surface area and surfaces can change due to oxidation.

3.3.2 Preliminary uranium sorption studies

The effect of pH on the sorption of aqueous uranyl nitrate to a range of solid phases relevant to geological disposal was investigated. The powders studied were

(i) Ca(OH)\(_2\)
(ii) Fe\(_{1-x}\)O
(iii) Fe\(_3\)O\(_4\)
(iv) Fe\(_2\)O\(_3\)

The greatest sorption of uranium was observed when using the Ca(OH)\(_2\) powder with the least sorption being observed on the Fe\(_3\)O\(_4\) powder. Increased sorption to all materials was observed in
the 95% saturated Ca(OH)$_2$ solution; this would suggest the matrix has a key effect on sorption or possible evidence for precipitate formation.

The pH was recorded when the solids had been separated from the solution. As expected, in the case of the Ca(OH)$_2$ the pH had been buffered by dissolution of the Ca(OH)$_2$, which at room temperature has a solubility of 0.173 g per 100 cm$^3$. In the case of the FeO and Fe$_2$O$_3$ the pH remained close to the initial pH with little variance. Therefore, not surprisingly when the results for the Ca(OH)$_2$ sorption experiment were plotted as a function of pH, within errors, a straight line was observed as is shown in figure 3.56.

The extent of sorption to calcium hydroxide is high, especially under the hyperalkaline conditions. As the surface, will be negatively charged and as the two dominant species of uranium in solution are both anionic uranium hydroxides, UO$_2$(OH)$_2$ and UO$_2$(OH)$_4$$^{2-}$, then surface sorption is unlikely due to electrostatic repulsion. The concentration of uranium used is under the saturation limit and verified by the control experiments. Therefore, the two possible reasons explaining the increased sorption are a calcium uranate CaUO$_4$ phase formed only when the uranium is exposed to the calcium.

![Figure 3.56 Plot of Rd for Uranium against pH for Ca(OH)$_2$](image-url)
hydroxide solid or incorporation into the solid phase; a phenomenon that has been reported in both similar systems namely calcite and dissimilar systems.

The results of the uranyl nitrate sorption experiments to the Fe$_{1-x}$O surface show initially a high level of sorption at near neutral pH. However, for the non-calcium hydroxide solutions, the extent of sorption decreases, this suggests that the primary sorption mechanism is surface complexation. As the pH increases, the speciation of uranium is dominated by anionic uranium species and so binding to the surface will be hindered as the alkalinity is increased. However, it has been shown that uranium incorporation into iron oxides is possible, also as Fe$_{1-x}$O is an iron 2+ oxides the uranium can be reduced by the iron oxide. The uranium-iron redox couple is well known and has been studied extensively.$^{46,78,79,81,84,86,88,134–153}$

![Figure 3.57 Rd values as a function of pH for Uranium for Fe$_{1-x}$O 95% saturated calcium hydroxide value shown in red](image-url)
Uranyl nitrate sorption to Fe$_2$O$_3$ is shown in figure 3.57. The trend in the results is similar to the Fe$_{1-x}$O although the extent of sorption under near neutral conditions is not as significant. As with the Fe$_{1-x}$O example the most likely description of what the results is that the sorption is due to surface complexation. In the case of Fe$_2$O$_3$, redox is unlikely to be a significant factor since iron is in the trivalent state and there is not significant evidence in the literature for uranium substitution for iron(III).

Sorption of uranyl nitrate to Fe$_3$O$_4$ surface is shown in figure 3.58. The results follow a similar trend to the other iron oxides previously studied, however the extent of sorption is significantly lower in all cases. This can be explained by the point of zero charge for Fe$_3$O$_4$ being lower than that of the other iron oxides resulting in less sorption.
Figure 3.59: Plot of $R_d$ values for Uranium against pH with Fe$_3$O$_4$
3.3.3 Effect of pH on uranyl sorption to iron oxides

Since the results from the preliminary sorption experiments indicated that the extent of sorption is dependent on the pH, the effect of pH was investigated further by generating more data points to allow the trend to be observed. Care was taken to ensure that the particle sizes used were similar to eliminate the effect of a change in surface area. The results are shown in figure 3.60.

![Graph showing the effect of pH on uranyl sorption](image)

**Figure 3.60: Comparison of Rₐ values as a Function of pH for FeO (black circles), Fe₂O₃ (red triangles) and Fe₃O₄ (green triangles)**

The plot of Rd against pH shows the same trend for each of the iron oxides with no discernible difference between any of the iron oxides used in this study. The sorption results show a steady decrease until the pH reaches approximately pH 10. At pH 10 and above, sorption decreases to almost zero. An explanation for the lack of uranium sorption is because the aqueous uranium species is negatively charged at these pHs and, the iron surface is also negatively charged because of deprotonation of the OH groups on the surface. Thus, electrostatic repulsion dominates.
4.3.4 Effect of dissolved carbonate on uranyl sorption to iron oxides

The effect of dissolved carbonate on the sorption of uranyl nitrate to the three iron oxides at both near neutral and hyper alkaline pH was investigated. The results of the experiments are shown in figure 3.61.

![Figure 3.61 R_d values for Uranium as a Function of Carbonate Concentration at variable pH](image)

These results show that at pH 7, uranium sorption decreases to all three solids as aqueous carbonate concentration increases due to the formation of soluble uranium carbonate species. Uranium sorption is much less at higher pH because of reasons discussed in section 3.3.

3.3.5 Summary of uranium batch sorption experiments

The sorption of uranium to a selection of iron solids was investigated as a function of pH. Under all conditions there was evidence for uranium sorption. The greatest sorption was found when Ca(OH)₂ was present. The increased removal of uranium from the aqueous phase is possibly due to a calcium uranate (CaUO₄) phase being precipitated, which is surprising as the system is not saturated. Sorption to the iron oxide solids in all cases shows a decrease in sorption as the pH is increased. Further investigation of the uranium sorption to iron oxides has shown that the extent of sorption
decreases as the pH becomes more alkaline and all the uranium remains in solution past pH10 which coincides with the surface being negatively charged as well as the dominant aqueous species being anionic in nature. It has also been shown that as the carbonate concentration increases the extent of sorption decreases. This can be attributed to uranyl carbonate species being soluble and hence the extent of surface bound uranium.
3.4 Aqueous Speciation of the Uranyl Carbonate

The aqueous speciation of uranium is of importance in gaining a deeper understanding into the interactions with mineral surfaces that may be pertinent to geological disposal. This requires the use of spectroscopic techniques. This section discusses the use of optical spectroscopy and NMR to study the uranium and carbonate respectively. A large portion of this work involves establishing experimental methods for both the uranium fluorescence spectroscopy and to a lesser extent the $^{13}$C NMR.

3.4.1 Photochemical Measurements of Uranium Species

Time Resolved Fluorescence Spectroscopy as discussed in section 2.2.1.1 is a useful technique for differentiating the chemical species of a fluorescent metal ion through analysis of characteristic excitation and emission spectra and decay (relaxation) lifetimes. The principal advantage over other spectroscopic techniques is the ability to determine in-situ metal speciation at environmentally relevant concentrations in solution and on ultra-thin surfaces.$^{152-158}$

Due to the spectral and temporal data being orthogonal to each other, it is possible to differentiate the metal species by two discrete variables allowing speciation to be determined, which is difficult by any other laboratory based method.

The technique is becoming a widely-used method for fundamental actinide & lanthanide studies. TRLFS is unique in being able to determine in-situ metal speciation at picomolar concentrations, which is essential when dealing with incipient corrosion of speciality metals or the alteration of ceramic and other materials used in the nuclear fuel cycle.

3.4.1.1 Determination of Uranium Molar Absorption Coefficient by UV-Vis Spectroscopy

To determine the experimental parameters required, as well as ascertaining whether it was possible to measure the uranium fluorescence with the fluorimeter mentioned previously, the absorption spectroscopy was studied. The uranyl solution was placed into a 4 cm$^3$ quartz cuvette, with a path length of 1 cm$^3$ and the absorption spectrum was collected between 350 and 550 nm using a Cary 500s uv-vis spectrophotometer. The absorption spectrum is shown in figure 3.62 and clearly shows an increase in absorption as expected, the absorption maximum is not greater than one in any of the measurements obtained ensuring all measurements were within the linear dynamic range of the spectrophotometer.
The peak maximum at 412 nm was used to determine the molar absorption coefficient. This was obtained by plotting absorption against concentration, and as the path length is 1 cm$^3$ the molar absorption coefficient was determined from the slope of the line. The plot is shown below in Figure 3.63.
The molar absorption coefficient for aqueous uranyl nitrate was determined to be 9.05 dm$^3$ mol$^{-1}$ cm$^{-1}$. This is a comparatively small value when compared to most dyes$^{161}$, which would suggest that the emission intensity may be low which could result in poor sensitivity.

**3.4.1.2 Uranyl Nitrate Emission Measurements**

A series of uranyl nitrate samples were prepared by serial dilution of the 0.1 mol dm$^{-3}$ to a concentration of 1x10$^{-4}$ mol dm$^{-3}$ in factors of 10. All measurements were made using the Edinburgh instruments FLS 900 using a picosecond pulsed diode laser emitting at 375 nm. The obtained spectra are shown in figure 3.64.
The obtained spectra show that with an excitation wavelength of 375 nm, the emission spectra intensity is reduced rapidly as the uranium concentration is decreased, and as a result the $0.1 \times 10^{-3}$ mol dm$^{-3}$ is barely visible, this is in agreement with the absorption data and the low molar absorption coefficient.
3.4.1.3 Investigation of the effect of bandwidth on the fluorescence intensity of 0.1 mol dm$^{-3}$ uranyl nitrate solution

In an attempt to gain extra signal to noise, the effect of altering the bandwidth of both the entrance and exit slits was investigated. The 0.1 mol dm$^{-3}$ solution was used in all measurements discussed in this section. Instead of using the laser, the xenon arc lamp was used as the excitation source again with an excitation wavelength of 375 nm. The overlay plot of the emission spectrum for bandwidths ranging from 1 to 7 nm is shown in figure 3.65.

![Figure 3.65 Emission Spectrum of Uranyl Nitrate as a Function of Wavelength](image)

The plot shown in Figure 3.66 is a clear trend that depicts the fluorescence intensity increasing as the sample is exposed to more light. As the detector was exposed to more light, and as expected the signal intensity is increased, care was taken to not over expose the detector and therefore intensities were kept well below $10^6$ counts per second at all times.

Further analysis of the data shows that the process is not linear. Figure 3.65 plots fluorescence intensity at the 510 nm peak as a function of bandwidth.
The results show an increase in intensity when increasing the bandwidth. This suggests that previous measurements were not allowing the cross section to be saturated and hence the emission intensity was not sufficient to allow lower concentrations to be observed.

As the bandwidth increased it was determined, by peak and trough analysis, that the resolution decreased and so the gain in intensity by opening the bandwidth increases the light intensity. In addition, the gain in intensity is achieved because of a decrease in resolution and so for some samples this will need to be considered.
3.1.4.4 Quantum Efficiency of Uranyl Nitrate

The quantum efficiency of uranyl nitrate was investigated. This process involved measuring the absorbance and emission of the sample as well as a known standard. Samples with an absorbance of 0.1 corresponding to a concentration of 0.01 mol dm$^{-3}$ of uranyl nitrate were measured. The reference used was sodium anthracene figure 3.49. To determine the quantum efficiency of the unknown sample, equation 3.10 was used.

$$\phi_{unk} = \frac{\phi_{std} \cdot F_{unk} \cdot q_{std} \cdot A_{std}}{q_{unk} \cdot A_{unk}}$$

Equation 3.10

Where $\phi_{unk}$ and $\phi_{std}$ are quantum yields of the unknown and standard respectively, and $F$, $q$ and $A$ are their respective fluorescence values ($F$), number of photons emitted by the excitation source ($q$), and the absorbance values of the unknown and standard.

![Figure 3.67 Structure of Sodium Anthracene](image)

By comparing the absorbance and emission values for the uranyl nitrate from section 3.4.1.1 and 3.4.1.2 and the sodium anthracene solution, it was determined that the quantum efficiency of uranyl nitrate was 0.83 %.
3.4.1.5 Effect of a Non-Complexing Ligand on the Uranyl Nitrate Emission Spectrum

The uranyl nitrate spectra shown in figure 3.63 show that at lower concentrations the background is increased and so there is a significant error in the quantification of low concentrations of uranium. Previous studies suggest that the best uranium fluorescence spectra are obtained when the anion present in solution is non complexing and so perchlorate is preferred.$^{115}$

Aqueous uranyl perchlorate was obtained from precipitating sodium diuranate ($\text{Na}_2\text{U}_2\text{O}_7$) by the addition of sodium hydroxide to a uranyl nitrate solution, and then dissolving the precipitate in dilute perchloric acid using the experimental described in section 2.2.2.4. The powder diffraction pattern of sodium diuranate ($\text{Na}_2\text{U}_2\text{O}_7$) is shown in figure 3.69.
3.4.1.6 Uranyl Perchlorate Limit of Detection

The effect of having a non-complexing ligand on the emission spectra was studied by preparing a dilution series of uranyl perchlorate spectra by dissolving sodium diuranate in 2 mol dm$^{-3}$ perchloric acid. All samples were prepared under a nitrogen atmosphere and with boiled and degassed deionised water. The concentration range was between 10 $-0.1 \times 10^{-3}$ mol dm$^{-3}$. The samples were then placed into 4 cm$^3$ plastic cuvettes fitted with stoppers and the lids sealed with parafilm. Measurements were collected using the Edinburgh instruments FLS 900, using the 375 nm picosecond pulsed diode laser as the excitation source and with the bandwidth set to 1 nm. The spectra obtained are shown in figure 3.70.

Figure 3.69 Reflectance Powder Diffraction Pattern of Sodium diuranate ICCD pattern 01-072-2295 shown in pink.
Figure 3.70 Spectra of Uranyl Perchlorate in Perchloric Acid as a Function of Concentration

The uranyl perchlorate spectra are similar to those obtained for uranyl nitrate under similar conditions, where all emission peaks are observed in the same region of the spectrum, which shows that by substituting the nitrate for perchlorate the aqueous uranium chemistry remains unaltered. The resulting uranyl perchlorate results are smoother than those obtained for the uranyl nitrate, and as a result the signal to noise is improved. Through extrapolation, the limit of detection was determined to be in the order of $1 \times 10^{-6}$ dm$^{-3}$. This will allow environmentally relevant uranium concentrations to be studied by this technique using this system.

3.4.1.7 Temporally Resolved Uranium Emission Data

The fluorescence lifetime of the excited uranyl nitrate species was studied using the Edinburgh instruments FLS900 using a 375 nm picosecond pulsed diode laser as the excitation source.
In this experiment a 0.1 mol dm$^{-3}$ uranyl nitrate solution was placed into a sealed quartz cuvette and placed into the fluorimeter. The sample was excited at the 510 nm peak using a 375 nm diode laser operating at 50 MHz repletion rate. The decay of the excited uranyl species was observed by TCSPC with a time base of 20 microseconds the resulting decay profile is shown below in Figure 3.70.

![Figure 3.71 Decay of Uranyl Nitrate fluorescence lifetime](image)

The results obtained for the decay of the uranyl nitrate shows evidence for a signal exponent which fits to a decay lifetime of 1.372 μs. This agrees with the values obtained by other spectroscopic methods.

### 3.4.1.8 The Effect of Sodium Carbonate on the Uranyl Absorbance and Emission Spectra

The effect of inorganic complexants on the solubility of uranium has been an area of interest for some time, and is pertinent to geological disposal$^{20,162}$. The uranyl carbonate system has been shown to increase the solubility of uranium, therefore understanding the speciation of uranyl carbonate complexes formed is of interest. This work focusses on the effect of aqueous sodium carbonate on the absorbance and emission spectra of uranyl perchlorate under near neutral conditions.
The absorbance spectra are shown in Figure 3.72. The absorbance is shown to increase as the carbonate concentration increases until the carbonate uranyl ratio reaches 2:1 in which case the absorbance decreases sharply. This can be better observed by focusing on the absorbance at 330 nm a plot of which can be seen in Figure 3.56. One possible explanation for this is that when the carbonate uranyl ratio reaches 3:1 the uranyl tricarbonate species $\text{UO}_2(\text{CO}_3)_3^{4-}$ is dominant. The species has been shown to quench the fluorescence emission which could result from the lack of absorbance seen in figure 3.72.
The linear section of the plot can be seen in Figure 3.74. This part of the spectrum can also be attributed to aqueous speciation and the promotion of ligand to metal charge transfer; a phenomenon that is commonly observed with other actinides and lanthanides\textsuperscript{163}. This effect is concentration dependant and will produce a linear response until the tricarbonate species is formed and then the absorbance decreases.
Figure 3.74 Plot of Absorbance against Uranium:Carbonate Ratio.

Figure 3.75 Graph of Intensity against Wavelength

Absorbance at 330 nm with varying uranium:carbonate mol ratios

Figure 3.74 Plot of Absorbance against Uranium:Carbonate Ratio.

Figure 3.75 Graph of Intensity against Wavelength
However, the results shown in figure 3.72 and 3.73 do not agree with the emission data shown in figure 3.74. The emission data show a linear rise as seen in the absorbance spectrum however this begins to decrease steadily after carbonate uranyl ratio of 0.5 is achieved and again all emission decreases past the carbonate uranyl ratio 2:1. This is better observed by looking at the maximum intensity as a function of the carbonate to uranyl ratio figure 3.75.

![Emission at 515 nm for varying uranium:carbonate mol ratios excitation 330 nm](image)

**Figure 3.76. Emission Spectrum Intensity at 515nm for varying U:CO$_3^{2-}$ Concentrations**

This can be attributed to uranyl self-absorption, or additionally, the carbonate could be quenching the emission. In order to determine which one of these possibilities is most likely this would require a temperature study to be performed as the effect of the quencher should be reduced as the temperature is decreased.
3.4.2 Effect of Uranyl on Carbonate NMR Spectrum

This section will discuss the limit of detection for the instrumentation used, the carbonate system as a function of pH in the absence of any uranyl species and the effect of temperature. The uranium carbonate system was studied using a Bruker 500 MHz spectrometer, in order to increase the signal to noise, all measurements were recorded using Na$_2^{13}$CO$_3$. All uranium containing samples use a FEP insert as a safety precaution in case the NMR tube breaks while in the magnet.

Before running any NMR samples containing uranium it was necessary to determine whether the samples were diamagnetic or paramagnetic, as diamagnetic molecules have a negative effect on any spectra obtained.

3.4.2.1 Magnetic Susceptibility Measurements of Uranyl Nitrate and Uranyl Carbonate

The calculated magnetic moments are shown below:

\[
\begin{align*}
\text{UO}_2(\text{NO}_3)_2.6\text{H}_2\text{O (solid)} & = 0.57 \text{ BM} \\
\text{UO}_2\text{CO}_3 \text{ (aqueous)} & = 0.37 \text{ BM}
\end{align*}
\]

The experimental values for both the solid uranyl nitrate and the aqueous uranyl carbonate are consistent with the compounds having no unpaired electrons. This is in agreement with the uranyl molecular orbital diagram shown in figure 3.77. Both compounds are negligibly paramagnetic, this was determined by the small negative readings obtained from the Evans balance as paramagnetic species are repelled by an external magnetic field.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{molecular_orbital_diagram.png}
\caption{Generic molecular orbital diagram of actinyl ion}
\end{figure}
3.4.2.2 The Effect of Using a FEP Insert on Signal to Noise

Due to the uranium being both chemically toxic and radiotoxic, as well as the spectrometer being used not being solely dedicated to examining radioactive species, an inert plastic insert was used to limit the likelihood of the spectrometer becoming contaminated in the event of failure of the glass NMR tube.

In order to assess the effect of the FEP insert on the signal to noise, a 0.03 mol dm$^{-3}$ solution of sucrose was prepared by dissolving 0.1027 g in 10 cm$^3$ of D$_2$O. The sample was then placed into a glass NMR tube, as well as the FEP insert. Both samples were filled with sufficient volume to achieve the required height of solvent in the NMR tube for the instrument to allow the shim settings to achieve good signal line-shape.

The NMR spectrum shown in Figure 3.78 compares the sample in presence and absence of the FEP insert. In the spectrum acquired with the insert, the baseline has a distinctive broad peak with a range of 100 ppm at approximately 120 ppm; this can be attributed to the insert itself. This is consistent with a solid fluorinated plastic that displays significant chemical shift anisotropy.

There is a significant difference in the time taken to achieve comparable signal to noise in the instance of the glass NMR tube signal to noise of 18.6 was achieved in 5 h, where the FEP sample
required 20 h. This can almost certainly be attributed to the decreased sample volume due to the smaller diameter of the liner approximately a 2 fold decrease 0.7 cm³ to 0.35 cm³.

3.4.2.3 Isotopically Enriched Sodium Carbonate Limit of Detection

Due to the small difference between the populations of the ground and excited states, NMR is not one of the most sensitive spectroscopic techniques, and therefore the limit of detection for the carbonate/bicarbonate system was investigated.

The overlay NMR spectrum is shown below in figure 3.79, with ascending spectra decreasing in concentration.

![Figure 3.79 NMR spectra as a Function of Concentration](image)

The spectra clearly show a decrease in signal intensity as the concentration is decreased as expected, however there was also a clearly visible trend that as the concentration decreased the signal observed shifted to the right suggesting that the carbonate was becoming gradually more shielded as the concentration was decreased.
This was determined to be due to a change in the solution chemistry of the system as the carbonate/bicarbonate system is a complex equilibrium with the carbonate and bicarbonate being the two dominant species.

\[ \text{HCO}_3^- \rightarrow \text{CO}_3^{2-} \]

Equation 3.11

One parameter that is able to alter the equilibrium of the two aqueous species is pH. As carbonate concentration is known to affect the pH of a solution, this was a possible source of the observed shift. As there was no buffer added to the system to prevent adding complexity to an already challenging system, there was a strong possibility that absorption of carbonate from the carbon dioxide in the air was the cause of the shift. pH measurements and modelling of the solution using the program JCHESS confirmed that the pH was likely to have drifted. The results of these calculations are given in table 3.3

<table>
<thead>
<tr>
<th>pH</th>
<th>Calculated Chemical shift / ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.00</td>
<td>149.76</td>
</tr>
<tr>
<td>7.50</td>
<td>149.83</td>
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<tr>
<td>8.00</td>
<td>149.97</td>
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<td>150.64</td>
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<td>9.00</td>
<td>151.88</td>
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<td>9.50</td>
<td>156.52</td>
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<tr>
<td>10.00</td>
<td>161.54</td>
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<tr>
<td>10.50</td>
<td>168.01</td>
</tr>
<tr>
<td>11.00</td>
<td>170.22</td>
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<td>11.50</td>
<td>171.50</td>
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<td>171.78</td>
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<td>12.50</td>
<td>171.92</td>
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<tr>
<td>13.50</td>
<td>171.97</td>
</tr>
<tr>
<td>14.00</td>
<td>171.97</td>
</tr>
</tbody>
</table>

4.4.2.4 Effect of pH on the $^{13}\text{CO}_3^{2-}/H^{13}\text{CO}_3^-$ chemical shift

Upon closer investigation of the results obtained from the limit of detection experiments, a chemical shift was detected that was associated with the carbonate bicarbonate ratio. The change in chemical shift of the $^{13}\text{C}$ signal could be attributed to the change in pH and this effect was investigated further. Moret et al identified a similar result in their work with carbonate and acetate$^{164}$. 
The chemical shift expected for the carbonate and bicarbonate species were modelled using Gaussian 05 with the B3LYP basis set, where the two species were relaxed in order to obtain the minimum energy structure. The chemical shift was then predicted for both species with a chemical shift of 149.74 ppm obtained for the hydrogen carbonate and 171.97 ppm for the carbonate. The chemical shifts were normalised by referencing to the predicted chemical shift of benzene to allow usable values to be obtained.

These values were then used along with the mole ratio of the carbonate/bicarbonate predicted by JCHESS to allow theoretical chemical shift data to be obtained as a function of pH, the modelled results are depicted in figure 3.80.

![Figure 3.80 Predicted Mole Fraction of Carbonate/bicarbonate as a Function of pH](image)

The modelling suggests that the chemical shift can be correlated with the change in pH as the solution equilibrium shifts towards the carbonate species.

A series of samples ranging from pH 7 to 13 were prepared where the concentration was fixed at 0.1 mol dm\(^{-3}\) to allow data with good signal to noise to be collected. The pH of the samples was controlled by the addition of NaOD and trace metal analysis grade HNO\(_3\), solution compositions are shown in table 3.4.
Table 3.4 Measured pH of Solution

<table>
<thead>
<tr>
<th>pH</th>
<th>$H^+$ added / mol dm$^{-3}$</th>
<th>$OH^-$ added / mol dm$^{-3}$</th>
<th>Measured pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.00</td>
<td>1.16E-02</td>
<td>N/A</td>
<td>7.04</td>
</tr>
<tr>
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<td>1.05E-02</td>
<td>N/A</td>
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<td>N/A</td>
<td>8.00</td>
</tr>
<tr>
<td>8.50</td>
<td>9.80E-03</td>
<td>N/A</td>
<td>8.55</td>
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<tr>
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<td>N/A</td>
<td>9.01</td>
</tr>
<tr>
<td>9.50</td>
<td>8.10E-03</td>
<td>N/A</td>
<td>9.45</td>
</tr>
<tr>
<td>10.00</td>
<td>5.50E-03</td>
<td>N/A</td>
<td>10.03</td>
</tr>
<tr>
<td>10.50</td>
<td>2.50E-03</td>
<td>N/A</td>
<td>10.59</td>
</tr>
<tr>
<td>11.00</td>
<td>N/A</td>
<td>N/A</td>
<td>10.97</td>
</tr>
<tr>
<td>11.50</td>
<td>N/A</td>
<td>3.00E-03</td>
<td>11.56</td>
</tr>
<tr>
<td>12.00</td>
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<td>1.40E-02</td>
<td>12.02</td>
</tr>
<tr>
<td>12.50</td>
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<td>4.00E-02</td>
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<tr>
<td>13.00</td>
<td>N/A</td>
<td>1.50E-02</td>
<td>13.09</td>
</tr>
</tbody>
</table>

The results clearly show agreement with the modelling where the chemical shift follows the pattern suggested; a chemical shift is observed at approximately 163 ppm at pH 7 and moves to 171 ppm at pH 13. There is also a peak observed at 125 ppm in the pH 7-9 samples which can be attributed to aqueous CO$_2$. The relative intensities between the 125 and 163 ppm peak are indicative of the conversion from CO$_2$ to HCO$_3^-$, where the 125 ppm peak decreases and the 163 ppm peak increases as pH increases. Another piece of information that supports the finding of the modelling is the variation in $T_1$ relaxation times of both the $^{13}$C and $^1$H nuclei. These results are presented in Table 3.5.
Table 3.5 T1 Relaxation Time Data as a Function of pH

<table>
<thead>
<tr>
<th>pH</th>
<th>$^{13}$C Chemical shift / ppm</th>
<th>$^{13}$C T1 relaxation / s</th>
<th>$^{1}$H Chemical shift / ppm</th>
<th>$^{1}$H T1 relaxation / s</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.00</td>
<td>163.08</td>
<td>26.71</td>
<td>4.77</td>
<td>22.05</td>
</tr>
<tr>
<td>7.50</td>
<td>163.10</td>
<td>27.60</td>
<td>4.77</td>
<td>17.36</td>
</tr>
<tr>
<td>8.00</td>
<td>163.10</td>
<td>58.20</td>
<td>4.78</td>
<td>22.06</td>
</tr>
<tr>
<td>8.50</td>
<td></td>
<td></td>
<td></td>
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<td>9.00</td>
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<td>9.50</td>
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<tr>
<td>10.00</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>10.50</td>
<td>163.54</td>
<td>43.27</td>
<td>4.78</td>
<td>15.76</td>
</tr>
<tr>
<td>11.00</td>
<td>167.55</td>
<td>29.08</td>
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<td>15.90</td>
</tr>
<tr>
<td>11.50</td>
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<td>57.45</td>
<td>4.79</td>
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<td>12.50</td>
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<td>56.18</td>
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</tr>
<tr>
<td>13.00</td>
<td>171.26</td>
<td>73.97</td>
<td>4.78</td>
<td>15.47</td>
</tr>
</tbody>
</table>

A trend is observed in the T1 relaxation data. The $^{13}$C T1 increases as the pH is increased, and this corresponds to a decrease in the T1 relaxation of the $^{1}$H signal. This can be justified by suggesting that as the pH is increased, the mole ratio of the HCO$_3^-$ decreases as does the dynamic exchange with the protons in solution and this is reflected in the T1 relaxation times.

These findings suggest that the free carbonate in a solution can be used to determine the pH of the solution in situ. It is particularly important to notice that the pH can be determined from a series of measurements that are independent of each other, not just relying on the chemical. This information can serve as a reference when studying the uranyl carbonate systems to reassure that the equilibria have remained constant when the pH has been adjusted.
Figure 3.81 Change in chemical shift as Function of pH
3.4.2.5 Effect of Temperature of the $^{13}$C Chemical Shift of Sodium Carbonate

To conclude the section on characterising the carbonate system in the absence of any uranyl species, it has been reported in the literature\textsuperscript{164} that temperature has an effect on the carbonate chemical shift.

Two variables were investigated – i) the effect of temperature and ii) the effect of concentration. Three samples were prepared from a 0.1 mol dm$^{-3}$ stock solution of Na$_2^{13}$CO$_3$ to give concentrations of 0.1, 0.01 and 0.001 mol dm$^{-3}$, as previously the samples were prepared in a nitrogen atmosphere and placed into an FEP insert before being placed into a glass NMR tube. The samples were placed into the NMR spectrometer and allowed to equilibrate, NMR spectra were recorded at temperatures between 25 and 50 °C with 5 °C intervals.

The spectral overlay for the 0.1 mol dm$^{-3}$ is shown in figure 3.82 the signal shifts in a linearly from 167.1 to 167.35 ppm, this gives a small but measurable shift of 0.25 ppm over a 25°C temperature range.

![Figure 3.82 Variation in NMR Chemical Shift of Carbonate as a Function of Temperature](image)

The aqueous speciation was subsequently modelled using JCHESS, and a plot of normalised concentration against temperature was generated as shown in figure 3.65. The model suggests that the pH should be decreasing but this theoretical situation does not account for the observed trend.
Another observation is that the carbonate concentration is increasing over the temperature range. An increase in the carbonate concentration could account for the shift observed because of the change in aqueous speciation predicted in figure 3.83.

A different trend is observed in the 0.01 mol dm$^{-3}$ spectra as shown in figure 3.84. In this instance the signal follows a polymeric trend from 166.8 to 166.65. As this does not follow the same trend as the 0.1 mol dm$^{-3}$ sample it would suggest that the process is kinetic as opposed to thermodynamic.

The modelled data are presented in a plot of normalised intensity as a function of temperature shown in figure 3.83.

Figure 3.83 Speciation as Function of Temperature
This shift can be explained as due to a decrease in the pH of the system and in the concentration of the \( \text{CO}_3^{2-} \). Where an increase in the other carbonate species is observed and hence the observed chemical shift.
A similar trend is observed in the 0.001 mol dm\(^{-3}\) spectra where the observed chemical shift moves from 164.5 to 164.0 ppm over the temperature range 25 to 45 °C, however the signal then moves in the opposite direction to 164.2 ppm at higher temperature.

The speciation modelling, figure 3.85, suggests that as previously seen in section 3.4.2.5, the pH decreases and the HCO\(_3^-\) increases. However, at ca. 50°C, the NaHCO\(_3\) trend change as is seen in the figure.

Therefore these experiments suggest that speciation modelling can aid in explaining the observed NMR spectra as well as showing that the effect that temperature has on the carbonate chemical shift is linked to the concentration.
3.4.2.6. Uranyl carbonate NMR Spectra

The effect of uranium on the carbonate NMR spectrum was studied by preparing a range of samples of varying carbonate concentration with a constant uranium concentration fixed at 1x10^{-3} mol dm^{-3} and a varying carbonate concentration between 1x10^{-3} mol dm^{-3} and 0.1 mol dm^{-3}. Samples were prepared from a stock solution of 0.1 mol dm^{-3} solution of Na\(_2^{13}\)CO\(_3\) and the correct volume of 1000 ppm (w.v) ICP standard uranium in 2% HNO\(_3\). All samples were fixed to pH 7 by the addition of deuterated sodium hydroxide in order for the data to be comparable with the fluorescence measurements discussed previously. All samples were prepared under a nitrogen atmosphere, samples were transferred to a FEP NMR tube insert and then placed into a glass NMR tube and the data collected using a Bruker 500 MHz NMR spectrometer. The spectra are shown in Figure 3.70.

The overlaid NMR spectra clearly show two signals. One signal at 163 ppm and another at 170 ppm. There is a trend whereby increasing the carbonate concentration increases the signal observed at 163 ppm. Previous literature suggests that the signals observed correspond to two separate uranyl
carbonate species \( \text{UO}_2(\text{CO}_3)_3^{4-} \) and \( \text{(UO}_2)_3(\text{CO}_3)_6 \). However, the signals observed in the experiment would suggest that the peak at 163 ppm corresponds to the free carbonate species which at pH 7 will be dominated by \( \text{HCO}_3^- \), the peak observed at 170 ppm remains relatively constant in height and so corresponds to the uranyl carbonate species,

### 3.4.2.6 Summary of uranium carbonate NMR measurements

Using both NMR and fluorescence spectroscopy to determine the aqueous speciation of the uranyl carbonate system shows promise. By using the free carbonate/bicarbonate peaks coupled with the variance in \( T_1 \) relaxation time, it is possible to accurately determine the pH or the sample in situ with great sensitivity. The expected chemical shift was predicted and modelled accurately and these results could prove to be a valuable resource in future work for others studying uranium speciation.
3.5 X-ray absorption measurements

The work in this section is focussed on the interaction of the uranyl ion with the Fe$_{1-x}$O surface. X-ray absorption spectroscopy will allow a holistic view of the binding mechanism to be determined. The work in this chapter has been published, and the manuscript can be found in the supplementary information section.

3.5.1 XANES analyses

The U LIII-edge XANES spectra for the Fe$_{1-x}$O samples show significant differences in the edge positions and intensities of spectral features. XANES spectra for uranium show that at near neutral to moderately alkaline pH, U(VI) is reduced to U(IV) by the iron oxide surface. The three lower spectra in figure 3.88 indicate reduction to U(IV), are similar to spectra previously published for uraninite$^{165}$ At pH 12, with high pCO$_2$ the solution pH drifted to pH 7, and therefore this spectrum resembles the experiments completed at near neutral pH. In contrast to the other uranium adsorption experiments onto Fe$_{1-x}$O, without carbonate present at pH 12 the oxidation state of U(VI) was unchanged with XANES similar to previously published U(VI) species$^{166}$. In this experiment the pH did not drift.

![Figure 3.88 U XANES spectra for uranium reacted with FeO](image)

**Figure 3.88 U XANES spectra for uranium reacted with FeO**
The XANES spectra collected at the iron K edge can be seen in figure 3.89 and show no evidence of changing which is consistent with other X-Ray experiments carried out previously in this thesis.

Figure 3.89 Fe XANES spectra for uranium reacted with FeO
3.5.2 EXAFS analyses

The results for the samples reacted with U(VI) are in good agreement with previous studies. Reduced species of U(IV) were also observed when the absorption of uranium onto iron-bearing minerals was investigated167–169.

The experimental and simulated k3-weighted χ spectra of the samples analysed by EXAFS are presented in Figure 3.89 and the Fourier Transform (FT) of these spectra are shown in Figure 3.90. The U(IV) adsorbed on Fe1-xO shows well resolved oxygen features. Fits of the Fourier transform resulted in a distorted polyhedron of 5-6 first shell oxygen atoms. One or two present at an average distance of R ≈ 2.25 Å and four additional oxygen’s at R ≈ 2.38 Å.

Figure 3.90 U EXAFS spectra for uranium reacted with FeO
Figure 3.91 U Fourier transform for uranium reacted with FeO

Table 3.6 U bond distances and coordination number for uranium reacted with FeO

<table>
<thead>
<tr>
<th></th>
<th>O/O</th>
<th>O/Oeq</th>
<th>O/Oeq2</th>
<th>C</th>
<th>Fe</th>
<th>Fe2</th>
<th>U</th>
</tr>
</thead>
<tbody>
<tr>
<td>U LIII-edge</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeO pH12 U + C</td>
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<td>1.7</td>
<td>4.5</td>
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<td>0.9</td>
<td>1.1</td>
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<tr>
<td></td>
<td>R (Å)</td>
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<td>3.55</td>
<td>3.77</td>
<td>3.88</td>
</tr>
<tr>
<td></td>
<td>s² (Å²)</td>
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<td>0.0094</td>
<td>–</td>
<td>0.0031</td>
<td>0.01</td>
<td>0.011</td>
</tr>
<tr>
<td>FeO pH6 U</td>
<td>CN</td>
<td>1.4</td>
<td>4.4</td>
<td>–</td>
<td>1</td>
<td>1.3</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>R (Å)</td>
<td>2.28</td>
<td>2.37</td>
<td>–</td>
<td>3.44</td>
<td>3.63</td>
<td>3.86</td>
</tr>
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<td></td>
<td>s² (Å²)</td>
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<td>0.0079</td>
<td>0.0093</td>
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<tr>
<td>FeO pH6 U + C</td>
<td>CN</td>
<td>1.9</td>
<td>4.0</td>
<td>–</td>
<td>1.5</td>
<td>1.6</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>R (Å)</td>
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<td>2.4</td>
<td>–</td>
<td>3.47</td>
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<td>0.0111</td>
<td>0.0148</td>
<td>0.0066</td>
</tr>
<tr>
<td>FeO pH12 U</td>
<td>CN</td>
<td>2.1</td>
<td>3.5</td>
<td>4.8</td>
<td>2.4</td>
<td>0.9</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>R (Å)</td>
<td>1.82</td>
<td>2.21</td>
<td>2.35</td>
<td>2.81</td>
<td>3.49</td>
<td>–</td>
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<tr>
<td></td>
<td>s² (Å²)</td>
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<td>0.0052</td>
<td>0.0061</td>
<td>0.0094</td>
<td>0.0014</td>
<td>–</td>
</tr>
</tbody>
</table>
Figure 3.92 presents a model of the EXAFS data for U(IV) on Fe$_{1-x}$O. In the fixed pH 12 solution, the FT profile resembles the U(VI) uranyl species with two axial oxygen atoms at R = 1.82 Å and six to eight oxygen atoms in a split equatorial plane at R = 2.21 Å and R = 2.35 Å respectively. The fit confirms that the linear uranyl (O=U=O)$_2^+$ configuration is maintained at high pH (see Figure). In order to improve the fit, three paths of multiple scattering (MS) involving the U-O$_{ax}$ path at twice the distance were included. In contrast with the high pH Fe$_{1-x}$O sample, only one oxygen atom could be fitted in the first shell at R = 1.96 Å and four to five in a split equatorial plane at a distance of R = 2.24 Å and R = 2.7 Å respectively. These results are similar of those found for an uranate [UO$_4$] species. Fe shells were resolved well in all samples at distances greater than those pertaining to the first shell oxygen atoms. The fitted U-Fe distances are in good agreement with those published for uranium adsorbed onto Fe-minerals$^{135,143}$ thus confirming surface attachment.

3.5.2.1 Summary

The aims of this section were to gain detailed insights into three aspects of reactivity pertinent to GDF conditions: (1) to investigate the surface changes of Fe$_{1-x}$O altered with hyperalkaline fluids, (2) to quantify the adsorption of U hyperalkaline conditions onto Fe$_{1-x}$O and (3) to determine the local coordination chemistry of the adsorbed radionuclides. SEM and HR-XRPD results indicated that the surface area of Fe$_{1-x}$O increased with increasing pH and carbonate concentration. In addition, pH and carbonate concentrations also affected the adsorption of uranium dramatically, with decreasing adsorption at increasing pH and carbonate concentrations. Furthermore, results of XRD and EXAFS analyses show that uranium is adsorbed directly onto material edge sites in Fe$_{1-x}$O.
3.6 Sandstone diffusion experiments

3.6.1 Introduction
In the absence of water movement by advection, radionuclides can move by diffusion. To investigate the diffusion of uranium, thorium and technetium through sandstone, experiments were conducted using the methods detailed in section 2.2.5.

3.6.2 Dynamic experiments
3.6.2.1 Porosity $^3$H
The porosity of the 45 cm$^3$ sandstone blocks was determined using a tritium tracer. In these experiments, it was assumed that the HTO interaction with the rock was negligible and the kinetic isotope effect was ignored. The diffusion experiments were allowed to run for a period of 20 days. Tritium was measured in the external fluid after approximately one day with $C_{\text{max}}$ being reached after 12 days.

![HTO Diffusion Sandstone Block Overlay C/C_{Max}](image)

**Figure 3.94 Diffusion Through Sandstone (3 replicates)**

The experiments were carried out in triplicate. The three replicates all show good agreement; however, there is some deviation in the time taken to reach $C_{\text{max}}$ which can be attributed to the experiments using core samples which will vary slightly in their characteristics since they are...
mineralogical in nature and suffer from geological variation. The results from the three replicates were therefore averaged as shown in Figure 3.95.

Figure 3.95 Averaged Diffusion Data for 3 Replicates

3.6.2.2 3H recovery from the sandstone core

The three sandstone cores were removed from the YCL solution and placed into fresh YCL. This alters the concentration encouraging mass transfer of tritium from the block to the receiving water.
Recovery of tritium was observed from all the cores. However, as most the HTO was in the receiving water the diffusion gradient is much less steep than in the previous experiment with the significantly higher HTO concentration. The results of the recovery experiments also suggesting that the majority of the HTO was recovered in the initial experiment.

3.6.2.3 $^{99}$Tc Diffusion

The migration of technetium through sandstone at high pH was investigated using a $^{99}$Tc spike. The technetium was present as TcO$_4^-$ and therefore was expected not to be retarded by the rock.
The experiment was conducted in duplicate. The results showed that Tc breakthrough was slightly retarded when compared to tritium breakthrough with $C_{\text{max}}$ of Tc being reached after 16 days. These results suggested that the rock slightly retards the diffusion of the pertechnetate ion. The results also show that, as with tritium, the activity of Tc in the external fluid reaches $C_{\text{max}}$. The experiment conducted in ICL, after ageing the cores in YCL for a period of 6 months, shows breakthrough after 4 days which is noticeably slower than with the YCL experiment. This may be due to the porosity of the system being decreased, because of precipitating calcium rich phases.

3.6.2.4 Uranium and Thorium

Experiments to study the migration of uranium and thorium under high pH conditions were conducted. Both thorium and uranium are largely insoluble at high pH, this experimental limitation was overcome by ensuring a constant source of uranium and thorium into the solution which was achieved by forming precipitates, which would ensure a source of uranium and thorium at their respective solubility limits.

Initially the results were surprising showing a significant uranium and thorium concentration in the receiving water after a relatively short period. It is unlikely that the uranium and thorium had reached breakthrough after a period of one week, due to the small concentration gradient that would be driving the diffusion within the system. It was also observed in all replicates which would suggest that it is an artefact of the system. Some sandstone deposits have been shown to contain
uranium, upon submerging the sandstone core in the highly alkaline simulant cement leachate it is plausible that the uranium and thorium have been leached from the sandstone core. This theory was given more validity upon acid digestion of the disaggregated sandstone.

Table 3.8 uranium and thorium concentration in Holligton sandstone

<table>
<thead>
<tr>
<th>Replicate</th>
<th>Conc $^{238}$U / mol dm$^{-3}$</th>
<th>Conc $^{232}$Th / mol dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.53E-07</td>
<td>6.13E-08</td>
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<tr>
<td>2</td>
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<tr>
<td>3</td>
<td>7.18E-07</td>
<td>9.62E-08</td>
</tr>
</tbody>
</table>

The acid digestion determined that the levels of uranium and thorium detected in the receiving water were less than the mass found within the sandstone block. This was further checked by analysing the receiving water of the experiments without the presence on any radionuclides. The results obtained show similar levels of both uranium and thorium in the receiving water.

Table 3.79 Uranium and thorium concentration in blank samples

<table>
<thead>
<tr>
<th>Blank No</th>
<th>Conc $^{238}$U / mol dm$^{-3}$</th>
<th>Conc $^{232}$Th / mol dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.46E-08</td>
<td>7.82E-08</td>
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<tr>
<td>2</td>
<td>4.22E-08</td>
<td>3.64E-08</td>
</tr>
<tr>
<td>3</td>
<td>5.44E-08</td>
<td>3.48E-08</td>
</tr>
<tr>
<td>4</td>
<td>2.89E-08</td>
<td>8.96E-08</td>
</tr>
</tbody>
</table>

This suggests that the uranium and thorium diffusion experiments had not reached breakthrough and that the concentration of uranium and thorium in the receiving water is part of the system.

To determine the solubility limited concentration of the two actinides in the YCL, the supernatant liquid from the precipitate formation was analysed. These results gave much higher concentrations that expected, especially in the case of the thorium which gave an average concentration of $1 \times 10^{-5}$ mol dm$^{-3}$. One possible cause of this is that a proportion of the colloidal thorium in solution may have passed through the 0.22µm filter stage and upon acidification of the sample resulted in a
higher concentration of thorium. More in depth solubility experiments will be conducted to determine the thorium concentration in the YCL.

**Figure 3.97: Uranium diffusion through sandstone as concentration against time**

**Figure 3.98: Thorium diffusion as a function of time**
In both cases of the uranium and thorium experiments breakthrough has not been observed. The sacrificed cores were then analysed by auto radiography to determine the extent of migration through the cores. No uranium was observed suggesting that migration had not occurred. This ties to some work carried out on a project that considered the migration of uranium and thorium through NRVB.

A similar set of experiments were conducted using cement cores showed a similar effect. Although these experiments were not conducted as part of the work reported in this thesis, the cores were analysed by EXAFS by the author of this thesis. The results are therefore reported here. The results of the EXAFS investigation are also included in a paper which is included Appendix 7.2.

Samples from the solubility experiments were ground for EXAFS analysis using an agate pestle and mortar before mixing with cellulose to yield a concentration of approximately 2000 ppm. A 40 mg sample was placed into a Perspex sample holder, sealed with three layers of Kapton® tape and then heat sealed under nitrogen atmosphere. The EXAFS measurements were performed at the B18 experimental station at the Diamond Light Source, UK\textsuperscript{122}. This beamline is designed to collect bulk EXAFS analyses rapidly by using the Quick EXAFS mode. The energy of the beam was calibrated against the K-edge first derivative of a Y foil, defined at 17,038 eV. Measurements were conducted at the U LIII-edge in fluorescence mode using a nine element Ge detector mounted perpendicular to the incoming beam. The sealed samples were placed into a clamp so that each sample was positioned at 45° relative to the incoming X-ray beam. The EXAFS spectra were further corrected for remaining self-absorption using the Fluo algorithm in Athena 0.9.18\textsuperscript{170}. EXAFS w(k) values were refined from the raw data by standard procedures, including background subtraction, normalization of absorption and conversion to momentum and k space. For each sample ~34 spectra were averaged to improve the signal-to-noise ratio. The spectra were then analysed with Artemis 0.9.18 and the phase/amplitude functions were calculated by FEFF6. The theoretical fits were performed in R-space.
EXAFS spectra for these precipitates resemble those collected from the solubility experiments described above. The latter were tentatively identified as U(VI) oxy-hydroxides as the data show a good fit to the co-ordination numbers and scattering paths from becquerelite crystal data.

A diffusion profile for HTO through the disaggregated sandstone under optimised conditions is shown below in figure 3.100.
3.6.3 Tc-99 diffusion through disaggregated sandstone using the diffusion cell method

The effects of the pH and matrix of the cement leachate have been investigated of the migration of TcO$_4^-$ through disaggregated Hollington sandstone. The cement leachates used are as follows:

- YCL - Young cement leachate (13.1)
- ICL – Intermediate cement leachate (12.3)
- OCL – Old cement leachate (10.4)
- GW – Ground water (7.2)

The cells were dismantled after a period of 20 Hours and analysed by liquid scintillation counting. The results were normalised and plotted in figure 3.101.
The overlay shows that as in the core diffusion experiments that the pertechnetate moves slower than the HTO. However there does appear to be a noticeable difference between the cement leachates. Below is a plot of distance from spike as a function of pH.

**Plot of distance from Max as a Function of pH**

\[ y = 0.1554x + 1.1652 \]

\[ R^2 = 0.9747 \]
The plot would suggest that as the pH of the system is increased the extent of transport is increased. This is not the same as observed in the core experiments. One possible explanation could be related to the trace iron minerals associated with the sample which above pH 10 the surface is negatively charged. This would result in the negatively charged pertechnetate ion being electrostatically repelled by the surface leading to increased transport as observed. The difference with the core experiments can be accounted for by the differences in the system. The material is disaggregated and so will have greater porosity and more flow paths, as well as the material not being aged in the cement leachates so in the diffusion cell case porosity is not a problem that is encountered and so the surface interaction is all that is being observed in this system.
Chapter Four: Conclusions
4.0 Conclusions

Iron oxides, calcium hydroxide and Sherwood sandstone were used in this thesis to represent stainless steel corrosion products, the cement matrix used to stabilise the radioactive waste form and the host rock surrounding the engineered facility respectively. In order to simplify the systems being studied, pure single phase materials were chosen where possible. Commercially available materials were purchased and subjected to powder X-ray diffraction and FT-IR analysis. The purity of the commercially available iron oxides was good for Fe$_2$O$_3$ and Fe$_3$O$_4$ with no crystalline impurity phases identified in the powder diffraction patterns. In the case of Fe$_{1-x}$O, small amounts of iron metal and Fe$_3$O$_4$ were evidenced in the powder diffraction pattern. In the case of calcium hydroxide, the commercially available sample was found to contain substantial amounts of calcium carbonate as an impurity phase. As sandstone is a natural material, there was no alternative but to use the material in its natural state which was shown by X-ray diffraction to contain majority impurity phases of quartz and feldspar. This material was also analysed using ICP-MS following total acid dissolution.

Calcium carbonate was identified as a problematic impurity in the calcium hydroxide phases, as calcium carbonate has been shown to be an efficient complexing agent for uranium and improve its solubility. There a method to product high purity calcium hydroxide in house was developed. The process took several iterations in order to be optimised, but the methodology always involved precipitation of calcium hydroxide from mixing two solutions of calcium chloride and sodium hydroxide. Preparing the compound under oxic conditions was initially problematic and so a procedure for synthesis under anaerobic conditions was developed. However subsequent attempts in oxic conditions with the calcium chloride and sodium hydroxide being prepared in a 10% by weight sucrose solution resulted in high purity calcium hydroxide being formed using a much simplified method.

As one of the primary aims of this thesis was to allow the interaction between the solid phases and specific radionuclides of interest to be determined, it was important to understand how the surface of the solid phases altered when exposed to the solution conditions of varying pH. A set of experiments to determine changes in the solid and solution composition were conducted on the iron oxides over a timescale of 720 hours. The X-ray diffraction patterns did not show any significant changes in the phases present, however this was explained by XRD only probing the bulk of the sample and so any surface phases are not likely to be included. SEM imaging of the surface of the powdered iron oxides was performed and the SEM images show a decrease in particle size as the
exposure time increased. In the case of the Fe$_{1-x}$O, evidence for the formation of needle like iron oxy-
hydroxide phases was observed which eventually from spherical crystals similar to those observed
for the Fe$_2$O$_3$ after aging. These findings are in full agreement with the literature and suggest that
Fe$_2$O$_3$ is the most stable iron oxide in GDF conditions. This phenomenon was observed for Fe$_{1-x}$O
under all conditions, however as the alkalinity increased, the transformation appeared to slow.

The solution chemistry was monitored for changes in pH and increase in iron concentration; the pH
remained stable throughout the period which suggested that the sampled had been sealed
appropriately and that carbonation had not occurred, as well as there being no significant
dissolution of the iron surface. This was supported by the ICP-MS results which showed the increase
in iron concentration in the solution was of the order of parts per billion. The increase in iron
concentration in the solution does reach equilibrium under the time scale measured. The results
were plotted in order for the rate of dissolution to be estimated, making the assumption that the
dissolution of the iron oxide surface would follow first order kinetics. This was determined to be a
good approximation for the Fe$_{1-x}$O and Fe$_3$O$_4$ systems; however the Fe$_2$O$_3$ system clearly shows the
kinetics is more complicated than first order. The introduction of the calcium hydroxide solutions
also appears to alter the kinetics. In all cases the rate constant for dissolution decreases as the
alkalinity increases which can attributed to the passive layer formation and is in agreement with the
SEM images.

As the Fe$_{1-x}$O surface is likely to be present as the geological disposal facility becomes deoxygenated
it was studied further, with the addition of aqueous sodium carbonate to see the effect of dissolved
carbonate species on the iron oxide surface. The X-ray diffraction patterns again do not show any
evidence for a change in phase; however the SEM images show that the extent of transformation of
the iron oxide surface is accelerated when the carbonate concentration is increased.

In order to assess the extent of sorption of uranium to the surfaces of interest, a typical batch
method was used. Initially a set of scoping experiments was conducted under a series of solutions
with varying pH where sodium hydroxide was used to vary the alkalinity. A 95% saturated calcium
hydroxide solution was also used to mimic cementitious conditions. In order to see the effect of
varying the pH, the uranium concentration was kept constant at 1x10$^{-6}$ mol dm$^{-3}$ to ensure the more
alkaline solutions were below the uranium solubility limit. The initial experiments determined that
the sorption decreased as the pH was increased. Except in the case of the calcium hydroxide or 95%
saturated calcium hydroxide solution where constant values were seen, typically much greater than
with the iron oxides. This was determined to be due to the dissolution of the calcium hydroxide
buffering the pH to approximately 12.3 resulting in all conditions being similar. The apparent increase in sorption can be attributed to co-precipitation of uranium with the calcium hydroxide as calcium uranate. The effect of pH on uranium sorption to the iron oxide surfaces was investigated further where a clear trend was observed as the pH was increased the extent of sorption decreased as seen previously. This was determined to be due to the formation of anionic uranium hydroxide species being formed as the pH is increased coupled with the iron oxide surface becoming negatively charged, the resulting electrostatic repulsion can be attributed to the decrease in sorption.

The effect of aqueous sodium carbonate on the sorption of uranium to iron oxides was investigated, again keeping the uranium concentration fixed and varying the carbonate concentration. The results show that as the carbonate concentration increased the extent of sorption decreased, suggesting that uranium affinity for the surface is decreased. This can be attributed to the formation of aqueous uranyl carbonate species which form preferentially over the iron oxide uranium surface complex.

The changes in behaviour observed in the uranium/iron oxide system in the presence of carbonate resulted in further investigations into the aqueous speciation of the uranium using spectroscopic methods. The fluorescent properties of uranium and the paramagnetic effect that the uranium has on the carbonate spectrum were utilised to investigate speciation by fluorescence and NMR spectroscopies. The aim was to determine the aqueous uranium speciation, which is typically hard to achieve with standard laboratory equipment. This resulted in the majority of the work focussing on instrument optimisation as well as the uranium free carbonate solutions being run as control experiments. The UV-Vis absorption measurements and fluorescence emission measurements are in good agreement with the literature, the molar absorption coefficient of 9.05 mol dm⁻³ cm⁻¹ and a quantum yield of 0.83%. It was determined that by using a non-complexing ligand such as perchlorate it was possible to measure uranium at concentrations relevant to geological disposal. A series of uranium carbonate samples were measured using the technique. Using NMR spectroscopy to determine the aqueous speciation within the uranyl/carbonate system has shown promise. By using the free carbonate/bicarbonate peaks coupled with the variance in T₁ relaxation time, it is possible to accurately determine the pH or the sample in situ with great sensitivity. The expected chemical shift was predicted and modelled accurately and these results could prove to be a valuable resource in future work for others studying uranium speciation.

Steady state diffusion of uranium, thorium and technetium was investigated using Hollington sandstone as a mimic of the extended natural environment of a GDF. These experiments adapted a
known technique for investigating the diffusion of radionuclides through cement to intact sandstone cores. The porosity measurements determined the technique was valid. The only radionuclide investigated that achieved breakthrough was the technetium, which is unsurprising as it will be present as the pertechnetate ion and anions are typically mobile in the environment. The uranium and thorium show no evidence for movement under the experimental conditions. This is further supported by analysis of a similar set of experiments where the precipitate was analysed by EXAFS and determined to be a becquerelite type phase which is very insoluble even at neutral pH values.
Chapter Five: Future Work
5.0 Future work

5.1 Iron oxide ageing experiments

In order to build on the iron oxide ageing experiments in this thesis, it would be of interest to examine the effect of particle size on the phases formed as a function of pH. This would allow a more accurate comparison of the change in surface morphology and iron dissolution. By using smaller particles, the rate should be increased as there is more reactive surface. In turn this may allow secondary minerals to be observed and characterised by X-ray diffraction which could not be achieved using the materials chosen due to the small quantity of corroded product in relation to large quantity of bulk. To allow for a more accurate estimation at the dissolution rate of the iron oxide surfaces, more sampling points should be investigated. It is suggested that these should be concentrated in the initial period and for the time periods between 168 and 720 hours as the gap between the two points may have biased the results and led to an inaccurate estimation of the dissolution rate. Due to the interesting results obtained from the samples exposed to the 95% saturated calcium hydroxide, it is suggested that this system should be investigated further to determine whether the calcium hydroxide affects the dissolution rate of the iron oxide surface. On a related note, adding in additional variables such as ionic strength and carbonate concentration which could be relevant to the GDF as the environment is expected to change as the repository ages.

5.2 Uranium sorption experiments

The uranium sorption experiments carried out show that as the pH of the solution is increased the degree of sorption to the iron oxide surfaces is decreased. In addition, as the concentration of carbonate is increased the affinity of the uranium for the iron oxide surface is also diminished. These experiments were conducted under very simplistic conditions to simplify the system and further work could focus on increasing the complexity of the experiments conducted to make them more reflective of the repository conditions. This could be achieved by investigating the effect of ionic strength since it has been shown in this work that the effect of calcium hydroxide on the system was to increase sorption. As all experiments used natural uranium the concentration was fixed, and so isotherms were unable to be plotted. By using an isotope of uranium with a higher specific activity such as $^{233}$U the measurements could be conducted radiometrically allowing much lower concentrations to be counted and so isotherms would be possible even under conditions where the uranium solubility limit is low.
5.3 Fluorescence Spectroscopy of Uranium

The fluorescence work is promising however using the current instrumentation it is only possible to analyse concentrations that are relevant under alkaline conditions. This is probably due to the low energy of the excitation source used in the measurements, which does not allow for saturation of the uranium cross section. Future work should consider using a laser excitation source with higher peak power to allow for this to occur. As the work has been in its infancy, there was not access to high quality reference spectra that would allow speciation to be determined, so future work could focus on analysing reference materials to allow a database to be established. This in turn would allow speciation to be determined in a laboratory setting. Cryogenic temperatures have been shown to increase the fluorescence yield as under cryogenic temperatures the analyte has fewer degrees of freedom and hence quenching is reduced, allowing lower concentrations to be detected.

5.4 NMR of Uranium Carbonate

The NMR work determined that the pH not only had an effect of the chemical shift of the associated carbonate peak but also the $T_1$ relaxation times of the carbonate and hydrogen carbonate. This could lead to extremely sensitive in situ pH measurements and so future work would focus on determining the efficacy of this. Due to the low concentrations of uranium that needed to be used to satisfy the safety criteria, the corresponding carbonate concentration was also decreased. These restrictions led to a large number of scans being needed to achieve suitable signal to noise which limited the number of measurements able to be completed. Repetitions/time requirements could be reduced by using a spectrometer with a more powerful magnet; however the more sensible option would be to run the samples at lower temperature as it decreases the line broadening and increases the resolution.

5.5 Diffusion of uranium, thorium and technetium through sandstone

The main drawback of the uranium and thorium diffusion experiments was that they used a solid source of uranium and thorium at the centre of the core. The precipitate was determined to be extremely stable and so limited movement was observed. By using radio-tracers with higher specific activity, low concentrations of radionuclide could be used and as a result diffusion could be observed. Finally adding a modelling approach to these measurements would allow a better understanding of the system and could be used to in a geological disposal safety case.
6.0 References


55. Chap-4-Freeze-and-Cherry-1979-GroundwaterGeology.pdf. 1979


57. Flow and Contaminant Transport in Fractured Rock - Jacob Bear, C-F.


115. Techniques, M. C. 2. Nuclear magnetic resonance spectroscopy. 30–61


118. Standardization, I. Environmental Analysis Using the ICS-3000 Ion Chromatography System.


166. Fletcher, K. E., Boyanov, M. I. & Thomas, S. H. U (VI) Reduction to Mononuclear U (IV) by Desulfitobacterium Species. 4705–4709 (2010).
7.0 Appendices

7.1 AMASS case for support
Atomic and Macro-scale Studies of Surface Processes: Towards a Mechanistic Understanding of Surface Reactivity and Radionuclide Blending Mechanisms (The AMASS Consortium)

Summary of the results and conclusions of recent work in the technological/scientific area. The research team has expertise in materials science and nanotechnology (Ryan1,3,5), environmental radiochemistry (Evans2, 7, Morris3), synchrotron-based spectroscopy and scattering (Morris, Mosselmans2, Ryan, Wogelius4), and computational and theoretical chemistry (Burton3, 1, 5). All members are experienced researchers with funding track records from e.g. NERC, EPSRC, EU, Leverhulme, Royal Society and work closely with the nuclear industry. Current funded research includes: membership of the NERC BIORAD Consortium (Morris (PI), Evans, Mosselmans); PI of the EPSRC Nanotechnology Grand Challenge for Solar (Ryan); and membership of the EPSRC DIAMOND Consortium (Evans, Morris, Ryan, Wogelius) and Nuclear FIRST and Materials DTCs (Burton, Morris, Ryan, Wogelius). We are currently involved in > £10 M active research in the nuclear area and have been awarded > 250 days beam time in competitive access bids to synchrotrons in the last 5 years. AMASS collaborators are members of research council (RC) colleges and have advisory roles in RC, EU and synchrotron related nuclear thematic programmes. Examples of recent work are:

1) Sorption mechanisms of actinyl complexes on calcite (Burton). We are investigating the sorption mechanisms of uranyl(VI) and neptunyl(V, VI), on the calcite 104 surface using both atomistic simulation and quantum (DFT) methods. Free energy paths have been computed which simulate reactions involving carbonate ligand exchange to understand the kinetics and stabilities of the species involved at the water-mineral interface. We are also studying actinyl adsorption on the mineral surface to interpret experimental observations. This approach provides fundamental understanding at an atomic / molecular level of RN sorption on calcite.

2) Organic complexants in radioactive waste disposal (Evans).

Recent work has focussed on the impact of organic complexants on the migration and sorption of radionuclides in the near- and far-fields of a GDF. Recent work examined the influence of humic acid (HA) on U(VI) sorption to kaolin. In the absence of HA 20-40% of the U(VI) was in solution, with more sorption occurring at higher pH. HA amended systems solubilised up to 90% of the uranium with higher solubilities at higher HA concentrations and higher pH values. When U sorption was mapped against HA sorption sensitivity analysis showed surface-bound HA is the controlling parameter for modelling these systems.

3) Radionuclide biogeochemistry (Morris). Recent work has focussed on radionuclide biogeochemistry in sediments with relevance to contaminated land. Most recently, we have for the first time observed microbiologically mediated reduction of the transuranic element neptunium, during ingrowth of Fe(II) bearing minerals in natural sediments. Reduction of Np(V) to Np(IV) had a significant effect on solubility. These results highlight the need for biogeochemical assessments of radionuclide behaviour in nuclear legacy management.

4) Atomic Structure of Oxide Surfaces (Ryan): Our work uses in-situ synchrotron techniques to probe structure and chemistry of materials. We are interested in the atomic arrangement of surface atoms and how this controls interactions with molecular species. In the figure, aLaO single crystal is found to be terminated by La-O planes with a 5% surface relaxation: this implies a new non-Ni mediated mechanism for surface O₂-exchange.
5) Polarization dependent EXAFS of uranyl surface complexes in simulated MAGNOX sludge. Comparison of glancing incidence radial distribution functions for uranyl a) co-precipitated and b) adsorbed onto a hydroxylated MgCl(111) surface which is structurally equivalent to Mg(OH)2, basal plane. Red is chi = 90, blue is chi = 0. c) Proposed uranyl-carbonato attachment mode based on EXAFS.

Where work has contributed to the UK’s competitiveness or to improving the quality of life. AMASS Consortium members have a significant body of research that has examined the fate of contaminants in natural and engineered environments and thus work on these issues continually. Our work has fed directly into the safety case for the UK Low Level Waste Facility; has been included in the CoRWM doc. 2543 R&D needs for geological disposal, and informs management and disposal of nuclear legacy materials at implementer, regulator and research council levels.

Specific expertise available for the research at the host organisations. All the institutions in this proposal have identified the nuclear sciences as a priority area and AMASS investigators have received £3.5M investment in state-of-the-art infrastructure and equipment to directly support their nuclear research over the last 2 years. AMASS members are networked into a vibrant research community, affiliations with EPSRC DIAMOND, NERC B/GRAD and the Nuclear FIRST- and Theory and Simulation of Materials-Doctoral Training Centres will benefit the proposed AMASS project. Additionally, we have expertise in the major synchrotron techniques including EXAFS (including μ-GH), XANES, SAXS, WAXS, reflectivity and diffuse scatter and have successfully applied for access to the major synchrotron facilities.

Mary Ryan (MR-Grant PI) is Reader in Materials Science and Nanotechnology at Imperial College London. Her research focuses on applied electrochemistry and in the processing, characterisation and surface stability of functional nanomaterials. She is an expert in the use of synchrotron approaches to studying materials in aqueous environments.

Neil Burton (NB) is Senior Lecturer in Computational and Theoretical Chemistry and he has been part of the pioneering effort in the UK into the development and application of hybrid, quantum mechanical and molecular simulation methods to study condensed phase reactivity and mechanism. Recent research focuses on the use of computational approaches to study radionuclide chemistry.

Nick Evans (NE) is Lecturer in Radiochemistry at Loughborough University. The majority of his research is on the chemistry of radioactive waste disposal, particularly the impact of organic complexants on the migration and sorption of radionuclides in GDF relevant environments. Katherine Morris (KM) is BNFL Endowed Research Chair in Geological Disposal at The University of Manchester. Her research interests focus on radionuclide biogeochemistry in natural and engineered environments specifically, in the processes controlling radionuclide fate in nuclear scenarios. She is an expert in the biogeochemistry and spectroscopy of long-lived radionuclides.

Fred Moselemans (FM) is Principal Beamline Scientist on the i18 Microfocus beamline at Diamond and has led the implementation of the UKs first μ-focused beamline. He has research interests in the actinides and lanthanides and is leading the implementation of a low-level radiochemistry lab at DIAMOND to facilitate in-situ measurements with U and Tc.

Roy Wogelius (RW) is Reader in Geochemical Spectroscopy at The University of Manchester. He is an expert in the use of synchrotron approaches in studying surface mineral reactivity in environmental systems. Current work includes diffusion in low permeability systems along with uranium speciation in magnesium-rich phases.

DESCRIPTION OF PROPOSED RESEARCH

1.1. Background and Motivation

The UK has an extensive and complex legacy of radioactive waste from over 60 years of military and civil nuclear technology and any 'new build' reactors will continue to add to this legacy. These wastes are some of the most hazardous materials ever generated by humans, and their appropriate management and secure disposal is vital. Management of these wastes has been described as 'one of the most demanding managerial, technical and environmental challenges facing the UK in the next century' and is likely to cost £100+ billion. Developing new, consortia in this area is particularly important given the erosion of the once world-leading UK science-base. Here, we bring together a new collaboration, the AMASS consortium, that proposes to examine surface reactivity and binding of key radionuclides at the mineral-fluid interface.

After many years of debate on the issue, deep geological disposal of the waste legacy was adopted as UK Government policy in 2008. At that time, the Nuclear Decommissioning Authority retained the Radioactive Waste Management Directorate (NWDA-RWM) for the delivery of a geological disposal facility (GDF) for higher activity wastes. The primary objectives of the GDF are isolation and containment of the radioactive material and several strategies will be employed within the engineered barrier system to optimize radionuclide (RN) retardation over geological timescales. As the radionuclides (RN) are solubilized their fate is determined by the conditions in the groundwater, and the surfaces of the constructed barrier system (EBS) encountered. For an adequate safety case to be developed the processes leading to radionuclide retardation, such as adsorption, co-precipitation, surface ligand exchange etc., must be mechanistically understood and quantified. Furthermore, for a predictive capability to be developed a holistic approach to the whole system must be adopted, and this must be studied at the length-scales appropriate to these processes, and models developed capable of describing the system at a molecular level. E.g. in the past sorption studies in this area have used the measurement of partition coefficients (Kd) to interpret RN behaviour in complex systems. This purely empirical approach is insufficiently robust to be used for mechanistic understanding of evolving, non-equilibrium systems.

Currently, there is no designated site for a Geological Disposal Facility (GDF); site selection will be completed by 2018. A volunteer host community, however, there is a clear need to continue to develop our understanding of the complex processes involved in geological disposal. For different waste types and different geological environments, a range of generic materials can be considered for use in the EBS (e.g. waste encapsulation materials, container materials and buffer, backfill and sealing materials) each with their own evolving function from short term physical containment to long term sorption and retardation properties.

This proposal describes integrated experimental and multi-scale modelling studies on selected key surfaces, which are designed to address fundamental questions about: (i) how the surfaces of candidate EBS materials behave in a typical disposal environment; and (ii) the effect of these alteration processes on RN/surface interactions. Crucially our approach represents fundamental, underpinning scientific research that will provide mechanistic understanding of key processes, simulating the range of post-closure RN retardation processes over candidate EBS and natural surfaces. Such an approach seeks to develop a methodology that is transferable to other materials and systems. This transferable approach supports the current generic stage of the UK disposal programme so that methods developed can be used to perform experiments on other materials using other RNs of interest as the UK geological concept progresses. It allows us to perform key experiments and underpin these with mechanistic prediction approaches. By quantifying energetics of reactions we will create predictive tools for use in developing and revising more accurate field-scale computational models. This will have profound impact on development of a new GDF safety case and has wider scientific implications.

Current state-of-the-art research in the study of molecular interactions with mineral surfaces: These are challenging areas to work in, even in the absence of active species, and this proposal will address some key knowledge and skills gaps. We have designed the AMASS programme of work in a staged fashion to allow delivery of scientifically world-leading research across the spectrum of experimental difficulty. There are few in-situ studies of mineral surfaces in hyperalkaline pH at the atomic-scale, dynamic studies of RN adsorption under these conditions are non-existent. Recently, however, surface analytical techniques have greatly enhanced our understanding of sorption processes at the mineral-fluid interface. This is important in understanding mass transfer of contaminants in complex systems. X-ray and infra-red techniques are especially powerful, for example glancing incidence EXAFS applied to radionuclide adsorption; X-ray Standing Waves applied to contaminant uptake in surface biofilm; combined X-ray Reflectivity/XANES/FTIR studies to provide coupled information about oxidation, chelation, and roughening of the surface as a function of time; and glancing incidence diffraction combined with imaging to constrain processes of contaminant uptake. Research published to date on RN sorption at the mineral-fluid interface has mainly focused on relatively ideal oxide and mineral surfaces, with an increasing interest in the interactions of aquated uranyl...
for example, on goethite. Little, if any, consideration has been given to modelling the sorption of different RN species or to the speciation mechanisms.

1.2 Research Hypotheses and Key Objectives

This proposal addresses fundamental questions about the structure, chemistry, and morphology of key material/groundwater interfaces involved in a GDF. A central hypothesis is that surface characteristics control several critical processes involved in the retardation of RN release (e.g., adsorption/desorption, incorporation, complexation). A key outcome will be how bulk solution properties such as pH, ionic strength and dissolved gases impact surface organization. In turn, we will explore how this affects RN binding mechanisms via both atomic scale modelling and select experimental approaches. Key macro-scale process information will be provided by allied larger-scale binding and reactivity studies to develop a multi-scale view of surface alteration and RN interactions. Outputs from experimentation will be used to constrain atomic-scale computational models such that the energetics of reactions may be understood and predicted. Our aim is to go beyond simplistic partitioning approaches by providing a mechanistic understanding of RN-surface interactions allowing non-equilibrium and kinetic considerations to be taken into account.

Key objectives are:
- To determine the atomic scale surface structure and chemistry of three model systems relevant to geological disposal, and to understand the key environmental factors that determine the evolution of these surfaces in a typical GDF environment;
- To determine the speciation of key long-lived RN upon their interaction with the three model systems and determine the effect of key environmental factors on RN speciation;
- To couple experimental and modelling approaches in order to gain mechanistic insights into the uptake of RN onto/from model surfaces as a function of the environmental conditions;
- To develop a generic experimental and predictive modelling approach that will allow an optimised approach to predicting RN binding onto model surfaces for a range of systems of relevance to the post-closure GDF groundwater pathway for RN transport.

2.1 Programme and Methodology

Until a site is identified and a concept selected and optimised for the site and UK wastes, different EBS options will be under consideration. It is important therefore to select materials and RNs that provide underpinning information relevant over a range of GDF scenarios. Our careful selection of materials and scenarios for study encompasses some of the most likely candidate materials/surfaces and geochemical conditions of importance for the range of GDF concepts under consideration in the UK. More significant, however, is that we have chosen to represent a range of model systems of increasing complexity and sensitivity to environment allowing development of an approach transferrable to other systems.

The systems considered are shown schematically in Figure 1. Whilst we recognise that the system is complex and there will be coupling between several of these parameters (e.g., bulk dissolution buffering the bulk pH) we have developed a systematic study to separate the effects of key variables. These parameters represent the starting point of our experiments: the material surface phase and solution speciation will in some cases change during experiments, reflecting the evolution that would occur in the GDF. Justification for choice of materials, environments and RNs is given below.

Environmental parameters: major variables will include pH, ionic strength, carbonate concentration and aeration. The pH of an LLW GDF will vary from hyperalkaline to ambient over millions of years. We therefore define a range of pH values that bracket likely conditions. Ionic strength is also a key variable as sub-surface groundwaters may be brines. Our experiments will explore two ionic strength (IS) end members: (i) low IS (deionised water), and (ii) high IS (sodium perchlorate at the same IS as a representative brine). Since carbonate will be significant in surface alteration reactions, and is a strong competitor for actinides, we will vary carbonate concentrations from ambient (pCO₂ = 10^{-3.5} atm; calcite equilibrated) to reduced partial pressures of CO₂ (pCO₂ = 10^{-4.5} atm). Deaeration will have significant impact on redox of both surfaces under consideration and RN speciation, ambient and Ar-surfced conditions will be investigated.

Mineral Surfaces: Portlandite (Ca(OH)₂), wollastonite (CaO), and bentonite will be studied. From a scientific point of view these materials offer a progression in complexity that allows development of both the experimental and computational methodologies and we justify this below.

Portlandite (Ca(OH)₂). Cementitious materials are used throughout radioactive waste management and across all geological disposal concepts. Portlandite has been selected as a model system as it will be a significant and evolving mineral surface during the period that ILW
packages will degrade and RNs will be released into the GDF environment. Furthermore, there is a paucity of information about the RN retention properties of this key phase. Our experiments will bracket cement degradation conditions from pH 13 when KOH/NaOH dominate dissolution through ~pH 12.5 where portlandite is in equilibrium with the groundwaters and finally to CSH gel buffered leachates at pH 12.5–10. Error! Bookmark not defined. Portlandite is an important starting point for our experimental design: the surface chemistry and reaction kinetics are relatively simple and we have experience with similar systems (see PTR). Carbonate mineral precipitates will most probably be calcite, and several relevant studies on RN uptake into calcium carbonates exist to constrain our approach.

Wüstite (FeI(II)). Iron will be present throughout the engineered GDF environment; corrosion of iron will lead to the formation of Fe-oxides, and as the GDF becomes de-oxygenated Fe(II) oxide phases will be stabilized. Fe(II)-phases have already been demonstrated to be significant in controlling RN solubility at ambient pH 5–6, and thus we have chosen to use a redox active model phase in our work. We realise that Fe-OH phase equilibria are complex and these phases will evolve with time and as a function of pH, pO2, and ionic strength of the environment. To constrain our experimental matrix initial work will focus on surface studies of FeO; however, we are responsive to studying alternate iron oxides as our understanding of this model system improves. Wüstite has increased complexity to portlandite; structurally simple but reductively active.

Bentonite. The clay mineral bentonite is important in many disposal concepts as a RN retarder due to its excellent sorption properties. It is likely to be important in engineered and geological portions of the UK GDF. Because of its key role in RN uptake there is a large amount of experimental data already produced and we will make use of this in our study. However, most existing work treats bentonite as a single entity. In reality it is a complex heterogeneous material, the result of this is a lack of mechanistic information concerning surface reactivity. In this study we will deconvolute the bentonite system into representative components. This work will build on the results from portlandite and wüstite to determine well-constrained data from this complex material.

Radioisotopes: The RNs of study will include the long-lived fission products and actinides whose potential mobility makes them critical species in any safety case - technetium, iodine, uranium and neptunium. We will work with U(VI), I(V), Tc(VII), and Np(VI) in our experiments reflecting an initially radiotoxic scenario. In addition, these species are a conservative choice as they are considered the most mobile species and provide reasonable solubility for experiments. RN speciation will change with solution conditions and proximity to redox surfaces, our experiments are designed to monitor this.

Modelling. The use of state-of-the-art computational modelling methods to simulate chemical processes occurring at the atomic and molecular scale, will give us direct mechanistic insight into sorption and incorporation processes for a range of surface morphologies. We will progress beyond purely thermodynamic reasoning (‘Kₐ approaches’) to build a more complete, explicit and justified understanding of RN retardation processes in dynamic systems. Our simulations will address mainly non-ideal sorption processes where the RNs are unlikely to bind as simple ions on to clean surfaces. Co-precipitation with counter-ions and later co-precipitation on the stable leading to alternative mineral phases will be addressed. This information will underpin NDA development of the safety case for the specific RNs in this proposal and provide a framework for more detailed assessment of key components once EBS and site selection process is complete.

2.2 Health, Safety and Regulatory Compliance. Work with radioactive, chemical and biological materials is subject to stringent controls and regulatory scrutiny. The Universities of Manchester and Loughborough have the facilities, management structures and experience to conduct the proposed radiochemical work and all partners have the facilities to conduct chemical work safely and correctly. Practical Approach. Radiochemistry experimental work will be developed across the spectrum of radiological hazard (U²³³Tc²⁹⁰Np). Experiments will become more selective as radiotoxicity constrains practical approaches; we anticipate running a full range of experiments with U, and progressively more select experiments with Tc and then Np. For I, we will use stable iodine and we recognise iodine speciation is challenging.

2.3 Experimental and Simulation Methodologies

Experimental. Surface structure, morphology and chemistry will be evaluated at atomic/nanoscale resolution using a combination of advanced surface science techniques and utilizing both lab- and synchrotron-based approaches. RN speciation / surface interactions will be monitored using both direct (spectroscopy) and indirect (extraction) approaches. The main techniques are:

- X-ray (Specular) Reflectivity and Diffuse Scatter. Specular reflectivity from an atomically flat surface gives X-ray information about the structure normal to the surface. Reflectivity can be used to constrain roughening processes during surface reactions. In the cases where surface films or reacted surface volumes occur, Kossel interference fringes appear providing information about differences between film and bulk. Specular reflectivity can be augmented with measurements of diffuse scatter which can be used to classify surface processes in terms of fractal dimension.

Synchrotron Surface X-ray diffraction: X-ray scattering is a powerful tool to determine surface atomic structure and can be used to study surface adsorption or reconstruction. In
diffraction experiments the crystalline surface results in additional intensity along linear regions in momentum space normal to the surface (crystal truncation rods), manifest as non-zero intensity away from the Bragg condition (see PTR4). Initially surface diffraction will be performed pre- and post-ageing. We will perform in-situ experiments on samples showing significant changes. Insights into surface termination, strain, chemical segregation and new phase formation will be obtained.

**Atomic Force Microscopy (AFM)**: AFM is a real-space technique for mapping surface morphology and can be used in-situ to monitor subtle changes in surface properties. It will provide complementary real-space information to the CTR/XRR on scales of a few nm. Topographical AFM will be particularly useful for following morphological changes in systems where amorphous phases may be formed. In addition it can be used to assess the microscopic ‘stickiness’ of a surface by assessing force-curve data or by operating in phase contrast mode. Our collaborators at PNNL have AFM system for active materials which will aspire to use in this work.

**Low Energy Ion Scattering (LEIS)**: provides non-destructive elemental and structural characterisation of the outermost atomic layer of a surface by monitoring the scattered intensity of a low energy noble gas ion. Quantitative matrix independent elemental profiles are produced so can be used to directly compare the chemical composition of different surface phases. Sensitivity is 10-50 ppm therefore subtle changes in surface chemistry can be assessed.

**RN/iodine speciation**: Solution phase speciation will be monitored using both indirect and direct approaches. Indirect approaches include liquid, liquid extraction and I, HPLC-ICPMS. Direct approaches allow characterisation of both solution and solids and include X-ray absorption spectroscopy (XAS) and IRRR (see below) and for U, time-resolved laser-induced fluorescence (TRLFS). TRLFS offers speciation insights in solution, suspension or solid surfaces.

**X-ray Absorption Spectroscopy / surface EXAFS**: XAS provides direct speciation information on the oxidation state and coordination environment of the target species. We will perform both bulk measurements to study RN speciation in mineral systems and grazing incidence EXAFS to provide surface sensitivity to determine the interaction with mineral surfaces. Polarization-dependent measurements will provide further information on surface conformation of adsorbed species. We have extensive experience in working with U, Ti, Ca and Mg and are in close dialog with DREAMS regarding radioactive samples (FM, KM). In selected systems, it will be possible to perform complementary XPS at PNNL to clarify EXAFS analysis.

**Computation and simulation**: We will use computational codes for the simulation and mechanistic studies, available under academic license: NWChem and Gaussian are appropriate for the DFT and quantum computations, although other first-principles DFT code, such as VASP may be utilised where the pseudopotentials and sizes of the systems permit. For atomic simulations, DLPol, NWChem (and Gulp) offer capability to handle large condensed phases and periodic systems and we will develop our collaboratation with EMSL and STFC to fully utilise these codes. We shall adapt previously successful computational protocols of surface studies and mechanistic modelling to the proposed systems and will validate and develop new protocols as required, the fundamental computational models will be an important output of the project, enabling more elaborate studies, refinements and extrapolations to macroscopic observations.

**Work packages**: The proposal is divided into a series of complementary work packages (WP) and the WPs divided into specific tasks. This structure, and resources required are outlined in Table 1.

<table>
<thead>
<tr>
<th>Work Package</th>
<th>Task</th>
<th>Resource (staff / time in months)</th>
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<tbody>
<tr>
<td>WP1. Mineral surface evolution (MR/RW)</td>
<td>1.1 ex-situ studies of mineral ageing</td>
<td>1.1 PDRA/15M PD/R01M</td>
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<td>1.2 in-situ surface ageing (Ca(OH)2, FeO)</td>
<td>1.2 PDRA/15M PD/R01M</td>
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<td>1.3 in-situ surface ageing (berillinite)</td>
<td>1.3 PDRA/15M PD/R01M</td>
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<tr>
<td>WP2. RN speciation during mineral evolution (KMINES)</td>
<td>2.1 Macro-scale studies of RN uptake &amp; speciation</td>
<td>2.1 PDRA/15M PD/R01M</td>
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<td></td>
<td>2.2 RN Surface complexation modelling</td>
<td>2.2 PDRA/15M PD/R01M</td>
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<td></td>
<td>2.3 RN in-situ surface ageing</td>
<td>2.3 PDRA/15M PD/R01M</td>
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<tr>
<td>WP3. Sorption and mechanic modelling</td>
<td>3.1 Portlandite U, Np, i, Tc,</td>
<td>3.1 PDRA/15M PD/R01M</td>
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<td></td>
<td>3.2 Iron oxyhydroxides</td>
<td>3.2 PDRA/15M PD/R01M</td>
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<td>3.3 Bentonite</td>
<td>3.3 PDRA/15M PD/R01M</td>
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Table 1: Work packages and resource. PDRA 1 Experimental (ICUMAN); PDRA 2 Modelling (MAN); PhD1 RN Binding and Surface Complexation Modelling (LB0); PhD 2. Spectroscopy and RN Speciation (MIA).

**WP1: Mineral Surface Evolution (MR/RW)**: The structural and chemical state of surfaces determine the energetic interactions with solution species and so control interface interactions. Surfaces are of course dynamic and evolve over time in response to environmental conditions. The surfaces of the systems of interest here are poorly understood in high pH environments and any model that tries to address the issue of RN interaction at present must start with an unknown. We aim to address this key knowledge gap using advanced surface science approaches capable of atomic-scale determination of surface properties under realistic GDF conditions.

**Task 1.1 ex-situ studies of mineral ageing**: Preliminary ex-situ studies of mineral ageing will be performed on all materials using single crystal substrates (where possible) that are: a) freshly cleaved in an inert environment, and b) post-exposure to the selected environments (Fig 1). The samples
will be examined at predefined timepoints from 1-100 h where we expect most systems to be at steady state. Samples will be examined in-house (LEIS, AFM) and solution chemistry measured (ICP-MS) to quantify dissolution. For synchrotron experiments, exposure will be performed on-site to minimise further changes that may occur during emersion, drying and transportation. These data will constrain initial and end point properties for simulations and guide in-situ experiments.

**Task 1.2** In-situ surface ageing experiments (Ca(OH)₂, FeO) will be performed where ex-situ analysis show significant changes in response to specific parameters. This will provide mechanistic information on surface transformation as well as directly measuring the kinetics of any transitions.

**Task 1.3** In-situ surface ageing (bentonite). Complex phyllosilicates such as bentonite are strongly anisotropic mixed oxides and are therefore experimentally challenging. We will simplify the systems by performing experiments with saponite (a tri-octahedral Mg-rich phase) and comparing them with nontronite (di-octahedral Fe-rich phase), to represent end-member bentonite surfaces. Previous work has indicated that the tri-octahedral phase is more stable at hyperalkaline pH. With first-principles calculations and flow experiments will be performed. Based on previous experience we will develop in-situ cells for dynamic flow experiments to allow real-time response to environmental parameters; this will provide optimised methodology for RN experiments (Task 2.3).

**WP2 Radionuclide Speciation During Mineral Evolution (KMNE)**. The physico-chemical and mineralogical properties of minerals in any environment, there is scant information on the molecular-speciation and mobility of RN on several of our model phases under the conditions we will study. In addition, there is little or no information on RN interactions with the evolving surfaces we wish to study in our dynamic experiments. To move toward addressing these key knowledge gaps, we will define the macro-scale and molecular speciation of RN with unreacted and end-member mineral surfaces using low-level batch, and in select systems XAS and TRLFS approaches (Task 2.1). These studies will be augmented by speciation/surface complexation modelling (Task 2.2). Finally we will, in key systems, examine the RN interactions under surface evolution conditions in dynamic experiments (for U and 1).

**Task 2.1** Macrosopic scale studies of RN uptake and speciation. There is a paucity of information on RN interactions with portlandite, and for bentonite and Fe(ii-iii)-bearing minerals at hyperalkaline pH. Work will explore sorption processes in fresh and end-member sorption batch experiments and in key systems we will use XAS/TRLFS to examine RN solid/solution speciation. Throughout, the approach will be to augment the available literature information with tailored experiments to gain an understanding of which sorption and radionuclides will be scientifically interesting and technically feasible to study under dynamic alteration processes (Task 2.3).

**Task 2.2** Surface Complexation Modelling (SCM). The empirical approach of using partition coefficients is insufficiently robust for a full mechanistic understanding of the non-equilibrium systems in a GDF. Hence, surface complexation modelling (SCM), using computer codes such as JC/HESS and PHREEQ will be used to model the experimentally-determined macro-scale sorption behaviour. This modelling will inform, and be informed by, the atomistic scale modelling performed by the PDRA2. This will lead to a synergy between the investigations and a scaled understanding of the systems. The SCM will be led by Loughborough, and enhanced by the active participation of PhD1 and PDRA1 & 2 who will provide data and gain training in SCM techniques.

**Task 2.3** Radionuclide in-situ surface ageing. When we have a good understanding of the surface alteration processes (WP1) and bulk radionuclide behaviour (Task 2.1, 2.2) we will, for highly selective systems, perform in situ surface ageing experiments with RN. We anticipate, in task 1.2 and 1.3 designing cells that will allow work with U in situ and we will explore whether work on Tc may be possible. Work with I will also be used to bridge from non-active, to active experiments and will provide a significant speciation challenge in itself. This Task will provide unique and highly novel fundamental information on RN interactions with surface transformed phases in dynamic systems.

**WP3 Sorption and Mechanistic Modelling (NB).** To model the sorption processes an iterative approach examining a range of simulation protocols will be necessary. This will range from determination of key stationary points on relevant potential energy surfaces, through to the use of rare-event sampling methods such as the analysis of potentials of mean force along defined reaction pathways. Quantum mechanical potentials, particularly density functional theory, will underpin the quantitative evaluation of the relative energetics and allow key properties such as structure and IR to be accurately computed. In addition, atomistic simulation with classical potentials will be essential in order to realistically model the condensed phase with appropriate sampling of solvent, counter-ions and surface relaxation/dissociation. An iterative approach, utilising experimental observations to inform computation will be essential and will be optimised by start-up of this WP at 18 months to enable realistic atomic scale models to be constructed and assessed alongside development of experimental approaches.

**Task 3.1** Interactions with Ca(OH)₂ surfaces: Simulation research will parallel experiments and focus on the sorption pathways of UO₂⁷⁻ onto Ca(OH)₂ surfaces under highly alkaline conditions. The computational studies investigate how and why the aqueous uranyl complexes coordinate to Ca(OH)₂ surface features. This will provide relative estimates of adsorption/desorption processes.

To understand the sorption mechanism from a kinetic perspective, ligand exchange processes for
direct interchange or reaction with surface or aquated species will be investigated. Currently, this type of modelling is restricted to CT binding.22 RN-ligand exchange has been extensively studied in aqueous phase, we aim to understand how process energetics are modified by surface and environment. Crucially, we will explore how counter-ions and variation in IS affect RN sorption mechanisms. The role of neutral complexes (Ce-UO4(2-)CO3(-)) in recrystallisation and mineralisation processes, and hetero-interaction of high oxidation-state actinides into the bulk, will be explored. 

**Task 3.2** Interactions with iron-oxide surfaces: Iron oxide surfaces provide a major challenge to computation, and we may need follow a more pragmatic approach to describe these sorption processes in comparison to portlandite. We shall draw upon the extensive literature on modelling simple sorption processes to active oxide surfaces, such as TiO2, and state-of-the-art studies such as those involving goethite.

Since modelling lower actinide oxidation states also necessitates special consideration, we will make judicious use of redox-inactive empirical data where possible. **Task 3.3** Interactions with bentonite surfaces: Modelling uptake of actinide species on to bentonite at the atomic scale will involve different computational challenges, mainly due to its more complex structure and compositional variations. The key bias of our simulations will be towards an understanding of the interactions with bentonite surface features representative of those likely to give rise to the batch-sorption properties. Input data from the experimental programme will facilitate a theoretical deconvolution of key properties. Again, interfacial solution speciation will be critical, and the presence of Na+ is in particular likely to result in quite different behaviour to portlandite.

**2.4 Summary.** The AMASS approach is required to deliver this programme of work as no single group has the breadth and depth to tackle the research as outlined. For each task, the team, under leadership, will develop the experience needed for successful delivery. The consortium structure (Table 1) highlights that completion of each task is essential to delivery of our overarching objectives. Finally, the structure uses a 4 year timeframe needed to allow incorporation of molecular-scale results into advanced modelling tools.

**2.5 Research Excellence and Novelty.** This proposal will provide for the first time an integrated and coherent approach towards understanding fundamental mechanisms of GDF-related surface-ownement-RN interactions, in particular the work in hyper-alkaline, dynamic environments and with RN is entirely novel. This work is only now possible because of (i) advances in experimental facilities and computational methodologies; and (ii) the bringing together of researchers with synergistic expertise in radiochemistry, computational chemistry, surface science, modelling and spectroscopy and who take a holistic view of the research problem. The experimental work will bridge both length and time-scales and provide key input data to computational simulations which will build predictive capability based on realistic conditions.

**3.1 Management.** The proposed team individually have a long track record of successful collaborative research. MR will be responsible for day-to-day management and reporting to EPSRC. Because of the high degree of interaction required for successful programme delivery quarterly meetings will be held, to which NDA representatives and other interested parties will be invited. A monthly e-conference will be held to ensure efficient communication and rapid transfer of information. A website with secure web-based file-share will be set up for ease of data transfer as demonstrated on BIGGRAD website (www.bigrad.nerc.com). The programme is set up such that it is essential for PhDs and PDRAs to spend significant time at partner institutions, working at the boundaries between disciplines to deliver the step-change science we propose. Formal visiting appointments for researchers will be set up at each institution to facilitate collaborative exchanges.

**3.2 External Linkages and Collaboration.** The ambitious programme of work involving active experimentation will be significantly enhanced by the interactions and support of key collaborators. The programme will be a strong interaction with DIAMOND Synchrotron and are already developing protocols for radioactive work (FromN). The NDA will have ongoing input and provide guidance throughout the programme. We have active collaborations with e.g. NNL and Sellafield Ltd that we will develop as appropriate. Scott Wilson will provide industry expertise in the form of a knowledge exchange partner. In Europe we will collaborate with KAT, ANKA and CTU Prague. In the US we will cement our existing successful relationships with SGRL and develop links with PNNL. In addition to providing world-class facilities for radioactive work there will be significant benefit to the PhD/PDRAs from exposure to different laboratories and research cultures. The PhDs will benefit from interactions with EPSRC Doctoral Training Centres: Nuclear FIRST (Man) and Material Theory & Simulation (IC).

(References are omitted for brevity. For the complete list, please refer to the original document.)
7.2 Published paper on uranium interaction with materials relevant to geological disposal

The author contributed to the work in the paper by drafting the manuscript, preparing the samples for surface alteration and sorption experiments. Assisting in the preparation of the samples for EXAFS analysis and the fitting of the data. The elemental analysis was carried out using the in house service at Loughborough and the BET measurements were conducted at the University of Manchester.
Uranium and technetium interactions with wüstite [Fe_{1-x}O] and portlandite [Ca(OH)_2] surfaces under geological disposal facility conditions


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[Received 28 November 2013; Accepted 5 May 2014; Associate Editor: R. Giere]

**ABSTRACT**

Iron oxides resulting from the corrosion of large quantities of steel that are planned to be installed throughout a deep geological disposal facility (GDF) are expected to be one of the key surfaces of interest for controlling radionuclide behaviour under disposal conditions. Over the lengthy timescales associated with a GDF, the system is expected to become anoxic so that reduced Fe(II) phases will dominate. Batch experiments have therefore been completed in order to investigate how a model reduced Fe-oxide surface (wüstite, Fe_{1-x}O) alters as a function of exposure to aqueous solutions with compositions representative of conditions expected within a GDF. Additional experiments were performed to constrain the effect that highly alkaline solutions (up to pH 13) have on the adsorption behaviour of the uranyl (UO_2^2+) ion onto the surfaces of both wüstite and portlandite [Ca(OH)_2]; representative of the expected cementitious phases. Surface co-ordination chemistry and speciation were determined by ex situ X-ray absorption spectroscopy measurements (both X-ray absorption near-edge structure analysis (XANES) and extended X-ray absorption fine structure analysis (EXAFS)). Diffraction, elemental analysis and XANES showed that the bulk solid composition and Fe oxidation state remained relatively unaltered over the time frame of these experiments (120 h), although under alkaline conditions possible surface hydroxylation is observed, due presumably to the formation of surface hydroxyl complexes. The surface morphology, however, is altered significantly with a large degree of roughening and an observed decrease in the average particle size. Reduction of U(VI) to U(V) occurs during adsorption in almost all cases and this is interpreted to indicate that wüstite may be an effective reductant of U during surface adsorption. This work also shows that increasing the carbonate concentration in reactant solutions dramatically decreases the adsorption coefficients for U on both wüstite and portlandite, consistent with U speciation and surface reactivity determined in other studies. Finally, the EXAFS results include new details about exactly how U bonds to this metal oxide surface.

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DOI: 10.1190/minmag.2014.0785.02

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This paper is published as part of a special set in *Mineralogical Magazine*, Volume 78(5), 2014, entitled 'GEOLIFE—Geomaterials for the environment, technology and human activities' arising out of papers presented at the Goldschmidt 2013 conference.
Keywords: Uranium, technetium, iron oxides, wüstit, portlandite, radionuclide behaviour, geological disposal.

Introduction

In the UK, significant amounts of nuclear waste generated from military, medical and civilian nuclear power sources have accumulated over a period of 60 years (Hastings et al., 2007; Department for Environment, Food and Rural Affairs and the Nuclear Decommissioning Authority, 2008). In combination with poor waste management in the past, the disposal and clean-up of this legacy waste is challenging and complex (Topping and Bruce, 2006). The international consensus for the safe disposal of the higher-activity wastes is a deep geological disposal facility (GDF) (Department for Environment, Food and Rural Affairs et al., 2008; Nuclear Decommissioning Authority, 2010a; Feiverson et al., 2011; Morris et al., 2011). Therefore, the Nuclear Decommissioning Authority (NDA), the body responsible for planning and implementing geological disposal, has established the Radioactive Waste Management Directorate (RWMD) which will be responsible for the delivery of the Geological Disposal Facility (GDF) (Department for Environment, Food and Rural Affairs et al., 2008). This method involves a multi-barrier approach with a waste form, a waste container and backfill; the waste will be stored underground within a suitable host rock. It is necessary to understand the complex processes associated with deep geological disposal in order to develop a robust safety case (Nuclear Decommissioning Authority, 2010a).

A significant part of the waste, by volume, is intermediate level waste (ILW) (Nuclear Decommissioning Authority, 2011). It is proposed that part of the ILW and the low level waste (LLW) are to be encapsulated in a cement matrix and placed into stainless steel containers, stored above ground and eventually transferred to the GDF where backfilling, possibly with a cementitious matrix, will occur. The canisters will be subject to changes in P\(_O_2\) and P\(_{CO_2}\), humidity and temperature, which will eventually lead to failure of the canisters (Féron et al., 2008).

Corrosion of stainless steel canisters

The corrosion of stainless steel has been studied widely and the corrosion products formed under many aqueous conditions are well understood (Braithwaite and Melecke, 1986; Yan-tao and Baorong, 1998; Quintessa, 2009; Zhang et al., 2012; Hazan et al., 2013). It has been shown that where toxic aqueous corrosion is the main failure mechanism, the expected corrosion products are magnetite (Fe\(_3\)O\(_4\)), hematite (\(\gamma\)-Fe\(_2\)O\(_3\)), goethite (\(\alpha\)-FeOOH) and lepidocrocite (\(\gamma\)-FeOOH) (Latta et al., 2011; Hazan et al., 2013; Ma et al., 2013).

Under repository conditions the canisters will be exposed to hyper-alkaline conditions associated with cementitious materials (grout, engineering cement, backfill) where the pH is likely to be >12. The steel is protected from corrosion by a thin passive film, which, over time, may lose its protective properties due to the presence of aggressive ions such as chloride. However, over time the GDF will also become deoxygenated (Smart et al., 2002). The strongly reducing geochemical conditions associated with the GDF environment (high pH, low Eh) mean that Fe(II)-bearing minerals and mixed oxidation state Fe(II)/Fe(III)-bearing minerals are likely to be part of the stable, long-term, solid-phase assemblage.

Uranium and technetium adsorption under GDF conditions

Uranium and technetium, a high-yield fission product, are common radionuclide contaminants in the subsurface at nuclear facilities and are thus of great environmental concern (Lloyd et al., 2000; Peretyazhko et al., 2008; McKenzie et al., 2011), and studies of U and Te mobility are of high importance (long half-life of U and Te) in relation to geological disposal. Under oxidizing conditions U and Te exist predominantly as the U(VI) (UO\(_2^2+\)) and Te(VII) (TeO\(_4^{2-}\)) species. These oxidized species are more mobile in aqueous systems than their reduced U(IV) and Te(IV) equivalents (Morris et al., 2008; Singer et al., 2012). In addition, the aqueous speciation of the uranyl ion changes as a function of pH. At acidic pH the uranyl ion dominates, however, as alkalinity increases, uranyl hydroxyl and carbonate species dominate (Langmuir, 1978).

Uranium and Te interaction with Fe oxides

Previous studies have shown that magnetite is an effective reductant for dissolved metal ions facilitated by coupled oxidation of structural Fe(II) (Cui and Eriksson, 1996b; Scott et al., 2005; Latta et al., 2011; Singer et al., 2012).
Bargar et al. (1999) studied the adsorption of U(VI) on hematite and noticed a surface-charge reversal in the presence of U(VI) at near-neutral pH. It was suggested that surface-charge adjustment may be attributed to the formation of anionic ternary surface complexes, such as uranyl carbonate and uranyl dicarbonate (Bargar et al., 1999; Wazne et al., 2003). O’Loughlin et al. (2010) investigated the adsorption of U(VI) on secondary mineralization products of bioreduced Fe(III) oxides under anoxic conditions. Their EXAFS results suggested an association of Fe oxides and uraninite nanoparticles on biogenic green rust and magnetite. Here, U was adsorbed preferentially onto edge sites rather than the basal plane sites of these crystals. These results are consistent with charge hopping, where any oxidized Fe(III) is reduced back to Fe(II), such that U(VI) reduction is continued (Wander et al., 2007; O’Loughlin et al., 2010; Singer et al., 2012b); however, this study also showed that the Fe(II)-bearing carbonate mineral, siderite (FeCO₃), did not show significant uptake of U(VI) and did not contribute to the reduction to U(IV). In addition, U mobility is also controlled by interactions with solution ions and mineral surfaces. Carbonates form strong complexes with U(VI), which increases the solubility of U (Bargar et al., 1999; Grenthe et al., 2004; Hieuntran et al., 2009). Wazne et al. (2003) have shown that adsorption of U(VI) decreases significantly with both increasing carbonate concentration and alkalinity. It is therefore important to determine exactly how U behaves in the presence of carbonate and Fe(II)-bearing oxides under the external pH conditions present at a proposed GDF in order to make reliable predictions concerning radionuclide mobility.

Similarly, the mobility of Tc is dependent on redox chemistry, as well as hydrolytic and complexation equilibria. Under oxic conditions, Tc(VII) is the predominant species, which is highly mobile as it adsorbs to mineral surfaces only very weakly at near-neutral and basic conditions (Cui and Erikson, 1996b; Fan et al., 2013; Thorpe et al., 2014). Reduced Tc(IV) is stable under anoxic conditions and in the absence of ligands such as carbonates and humic acids (Lloyd et al., 2000; Burke et al., 2005). Under these circumstances, Tc at high concentrations may precipitate as hydrous TeO₂-like phases (Morris et al., 2008; Fan et al., 2013) or may be adsorbed onto mineral surfaces (Bouchez and Francis, 1979; Burke et al., 2005). Recent work with ⁹⁹ᵐTc has shown that Tc(IV) is adsorbed even at picomolar concentrations, well below the predicted solubility of TeO₂ of 10⁻⁸ mol L⁻¹ (Leur et al., 2009). Therefore the redox chemistry of Tc is key in governing its mobility (Bouchez and Francis, 1979; Cui and Erikson, 1996a; Líoü et al., 2000; Itoh et al., 2004; Burke et al., 2005). In subsurface environments, Fe(II) is a key reducer. Several studies have shown sorption of Tc and enhanced reduction on the surfaces of Fe oxides, with Tc present as inclusions in Fe(II)-containing minerals and in fracture-filling materials (Bouchez et al., 1984; Buró et al., 2005; Liu et al., 2012). The EXAFS results of Liu et al. (2012) showed the reduction of Te(VII) on titanomagnetite [Feₓ₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋_-
Although adsorption and reduction of both U(VI) and Tc(VII) have been studied extensively, relatively little is known about U and Tc adsorption under the hyper-alkaline conditions which will be present in a GDF. Secondary cementitious and Fe materials (analogs: portlandite and wüsite, respectively) will probably be present throughout the ILW disposal area of a GDF. Under GDF conditions, the exposed surfaces of Fe-oxide precipitates and portlandite are likely to be altered significantly, both chemically and structurally, which will have implications for adsorption and reduction reactions. Surface alteration may result in decreased retention of both U and Tc in the solid phase and thus needs to be accounted for when considering environmental risk. In order to build a robust safety case, surface alteration and adsorption under these extreme conditions needs to be fully understood. Portlandite and wüsite have been selected in this present study as model systems to represent degradation of the cement and steel materials, respectively, in a GDF. In this study two sets of experiments are presented. The first set of experiments focused on the transformation of the mineral wüsite in the presence or absence of carbonates at near-neutral and hyper-alkaline conditions, which would be expected in an ILW disposal area of a GDF. Wüsite was also chosen as a model reactant solid because it contains only ferrous Fe and hence should make determination of oxidation more straightforward than in mixed Fe(II)/Fe(III) phases such as magnetite. Furthermore, wüsite is structurally simple and comparable to MgO and CaO, so subtle adjustments in atomic configurations during reactions may be more easily discernible than with more complex phases. Solids were characterized using standard X-ray diffraction (XRD) and high-resolution synchrotron powder XR (HR-PXRD) and field emission gun scanning electron microscopy (FEG-SEM). The second set of experiments focused on the adsorption behaviour of U and Tc, where the amount adsorbed was determined by the difference in solution concentration before and after the reaction. This was measured using either inductively-coupled plasma mass spectrometry (ICP-MS) or inductively-coupled plasma atomic emission spectrometry (ICP-AES). Under hyper-alkaline conditions, cementitious materials will degrade such that portlandite will be in equilibrium with groundwater. Therefore, adsorption onto portlandite was also included in this second set of experiments in order to compare results from a non-redox active surface to the results from the reaction with wüsite. Local coordination chemistry of both U and Tc was determined using X-ray absorption spectroscopy (XAS), and the solids were again characterized using XRD.

The goals of this study are: (1) to quantify changes in wüsite surface chemistry and morphology during alteration with solutions that simulate GDF conditions; (2) to determine how pH and dissolved carbonate affect U and Tc adsorption onto wüsite and portlandite; and (3) to use XAS to provide details of how U and Tc interact with these surfaces.

**Experimental**

**Surface alteration experiments**

Surface alteration experiments were conducted using a batch method: 0.5 g of wüsite [Fe₆₋₇O] (as received; Sigma-Aldrich 99.99% pure, particle size <212 μm) was placed into a 50 ml Perspex centrifuge tube. Solutions were prepared with deionized water that had been boiled and degassed and the pH was adjusted using NaOH to give values of 7 or 12. Each solution was then divided into two parts and 0.1 mol l⁻¹ anhydrous Na₂CO₃ was added to half of them (for details, see Supplementary Data, Table S1A). The Supplementary Data, Tables S1–3 and Fig. S1, have been deposited with the Principal Editor of *Mineralogical Magazine* and are available from [www.minersoc.org/pages/e_journals/dep_mat_mm.html](http://www.minersoc.org/pages/e_journals/dep_mat_mm.html). Then 50 ml of each relevant solution was added to the Perspex tube experiments. Alteration was conducted under either atmospheric conditions or within a nitrogen atmosphere using a Braun glove box. Following a 120 h (±2 h) incubation the supernatant was then separated and filtered (0.22 μm) to remove any particulate material. The reacted wüsite was then washed with isopropyl alcohol and dried under a nitrogen atmosphere.

The supernatant was analysed by ion chromato-graphy and ICP-MS. The wüsite powders were analysed by standard XR, HR-PXRD, FEG-SEM and elemental analysis (Exeter Analytical CE-440, optimized for C, H and N). In addition, the surface area was measured before the reaction via Brunauer-Emmett-Teller (BET) analysis using a Gemini 2360 V5.00.

**Effect of pH on uranyl sorption**

Sorption experiments were carried out in 50 ml plastic centrifuge tubes containing ~0.1 g of
U AND Tc INTERACTIONS WITH WÜSTITE AND PORTLANDITE

wüstite (particle size <212 μm, as above) and 10 ml of ~200 ppb UO₂(NO₃)₂·5H₂O. The pH was adjusted using NaOH to obtain pH values in the range of 7–13 (see Supplementary Data, Table S1B). Total contact time was 120 h (±2 h) at room temperature, after which the samples were centrifuged at 6000 rpm (2000–2500 g). The supernatant was then pipetted out and filtered through a 0.22 μm syringe filter and then prepared for ICP-MS analyses using bismuth as an internal standard. All experiments were carried out in triplicate, in both standard atmosphere and anaerobic conditions.

Effect of carbonate on uranyl sorption

The effect of dissolved carbonate on uranyl sorption to wüstite was investigated using a batch method similar to the batch sorption experiments discussed previously. Experiments were carried out in 50 ml plastic centrifuge tubes containing ~0.1 g of wüstite (particle size <212 μm, as above) and 10 ml of ~200 ppb UO₂(NO₃)₂·5H₂O. A series of Na₂CO₃ solutions was prepared such that the carbonate concentration varied between 1 × 10⁻⁵–1 × 10⁻⁶ mol l⁻¹ but the U concentration remained constant (see Supplementary Data, Table S1C). Total contact time was 120 h (±2 h) at room temperature after which the samples were centrifuged at 6000 rpm (2000–2500 g). The supernatant was then pipetted out, filtered through a 0.22 μm syringe filter and then prepared for ICP-MS analyses using bismuth as an internal standard. All experiments were carried out in triplicate, in both atmospheric and anaerobic conditions.

In order for the results of the U sorption batch tests to be compared with literature data, Rₛ values were calculated using the equation below:

\[ Rₛ = \frac{Aᵢ - Aᵢ'}{Aᵢ'} × \frac{V}{M} \]

where Aᵢ is the initial concentration (mol l⁻¹), Aᵢ' is the final concentration (mol l⁻¹), V is the volume (ml) and M is the mass (g).

Field emission gun-scanning electron microscopy (FEG-SEM)

The powdered wüstite samples, both unreacted and reacted, were mounted on carbon tape and gold coated at 25 mA for 2 min giving a coating thickness of 15 nm. The prepared samples were then analysed using a Gemini 1525 high-resolution FEG-SEM. Secondary electron imaging was performed with an accelerating voltage of 5 keV with a working distance varying from 4.5–8.5 mm.

Standard XRD

Powder diffraction measurements were performed in 0–2θ geometry (CuKα; λ = 1.5418 Å) on both wüstite and portlandite using a Bruker D8 Advance diffractometer. An internal standard of silicon was used for calibration so as to allow the detection of minor peak shifts.

High-resolution synchrotron powder XRD (HR-PXRD)

The HR-PXRD measurements were performed at beamline I-11 at the Diamond Light Source. Measurements were conducted with monochromatic X-rays (Si(111)) using a beam energy set at 15 keV (λ = 0.827 Å). Spectra were collected using five multi-analysing crystal detectors (MAC's) from 0–15°2θ with a 0.005° step-size. TOPAS software (Bruker) was used to perform Rietveld refinement and Scherrer analysis of the data.

X-ray absorption spectroscopy (XAS) bulk adsorption experiment

Mineral solids preparation

The wüstite [Fe₇,₉2O] and portlandite [Ca(OH)₂] mineral solids used in the XAS experiments were prepared in an anaerobic chamber (under argon) to prevent oxidation of wüstite and possible carbonation of the portlandite. Powders were sieved and the size fraction with an average particle diameter <88 μm was used in these experiments.

Mineral reaction with U and Tc for XAS analysis

Solutions with relatively high concentrations of adsorbates were prepared in order to ensure high surface uptake and to optimize the signal-to-noise ratio in the spectroscopic data. A stock solution of 1000 ppm U(VI) from an isotopically depleted UO₂⁺(NO₃)₂·5H₂O source was used in this experiment. For Tc a stock solution of 1000 ppm pertechnetate (TcO₄⁻) was prepared. Then 0.25 ml of stock solution was diluted in 25 ml Milli-Q water to produce a precipitate-free
final stock solution of 10 ppm dissolved U(VI) or Tc(VII). The pH was not adjusted for the pH equilibrated samples. The pH for hyperalkaline solutions was adjusted by adding 0.01 M NaOH to produce a final pH ~12. For the portlandite sample, portlandite-equilibrated Milli-Q water was used in order to prevent dissolution of portlandite during the reaction.

Powders were transferred into 30 ml crimp bottles in a sample-to-solution ratio of 1:100 for the reactions, so that, assuming complete uptake, the total final loading on the solid phase would be 1000 ppm U(VI). The contact time was 120 h (±2 h) after which the samples were transferred, under atmospheric controlled conditions, into centrifuge tubes and centrifuged at 5000 rpm (4500–5000 g). The supernatant was decanted and the paste was transferred into a Perspex sample holder with a drill hole diameter of 2 mm. The wet solids were then further dried by brief wicking to provide a moist paste. The top of the hole was then sealed by a layer of Kapton tape and the samples were double contained in vacuum-sealed bags under argon.

**BET analysis of wustite used in adsorption**

The multipoint N₂-BET method was used to measure the surface area of the starting materials. Samples were dried overnight under helium at room temperature and the surface area was then determined using the BET (Brunauer et al., 1938) N₂ gas adsorption technique with a Micromeritics Gemini 2360 gas adsorption BET analyser adapted for materials with small surface areas. A reference material (carbon black) was also analysed. The estimated 2σ relative error for these samples is 10%.

**Bulk EXAFS analyses**

The EXAFS measurements were performed at the B18 experimental station at the Diamond Light Source, UK (Dent et al., 2009). This beamline is designed to collect bulk EXAFS analyses rapidly, by using the Quick EXAFS mode. The energy of the beam was calibrated against the K-edge first derivative of a Y foil, defined at 17,038 eV. The measurements were then conducted at the U L\textsubscript{γ}-edge in fluorescence mode using a nine element Ge detector mounted perpendicular to the incoming beam. The double contained sealed samples were placed into a clamp so that each sample was positioned at 45° relative to the incoming X-ray beam.

Technetium EXAFS were collected at the K-edge in fluorescence mode. The energy of the beam was calibrated against the first derivative of the Mo K-edge, defined at 20 keV. Iron bulk EXAFS were collected at the Fe K-edge. An unreacted wustite pellet was prepared and measured in transmission mode. Unfortunately the design of the sample holders and density of the reacted substrate precluded data collection for the product solids in transmission mode. Therefore these measurements were completed in fluorescence mode similar to that described above, except that the surface of the sample holder was positioned nearly normal to the incident beam. This resulted in a glancing exit angle which decreases the impact of self-adsorption on the measured intensity. The EXAFS spectra were further corrected for remaining self-absorption using the Fluor algorithm in athena (Newville et al., 1995).

The EXAFS, χ(̅r), were refined from the raw data by standard procedures, including background subtraction, normalization of absorption, conversion to momentum and k space. For each sample ~34 spectra were averaged to improve the signal-to-noise ratio. The spectra were then analysed with athena (Newville et al., 1995) and the phase/amplitude functions were calculated by FEFF6L (Newville et al., 1995). The theoretical fits were performed in k-space.

**Results and discussion**

**Surface alteration experiments**

Standard XRD was unable to determine any new phases after the reactions. HR-XRPD analysis on the reacted and unreacted samples agreed with these findings, but was able to show the presence of trace quantities of α-iron (Fe\textsuperscript{3+}) impurities in the starting material which persist after the reaction (Fig. 1). Rietveld refinement quantified 2.8 ± 0.2% and 4.0 ± 0.1% of α-iron in unreacted and reacted wustite respectively. The observed difference in α-iron content is most likely due to heterogeneity in the starting material.

The FEG-SEM results show that all reacted materials display varying degrees of surface morphological alteration compared to the unreacted starting material (Fig. 2). The systems that show the most significant alteration are those containing high concentrations of dissolved carbonate (Figs 2d, e and h). All three of these images are similar, clearly showing the formation of plate-like features. The systems with no
dissolved carbonate were reacted under a controlled atmosphere and also showed alteration over the timeframe of these experiments but show no evidence of platelets. Samples reacted either in deionized water (Figs 2b and c) or in hydroxide solution only (Figs 2f and g) show signs of surface roughening attributed to dissolution plus micro-crystalline features with contrasting morphology. Differences in alteration for samples with and without Na₂CO₃ are especially pronounced under hyper-alkaline conditions. The experiments without Na₂CO₃ were completed in an anaerobic chamber to decrease P₉O₅, hence this difference can probably be attributed to the lack of an oxidized surface layer: i.e. under atmospheric conditions at high pH, surface Fe will rapidly oxidize to insoluble Fe(III) and passivate the surface. Under anaerobic conditions however, the much more soluble Fe(II) will be released without impediment and the starting material may be more easily broken down into finer particle sizes. X-ray diffraction did not show secondary phase precipitation in any of the experiments, and therefore the fine-grained materials in Fig. 2 probably represent an extremely small volume of non-wüstite precipitates and most likely include fine-grained fragments and re-precipitates of wüstite.

These findings are corroborated by Scherrer analyses of the powders performed on the HR-PXRD spectra. Peak-width analysis revealed that alteration caused a significant decrease in particle size. The particle size of the unreacted starting material was too coarse to resolve accurately from peak-width analysis, however after 120 h of reaction the mean particle size decreased to 164.7 ± 10.7 nm. This indicates that the particle size decreased dramatically during the reactions and that the specific surface area of wüstite (initially 0.07 m² g⁻¹) increased significantly (Table 1), which could potentially lead to significant effects on the adsorption of radio-nuclides and on other surface area dependent processes such as dissolution.

Elemental analyses (Supplementary Data, Table S2) revealed that in all hyper-alkaline experiments a possible incorporation of hydrogen into the solid took place. We interpret this as due to the formation of surface hydroxyl species. Carbon and nitrogen contents showed no changes.
Fig. 2. Whźlittle surface alterations caused by changing pH and carbonate concentrations, imaged using a FEG-SEM) (altered images labelled (b–h)). The greatest degree of alteration occurred in systems containing carbonate (images (f), (e) and (h)). The constant and even-spaced swirl patterns in images (f) and (g), possibly represent preferential surface-mediated reactions on the octahedral edges of whźlilite.
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Table 1. BET surface area measurements of wüstite under various conditions.

<table>
<thead>
<tr>
<th></th>
<th>Na₂CO₃ (mol l⁻¹)</th>
<th>NaOH</th>
<th>Surface area (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wüstite unreacted</td>
<td>—</td>
<td>—</td>
<td>0.07</td>
</tr>
<tr>
<td>Wüstite pH 7</td>
<td>0</td>
<td>0</td>
<td>0.10</td>
</tr>
<tr>
<td>Wüstite pH 7 + C</td>
<td>0.1</td>
<td>0</td>
<td>1.14</td>
</tr>
<tr>
<td>Wüstite pH 12</td>
<td>0</td>
<td>0.01</td>
<td>0.05</td>
</tr>
<tr>
<td>Wüstite pH 12 + C</td>
<td>0.1</td>
<td>0.01</td>
<td>1.36</td>
</tr>
</tbody>
</table>

Ion chromatography results also show that nearly all added carbonate remained in solution. Given the fact that XRD did not show secondary precipitates, hydroxyl and any unresolved carbonate uptake must be limited to thin surface films composed of <5% of the solid by volume (i.e. below the detection limit).

Adsorption experiments

**Uranium adsorption on wüstite, 200 ppb initial concentration**

Figure 3 shows the combined results of all the adsorption experiments with identical starting concentrations of U onto wüstite, but under conditions of variable pH or carbonate concentration (all data on this Figure are included in the Supplementary Data, Table S3). Adsorption is strongly pH-dependent (Fig. 3a). In the near-neutral region, adsorption is a strong function of carbonate concentration, but this is not the case in hyper-alkaline solutions, where adsorption is minimal across the experimental range (Fig. 3b). When carbonate concentration increased in solutions at pH 7, adsorption of uranyl decreased (Fig. 3b). This trend, even though the surface area of the solid increases, reflects the fact that uranyl adsorption is affected strongly by complexation with dissolved carbonate. At high pH and high carbonate concentrations, aqueous uranyl-triscarbonato complexes are formed that do not attach easily at solid surfaces, hence uranyl remains dominantly in the aqueous phase (Wan et al., 2003; Grinter et al., 2004; Greathouse and Cygan, 2005). Additionally, at hyper-alkaline pH, the nearly complete deprotonation of the mineral results in a negatively charged surface (Hemstra et al., 1996), such that electrostatic repulsion between the negative mineral surface and the anionic solute will minimize adsorption.

**Uranium and Tc adsorption on wüstite and portlandite, 10 ppm initial concentration**

In agreement with the experiments shown on Fig. 3, uranium and Tc adsorption on wüstite from solutions with higher starting concentrations show

**Fig. 3.** Calculated $R_d$ values of U adsorbed on wüstite with changing pH (a) and carbonate concentrations (b).
similar trends, with large amounts of adsorption in the near-neutral region and decreasing adsorption in hyperalkaline solutions (Table 2). When taking into account the dissolution of Fe, we suggest that surface-mediated reactions affect U adsorption onto wortelite. Portlandite, however, exhibits a high uptake of U(VI) in hyper-alkaline solutions consistent with previous work on cementitious phases (Tis et al., 2011).

The XRD results on all solids used for XAS measurements showed no significant shift in peaks or appearance of new peaks between the unreacted and reacted minerals. This indicates that U has not been incorporated in large quantities into the crystal structure, as this would distort the distances between crystallographic planes (Hudson et al., 1999).

**XANES analyses**

The U L₂₃-edge XANES spectra for the wortelite samples show subtle differences in edge positions (Fig. 4a) and the intensities of certain spectral features (see Fig. 4a, features 1 and 2). The XANES spectra for both U and Te show that, at near-neutral to moderately alkaline final pH, U(VI) and Te(V) are reduced to U(IV) and Te(IV), respectively (Fig. 4a). The three lower spectra in Fig. 4a, which indicate reduction to U(IV), are similar to spectra published previously for uraninite (especially note feature 1) (Olmukka et al., 2005; Kelly, 2010; O’Loughlin et al., 2010; Marshall et al., 2014). At pH 12 with high PCO₂ (lowermost spectra of Fig. 4a), the pH of the solution drifted to pH 7, and therefore this spectrum resembles the experiments completed at near-neutral pH. The XANES spectra for Te samples resembles previously published reference spectra of TeO₂N₂H₂O (Fig. 4c, feature 3 and 4) (Lloyd et al., 2008; Hess et al., 2004; Liu et al., 2012). In contrast to the other U adsorption experiments onto wortelite, without the presence of carbonate at pH 12, the oxidation state of U(VI) was unchanged (Fig. 4a, fourth spectrum from top: edge position and feature 2 are diagnostic), with XANES similar to previously published U(IV) species (Kelly, 2010; Marshall et al., 2014). In this experiment the pH did not drift. The XANES spectrum of U on portlandite (Fig. 4a, third from top) suggests an alkaline earth complex CaUO₄⁺, similar to that published by Macé et al. (2013).

In contrast with the oxidation-state changes of U and Te, the Fe K-edge XANES showed no

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**Table 2. EXAFS sample conditions.**

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Mass solid (g)</th>
<th>Volume (ml)</th>
<th>Ψ₀ (°)</th>
<th>P₂₂₀ (º)</th>
<th>α (º)</th>
<th>Fe₃⁺ (ppm)</th>
<th>α₃⁺ (º)</th>
<th>Fe₅⁺ (ppm)</th>
<th>α₅⁺ (º)</th>
<th>Fe₇⁺ (ppm)</th>
<th>α₇⁺ (º)</th>
<th>Fe₉⁺ (ppm)</th>
<th>α₉⁺ (º)</th>
<th>Fe₁₁⁺ (ppm)</th>
<th>α₁₁⁺ (º)</th>
<th>Fe₁₃⁺ (ppm)</th>
<th>α₁₃⁺ (º)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₅⁺ + U</td>
<td>0.25</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
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<td>Fe₅⁺ + U + C</td>
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<td>Fe₅⁺ + U + C</td>
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<td>CaUO₄⁺</td>
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*RXS refers to the average 120 h (2σ) content line calculated using average concentrations measured in the anemometer chamber.
changes in edge position or amplitude frequency (Fig. 4b). Although U(IV) and Tc(IV) XANES suggest that part of the wüstite substrate should be oxidized due to electron transfer catalysed by surface-mediated reactions; within the error of this technique the main bulk still remains apparently fully reduced. It is therefore suggested that the oxidized layer is too small proportionally to be detected in the bulk XANES spectra. Therefore, in order to constrain the oxidized layer and mechanisms of incorporation of U and Tc in the crystal structure, grazing incidence EXAFS (GIXAFS) on flat single crystals of wüstite is necessary. Farquhar et al. (2003) used this technique to profile the oxidation state of Mn in rhodonite [MnSiO₃] vs. depth of the mineral. In addition X-ray Photoelectron Spectroscopy (XPS) measurements on single crystals could potentially quantify the change in redox couples in the substrate and adsorbate.

EXAFS analyses

The results for the samples reacted with U(VI) and Tc(VII) resemble the reduced species of U(IV) and Tc(IV) determined in other studies for U and Tc adsorbed onto Fe-bearing minerals (Bargar et al., 1999; Boyanov et al., 2007; Iton et al., 2012; Liu et al., 2012; Fan et al., 2013). The experimental and simulated K-weigh ted x spectra of the samples analysed by EXAFS are presented in Fig. 5a and the Fourier Transform (FT) of these spectra are shown in Fig. 5b.

The U(IV) adsorbed on wüstite shows well resolved oxygen features. Fits of the FT resulted in a distorted polyhedron of five to six first shell oxygen atoms. One or two present at an average distance of R ≈ 2.25 Å and four additional oxygens at R ≈ 2.38 Å (Table 3). Figure 5a presents a model of the EXAFS data for U(IV) on wüstite. In the fixed pH 12 solution, the FT profile resembles that for the U(VI) uranyl species with two axial oxygen atoms at R = 1.82 Å and six to eight oxygen atoms in a split equatorial plane at R = 2.21 Å and R = 2.35 Å, respectively. The fit confirms that the linear uranyl (O–U–O)₂⁻ configuration is maintained at high pH (see Fig. 6b). In order to improve the fit, three paths of multiple scattering (MS) involving the U–O₃ nitrogen path at twice the distance were included.

On portlandite, five to six oxygen atoms were required to fit the amplitude of the first shell peak. In contrast to the high-pH wüstite sample, only one oxygen atom could be fitted in the first shell at R = 1.96 Å and four to five in a split equatorial plane at a distance of R = 2.24 Å and R = 2.7 Å,
Fig. 5. EXAFS spectra k3-weighted (a) and their Fourier transform (b) for U adsorbed on wüsite and portlandite and Tc on wüsite in extreme alkaline and near-neutral solutions. Black — experimental data; red — best fit model.

Table 3. Shell-by-shell fit results of bulk EXAFS.

<table>
<thead>
<tr>
<th></th>
<th>O/Oax</th>
<th>O/Oeq</th>
<th>O/Oeq2</th>
<th>C</th>
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<th>Fe2</th>
<th>Cu</th>
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<tr>
<td>Te K-edge</td>
<td>CN*</td>
<td>5.1</td>
<td>-</td>
<td>-</td>
<td>0.8</td>
<td>-</td>
<td>-</td>
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<tr>
<td>FeO pH6 Tc</td>
<td>R (Å)</td>
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<td>2.59</td>
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<tr>
<td>U Lm-edge</td>
<td>CN</td>
<td>1.7</td>
<td>4.5</td>
<td>-</td>
<td>0.9</td>
<td>1.1</td>
<td>-</td>
<td>4.1</td>
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<tr>
<td>FeO pH112 U + C</td>
<td>R (Å)</td>
<td>2.27</td>
<td>2.38</td>
<td>-</td>
<td>3.55</td>
<td>3.77</td>
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<tr>
<td>σ (Å²)</td>
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<td>0.0094</td>
<td>-</td>
<td>0.0031</td>
<td>0.01</td>
<td>-</td>
<td>0.011</td>
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<td>FeO pH16 U</td>
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<td>2.37</td>
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<td>σ (Å²)</td>
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<td>0.0123</td>
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<td>0.0079</td>
<td>0.0093</td>
<td>-</td>
<td>0.0068</td>
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<td>FeO pH6 U + C</td>
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<td>1.9</td>
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<td>1.5</td>
<td>1.6</td>
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<td>R (Å)</td>
<td>2.24</td>
<td>2.4</td>
<td>-</td>
<td>3.47</td>
<td>3.71</td>
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<td>σ (Å²)</td>
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<td>0.0044</td>
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<td>0.0111</td>
<td>0.0148</td>
<td>-</td>
<td>0.0066</td>
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<tr>
<td>FeO pH12 U</td>
<td>CN</td>
<td>2.1</td>
<td>3.5</td>
<td>4.8</td>
<td>2.4</td>
<td>0.9</td>
<td>-</td>
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<tr>
<td>R (Å)</td>
<td>1.82*</td>
<td>2.21</td>
<td>2.35</td>
<td>2.81</td>
<td>3.49</td>
<td>-</td>
<td>-</td>
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<tr>
<td>σ (Å²)</td>
<td>0.0017</td>
<td>0.0052</td>
<td>0.0061</td>
<td>0.0094</td>
<td>0.0014</td>
<td>-</td>
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<tr>
<td>Ca(OH)₂ pH12 U</td>
<td>CN</td>
<td>1.2</td>
<td>2.8</td>
<td>1.8</td>
<td>0.7</td>
<td>-</td>
<td>5</td>
<td>4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>R (Å)</td>
<td>1.96*</td>
<td>2.24</td>
<td>2.7</td>
<td>2.88</td>
<td>3.49</td>
<td>-</td>
<td>-</td>
<td>4.09</td>
<td>3.79</td>
</tr>
<tr>
<td>σ (Å²)</td>
<td>0.0025</td>
<td>0.0043</td>
<td>0.0148</td>
<td>0.0095</td>
<td>0.0041</td>
<td>0.0046</td>
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</table>

* CN – coordination number (±25%)
* contributions from three multipole scattering (MS) paths were taken into account.
respectively. These results are similar to those found for a uranate [UO₄] species (Macê et al., 2013).

Fe/Ca shells were resolved well in all samples at distances greater than those pertaining to the first-shell oxygen atoms. The fitted U–Fe distances are in good agreement with those published for U adsorbed onto Fe-minerals (Bargar et al., 1999; Boyanov et al., 2007), thus confirming surface attachment. In addition, U–U shells (R = 3.79–3.88 Å) were resolved in all the samples except for wüsite at pH 12 due to its poor signal-to-noise ratio. These distances show remarkable similarities with the results of Bargar et al. (2000) on hematite. The presence and distance of this U–U suggests a nanoparticulate or precipitate of uraninite on wüsite (Latta et al., 2012).

The Tc on wüsite spectrum showed two well resolved peaks, one for oxygen and one resulting from combined Tc and Fe scattering paths. Fits suggest a reduced species of Tc(IV), with a Tc–O bond length of R = 2.02 Å in the first shell and in the second shell Tc–Tc at R = 2.58 Å plus the presence of Tc–Fe at R = 2.59 Å (Fig. 6c). These data are in good agreement with results found for TcO₂-nH₂O (Morris et al., 2008; Peretyazhko et al., 2008; Fan et al., 2013).

For all the EXAFS with wüsite in near-neutral conditions, U and Tc were reduced. EXAFS results on the reacted minerals showed that U and Tc form inner-sphere complexes on the surfaces, bound in a bidentate fashion to two surface oxygen atoms with all four first-shell oxygens arranged in a square planar configuration. The surface oxygens resolved in this shell are consistent with oxygen atoms positioned along edge-sharing octahedral sites of Fe in wüsite. In addition, results for the uranyl ion on wüsite at high pH also suggest adsorption in a bidentate fashion via the equatorial plane, so that the uranyl axis would be parallel to the plane of the surface. This configuration is similar to that found for uranyl on α-Al₂O₃ (Denecke et al., 2003) and on Fe₃O₄(111) (Singer et al., 2012a). However, polarization-dependent GIXAFS on single crystals would constrain unambiguously this attachment by resolving directly the orientation of the linear uranyl complex relative to the surface plane. The well resolved Fe shells in combination with XRD results suggest that these attachment modes of U(IV), U(VI) and Tc(IV) are relatively stable inner-sphere adsorbates.

Uranium EXAFS results on portlandite resemble six-fold coordination in another alkaline earth phase, comparable to that of SrUO₄ (Randall and Ward, 1959) and CaUO₄ (Macê et al., 2013). The large number of Ca atoms surrounding the U central absorber is a strong indication that this is a co-precipitate. The fit suggests that this is a Ca-uranate [CaUO₄] species.

Conclusions

The goals of this study were to gain detailed insights into three aspects of mineral reactivity pertinent to GDF conditions: (1) to investigate the surface changes of wüsite altered with hyperalkaline fluids; (2) to quantify the adsorption of the radionuclides U and Tc under hyper-alkaline conditions on wüsite and portlandite; and (3) to determine the local coordination chemistry of these adsorbed radionuclides. The SEM and HRXRPD results indicated that the surface area of wüsite increased with increasing pH and carbonate concentration. In addition, pH and
carbonate concentrations also affect the adsorption of U and Tc dramatically, with decreasing adsorption at increasing pH and carbonate concentrations. Furthermore, results of XRD and EXAFS analyses show that U and Tc are adsorbed directly onto mineral edge sites in water. In portlandite, U showed a coordination shell involving Ca, which suggests a co-precipitate. These results will feed into risk assessments for the safe disposal of spent nuclear waste in GDFs and will form the basis for future surface-sensitive spectroscopy.

Acknowledgements

The authors gratefully acknowledge financial support for this research from the UK Nuclear Decommissioning Agency (RWMD) via EPSRC grant EP/1036389/1. The following authors contributed to this manuscript: OP, JQ and MPR performed the surface alteration and adsorption experiments and created the HR-XRPD and FEG-SEM images. AVV and KM prepared the EXAFS samples and AVV, JQ, MPR, JFWM and RAW performed the EXAFS measurements at Diamond. AVV and RAW analysed, fitted and interpreted the EXAFS results. AVV and RAW wrote the manuscript and OP, JQ GTW, KM, JFWM, MPR and NDME had equal input in finalizing the manuscript.

References


lessons from a 16-country study available at http://
thebulletin.org/managing-nuclear-spent-fuel-policy-
lessons-10-country-study. Accessed on 24 November
2013.
issues in nuclear waste disposal. Journal of Nuclear
dynamics simulation of uranyl(VI) adsorption
equilibria onto an external montmorillonite surface.
Physical Chemistry Chemical Physics, 7, 3580 – 3586.
Grenthe, I., Fuger, J., Konings, R.J.M., Lemire, R.J.,
Matier, A.B., Nguyen-Trung, C. and Wanner, H.
Organisation for Economic Co-operation and
Development. Nuclear Energy Agency. Data Bank,
Issy-les-Moulineaux, France.
Hastings, J.J., Rhodes, D., Fellerman, A.S.,
approaches for sludge management in the nuclear
Characterization of AISI 4340 corrosion products
using Raman spectroscopy. Corrosion Science, 74,
414 – 418.
Thermodynamic model for the solubility of TeO2-
2xH2O(ion) in the aqueous Te(V) – Na+ – Cl– – H+
– OH− – H2O system. Journal of Solution
Chemistry, 33, 199 – 226.
Hiemstra, T., Vanema, P. and van Riemslag, W.H.
(1996) Intrinsic proton affinity of reactive surface
groups of metal (hydr)oxides: The bond valence
principle. Journal of Colloid and Interface Science,
184, 680 – 692.
Hiemstra, T., Riemslag, W.H., Rosberg, A. and
Ulrich, K.-U. (2009) A surface structural model for
ferricydrite II: Adsorption of uranyl and carbonate.
Geochimica et Cosmochimica Acta, 73, 4437 – 4451.
Hudson, E.A., Terminello, L.J., Vian, R.E., Denecolin,
adsorption complexes on vermiculite and hydrobiotite.
Ilcz, E.S., Pacheco, I.S.L., Bugur, J.R., Shi, Z., Liu, J.,
Kovarik, L., Ingelhard, M.H. and Felmy, A.R.
(2012) Reduction of U(VI) incorporated in the
structure of hematite. Environmental Science &
Technology, 46, 9428 – 9436.
Itoh, J.D., Sesko, J.M., Krumholtz, L.R., Watson, D.,
Bogie, M.A., Penczek, A., Chang, Y.J. and White,
D.C. (2004) In situ bioreduction of technetium and
uranium in a nitrate-contaminated aquifer.
Environmental Science & Technology, 38, 468 – 475.
Kelly, S.D. (2010) Uranium chemistry in soils and
science, Vol. 34 (S. Bulwnt and G. Markus, editors).
Elsevier, Amsterdam.
Kelly, S.D., Newville, M.G., Chong, L., Kenner, K.M.,
Sutton, S.R., Fenter, P., Shurcho, N.C. and Spötl, C.
Environmental Science & Technology, 37,
1284–1287.
Kelly, S.D., Rashby, E.T., Chattopadhyay, S., Kroop,
uranium site in ancient organic-rich ecalite.
Environmental Science & Technology, 40,
2262–2268.
at low-temperatures with applications to
sedimentary ore deposits. Geochimica et
Cosmochimica Acta, 42, 547 – 569.
Latta, D.E., Gorski, C.A., Boyanov, M.I., O’Loughlin,
Influence of magnetic stoichiometry on U(VI)
reduction. Environmental Science & Technology,
46, 778 – 786.
Latta, D.E., Boyanov, M.I., Kenner, K.M., O’Loughlin,
E.J. and Scherer, M.M. (2012) Anionic reduction of
uranium by Fe(II) in soil. Applied Geochemistry, 27,
1512 – 1524.
Lear, G., McBeth, J.M., Boothman, C., Gunnig, D.J.,
Ellis, B.L., Lawson, R.S., Morris, K., Burke, I.T.,
Bryan, N.D., Brown, A.P., Livens, F.R. and Lloyd,
J.R. (2009) Probing the biogeochemical behavior of
technetium using a novel nuclear imaging approach.
Environmental Science & Technology, 44,
156 – 162.
Liu, J., Peerce, C.I., Qafoku, O., Arenholz, E., Heald,
tetramagnete (Fe₃O₄) nanoparticules. Geochimica &
Lloyd, J.R., Soile, V.A., Van Praagh, C.V.G. and Lovley,
D.R. (2000) Direct and Fe(II)-mediated reduction of
technetium by Fe(III) reducing bacteria. Applied
and Environmental Microbiology, 66, 3743 – 3749.
synthesis of ultrathin magnetic iron oxide nanoparticles
by schlor reaction. Nanoscale Research Letters,
Macel, N., Wieland, E., Dihm, R., Tiba, J. and Scheluwitz
Andreas, C. (2013) EMAF investigation on U(VI)
immobilization in hardened cement paste: Influence
of experimental conditions on speciation.
Radiocimica Acta International Journal for
Chemical Aspects of Nuclear Science and
Marsden, T.A., Morris, K., Law, G.T.W., Livens, F.R.,
Incorporation of uranium into hematite during
crystallization from ferricydrite. Environmental
Science & Technology, 48, 3724 – 3731.
U AND Te INTERACTIONS WITH WÜSTITE AND PORTLANDITE


RETARDATION OF URANIUM AND THORIUM BY A CEMENTITIOUS BACKFILL DEVELOPED FOR NUCLEAR WASTE DISPOSAL

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Abstract

This work describes the solubility of uranium and thorium under the chemical conditions anticipated in a cementitious repository for low and intermediate level radioactive waste. Similar solubilities were obtained for Th in all aqueous media, comprising NaOH (representing fresh cement pore water), Ca(OH)2 and water equilibrated with a bespoke limestone-rich cement designed specifically for application as a repository backfill. In contrast, the solubility of U(VI) was one order of magnitude higher in NaOH, whereas the presence of cellulose degradation products resulted in increased solubility for both elements by a comparable degree. Data from EXAFS (Extended X-ray Absorption Fine Structure) analysis suggested that the solubility limiting phase in the uranium experiments corresponds to a becquerelite-type solid, irrespective of whether cellulose degradation products are present. However, modelling using current thermodynamic data indicates a poorly crystalline, hydrated Ca-uranate phase. The solubility limiting phase for Th was ThO2 of intermediate crystallinity. No breakthrough of either U or Th was observed in diffusion experiments involving the backfill formulation after three years. Nevertheless, backscattering electron microscopy and microfocus X-ray fluorescence confirmed that uranium had penetrated 40 µm into the cement, implying active diffusion governed by slow dissolution-precipitation kinetics. As for the solubility experiments, precise identification of the uranium solid proved difficult, the latter displaying characteristics of both Ca-uranate and becquerelite. This highlights the ongoing need for standard reference spectra allowing reliable identification of waste-relevant solid phases by EXAFS.

Keywords: uranium, thorium, solubility, through-diffusion; cement; cellulose degradation products; repository backfill; radioactive waste.
1. Introduction

Cement is used widely for stabilisation of hazardous material owing to its capacity for both physical and chemical immobilisation of contaminant species (e.g. Wilk, 2004; Jantzen et al., 2010). For example, the present concept for the disposal of long-lived, low (LLW) and intermediate level (ILW) radioactive waste in the UK is based on grouting the waste in stainless steel canisters, placing the containers in a geological disposal facility (GDF) deep underground and backfilling with a bespoke cement matrix such as the Nirex Reference Vault Backfill (NRVB, Francis et al., 1997). In this multi-layered system, the cement acts not only as a physical barrier to migration but also contributes to the chemical containment of waste components by buffering the groundwater to a high pH, whereby the solubility of many target species is limited (Francis et al. 1997). Atkins and Glasser (1992) have defined five processes that affect the retardation of radionuclides in cementitious systems: (i) precipitation as a simple salt, typically a hydroxide; (ii) co-precipitation resulting in mixed salts; (iii) lattice incorporation in major cement hydration products; (iv) adsorption to hydrous surfaces and (v) formation of soluble complexes and colloids in the pore water.

Numerous examples can be found in the literature regarding the solubility, under hyper-alkaline conditions, of respectively, U(IV) (Baston et al., 1993; Fujiwara et al., 2005), U(VI) (Ewart et al., 1992; Baston et al., 1993; Sutton et al., 1999; Yamamura et al., 1998; King et al., 2008) and Th (Ewart et al., 1992; Thomason and Williams, 1992; Wierczinski et al., 1998; Neck et al., 2002, 2003; Brendebach et al., 2007; Kitamura et al., 2013). In the majority of cases, an attempt has been made to characterise the solid phase(s) responsible for limiting U concentrations in solution, though this was not always possible owing to the complexity of the matrix and the amorphous nature of the solids. Most studies on thorium focus on solubility measurements and colloid generation phenomena (e.g. Fanghänel and Neck, 2002) given its low solubility and tendency to hydrolyse. Less attention has been paid to Th adsorption (Wierczinski et al., 1998; Felipe-Sotelo et al., 2012) or incorporation into cement phases.

Bayliss et al. (1996) report partition coefficients ($R_d$) for the adsorption of U(VI) onto NRVB; values of 6 dm$^3$ g$^{-1}$ and 5 dm$^3$ g$^{-1}$ were obtained under non-saline and hypersaline conditions, respectively. More recent studies (Baston et al., 2012; Felipe-Sotelo et al., 2012) obtained $R_d$ values that were one order of magnitude higher for the same system. Baston et al. (2010, 2012) carried out batch sorption tests of U(VI) onto untreated and artificially aged
NRVB (either leached or leached followed by hydrothermal treatment at 80°C). These authors reported that, although ageing caused complete removal of portlandite and a reduction in pH, there were no significant changes to the sorptive capacity of the NRVB. Baston et al. (2010, 2012) attributed the capacity of NRVB for U(VI) uptake to calcium silicate hydrogel (CSH), which constitutes a large fraction of the hydrated cement. In related studies, Wieland et al. (2010) compared the R\textsubscript{d} values obtained for U(VI) onto cured sulphate-resistant ordinary Portland cement (R\textsubscript{d} = 2.5 dm\textsuperscript{-3} g\textsuperscript{-1}) with those for CSH (R\textsubscript{d} = 5 dm\textsuperscript{-3} g\textsuperscript{-1}, Harfouche et al., 2006). Assuming that CSH constitutes around 50% of the weight of the cured cement paste, they concluded that CSH must be the phase responsible for U(VI) retention.

EXAFS (Extended X-ray Absorption Fine Structure) analyses of UO\textsubscript{2}\textsuperscript{2+} loaded onto untreated and hydrothermally treated cement have been carried out by Sylwester et al. (2000). The uranyl ion appears to remain largely intact although, in the case of hydrothermally treated cement, there is some evidence of U-U bonding, indicative of oligomer formation or surface precipitation. Their study suggests that the uranyl ion interacts with cement minerals through an inner-sphere mechanism by sharing equatorial oxygen atoms.

One of the characteristics of the LLW and ILW inventory in the UK is the presence of cellulose residues, which degrade under alkaline conditions to give a complex mixture of carboxylated compounds (Pourchez et al., 2006) known collectively as cellulose degradation products (CDP). These compounds have the potential to complex radionuclides and inhibit their retention (van Loon and Glaus, 1998), either by increasing their solubility or by modifying the surface characteristics of the cement. Baker et al. (2003) studied the diffusion of U(VI) and Th through intact NRVB discs in the presence and in the absence of CDP. No breakthrough was observed on timescales up to 1000 days. However, subsequent analysis of the discs showed that U(VI) had penetrated 1.5 - 2 mm into the cement; diffusion of uranium appeared to be slower in the presence of CDP. Their findings match the results of batch tests reported by Felipe-Sotelo et al. (2012), who observed an increase in R\textsubscript{d} values for the adsorption of U(VI) onto NRVB from 33.7 dm\textsuperscript{3} g\textsuperscript{-1} to 282 dm\textsuperscript{3} g\textsuperscript{-1} in the presence of CDP. In comparison, Baker et al. (2003) derived R\textsubscript{d} values from the diffusion profiles of 18-22 dm\textsuperscript{3} g\textsuperscript{-1} without CDP and 62 dm\textsuperscript{3} g\textsuperscript{-1} with CDP, respectively. Unfortunately, the authors did not attempt to characterise the solid phase(s) responsible for U retention.
Rothe et al. (2013) and Bube et al. (2014) have characterised U(VI) phases in doped Ordinary Portland Cement (OPC) stored for two decades in NaCl and MgCl₂ brines. X-ray Absorption Near-edge Structure (µ-XANES) and Raman spectroscopy indicated that the uranium solids formed were similar to diuranates (CaU₂O₇/Na₂U₂O₇·xH₂O). The phases were largely amorphous; some localised formation of a uranophane-like (Ca(UO₂)₂(SiO₃OH)₂·5H₂O) phase suggesting metastability and that the transition to more thermodynamically stable mineral silicates is kinetically hindered. On the basis of EXAFS results, Wieland et al. (2010) also suggest that U(VI) in cement pastes presents a coordination environment comparable to uranophane. However, similar structural parameters were observed for U(VI) uptake by CSH (Harfouche et al., 2006), reinforcing the hypothesis that CSH is the main phase responsible for the retardation of U(VI) by cement.

The above studies serve to illustrate the difficulty in identifying uranium-containing phases in Portland cements. In the present work, a series of solubility experiments was carried out in alkaline solutions of increasing complexity, from NaOH, through Ca(OH)₂ and NRVB-equilibrated waters to solutions amended with CDP. The solubility values obtained in the various aqueous media were compared to those predicted by thermodynamic modelling using the JCHESS code (van der Lee, 1998) and published thermodynamic data (HATCHES Chemical Thermodynamic Database, version 20, freely available at http://www.hatches-database.com). Diffusion experiments were also carried out using NRVB monoliths, again with and without CDP. Identification of the solid phases responsible for retardation was attempted using EXAFS and complementary microscopic techniques.

2. Experimental

2.1. Solubility experiments

The solubility of uranium and thorium was assessed in six different media of increasing complexity in an attempt to represent analogue chemical conditions to those found in the near field of a cementitious repository. The solubility tests are part of a wider experimental programme devised by the Nuclear Decommissioning Authority, UK (NDA) to provide confidence in the concept of chemical containment. The solubility of several radioelements, namely Cs⁺, Ni²⁺, Eu³⁺, Th⁴⁺, UO₂²⁺/U⁴⁺, SeO₃²⁻ and I⁻, is being investigated to cover a range of oxidation states. The present work focuses on the results obtained for uranium and thorium.
Solubility measurements were approached from both the over- and under-saturation directions. The aqueous media tested were 0.02 mol dm$^{-3}$ NaOH, 95%-saturated Ca(OH)$_2$, NRVB-equilibrated water and cellulose degradation products generated in the presence of NRVB.

Deionised water (18 MΩ, Purite Neptune) was boiled and sparged for 1 hour with N$_2$ prior to the preparation of the NaOH (laboratory reagent grade, > 98%, Fisher Scientific) and Ca(OH)$_2$ (laboratory reagent grade, Fisher Scientific) solutions. A supersaturated Ca(OH)$_2$ solution was prepared by addition of excess of Ca(OH)$_2$ to the degassed, deionised water, followed by equilibration under N$_2$-atmosphere for 72 hours, after which the excess of Ca(OH)$_2$ was removed by filtration. The concentration was then reduced to 95% saturation by dilution with degassed deionised water, to avoid precipitation of Ca(OH)$_2$ during the experiments owing to changes in pressure or temperature. Full details regarding the preparation of the NRVB and CDP solutions, as well as compositional information, can be found in Felipe-Sotelo et al. (2014).

In order to assess the chemical conditions that would promote reduction of U(VI) to U(IV), additional experiments were carried out in which reducing agents were added to the CDP solutions; either Na$_2$S$_2$O$_4$ or solid Fe. In both cases, after filtration of the CDP solution, it was left to equilibrate with iron fillings (1 g Fe dm$^{-3}$, 1-2 mm granules, 99.98% (metal basis) Alfa Aesar®, Karlsruhe, Germany) for a period of 72 hours under N$_2$-atmosphere. After removal of the Fe fillings by filtration, 0.03 mol dm$^{-3}$ Na$_2$S$_2$O$_4$ (ca. 85% tech., Acrös Organics) was added as a holding reductant to a fraction of the CDP batch. All the solutions employed in the solubility experiments were subjected to ultrafiltration (30 kDa regenerated cellulose membranes, Millipore Amicon® Bioseparations, USA) for removal of any colloidal particles before the addition of the radionuclides. The membranes were pre-soaked in 0.1 NaOH before use and were fitted to an Amicon stirred cell (Model 8400, Merck Millipore) for ultrafiltration under N$_2$ pressure. 100 cm$^3$ aliquots of the solutions were then transferred to Teflon® containers.

For experiments using CDP with Fe as the reducing agent, two coupons of Fe (90mm $\times$ 15mm $\times$ 0.5mm, iron metal, general purpose grade, Fisher Scientific), were attached to the caps of the Teflon® containers with epoxy resin, so that 60 mm of the metal strips remained submerged in the CDP solution. For the over-saturation experiments, the solutions were spiked with 0.2 mol dm$^{-3}$ solutions of Th(NO$_3$)$_4$ (thorium nitrate hydrate puriss. 99%, Fluka)
and UO$_2$(NO$_3$)$_2$ (UO$_2$(NO$_3$)$_2\cdot$6H$_2$O, TAAB, UK) prepared in deionised water in order to provide a total inventory of $10^{-4}$ mol of either Th or U. The same total inventory of Th and U was added in the under-saturation experiments but, in this case, the radionuclides were added as a slurry. The precipitates had been generated in each of the aqueous media tested by addition of either Th(NO$_3$)$_4$ or UO$_2$(NO$_3$)$_2$ solutions to 15 cm$^3$ polypropylene centrifuge tubes. The resulting precipitates were left to age in contact with the supernatant solution for 28 days, after which the suspensions were centrifuged at 6000 rpm for 20 minutes and the supernatant removed; the resulting precipitate pellets were transferred to the Teflon® containers with the tests solutions. Ten replicates were prepared for each aqueous medium and saturation direction. The concentrations of U and Th were measured in the supernatant by inductively coupled plasma mass spectrometry (ICP-MS). For this purpose, 1 cm$^3$ samples were taken from each of the solutions and filtered with 0.2 µm PES syringe-top filters (Jaytee Biosciences Ltd) and acidified with HNO$_3$ (TraceSELECT®Ultra from Fluka, Steinheim, Germany), resulting in a final acid concentration of 2% v/v. The ICP-MS (Agilent, 7700x Series, Stockport, UK) was tuned and calibrated on a daily basis with traceable U and Th standards (Assurance from Spexcertiprep, Metuchen, NJ, USA), using Bi as internal standard (Assurance from Spexcertiprep). The limits of detection (LOD), based on three times the standard deviation of the blanks, were $4.1 \times 10^{-10}$ and $4.9 \times 10^{-10}$ mol dm$^{-3}$ for U and Th, respectively. Sampling was carried out in a glove box on a weekly basis over the first month of equilibration, moving to monthly sampling for the first year of the experiments and finally, to quarterly sampling for the remaining three years.

2.2. Through-diffusion experiments

The diffusion of uranium and thorium through NRVB was assessed using a radial diffusion configuration adapted from Markovaara-Koivisto et al. (2009) and successfully applied previously for the diffusion of Cs$^+$, I$^-$ (Felipe-Sotelo et al., 2014) and Cl$^-$ (van Es et al., 2015) through similar samples. The latter consisted of cylinders of cured NRVB with a central well where spikes containing either U or Th could be added. Full details regarding the preparation, curing and dimensions of the NRVB blocks are provided in Felipe-Sotelo et al. (2014). Two sets of experiments were carried out; in NRVB–equilibrated water and in CDP solution. Uranium and thorium slurry precipitates were produced by addition of a solution of either UO$_2$(NO$_3$)$_2$ or Th(NO$_3$)$_4$ to 0.5 mol dm$^{-3}$ NaOH and, after centrifugation (6000 rpm, 20 minutes) and removal of the supernatant solution, mixing and re-suspension in either
cement-equilibrated water or CDP solution. After placing the slurry in the central well of the NRVB cylinders, they were sealed, submerged in the appropriate solution and left in a glove box under N₂-atmosphere. The total inventory of U and Th added to the central well of the NRVB blocks was \(2.5 \times 10^{-4}\) mol. In all cases the NRVB blocks had been pre-equilibrated with the NRVB or CDP solution prior to introduction of the radionuclide precipitates (Felipe-Sotelo et al., 2014). Breakthrough was monitored by taking a 1 cm³ sample of the solution surrounding the cylinders and analysing by ICP-MS. Samples were filtered with a 0.2 µm PES syringe top filter in order to remove any debris from the NRVB blocks and then acidified before analysis. The solution taken from the containers was not replaced with fresh solution.

### 2.3. Solid characterisation

The nature and evolution of the solid phases formed was investigated by sacrificing two replicates at the end of each year of the solubility experiments. The samples were centrifuged and the aqueous supernatant removed, after which 1 cm³ of acetone (HPLC grade, 99.5% min, Fisher Scientific) was added to the precipitates followed by further centrifugation in order to remove any residual alkaline solution. After removal of the organic solvent, the solids were left to dry in a N₂-atmosphere glove box. In experiments in which the CDP solutions were in contact with Fe coupons, the latter were removed from solution and gently washed with a small amount of acetone to remove any trace of alkaline solution and then left to dry in the glove-box.

Samples from the solubility experiments were ground for EXAFS analysis using an agate pestle and mortar before mixing with cellulose to yield a concentration of approximately 2000 ppm. A 40 mg sample was placed into a Perspex sample holder, sealed with three layers of Kapton® tape and then heat sealed under nitrogen atmosphere. The EXAFS measurements were performed at the B18 experimental station at the Diamond Light Source, UK (Dent et al., 2009). This beamline is designed to collect bulk EXAFS analyses rapidly by using the Quick EXAFS mode. The energy of the beam was calibrated against the K-edge first derivative of a Y foil, defined at 17,038 eV. Measurements were conducted at the U LIII-edge in fluorescence mode using a nine element Ge detector mounted perpendicular to the incoming beam. The sealed samples were placed into a clamp so that each sample was positioned at 45° relative to the incoming X-ray beam. The EXAFS spectra were further corrected for remaining self-absorption using the Fluo algorithm in Athena 0.9.18 (Newville
et al., 1995). EXAFS w(k) values were refined from the raw data by standard procedures, including background subtraction, normalization of absorption and conversion to momentum and k space. For each sample ~34 spectra were averaged to improve the signal-to-noise ratio. The spectra were then analysed with Artemis 0.9.18 and the phase/amplitude functions were calculated by FEFF6L (Newville et al., 1995). The theoretical fits were performed in R-space.

At the end of the equilibration period, the cylinders used for diffusion experiments were cut axially with a diamond saw to expose the inner surface of the cement. The sectioned half cores were examined uncoated under variable pressure conditions using both backscatter scanning electron microscopy (BSEM) and large field detection (LFD, variable pressure ‘secondary’ imaging). Prior to BSEM- energy-dispersive X-ray analysis (EDXA), the samples were coated with a thin layer (25 nm) of carbon by carbon evaporation under vacuum using an EMITECH 960L evaporation-coating unit. EDXA data were acquired and processed using the Oxford Energy INCA Suite Version 5.04 Issue 21a+SP2 (2012) software package. All imaging was carried out using a FEI Company QUANTA 600 environmental scanning electron microscope (ESEM) equipped with an Oxford Instruments INCA EDXA system and a 50 mm² Peltier-cooled silicon drift detector (SSD) X-ray detector.

After the SEM-EDXA was complete, the half core samples were prepared for X-ray fluorescence mapping. The cores were dissected further to yield a wedge approximately 1 cm in thickness and with an area of 3 cm². The samples were then wrapped in Kapton® tape and placed into a heat sealed bag. X-ray fluorescence mapping was performed at the I18 station at the Diamond Light Source (Harwell, UK). The samples were analysed for uranium, calcium and iron using a beam size of 3 µm. Data were collected using a 9 element solid state detector. The resulting maps were analysed using the freely available software package, PyMCA. Precipitates mechanically removed from the central well of the diffusion cylinders were also analysed by EXAFS, as above.

3. Results

3.1. Concentrations of U and Th in solution

Significant differences were observed between uranium concentrations in the over-saturation, as opposed to the under-saturation, experiments (Figures 1a, 2 and 3). Concentrations for the former were approximately one order of magnitude higher than for under-saturation over the
entire duration of the experiments. The sole exception to this trend was found in the reducing CDP solution containing 0.03 mol dm\(^{-3}\) Na\(_2\)S\(_2\)O\(_4\) (Figure 3c), where both saturation directions gave similar results, at least at the beginning of the experiment. Again however, the results began to diverge beyond 200 days. Such differences should not occur in a system at true equilibrium. The fact that they do points to the slow dissolution of pre-existing uranium solid phases and the difficulty in separating ultra-fine particulates.

In the absence of organic ligands, NaOH exhibited the highest concentration of U in solution; experiments in 95%-saturated Ca(OH)\(_2\) and NRVB-equilibrated water gave solubility values approximately one order of magnitude lower and follow very similar trends (Figure 1a). For the over-saturation experiments, U concentrations decrease markedly over the first 28 days and then more gradually before stabilising after approx. 250 days (Figure 2). The trend is less clear in the under-saturation experiments. Uranium solubility shows an initial fall in NaOH but there is considerable variability in the data for Ca(OH)\(_2\) and NRVB solutions. The presence of CDP increased the solubility of uranium in all of the experiments (Figure 3). Initial concentrations of U in solution for the over-saturation tests were around \(10^{-5}\) mol dm\(^{-3}\), followed by a decrease of one order of magnitude over a period of 100 - 200 days. Addition of Fe coupons to the CDP solution had no significant impact on U solubility (Figure 3c). However, Na\(_2\)S\(_2\)O\(_4\), at a concentration of 0.03 mol dm\(^{-3}\), was effective in reducing U(VI) to U(IV) and this counteracts the solubilising influence of the CDP (Figure 1a).

The average concentrations of thorium measured in 0.02 mol dm\(^{-3}\) NaOH, 95%-saturated Ca(OH)\(_2\) and NRVB–equilibrated water overlap for both the over- and under-saturation experiments (Figure 4). As for uranium, solubility increases by approximately one order of magnitude in the presence of CDP (Figure 5).

3.2. Solid phase characterisation

A subset of precipitates from the over-saturation solubility experiments was subjected to EXAFS analysis in order to identify the solubility-limiting phases for uranium in each aqueous system. The analyses focussed predominantly on samples in the CDP-amended NRVB solution with reducing agents present, either 0.03 mol dm\(^{-3}\) Na\(_2\)S\(_2\)O\(_4\) or Fe coupons. EXAFS spectra and corresponding Fourier transforms with modelled data are shown in Figure 6.
The best fit for the uranium precipitates formed in the presence of elemental iron indicates that the uranium is in the (VI) oxidation state, with two axial oxygen at 1.8 Å and five equatorial oxygen atoms at distances between 2.32 and 2.42 Å. In order to improve the fit, it was necessary to consider the presence of second shell of four uranium atoms at between 3.70 and 3.83 Å. The fit was further improved by adding a path for a single calcium atom at a distance of 4.09 Å. The co-ordination numbers and bond distances are consistent with a U(VI) oxy-hydroxide such as becquerelite (Ca(UO$_2$)$_6$O$_4$(OH)$_6$·8H$_2$O). Thus, the scattering paths and co-ordination numbers taken from becquerelite crystallographic data (Pagoaga et al., 1987) were used to fit the EXAFS data.

In the case of uranium precipitates generated in CDP and 0.03 mol dm$^{-3}$ Na$_2$S$_2$O$_4$, there is a noticeable shift of the absorption edge to the left, indicating partial reduction of the uranium to U(IV). The EXAFS results were fitted using becquerelite crystallographic data, as for the previous sample; however, it was necessary to add a single scattering path from uraninite (UO$_2$) at 2.37Å to adequately describe the data. All fitting parameters for both precipitates are shown in Table 1.

3.3. Through-diffusion experiments

For the diffusion experiments through NRVB in radial configurations no breakthrough of uranium was observed after three years. Despite the increase of solubility observed for U caused by CDP, no breakthrough was for the NRVB blocks in contact with the organic compounds. The concentrations of Th in solution were below the limits of detection for the through diffusion experiments with and without CDP.

4. Discussion

4.1. Solubility

4.1.1. Concentrations of U and Th in solution

In the absence of organic ligands, uranium showed its highest solubility in 0.02 mol dm$^{-3}$ NaOH. Although the solubility of U suffered a marked reduction over the first 28 days of the experiments, it did not reach the levels attained in either saturated Ca(OH)$_2$ or NRVB solutions. Fanghænel and Neck (2002) attributed the reduction in solubility observed for
U(VI) in NaOH to changes in the solubility controlling phase and transformation of UO₂(OH)₂(s) to NaUO₂(OH)₃(s).

Overall, values obtained for the solubility of U(VI) from the under-saturation direction are lower than concentrations reported in the literature under similar experimental conditions (Table 2). The final concentration of U in 0.02 mol dm⁻³ NaOH was 5.8 × 10⁻⁸ mol dm⁻³; three orders of magnitude below that reported by Gayer and Leider (1955), who obtained 4.45 – 7.9 × 10⁻⁵ mol kg⁻¹. These authors studied the dissolution of UO₃H₂O, which is not crystallographically identical to the phase formed here. Moreover, incomplete filtration of particulates could account for the high concentrations observed in these early studies. The solubility of U(VI) in 95%-saturated Ca(OH)₂ (5.2 × 10⁻⁹ mol dm⁻³) is also significantly lower than the value obtained by Valsami-Jones and Ragnarsdóttir (1997) for microcrystalline UO₃ (5 × 10⁻⁷ mol dm⁻³) and CaU₁.₆O₅.₈·H₂O (8 × 10⁻⁷ mol dm⁻³). Slight differences in pH between the two studies may account in part for the discrepancy.

The final concentrations of U from the over-saturation direction were 1.9 × 10⁻⁶ mol dm⁻³ and 6.4 × 10⁻⁸ mol dm⁻³ in 0.02 mol dm⁻³ NaOH and 95%-saturated Ca(OH)₂ respectively. These results fit well with the data of Lucchini et al. (2007) who reported concentrations ranging from 7 × 10⁻¹⁰ to 10⁻⁷ mol dm⁻³. It should be noted that, although the experiments reported by Lucchini et al. (2007) were carried out at similar pH (12), the ionic strength of the solutions was much higher than in the present work (Table 2).

The average concentrations of U(VI) in the NRVB-equilibrated water were 7.3 ± 3.8 × 10⁻⁸ mol dm⁻³ and 4.6 ± 3.6 × 10⁻⁹ mol dm⁻³ for the over- and under-saturation experiments, respectively. These values are very similar to the data for Ca(OH)₂, suggesting that portlanditite plays a major role in NRVB solution chemistry. Uranium solubilities 2 - 4 orders of magnitude higher have been reported in earlier over-saturation experiments in cement-equilibrated water: Ewart et al. (1992) and Baston et al. (1993) obtained U(VI) ≈ 5 × 10⁻⁶ mol dm⁻³ at pH 12 and 2 × 10⁻⁵ mol dm⁻³ at pH 13. These authors used Ordinary Portland Cement: Blast Furnace Slag (OPC:BFS) at a ratio of 1:9 and consequently, the two systems are not directly comparable.

Uranium solubility determined in the presence of CDP is similar to previous results obtained by Baston et al. (1993) for OPC:BFS cement waters and by Greenfield et al. (2000) in an NRVB solution (Tables 2 and 3). Higher solubility values quoted by Greenfield et al. (2000)
reflect CDP with 10% cellulose loading compared to the 5% w/w loading in the present study.

Brendebach et al. (2007) reported a significant increase in Th solubility to \( \sim 10^{-7} - 10^{-3} \) mol dm\(^{-3}\) under alkaline solutions (pH 11-12) with CaCl\(_2\) present owing to formation of the \( \text{Ca}_4[\text{Th(OH)}_8]^{4+} \) complex, the latter identified by EXAFS. A similar increase was not apparent in the present work and there is little difference between the solubility of Th measured in NaOH, Ca(OH)\(_2\) or NRVB solutions ([Ca] \( \approx 0.01 \) mol dm\(^{-3}\)). It should be noted that the concentrations of Ca employed by Brendebach et al. (2007) were up to two orders of magnitude higher than those considered here. The variability in results with time is due in part to limitations in the measurements since the concentrations of thorium in solution are very close to the limit of detection of the ICP-MS. Another factor could be incomplete removal of colloidal particles, given the tendency of thorium to hydrolyse (Neck et al., 2002).

The final concentrations obtained for thorium after 1340 days equilibration are listed together with literature values in Table 4. Thorium solubility in NaOH ranged between \( 2.1 \times 10^{-10} \) and \( 3.7 \times 10^{-8} \) mol dm\(^{-3}\), which compares reasonably well with the values reported by Neck et al. (2002) for the same solution (\( 1.8 \times 10^{-9} - 6.8 \times 10^{-7} \) mol dm\(^{-3}\)). The average concentration for Th in NRVB-equilibrated water over the whole experimental period was \( (4 \pm 6) \times 10^{-9} \) mol dm\(^{-3}\) for both over- and under-saturation experiments; again, this value compares well with values reported previously by Ewart et al. (1992), \( \sim 4 \times 10^{-9} \) mol dm\(^{-3}\) in two cement- (OPC: BFS and OPC: limestone) equilibrated waters at pH 12. More recently, Kitamura et al. (2013) obtained \( 7 \times 10^{-10} \) to \( 2 \times 10^{-8} \) mol dm\(^{-3}\) in squeezed OPC pore water at pH 13.5. Wierczinski et al. (1998) measured the solubility of microcrystalline ThO\(_2\) in fresh cement (pH 13.22) and aged cement-equilibrated water (pH 12.45), obtaining \([\text{Th}] \approx 10^{-9} \) mol dm\(^{-3}\) and \( \approx 10^{-10} \) mol dm\(^{-3}\), respectively.

4.1.2. Comparison with modelling predictions

The solubilities of U and Th in the six aqueous media studied were modelled with the JCHESS code (van der Lee, 1998) and published thermodynamic data (HATCHES Chemical Thermodynamic Database, Version 20) and compared to the experimental data.

For uranium in 0.02 mol dm\(^{-3}\) NaOH, the model predicts the formation of Na\(_2\)U\(_2\)O\(_7\) as the solubility-controlling phase, with concentrations in solution ranging between 1.3 and \( 3.3 \times 10^{-7} \) mol dm\(^{-3}\). These values are around one order of magnitude lower than the concentrations
obtained for the over-saturation experiments (Figure 2a). Gorman-Lewis et al. (2008) pointed out that one of the sources of variability in the calculation of solubility products for uranyl minerals is related, among other factors, to particle size since a reduction in size would lower the interfacial free energy of the solid phase and therefore, increase its solubility. They reported differences of 2 to 3 orders of magnitude in the calculated solubility of U due to such variability, in view of which, agreement between theory and experiment is reasonable. The thermodynamic data used to predict uranium solubility in NaOH correspond to crystalline Na$_2$U$_2$O$_7$ with a solubility product of log $K_{sp} = 22.6$ (for the reaction $\text{Na}_2\text{U}_2\text{O}_7 + 6\text{H}^+ \leftrightarrow 2\text{Na}^+ + 2\text{UO}_2^{2+} + 3\text{H}_2\text{O}$). However, when considering only poorly crystalline Na$_2$U$_2$O$_7$ or NaUO$_2$(OH)$_3$(s) with log $K_{sp} = 25.1$ (Yamamura et al., 1998), the predicted solubility is $(2.3 - 5.9) \times 10^{-6}$ mol dm$^{-3}$, which is in better agreement with the results obtained, at least for the over-saturation experiments. The models overestimate the solubility obtained for the under-saturation experiments, irrespective of whether constants for Na$_2$U$_2$O$_7$(hydr) or Na$_2$U$_2$O$_7$(cr) are considered (Figure 2a) serving to highlight the degree of uncertainty associated with different experimental protocols.

For both the Ca(OH)$_2$ and NRVB systems, the model predicts precipitation of CaUO$_4$ as the solubility controlling phase and equilibrium aqueous U concentrations of around $3 \times 10^{-14}$ mol dm$^{-3}$. The calculated concentrations are unrealistically low and several orders of magnitude below the experimental values. Changing the solubility product reported in the HATCHES database from log $K_{sp} = 15.9$, taken from Wanner and Forest (1992), to 23.1, as reported by Moroni and Glasser (1995) for the reaction $\text{CaUO}_4 + 4\text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{UO}_2^{2+} + 2\text{H}_2\text{O}$, results in an increase in the calculated solubility to $(4 - 9) \times 10^{-7}$ mol dm$^{-3}$. These values are in much better agreement with the experimental results for Ca(OH)$_2$ and NRVB-equilibrated water (Figures 2b and c2).

Taking isosaccharinic acid (ISA) as a surrogate of CDP and without reducing agents, the main species in solution, as predicted by the models, is UO$_2$ISA$^{3-}$. It is necessary to introduce the solubility product for CaUO$_4$ reported by Moroni and Glasser (1995) in order to approximate the concentrations of U observed experimentally ($10^{-6}$ - $2 \times 10^{-6}$ mol dm$^{-3}$, for over-saturation; Figures 3a,c). The models indicate no significant reduction of U(VI) to U(IV) in the presence of Fe coupons at $E_{h}$ -34 mV (standard hydrogen electrode, SHE), as observed experimentally. With the addition of 0.03 mol dm$^{-3}$ Na$_2$S$_2$O$_4$ to the CDP system, the model predicts precipitation of UO$_2$(cr) and formation of UISA$^-$ as the main species in
solution. Allowing only for precipitation of UO$_2$(am), the predicted aqueous concentrations increase to \((4 - 6) \times 10^{-7}\) mol dm$^{-3}$, in good agreement with the solubility obtained in the over-saturation experiments (Figure 3b), with similar contributions from U(OH)$_4$(aq) and UISA$^-$ to the total U concentration in solution.

In broad terms, consideration of amorphous solubility-controlling phases allowed satisfactory prediction of U concentrations in all of the six aqueous media investigated. Systematic overestimation of the concentration in solution for experiments carried out from the undersaturation direction suggests that the solid phases produced exhibit an intermediate crystallinity between purely crystalline and amorphous Na$_2$U$_2$O$_7$ (in NaOH), CaUO$_4$ (in CaOH and NRVB, including experiments with CDP) or UO$_2$ (CDP + Na$_2$S$_2$O$_4$). However, characterisation of the solids by EXAFS raises the possibility that becquerelite may be the solubility-controlling phase in Ca-rich systems; therefore, new calculations were carried out allowing only this solid to form. With an average log $K_{sp}$ = 42.45 calculated from the published solubility products of respectively, Rai et al.(2002), Sandino and Grambow (1994) and Vochten and van Haverbeke (1990), precipitation of becquerelite is not predicted and the U concentration in solution corresponds to the total inventory added (10$^{-3}$ mol dm$^{-3}$). Casas et al. (1997) reported a much lower solubility product for becquerelite (log $K_{sp}$ = 29 ± 1). Taking this value, the U concentration predicted in the NRVB solution is $6.5 \times 10^{-7}$ mol dm$^{-3}$. This result tallies better with measured data but nevertheless, still overestimates solubility obtained experimentally by at least an order of magnitude. It is noted that the EXAFS spectra interpreted as becquerelite are merely indicative of this phase (Smith et al., 2015) and by no means definitive in the absence of certified reference material.

Initial predictions of thorium solubility using the published HATCHES database (http://www.hatches-database.com/) gave the unrealistically low $2.2 \times 10^{-16}$ mol dm$^{-3}$, controlled by thorianite (ThO$_2$); some 7 - 8 orders of magnitude below the values obtained experimentally. Fanghänel and Neck (2002) speculated that the very large variability in reported solubility values for Th as well as widespread discrepancies between experimental and thermodynamic modelling results could be due to control of experimental conditions, leading to a variety of oxy-hydroxides displaying different degrees of hydration (ThO$_n$(OH)$_{4-2n}$(am)). The difference in solubility between crystalline ThO$_2$ (log $K_{sp}$ = -54.2 ± 1.3), microcrystalline ThO$_2$ (log $K_{sp}$ = -53.2 ± 0.4) and ThO$_2$(am, hyd) or Th(OH)$_4$(am) (log $K_{sp}$ = -47.8 ± 0.3) could be explained on the basis of the particle size and incomplete removal of colloids,
which contribute to the measured concentration. Fanghänel and Neck (2002) highlighted the fact that, for very small particles with highly hydrated surfaces, the OH− groups would determine their chemical properties. Thus, Neck et al. (2003) observed that, in undersaturation experiments using ThO2(cr) and alkaline conditions, Th concentrations in solution were more consistent with the dissolution of Th(OH)4(am) and five orders of magnitude higher than for the original crystalline phase (5 × 10^{-10} as opposed to 2 × 10^{-16} mol dm^{-3}). These authors concluded that an amorphous layer forms on the surface of ThO2(cr), as result of the adsorption of monomeric or polymeric hydroxide complexes and it is this amorphous layer rather than the bulk crystalline solid that controls thorium solubility. Therefore, new calculations were performed allowing only for the precipitation of amorphous ThO2 (either “fresh” or “aged”, with log Ksp = 9.30 and 8.50 respectively, for the reaction ThO2 + 4H+ ↔ Th^{4+} + 2H2O). As expected, the calculated values provide a much better fit to the experimental measurements (Figure 4).

The HATCHES database (http://www.hatches-database.com/) provides stability constants for the complexation of Th with only two relevant organic ligands, isosaccharinate and acetate, (ThISA−, log K = -10.5 and ThAcet^{3+}, Th(Acet)_{2}^{2+}, Th(Acet)_{3}^{+}, Th(Acet)_{4}, Th(Acet)_{5} with log K = -0.57, -4.47, -3.93, -6.06 and -10.10, respectively) and the resulting model predicts no significant complexation of Th with either ligand under these experimental conditions. Mixed hydroxyl-ISA complexes, such as Th(OH)ISA^{2+}, Th(OH)_{3}(ISA)_{2}^{−} and Th(OH)_{4}(ISA)_{2}^{3−} have been reported by Rai et al. (2009), albeit in the absence of calcium. Some authors have suggested the formation of a calcium-thorium-ISA (Ca:ISA:Th = 1:2:1) complex in solution (Vercammen et al., 1999, 2001; Wieland et al., 2002; Tits et al., 2005). Gaona et al. (2008) carried out a comprehensive review of the stability constants for the complexation of ISA with tetravalent actinides. Re-calculating the values to ensure internal consistency resulted in log K = 64.04 for the formation of CaTh(OH)_{4}(ISA)_{2} for the reaction Th^{4+} + Ca^{2+} + 2ISA^{5−} + 4H_{2}O ↔ CaTh(OH)_{4}(ISA)_{2}. Using this constant for CaTh(OH)_{4}(ISA)_{2} has little impact on the calculated solubility of Th in CDP solution; the dominant aqueous species remains Th(OH)_{4(aq)}. Assuming that the entire inventory of organic compounds in the CDP mixture behaves as ISA (TOC = 187 mg dm^{-3} ≡ 2.6 mol dm^{-3} ISA), an estimated stability constant of log K = 50 for the ThISA− complex would be needed to reproduce the experimental results (predicted Th_{aq} = 1.8 × 10^{-8} mol dm^{-3}, Figure 5). Thus, unless there are gross errors in published constants for thorium-ISA complexation, it is concluded that ISA is a poor surrogate for the assemblage of organic moieties that comprise
CDP. The importance of re-evaluating stability constants for all organic ligands under Ca-rich, alkaline conditions has been highlighted recently by Pallagi et al. (2014).

4.2. Through-diffusion experiments

4.2.1. Diffusion of U(VI) through NRVB

Since no breakthrough of uranium was observed after three years of the diffusion experiments, two replicates were sacrificed, one with and one without CDP, in order to determine the extent of diffusion. The central well is clearly visible in each cylinder, displaying the characteristic yellow coating of a U(VI)-rich precipitate (Figure S1 in Supplementary Information, SI). Samples of the precipitate were removed from the surface of the cements and compositional data collected by EDXA from 10 locations. The resulting data gave average Si:Ca:U:O atomic ratios of 0.1: 0.9: 1: 4, which match closely with the composition of calcium uranate (i.e. CaUO₄). The presence of minor silicon may indicate incipient formation of a uranyl silicate, such as uranophane, but equally could be due to the overlapping spectrum of an unresolved microcrystalline cementitious (CSH) phase. The presence of CDP does not lead to any discernible change in mineral composition, suggesting that precipitate formation is not affected by the organic compounds.

In contrast, EXAFS spectra for these precipitates resemble those collected from the solubility experiments described above. The latter were tentatively identified as U(VI) oxy-hydroxides as the data show a good fit to the co-ordination numbers and scattering paths from becquerelite crystal data (all fitting parameters are tabulated in Table 5). This apparent conflict when attempting to identify uranium precipitates in hyper-alkaline, calcium-rich systems has been reported by other workers. Smith et al. (2015) found that electron diffraction images as well as TEM-EDX data (transmission electron microscopy – EDX) correspond to calcium uranate for uranium solids formed in ‘old cement leachates’ (U concentration 4.2 × 10⁻⁶ mol dm⁻³). However, the results of X-ray Absorption Spectroscopy for solids generated at higher uranium concentrations (2 × 10⁻⁵ mol dm⁻³) fit better with a uranyl oxy-hydroxide solid, such as becquerelite. These authors attributed the discrepancy between the two sets of data to changes in speciation caused by differences in the concentration of U used in the experiments. In the present work, both EDXA and EXAFS analyses were carried out on the same sample; therefore, any disagreement between the two techniques cannot be attributed to differences in U concentration.
It is worth noting that, although the uranium solids originally introduced into the central well of the diffusion blocks were precipitated in NaOH solution, the solids at the end of the diffusion experiment correspond to Ca-U compounds, proving that the transformation of Na-U into Ca-U solids is not only possible at high pH, but also a rapid process.

Backscattering (BSEM) images of the central well (Figure S2 in SI) show that, in the absence of CDP, the U(VI) precipitates do not penetrate into the cement matrix. This was further confirmed by EDXA mapping of the edge of the well (Figure 7a) and by micro-focus X-ray fluorescence mapping coupled with EXAFS. When CDP are present, BSEM, in combination with EDXA (Figure 7b) and micro-focus X-ray fluorescence mapping, indicate discreet areas of higher uranium concentration clearly visible within the NRVB matrix. Uranium penetrated into the NRVB cylinder to a depth of approximately 40 µm during the three years of the diffusion experiment; a slow but nevertheless measurable rate. Whether this is due to complexation by the organics or modification of cement surfaces (van Es et al., 2015) is not yet known. EXAFS analysis of the uranium phase within the cement matrix corresponds to a U(VI) oxy-hydroxide precipitate, consistent with results for bulk precipitates removed from the central well.

4.2.2. Diffusion of Th though NRVB

There was no evidence of thorium breakthrough after three years in either of the diffusion experiments and, as for uranium, two of the replicates were sectioned longitudinally to study diffusion profiles. BSEM images of Th-rich precipitates collected from the central well of the first cylinder, representing diffusion in the absence of CDP, show a thick (~ 100 µm) gel coating the wall (Figure S3a) above a layer of dendritic (Figure S3b) and acicular crystals (Figure S4). These morphologies suggest rapid precipitation of hydrous phases from solution. Backscattering images of the edge of the well and EDXA elemental mapping across the boundary area show high concentrations of thorium within the well but no indication of diffusion into the cement matrix. There is a negative correlation with Ca concentrations and no apparent relationship to either silicon or iron (Figure 8a).

Broadly similar crystal forms were found in the experiment with CDP; however in this case, the Th-rich coating is much thinner at ~ 10 µm. Again, elemental mapping suggests insignificant diffusion of Th into the NRVB (Figure 8b).
5. Conclusions

Uranium solubility measurements undertaken on a series of hyper-alkaline solutions revealed systematic and significant differences between values obtained from the over- and undersaturation directions. The former are generally higher, which may reflect incomplete removal of ultra-fine particulates. However, the bias persists over an extended time frame and could equally well reflect the slow dissolution kinetics of solids used in the under-saturation tests.

Uranium solubility in a bespoke backfill, NRVB, is similar to that in 95%-saturated Ca(OH)\textsubscript{2} solution and an order of magnitude lower than in NaOH. The addition of cellulose degradation products increased the solubility of U by a further order of magnitude in comparison to NRVB alone. The presence of CDP appeared to affect only aqueous speciation; there is no evidence of any change in the solubility-controlling phases produced. Previous studies (Atkins and Glasser, 1992 and references therein) identified several mineral phases that could be responsible for the immobilisation of U(VI) in cement systems; these include two mineral phases present in nature, becquerelite (Ca(UO\textsubscript{2})\textsubscript{6}O\textsubscript{4}(OH)\textsubscript{6}·8H\textsubscript{2}O) and uranophane (Ca(UO\textsubscript{2})\textsubscript{2}·2H\textsubscript{2}O·SiO\textsubscript{2}·6H\textsubscript{2}O) as well as synthetic phases such as Ca\textsubscript{2}UO\textsubscript{5}·1.3-1.7H\textsubscript{2}O. There was little evidence of uranophane or other silicate formation in the present study. Compositionally, the solids most closely resemble calcium uranate (CaUO\textsubscript{4}) whereas EXAFS spectra suggest a uranyl oxy-hydroxide, possibly becquerelite.

Metallic iron, employed as a surrogate for corroding steel, also caused no change in mineralogy or uranium oxidation state. Characterisation of the solids generated when a more potent reducing agent, Na\textsubscript{2}S\textsubscript{2}O\textsubscript{4}, is used revealed only partial reduction of U(VI) to U(IV). EXAFS analysis of the solids indicated U atoms in a chemical environment intermediate between uraninite and becquerelite.

Thorium results are less conclusive owing to the limited solubility of this element at high pH. Nevertheless, thermodynamic modelling using amorphous ThO\textsubscript{2} as the solubility-controlling phase generally provided a satisfactory fit to the experimental data. CDP cause an increase in thorium solubility for all of the alkaline solutions tested. However, thermodynamic models using surrogate ligands (e.g. ISA) underestimated the effect of CDP by more than an order of magnitude. This highlights the need for critical revision of the stability constants for Th with ISA and other CDP components under hyper-alkaline conditions.
No breakthrough was observed for either U or Th in diffusion experiments through intact cylinders of NRVB. Subsequent BSEM imaging and micro-focus X-ray fluorescence on cut sections confirmed that U had in fact penetrated 40 µm into the cement matrix over the three-year duration of the experiments, but only in a solution containing CDP. No migration of uranium was apparent in the absence of organics. Thorium rapidly precipitates forming a gel-like coating in the central well of the NRVB cylinders and does not penetrate into the matrix whether or not CDP are present.

As noted above, some discrepancies were found when attempting to identify largely amorphous, uranium phases using complementary techniques. Whereas SEM-EDX analyses on precipitated solids indicate formation of calcium uranate, EXAFS data for the same material suggest a closer fit to becquerelite. This inconsistency may reflect the fact that the solubility-controlling phase is not pure or presents an intermediate chemical composition that has not yet been fully described. It also highlights the complexity of cementitious systems and the need for standard matrices allowing reliable identification of solid phases by advanced spectroscopic methods.

6. Acknowledgements

We are grateful to the Nuclear Decommissioning Authority - Radioactive Waste Management Directorate (NDA-RWMD) for funding this work. The authors would like to thank the Diamond Light Source for access to beamlines I18 and B18, in particular, Prof Fred Mosselmans, Prof Andy Dent, Dr Steve Parry (Diamond Light Source Ltd) and Dr Sam Shaw (Manchester University, Env-Rad-Net) for their assistance. The authors acknowledge Prof Peter Warwick for his support during the first stages of this project. A.E.M. and L.P.F. publish with the permission of the Executive Director of the British Geological Survey (NERC).

7. References


Figure captions

Figure 1.- Final concentrations after 1340 days equilibration for (a) U and (b) Th in alkaline media.

Figure 2.- Total uranium (as determined by ICP-MS) and calculated concentration (dotted lines) in: (a) 0.02 mol dm$^{-3}$ NaOH; (b) 95%-saturated Ca(OH)$_2$ and (c) NRVB-equilibrated water. Each point corresponds to the average and ± SD of the available replicates.

Figure 3.- Total uranium (as determined by ICP-MS) and calculated concentration (dotted lines) in: (a) CDP produced in NRVB; (b) CDP in the presence of Fe coupons and (c) CDP in the presence of 0.03 mol dm$^{-3}$ Na$_2$S$_2$O$_4$. Each point corresponds to the average and ± SD of the available replicates.

Figure 4- Total thorium (as determined by ICP-MS) and calculated concentration (dotted lines) in: (a) 0.02 mol dm$^{-3}$ NaOH; (b) 95%-saturated Ca(OH)$_2$ and (c) NRVB-equilibrated water. Each point corresponds to the average and ± SD of the available replicates.

Figure 5- Total thorium (as determined by ICP-MS) and calculated concentration (dotted lines) in CDP produced in NRVB. Each point corresponds to the average and ± SD of the available replicates.

Figure 6- $k^3$-weighted $\chi$ functions with Fourier transforms for: U precipitates in the presence and absence of CDP. Blue lines represent experimental data and red lines are the fits using the parameters listed in Tables 4 and 5.

Figure 7- Backscattering images and EDXA elemental mapping of the edge of the central well in the NRVB blocks used in the diffusion of U(VI): (a) in the absence of CDP and (b) in the presence of CDP (note that heavier elements such as uranium appear bright white in the backscattered images).

Figure 8- Backscattering images and EDXA elemental mapping of the edge of the central well in the NRVB blocks used in the diffusion of Th: (a) in the absence of CDP and (b) in the presence of CDP (note that heavier elements such as thorium appear bright white in the backscattered images).
Figure 1

(a) U concentration (mol dm$^{-3}$) vs. NaOH, Ca(OH)$_2$, NRVB, CDPs, CDP + Na$_2$S$_2$O$_4$, CDP + Fe.

(b) Th concentration (mol dm$^{-3}$) vs. NaOH, Ca(OH)$_2$, NRVB, CDP.

Figure 1
Figure 2
Figure 3

(a) CDP -- Oversaturation
CDP -- Undersaturation
Moroni & Glasser (1995) -- pH 12.3
Moroni & Glasser (1995) -- pH 13.3

(b) CDP + Na2S2O4 -- Oversaturation
CDP + Na2S2O4 -- Undersaturation
UO2(am) -- pH 11.8
UO2(am) -- pH 12.7

(c) CDP + Fe -- Oversaturation
CDP + Fe -- Undersaturation
Figure 4

(a) [Graph showing colloidal growth of Th(IV) for NaOH oversaturation and undersaturation, amorphous ThO$_2$ (aged and fresh), and HATCHES 20.

(b) [Graph showing colloidal growth of Th(IV) for Ca(OH)$_2$ oversaturation and undersaturation, amorphous ThO$_2$ (aged and fresh), and HATCHES 20.

(c) [Graph showing colloidal growth of Th(IV) for NRVB oversaturation and undersaturation, amorphous ThO$_2$ (aged and fresh), and HATCHES 20.]

Figure 4

-271-
Figure 5

-272-
Figure 6
Table 1.- EXAFS best fit parameters for the uranium precipitates generated in the CDP solutions in the presence of reducing agents

<table>
<thead>
<tr>
<th></th>
<th>CDP in NRVB with Na$_2$S$_2$O$_4$</th>
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<th>CDP in NRVB with solid Fe</th>
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<tr>
<td></td>
<td>N</td>
<td>R/Å</td>
<td>σ$^2$</td>
<td>N</td>
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<td>U-O$_{ax}$</td>
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<td>2</td>
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<td>U-O$_{eq1}$</td>
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<td>1.91</td>
<td>0.0011</td>
<td>2.5</td>
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<tr>
<td>U-O$_{eq2}$</td>
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<td>2.16</td>
<td>0.0006</td>
<td>2.5</td>
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<td>U-U$_1$</td>
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<td>0.0017</td>
<td>2</td>
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<td>U-U$_2$</td>
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<td>0.0037</td>
<td>2</td>
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<td>U-Ca</td>
<td>1</td>
<td>4.21</td>
<td>0.0100</td>
<td>1</td>
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<tr>
<td>U-O$_{uraninite}$</td>
<td>8</td>
<td>2.37</td>
<td>0.0076</td>
<td>---</td>
</tr>
<tr>
<td>S0$^2$</td>
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<td>E0</td>
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<td>4.72</td>
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<td>Reduced χ$^2$</td>
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<td>3.29</td>
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<td>R</td>
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<td>0.017</td>
<td>0.036</td>
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</table>
Table 2.- Summary of the solubilities obtained for U(VI) and comparison with published data

<table>
<thead>
<tr>
<th>Liquid medium</th>
<th>Method</th>
<th>[U] (mol dm(^{-3}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02 mol dm(^{-3}) NaOH</td>
<td>Oversaturation</td>
<td>(1.9 \times 10^{-6})</td>
<td>This work(^a)</td>
</tr>
<tr>
<td>0.0230-0.0199 mol kg(^{-1}) NaOH</td>
<td>Undersaturation</td>
<td>((4.45 - 7.9) \times 10^{-5}) mol kg(^{-1})</td>
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<td>pH 12, (I = 4.965)</td>
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<td>(7 \times 10^{-10}) - (10^{-7})</td>
<td>Lucchini et al. (2007)(^c)</td>
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<tr>
<td>0.02 mol dm(^{-3}) NaOH</td>
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<td>(5.8 \times 10^{-8})</td>
<td>This work(^a)</td>
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<tr>
<td>95%-saturated Ca(OH)(_2)</td>
<td>Oversaturation</td>
<td>(6.4 \times 10^{-8})</td>
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<tr>
<td>Saturated Ca(OH)(_2), pH = 12.2</td>
<td>Undersaturation</td>
<td>(5 \times 10^{-7})</td>
<td>Valsami-Jones and Ragnarsdóttir (1997)</td>
</tr>
<tr>
<td></td>
<td>Undersaturation</td>
<td>(8 \times 10^{-7})</td>
<td></td>
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<tr>
<td>95%-saturated Ca(OH)(_2)</td>
<td>Undersaturation</td>
<td>(5.2 \times 10^{-9})</td>
<td>This work(^a)</td>
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<tr>
<td>BFS:OPC equilibrated water (pH 13)</td>
<td>Oversaturation</td>
<td>(10^{-5})</td>
<td>Baston et al. (1993)</td>
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<td>NRVB equilibrated water</td>
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<td>Greenfield et al. (2000)</td>
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<td>(2 \times 10^{-6})</td>
<td>Biddle et al. (2000)</td>
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<td>(3.7 \times 10^{-9})</td>
<td>This work(^a)</td>
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<tr>
<td>10% cellulose CDP in NRVB</td>
<td>Oversaturation</td>
<td>(1 \times 10^{-9})</td>
<td>Greenfield et al. (2000)</td>
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<td>1% cellulose CDP in NRVB</td>
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<td>(2 \times 10^{-9})</td>
<td>Biddle et al. (2000)</td>
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<tr>
<td>CDP in NRVB(^b)</td>
<td>Oversaturation</td>
<td>(1.5 \times 10^{-6})</td>
<td>This work(^a)</td>
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<tr>
<td>CDP in NRVB(^b)</td>
<td>Undersaturation</td>
<td>(3.0 \times 10^{-8})</td>
<td>This work(^a)</td>
</tr>
</tbody>
</table>

\(^a\) Final results after 1340 days equilibration

\(^b\) 5\% cellulose load; 187 mg dm\(^{-3}\) TOC

\(^c\) From graph
Table 3.- Summary of the solubilities obtained for U(IV) and comparison with published data

<table>
<thead>
<tr>
<th>Liquid medium</th>
<th>Holding reagent</th>
<th>Method</th>
<th>[U] (mol dm⁻³)</th>
<th>Reference</th>
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<tr>
<td>NaOH pH = 12.36 / 0.5 mol dm⁻³ HClO₄</td>
<td>Na₂S₂O₄</td>
<td>Oversaturation</td>
<td>2.59 × 10⁻⁸</td>
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<tr>
<td>BFS:OPC equilibrated water (pH &gt; 10.5)</td>
<td>0.05 mol dm⁻³ Na₂S₂O₄</td>
<td>Oversaturation</td>
<td>3 × 10⁻⁷</td>
<td>Baston (1993)</td>
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<tr>
<td>NRVB equilibrated water</td>
<td>Na₂S₂O₄</td>
<td>Oversaturation</td>
<td>8 × 10⁻⁷</td>
<td>Greenfield et al. (2000)</td>
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<tr>
<td>BFS:OPC equilibrated water (pH 12.3)</td>
<td>0.05 mol dm⁻³ Na₂S₂O₄</td>
<td>Undersaturation</td>
<td>2 × 10⁻⁷</td>
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<td>10% cellulose CDP in NRVB</td>
<td>Na₂S₂O₄</td>
<td>Oversaturation</td>
<td>1 × 10⁻⁴</td>
<td>Greenfield et al. (2000)</td>
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<tr>
<td>CDP in NRVB&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.03 mol dm⁻³ Na₂S₂O₄</td>
<td>Oversaturation</td>
<td>8.2 × 10⁻⁷</td>
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<td>0.03 mol dm⁻³ Na₂S₂O₄</td>
<td>Undersaturation</td>
<td>1.8 × 10⁻⁷</td>
<td>This work&lt;sup&gt;a&lt;/sup&gt;</td>
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<sup>a</sup> Final results after 1340 days equilibration
<sup>b</sup> 5% cellulose load; 187 mg dm⁻³ TOC
Table 4.- Summary of the solubilities obtained for Th and comparison with published data

<table>
<thead>
<tr>
<th>Liquid medium</th>
<th>Method</th>
<th>$\left[\text{Th}\right]$ (mol dm$^{-3}$)</th>
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<tr>
<td>0.02 mol dm$^{-3}$ NaOH</td>
<td>Oversaturation</td>
<td>$5.8 \times 10^{-10}$</td>
<td>This work$^a$</td>
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<tr>
<td>0.02 mol dm$^{-3}$ NaOH</td>
<td>Undersaturation</td>
<td>$2.8 \times 10^{-9}$</td>
<td>This work$^a$</td>
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<tr>
<td>0.5 mol dm$^{-3}$ NaCl / 0.02 mol dm$^{-3}$ NaOH</td>
<td>Undersaturation (ThO$_2$(am))</td>
<td>$6.6 \times 10^{-7}$ -- $1.8 \times 10^{-9}$</td>
<td>Neck et al. (2002)</td>
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<tr>
<td>0.5 mol dm$^{-3}$ NaCl/NaOH (pH 11.0 – 13.5)</td>
<td>Undersaturation (ThO$_2$(cr))</td>
<td>$5 \times 10^{-10}$</td>
<td>Neck et al. (2003)</td>
</tr>
<tr>
<td>0.1 – 0.5 mol dm$^{-3}$ NaCl / NaClO$_4$ (pH= 6-14)</td>
<td>Undersaturation (ThO$_2$·xH$_2$O)</td>
<td>$3.2 \times 10^{-9}$</td>
<td>Brendebach et al. (2007)</td>
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<tr>
<td>95%-saturated Ca(OH)$_2$</td>
<td>Oversaturation</td>
<td>$8.0 \times 10^{-7}$</td>
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<td>95%-saturated Ca(OH)$_2$</td>
<td>Undersaturation</td>
<td>$2.8 \times 10^{-9}$</td>
<td>This work$^a$</td>
</tr>
<tr>
<td>BFS:OPC:limestone equilibrated water</td>
<td>Oversaturation</td>
<td>$4 \times 10^{-9}$</td>
<td>Thomason and Williams (1992); Ewart et al. (1992)</td>
</tr>
<tr>
<td>NRVB equilibrated water</td>
<td>Oversaturation</td>
<td>$&lt;2 \times 10^{-10}$</td>
<td>Greenfield et al. (2000)</td>
</tr>
<tr>
<td>OPC squeezed pore water</td>
<td>Oversaturation</td>
<td>$7.1 \times 10^{-10}$ -- $2.4 \times 10^{-8}$</td>
<td>Kitamura et al. (2013)</td>
</tr>
<tr>
<td>NRVB equilibrated water</td>
<td>Oversaturation</td>
<td>$1.6 \times 10^{-10}$</td>
<td>This work$^a$</td>
</tr>
<tr>
<td>CEM I 42.5 HS equilibrated water (pH 12.45)</td>
<td>Undersaturation (ThO$_2$(micro))</td>
<td>$10^{-10}$ -- $10^{-9}$</td>
<td>Wierczinski et al. (1998)</td>
</tr>
<tr>
<td>NRVB equilibrated water</td>
<td>Undersaturation</td>
<td>$3.3 \times 10^{-10}$</td>
<td>This work$^a$</td>
</tr>
<tr>
<td>10% cellulose CDP in NRVB</td>
<td>Oversaturation</td>
<td>$2 \times 10^{-9}$</td>
<td>Greenfield et al. (2000)</td>
</tr>
<tr>
<td>1% cellulose CDP in NRVB</td>
<td>Oversaturation</td>
<td>$10^{-8}$</td>
<td>Biddle et al. (2000)</td>
</tr>
<tr>
<td>CDP in NRVB$^b$</td>
<td>Oversaturation</td>
<td>$7.3 \times 10^{-8}$</td>
<td>This work$^a$</td>
</tr>
<tr>
<td>$4 \times 10^{-4}$ mol kg$^{-1}$ ISA at pH 12.01 (NaOH/HCl)</td>
<td>Undersaturation (ThO$_2$(am))</td>
<td>$1.6 \times 10^{-9}$ mol kg$^{-1}$</td>
<td>Rai et al. (2009)</td>
</tr>
<tr>
<td>CDP in NRVB$^b$</td>
<td>Undersaturation</td>
<td>$2.7 \times 10^{-9}$</td>
<td>This work$^a$</td>
</tr>
</tbody>
</table>

$^a$ Final results after 1340 days equilibration

$^b$ 5% cellulose load; 187 mg dm$^{-3}$ TOC
Table 5.- EXAFS best fit parameters for the uranium precipitates deposited in central well of the NRVB blocks used for diffusion with and without CDP

<table>
<thead>
<tr>
<th></th>
<th>NRVB</th>
<th></th>
<th>CDP in NRVB</th>
<th></th>
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<tr>
<td></td>
<td>N</td>
<td>R/Å</td>
<td>σ²</td>
<td>N</td>
</tr>
<tr>
<td>U-O_{ax}</td>
<td>2</td>
<td>1.79</td>
<td>0.0005</td>
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<tr>
<td>U-O_{eq1}</td>
<td>3</td>
<td>2.40</td>
<td>0.0057</td>
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<tr>
<td>U-O_{eq2}</td>
<td>2</td>
<td>2.25</td>
<td>0.0032</td>
<td>2</td>
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<tr>
<td>U-U_{1}</td>
<td>3</td>
<td>3.78</td>
<td>0.0110</td>
<td>3</td>
</tr>
<tr>
<td>U-U_{2}</td>
<td>1</td>
<td>3.62</td>
<td>0.0028</td>
<td>1</td>
</tr>
<tr>
<td>U-Ca</td>
<td>1</td>
<td>4.01</td>
<td>0.0050</td>
<td>1</td>
</tr>
<tr>
<td>S0²</td>
<td>1.00</td>
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<td></td>
<td>0.64</td>
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<tr>
<td>E0</td>
<td>4.87</td>
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<td></td>
<td>9.93</td>
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<tr>
<td>Reduced χ²</td>
<td>30.70</td>
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<td></td>
<td>39.48</td>
</tr>
<tr>
<td>R</td>
<td>0.012</td>
<td></td>
<td></td>
<td>0.017</td>
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