Radionuclide Speciation During Mineral Reactions in the Chemically Disturbed Zone Around a Geological Disposal Facility

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<th>Definition</th>
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<tbody>
<tr>
<td>ALARP</td>
<td>As Low As Reasonably Practicable</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller method of specific surface area analysis</td>
</tr>
<tr>
<td>BIGRAD</td>
<td>Biogeochemical Gradients and Radionuclide Transport</td>
</tr>
<tr>
<td>Bq</td>
<td>Becquerel, SI unit of radioactivity defined as one nuclear disintegration per second</td>
</tr>
<tr>
<td>C-A-S-H</td>
<td>Calcium-Aluminium-Silicate-Hydrate</td>
</tr>
<tr>
<td>CDZ</td>
<td>Chemically Disturbed Zone</td>
</tr>
<tr>
<td>CIF</td>
<td>Crystallographic Information File</td>
</tr>
<tr>
<td>CNMMN</td>
<td>Commission on New Minerals and Mineral Names</td>
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<tr>
<td>CoRWM</td>
<td>Committee on Radioactive Waste Management</td>
</tr>
<tr>
<td>cpm</td>
<td>Counts per minute</td>
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<td>C-S-H</td>
<td>Calcium-Silicate-Hydrate</td>
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<tr>
<td>DECC</td>
<td>Department for Energy and Climate Change</td>
</tr>
<tr>
<td>Defra</td>
<td>Department for Environment, Food and Rural Affairs</td>
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<tr>
<td>DMRB</td>
<td>Dissimilatory Metal-Reducing Bacteria</td>
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<tr>
<td>DWF</td>
<td>Debye-Waller Factor</td>
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<tr>
<td>EDS / EDX</td>
<td>Energy Dispersive X-Ray Spectroscopy</td>
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<td>Electron Energy Loss Spectroscopy</td>
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<td>Electron Microscopy</td>
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<tr>
<td>EXAFS</td>
<td>Extended X-Ray Absorption Fine Structure</td>
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<tr>
<td>FHY</td>
<td>Ferrihydrite</td>
</tr>
<tr>
<td>FT</td>
<td>Fourier Transform</td>
</tr>
<tr>
<td>Ga</td>
<td>Gigaannus ((10^9 \text{ years}))</td>
</tr>
<tr>
<td>GBq</td>
<td>Gigabecquerel ((10^9 \text{ Bq}))</td>
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<td>GDF</td>
<td>Geological Disposal Facility</td>
</tr>
<tr>
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<td>HAW</td>
<td>Higher Activity Wastes</td>
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<td>High Level Waste</td>
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<td>IAEA</td>
<td>International Atomic Energy Agency</td>
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<tr>
<td>IC</td>
<td>Ion Chromatography</td>
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<td>ICDD</td>
<td>International Centre for Diffraction Data</td>
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<td>ICL</td>
<td>Intermediate Cement Leachate</td>
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<td>IGDTP</td>
<td>Implementing Geological Disposal of Radioactive Waste Technology Platform</td>
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<td>Intermediate Level Waste</td>
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<td>kBq</td>
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<td>PTFE</td>
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</tr>
<tr>
<td>SKB</td>
<td>Svensk Kärnbränslehantering AB, Swedish Nuclear Fuel and Waste Management Company</td>
</tr>
<tr>
<td>SLC</td>
<td>Site Licence Company</td>
</tr>
<tr>
<td>SNF</td>
<td>Spent Nuclear Fuel</td>
</tr>
<tr>
<td>SSA</td>
<td>Specific Surface Area</td>
</tr>
<tr>
<td>TBq</td>
<td>Terabecquerel ($10^{12}$ Bq)</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>THMC</td>
<td>Thermal, Hydrological, Mechanical, Chemical</td>
</tr>
<tr>
<td>US-DOE</td>
<td>United States Department of Energy</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultra-Violet – Visible light photospectrometry</td>
</tr>
<tr>
<td>VLLW</td>
<td>Very Low Level Waste</td>
</tr>
<tr>
<td>WIPP</td>
<td>Waste Isolation Pilot Plant, New Mexico, USA</td>
</tr>
<tr>
<td>XANES</td>
<td>X-Ray Absorption Near Edge Structure</td>
</tr>
<tr>
<td>XAS</td>
<td>X-Ray Absorption Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>YCL</td>
<td>Young Cement Leachate</td>
</tr>
</tbody>
</table>
List of Symbols

\( \sigma_f \)  Combined error
\( \bar{x}_i \)  Arithmetic mean of a triplicate set of measurements
\( \sigma_i \)  Standard deviation of \( \bar{x}_i \)
\( \mu(E) \)  Energy absorption function
\( \lambda \)  Wavelength of electron beam
\( d \)  Lattice diffraction plane spacing
\( L \)  Camera focal length
\( \chi(k) \)  EXAFS function
\( E_0 \)  Absorption edge energy
\( \mu_0(E) \)  Edge-step at the absorption edge
\( S_0^2 \)  EXAFS amplitude reduction factor
\( N \)  Coordination number
\( R \)  Interatomic distance
\( \sigma^2 \)  Debye-Waller factor
\( R \)  EXAFS goodness of fit parameter
\( \chi^2 \)  Chi square function
\( \chi^2_0 \)  Reduced Chi square function
\( \varepsilon_i \)  EXAFS measurement uncertainty
\( F \)  F-test function to compare two EXAFS fits
\( n \)  Number of independent data points in a range of EXAFS data
\( m \)  Number of independent variables used in an EXAFS fit
\( b \)  Dimension of hypothesis between two EXAFS fits compared via an F-test
\( \alpha \)  Confidence level at which two EXAFS fits are considered significantly different to each other
Geological disposal of radioactive wastes currently stored at Earth's surface is now the favoured management pathway for these materials. Typically, intermediate level wastes (ILW) are grouted and emplaced in a geological disposal facility (GDF) which will be backfilled, possibly with cementitious materials. Post-closure leaching of the cementitious materials in a GDF is expected to create hyperalkaline conditions in and around the repository, resulting in mineral alteration and crystallisation, both within the engineered barrier and host rock; creating a persistent chemically disturbed zone (CDZ). Iron derived from within the host rock as a result of alkaline breakdown of Fe-bearing silicate minerals (e.g. biotite, chlorite); corrosion products formed within the repository; or iron contained within the waste; will form secondary iron (oxyhydr)oxide minerals. The formation and re-crystallisation of these reactive mineral phases may sequester radionuclides through a host of processes: surface-mediated reduction to less soluble forms; adsorption onto, and/or incorporation into stable secondary or tertiary iron oxide phases. Therefore iron (oxyhydr)oxides will be key to the fate of radionuclides potentially released from within radioactive wastes disposed of in a GDF.

In this study, the fate of U(VI) and Tc(VII) was considered during crystallisation of ferrihydrite to more stable iron oxide phases (e.g. hematite and magnetite) and, in three synthetic cement leachates (pH 13.1, 12.5, 10.5) designed to reflect the early-, middle- and late-stage evolution of the CDZ. XRD and SEM/TEM have been used to characterise the mineralogy during crystallisation. Partitioning of U(VI) and Tc(VII) between the solid and solution has been followed throughout, with chemical extractions used to determine the distribution of the radionuclides adsorbed to, and incorporated within the solid. Synchrotron-based XAS techniques have been utilised to probe the oxidation state and molecular scale bonding environment of the radionuclides associated with the solids. The data suggest that: U(VI) is incorporated into the hematite structure in place of Fe(III), in a distorted octahedral environment with elongation of the uranyl bond; Tc(VII) is reduced to Tc(IV) and incorporated into the octahedral site within the magnetite structure in place of Fe(III), and is retained in the same environment even after extensive oxidation of the magnetite to maghemite; and that U(VI) may also be incorporated as U(V) or U(VI) into the magnetite structure, with similar recalcitrant behaviour during oxidation. These results highlight the importance of mineral reactions within the CDZ as potentially significant pathways for immobilising radionuclides released from a GDF.
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Acknowledgements

First and foremost, I would like to extend my deepest thanks and gratitude to my two supervisors, Sam Shaw and Kath Morris, for giving me the opportunity to undertake this project; for their continuing support and guidance; for providing a stimulating and challenging environment in which to work; and for their confidence in me to succeed.

Another constant source of support and advice, both academic and personal, has been Gareth Law. Gareth has been ever ready to offer advice on laboratory techniques, conference presentations and manuscript preparation; in addition to how to manage a PhD.

I am indebted to Fred Mosselmans for his ability to both enlighten and infuriate in equal measure. Fred’s knowledge of XAS data collection and analysis has been invaluable and essential for the successful completion of this project, even if his special way with words and seemingly incomprehensible thought process have required often more brain power to follow and understand than the science originally under discussion.

This project has involved a significant element of synchrotron science, with many long hours spent in various beamline hutch. My thanks go to all those fellow researchers with whom I have shared those hours, especially to Adam Williamson for late night pot noodle and 80s power ballads, and to Nick Masters-Waage for the world record score on GeoGuesser.com.

My thanks also go to all in the Cohen Labs in Earth Sciences at The University of Leeds. The first two years of my PhD were made easier and happier by their support both in the labs and in the pub. Special thanks must be reserved for Lizzy Moyce for her help with experimental setup, for looking after my experiments after I departed for Manchester, and for being a great conference buddy.

I must thank the contributions from all those who have assisted with the various analytical techniques I have utilised during the last four years: Sam Allshorn for all his general help in the Cohen Labs and for IC; Leslie Neve and John Waters for their assistance with XRD in Leeds and Manchester, respectively; Mike Ward and Andy Brown for driving the TEM on my behalf; Paul Lythgoe for undertaking all the ICP-MS and ICP-OES analyses; and finally, Chris Boothman for his general assistance in the labs in Manchester.

This whole period of my life and education was possible thanks to the counsel of my former line manager, Mark Cowper, who, over an Asahi beer - on the top floor of a Tokyo hotel - encouraged me to pursue my dreams. The rest, as they say, is history.

Finally, there is one person who above all deserves my sincerest thanks; without her all of this would be for nought. Her unwavering support and love has given me the strength of conviction to complete this thesis. This is for you, Rachel, my beautiful wife. Thank you.

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About The Author

Tim matriculated at the University of Oxford in October 2002, reading Earth Sciences at University College. He was admitted to the degree of Master of Earth Sciences (MEarthSci) in July 2006, being placed in the Second Class, Division One. Shortly after graduating, Tim joined Serco Assurance (later Serco Technical Assurance Services), a technical consulting business in the nuclear industry operating at Tier 3 level, based at Risley near Warrington. Whilst there, he worked on a range of projects for customers such as the Nuclear Decommissioning Authority, Sellafield, Magnox and the Japanese Atomic Energy Agency, focussing on radioactive waste disposal and characterisation of contaminated land at nuclear licensed sites around the UK. In October 2010, Tim left the nuclear industry to begin postgraduate study as part of the BIGRAD consortium, initially based at The University of Leeds, in the Earth Sciences Department, but moving across the Pennines in August 2012 to complete the project in the School of Earth, Atmospheric and Environmental Sciences at The University of Manchester.
Chapter 1  Project Introduction

This chapter will place the work presented in this thesis into context by giving a brief overview of radioactive waste arising out of power generation activities and the current internationally accepted best approach for managing and disposing of this waste. Radioactive waste is also generated through defence activities but these activities and the types of waste arising are not discussed here. The work contained in this thesis lies at the boundary of environmental mineralogy and radiochemistry and presents fundamental science of relevance to a wide range of scenarios where radioactivity is in contact with dynamic environmental systems, both at the Earth’s surface and deep within. The research hypotheses that have framed this project are detailed and a brief outline of the thesis’ structure is also given.

1.1  Context

The world’s first commercial nuclear power plant (NPP), Calder Hall in West Cumbria, was opened in 1956. According to the International Atomic Energy Agency (IAEA), as of 22nd September 2014, there are a total of 437 NPPs currently in operation around the world, with a further 70 under construction (www.iaea.org/PRIS). In the UK, there are currently 16 NPPs in operation whilst a further 29 NPPs have been permanently shut down and are undergoing decommissioning. Throughout the almost 60 years of nuclear power generation, the inventory of spent nuclear fuel (SNF) and other associated radioactive wastes has been steadily increasing, held in interim storage with no defined disposal route.

Radioactive wastes are classified into three main categories: low- (LLW), intermediate- (ILW) and high-level wastes (HLW). In the UK, radioactive wastes are classified based upon the nature and quantity of the radioactivity that they contain and their heat-generating capacity (Pöyry Energy, 2011) as outlined in Table 1-1. Typically SNF is classified as HLW, although in the UK SNF is still regarded as a resource and so is not formally declared as waste (Defra, 2008). Higher activity waste (HAW) consists HLW, ILW and a small fraction of LLW, and is currently planned for deep geological disposal in an engineered geological disposal facility (GDF), as stated in the UK Government’s Managing Radioactive Waste Safely White Paper (Defra, 2008). The total volume of radioactive waste from existing facilities within the UK is forecast to be 4.5 million m³, approximately 96 % of which has already been produced and 1 million m³ has already been disposed of as LLW and Very Low Level Waste (VLLW) (Pöyry Energy & Amec, 2013a). HLW contributes the majority of the radioactive content of the wastes (95 %), despite accounting for less than 0.1 % of the volume, whilst ILW accounts for 5% of the radioactivity and 6 % of the volume (Pöyry Energy & Amec, 2013b).
**Table 1-1** UK radioactive waste categories, classification criteria, disposal route and forecast volumes

<table>
<thead>
<tr>
<th>Waste Classification</th>
<th>Criteria</th>
<th>Disposal Route</th>
<th>Forecast Volume $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HLW</td>
<td>Wastes in which the temperature may rise significantly as a result of their radioactivity, so this factor has to be taken into account in the design of storage or disposal facilities.</td>
<td>Planned for disposal in a deep geological disposal facility for HAW</td>
<td>1,100 m$^3$</td>
</tr>
<tr>
<td>ILW</td>
<td>Wastes 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.</td>
<td>Near surface disposal in lined trenches at the Low Level Waste Repository. (Some LLW is earmarked as HAW)</td>
<td>290,000 m$^3$</td>
</tr>
<tr>
<td>LLW</td>
<td>Wastes having a radioactive content not exceeding 4 GBq per tonne of alpha, or 12 GBq per tonne of beta/gamma activity.</td>
<td>Disposal permitted to either: specified landfill sites unspecified destination with municipal, commercial or industrial waste</td>
<td>1,400,000 m$^3$</td>
</tr>
<tr>
<td>VLLW</td>
<td>A sub-category of LLW with lower specific activity limits: bulk disposal – maximum activity of 4 MBq per tonne ‘dustbin loads’ – less than 400 kBq per 0.1 m$^3$ with no single item greater than 40 kBq</td>
<td>Disposal permitted to either: specified landfill sites unspecified destination with municipal, commercial or industrial waste</td>
<td>2,800,000 m$^3$</td>
</tr>
</tbody>
</table>

$^a$Forecast volume is taken from the 2013 UK Inventory of Radioactive Wastes (Pöyry Energy & Amec, 2013a)

Disposal of radioactive waste in a GDF is the internationally accepted management pathway for disposing of these types of materials in the long-term. Currently there are several underground research facilities (e.g. Grimsel and Mont Terri, Switzerland; ONKALO, Finland; Horonobe, Japan; Bure, France) but only one operational disposal facility for higher activity wastes (WIPP, USA), which is solely for disposal of military derived waste. UK Nirex Limited announced plans to build a rock characterisation facility (RCF) at Longlands Farm, Cumbria. Between September 1995 and February 1996, an appeal was heard against Cumbria County Council’s decision to refuse planning permission for the RCF, which was rejected by the Secretary of State for the Environment on 17th March 1997 (Styche, 1997). The failure of the Nirex programme highlighted the need for greater emphasis on underpinning science over a reliance on sorption coefficient data. In 2003, the UK Government set up the Committee on Radioactive Waste Management (CoRWM) to consider the long-term management of the UK’s radioactive waste in the context of protecting the public and the environment. In 2004, The Nuclear Decommissioning Authority (NDA) was set up in order to manage the
decommissioning of the UK’s civil nuclear estate, with the remit for safe and secure disposal with their Radioactive Waste Management Directorate (RWMD). CoRWM reported to the Government in 2006 with the recommendation that safe and secure deep geological disposal was the preferred means of managing the legacy from nuclear operations (CoRWM, 2006). The Government accepted CoRWM’s recommendation and in 2008 published the Managing Radioactive Waste Safely White Paper (MRWS) (Defra, 2008) outlining the Government policy to seek a volunteer community to host a deep geological disposal facility for radioactive waste. In July 2011, the European Commission adopted the ‘Radioactive waste and spent fuel management directive’, explicitly stating that member states that have engaged in civil nuclear activities address the issue of their radioactive waste through a national program of research and development, leading to disposal in a GDF (Council Directive 2011/70/Euratom). However, on 30th January 2013 Cumbria County Council decided to withdraw from the MRWS process, despite both Allerdale and Copland Borough Councils’ decisions to continue with the process. As a result of the decision and since no other local communities had come forward to express a formal interest in participating, the MRWS process came to a close. In response to this and further Government consultation on the MRWS process, a new White Paper was published by the Department for Energy and Climate Change (DECC) on 24th July 2014 (DECC, 2014). This new process maintains the spirit of volunteerism but incorporates a national geological screening programme to help underpin development of a generic safety case and to inform discussions with interested communities.

1.2 Geological Disposal Concepts

![Figure 1-1 The multi-barrier principle for containment of radioactive wastes in a geological disposal facility.](image-url)
Various disposal concepts have been developed around the world upon which NDA-RWMD has drawn for its own generic design concepts. All disposal concepts utilise the multi-barrier approach Figure 1-1 which relies upon a series of independent engineered barriers, as well as the natural barrier provided by the host rock, to maintain isolation of the radioactive materials from the biosphere. Typically the engineered barrier system consists of the wasteform itself, which is encased in some form of canister or other containment to create the waste package. Waste packages are then emplaced in a drift or vault which has been excavated at depth in a suitable host rock. The waste packages are then backfilled with a suitable material to fully encase them. The access shafts and tunnels are then also backfilled and sealed. Various choices have been made regarding the materials used for each of the barriers which depend upon the waste type and the chosen host rock. For example, HLW is typically immobilised in a glass inside a steel canister, whereas ILW is more usually grouted using cementitious materials. Bentonite is the backfill of choice in an argillaceous host rock for its swelling capacity and low hydraulic conductivity. However, cementitious materials are a good option in hard rock scenarios (e.g. granite) where their geochemical impact is less severely adverse for the host rock but the induced conditions typically favour reduced radionuclide mobility.

The various generic disposal concepts currently being considered by NDA-RWMD are listed in Table 1-2, and Figure 1-2 illustrates the concept for ILW disposal in a higher strength rock. The engineered barrier will have a finite lifetime, on the order of $10^5$ years, beyond which it will no longer be able to guarantee the containment of the waste, leading to potential release of radionuclides into the geosphere. At this point, containment of radionuclides is provided by the natural barrier, i.e. the host rock. The efficacy of the natural barrier will be affected through thermal, hydrological, mechanical, or chemical (THMC) processes; e.g. leaching of a cementitious backfill will create a chemically disturbed zone (CDZ) in the host rock.

**Table 1-2** NDA-RWMD illustrative disposal concepts

<table>
<thead>
<tr>
<th>Host Rock Type</th>
<th>Illustrative Geological Disposal Concept Examples</th>
<th>ILW / LLW</th>
<th>HLW / SNF</th>
</tr>
</thead>
</table>
| Higher strength rocks | UK ILW/LLW concept  
(NDA, UK) | | KBS-3V concept  
(SKB, Sweden) |
| Lower strength sedimentary rocks | Opalinus Clay concept  
(Nagra, Switzerland) | | Opalinus Clay concept  
(Nagra, Switzerland) |
| Evaporites | WIPP Bedded Salt concept  
(US-DOE, USA) | | Gorleben Salt Dome concept  
(DBE-Technology, Germany) |

*Reproduced from Geosol Disposal: Steps towards implementation (Nuclear Decommissioning Authority, 2010)*
Figure 1-2 Illustrative UK concept for ILW/LLW disposal in a higher strength rock. Redrawn from Geological Disposal: Steps Towards Implementation (Nuclear Decommissioning Authority, 2010).

1.3 Radioactivity in the Environment

Anthropogenic radioactivity is found in the natural environment through both authorised and unauthorised discharges. For example, Sellafield and other nuclear licenced sites have authorised discharge limits whereby they are able to release limited quantities of radioactivity to the environment. Several studies have focussed on the retention of Sellafield discharges by the sediments along the Cumbrian coastline, in particular the Ravenglass Estuary (Eakins et al., 1990; Morris et al., 2000; Keith-Roach et al., 2003). There have also been numerous unauthorised discharges around the world, as in the case of the leaking storage tanks on the US-DOE Hanford site (Catalano et al., 2004; Ainsworth et al., 2005; Um et al., 2009) and in the highly publicised cases of the Chernobyl and Fukushima accidents. Further to these localised releases, the global background radioactivity was increased as a result of nuclear weapons testing between the 1940s and 1960s.

In the natural environment, radionuclide mobility is largely governed by the prevailing geochemical conditions, with pH, Eh and ionic strength having an impact upon the solubility of a particular radionuclide. In general, higher solubility equates to enhanced environmental mobility whilst when solubilities are lower mobility tends to be lower. However, formation of stable colloid phases may occur when the solubility limit is exceeded which may in turn create a very mobile phase. For the major contaminant radionuclides that exist in multiple oxidation states (e.g. actinides, technetium), the more oxidised states (e.g. U(VI), Tc(VII)) are generally more environmentally mobile than the reduced states (e.g. U(IV), Tc(IV)).

The mobility of radionuclides released into the environment may be attenuated by interactions with the geosphere, for example through adsorption to mineral surfaces or by
surface mediated precipitation. These processes are, however, reversible. A change in the prevailing geochemical conditions may induce desorption or increase the solubility product of precipitated phases. Such changes may be induced by a change in the groundwater pH or Eh, or by an influx of competing ions which may displace the radionuclides from the mineral surface or form stable solution complexes (e.g. \( \text{CO}_3^{2-} \)). The myriad processes that will occur in the dynamic and heterogeneous geosphere are complex, interrelated and location specific. It is therefore helpful to isolate certain processes in the laboratory to define the mechanisms of interaction. The research presented in this thesis contributes to the fundamental science of the behaviour of key radionuclides and their interactions with key mineral phases. Understanding the sequestration capacity of key components of the natural barrier is crucial to underpinning the case for safe disposal of radioactive waste in a GDF.

### 1.4 Research Hypotheses

The key aim of the project was to investigate mineral transformation processes that are likely to occur in and around the GDF and CDZ environments and determine the fate of uranium (U) and technetium (Tc) during these transformations. Uranium and its radiogenic daughter decay products are predicted to be the primary contributors to the radioactivity profile of ILW in the long term (beyond \( 10^5 \) – \( 10^6 \) years (Pöyry Energy & Amec, 2013b)) (Figure 1-3). Technetium is highly mobile in the aqueous environment; technetium derived from authorised discharges to the Irish Sea from Sellafield, UK, have been traced into the North Sea and arctic waters (Kershaw et al., 1999). Technetium in the natural environment also poses a hazard to human health after evidence of bioaccumulation in Irish Sea lobsters (Hunt et al., 2001).

![Figure 1-3](image.png)

**Figure 1-3** Predicted radioisotopic contributions to ILW activity. Reproduced from the 2013 UK Radioactive Waste Inventory (Pöyry Energy & Amec, 2013a, 2013b).
Previous research has shown that iron (oxyhydr)oxides are effective phases for reducing environmental mobility of radionuclides, particularly uranium and technetium (Nico et al., 2009; Skomurski et al., 2010; Boland et al., 2011; Um et al., 2011; Singer et al., 2012a), and typically these studies have focused on surface interactions. Incorporation of radionuclides into iron oxides has been shown to be possible but there is a discord between experimental data and modelling predictions regarding the structure around such substituted radionuclides.

Here, the aim was specifically to design a series of experiments to understand incorporation of radionuclides into key iron oxide phases and use state-of-the-art techniques to probe the atomic structure of the incorporated radionuclides. The following hypotheses, as illustrated in Figure 1-3, were used as motivation behind the experimental program:

- U(VI) will be incorporated into the structure of hematite as it crystallises from ferrihydrite
- Tc(VII) will be reduced and incorporated into the structure of magnetite as it crystallises from ferrihydrite
- U(VI) will be reduced and incorporated into the structure of magnetite as it crystallises from ferrihydrite
- Hyperalkaline alteration of Fe-bearing silicate minerals (e.g. biotite) will produce secondary iron oxide minerals which will sequester radionuclides from solution

![Figure 1-4 Schematic of PhD project hypotheses.](image-url)
The first three hypotheses target fundamental knowledge regarding radionuclide incorporation, mimicking transformation of amorphous iron oxyhydroxide precursor material (ferrihydrite) to stable iron oxides (hematite and magnetite). The last hypothesis focuses on exploration of how the precursor material may be generated through alkaline degradation of Fe-bearing silicate minerals likely to be present in many GDF designs. A simple batch experiment setup was utilised to generate multiple, repeatable data sets for the experimental matrix to which a combined analytical approach was applied, encompassing typical solution chemistry and solid characterisation techniques allied to synchrotron based spectroscopic techniques (Figure 1-4).

Figure 1-5 Combined analytical approach utilised in this thesis.

1.5 Thesis Structure

The structure of the thesis broadly follows the hypotheses outlined above, with a research chapter dedicated to each hypothesis, preceded by a discussion of the relevant literature and the analytical techniques shown in Figure 1-4.

Chapter 2 provides a more detailed account of the current state of knowledge in topics related to the scientific focus of this thesis.

Chapter 3 provides coherent coverage of the experimental and analytical techniques used in more detail, and provides a critical review of each technique in respect of the data obtained and associated uncertainties.

Chapter 4 presents the results of an experimental investigation into the behaviour of U(VI) present during the crystallisation of hematite from ferrihydrite conducted under oxidising conditions and details the incorporation mechanism and atomic arrangement around a U(VI) atom substituted in place of an Fe(III) atom in the hematite structure. This chapter is
presented here as a lead-author manuscript published in the journal Environmental Science and Technology in March 2014 (Marshall et al., 2014a). Author contributions are detailed in Table 1-3.

**Table 1-3 Author contributions to Chapter 4 (Marshall et al., 2014a)**

<table>
<thead>
<tr>
<th>Author</th>
<th>Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>T.A. Marshall</td>
<td>All laboratory work including experiment design, sampling, sample preparation; collection of XRD, TEM and XAS data; all data analysis (excluding qXRD) and modelling of XAS data; writing of manuscript and handling reviewers’ comments</td>
</tr>
<tr>
<td>K. Morris</td>
<td>Input to experimental concept; manuscript review pre- and post-submission</td>
</tr>
<tr>
<td>G.T.W. Law</td>
<td>Assistance with XAS data collection; manuscript review pre-submission</td>
</tr>
<tr>
<td>F.R. Livens</td>
<td>Manuscript review pre-submission</td>
</tr>
<tr>
<td>J.F.W. Mosselmans</td>
<td>Assistance with XAS data modelling; manuscript review pre- and post-submission</td>
</tr>
<tr>
<td>P. Bots</td>
<td>PHREEQC modelling of solution chemistry and Rietveld refinement of XRD data (qXRD)</td>
</tr>
<tr>
<td>S. Shaw</td>
<td>Input to experimental concept; assistance with XAS data modelling; manuscript review pre- and post-submission</td>
</tr>
</tbody>
</table>

Chapter 5 presents the results of an experimental investigation into the behaviour of Tc(VII) present during the crystallisation of magnetite from ferrihydrite conducted under anaerobic conditions and over the pH range 10.5 – 13.1, detailing the atomic arrangement around a reduced Tc(IV) atom substituted in place of an Fe(III) atom in the magnetite structure, along with an assessment of the longer-term stability of the incorporated Tc(IV) when exposed to oxidising conditions. This chapter is presented here as a lead-author manuscript published in the journal Environmental Science and Technology in September 2014 (Marshall et al., 2014b). Author contributions are detailed in Table 1-4.

Chapter 6 presents the results of an experimental investigation into the behaviour of U(VI) present during the crystallisation of magnetite from ferrihydrite conducted under anaerobic conditions and over the pH range 10.5 – 13.1, detailing the atomic arrangement around a reduced U(V)/U(VI) atom substituted in place of an Fe(III) atom in the magnetite structure, along with an assessment of the longer-term stability of the incorporated U(V)/U(VI) when exposed to oxidising conditions. This chapter constitutes the basis for a lead-author manuscript submitted in October 2014 to a special issue of the journal Mineralogical Magazine, arising from the Implementing Geological Disposal of Radioactive Waste Technology Platform (IGDTP) conference, 2014. Author contributions for the proposed manuscript are detailed in Table 1-5.
Table 1-4 Author contributions to Chapter 5 (Marshall et al., 2014b)

<table>
<thead>
<tr>
<th>Author</th>
<th>Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>T.A. Marshall</td>
<td>All laboratory work including experiment design, sampling, sample preparation; collection of XRD, TEM and XAS data; all data analysis (excluding qXRD) and modelling of XAS data; writing of manuscript and handling reviewers’ comments</td>
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<tr>
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<td>Assistance with XAS data modelling; manuscript review pre- and post-submission</td>
</tr>
<tr>
<td>P. Bots</td>
<td>PHREEQC modelling of solution chemistry and Rietveld refinement of XRD data (qXRD)</td>
</tr>
<tr>
<td>S.A. Parry</td>
<td>Assistance with XAS data collection</td>
</tr>
<tr>
<td>S. Shaw</td>
<td>Input to experimental concept; assistance with XAS data modelling; manuscript review pre- and post-submission</td>
</tr>
</tbody>
</table>

Table 1-5 Author contributions to Chapter 6

<table>
<thead>
<tr>
<th>Author</th>
<th>Contribution</th>
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<tbody>
<tr>
<td>T.A. Marshall</td>
<td>All laboratory work including experiment design, sampling, sample preparation; collection of XRD, TEM and XAS data; all data analysis (excluding qXRD) and modelling of XAS data; writing of manuscript</td>
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<tr>
<td>K. Morris</td>
<td>Input to experimental concept; manuscript review</td>
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<tr>
<td>G.T.W. Law</td>
<td>Assistance with XAS data collection</td>
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<td>J.F.W. Mosselmans</td>
<td>Assistance with XAS data modelling; manuscript review</td>
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<tr>
<td>P. Bots</td>
<td>PHREEQC modelling of solution chemistry and Rietveld refinement of XRD data (qXRD)</td>
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<td>S. Shaw</td>
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Chapter 7 contains the results of ongoing experiments investigating the long-term alteration of biotite, a common rock-forming Fe-bearing sheet silicate mineral, in a U(VI) containing synthetic cement leachate, representing the early stage groundwater around a cementitious geological disposal facility for radioactive waste. This chapter contributes to a co-authored manuscript in preparation for submission to the IGDTP Special Issue of Mineralogical Magazine. The work presented in Chapter 7 consists of solely the author’s work, with review from S. Shaw and K. Morris.

Chapter 8 provides a summary of the results and conclusions to be drawn from the work presented in this thesis, with reference to the original hypotheses, outlining the implications.
for consideration of radionuclide transport in environmental systems and the application to radioactive waste management and disposal in particular. Consideration of potential areas for future research to build upon that presented herein is also discussed.

A complete list of references is included after Chapter 8. Citations in chapters included as published manuscripts are maintained in the journal’s style, and as such, separate lists of references are included in Chapter 4 and Chapter 5.

Supplementary information to the research chapters is included in the appendices. Additionally, details of all travel grants are given along with a complete list of conference presentations made, and a copy of each poster presented by the author. Finally, contributions to other work not included for examination as part of this thesis are provided.
Chapter 2 Review of Relevant Literature

In this chapter, the relevant published literature will be discussed, placing the research described in this thesis into the context of the previously published research.

2.1 Nuclear Fuel Cycle and Radioactive Waste

Nuclear power provides energy through the fission of a nuclear fuel, typically uranium, which is then harnessed through heat exchange and used to generate electricity. There are numerous types of nuclear power plant (NPP) which broadly follow the same principle but do so in a number of ways which will not be discussed here. However, the common thread unifying all commercial NPPs is the use of a uranium derived fuel, either as low enriched uranium or as mixed oxide fuel (which also contains reprocessed plutonium). Uranium is the heaviest naturally occurring element and is mined from various ore minerals, the most common being uraninite (UO₂) (Wilson, 1996). The process of mining the uranium ore, fabricating the fuel, burning that fuel in an NPP, and then re-processing and disposing of the spent fuel is termed the nuclear fuel cycle (Wilson, 1996), illustrated in Figure 2-1.

![Figure 2-1 The nuclear fuel cycle. Redrawn from Wilson (1996).](image)

The process of nuclear fission is harnessed inside a nuclear reactor in a stable, self-sustaining critical reaction, where fission of one atom provides energy and neutron(s) for the next fission event. To obtain such a reaction, the nuclear fuel must contain sufficient fissile material.
U-235, the only naturally occurring fissile isotope, is the most commonly used fissile material in nuclear fuel. However, natural uranium ore is only approximately 0.7 % U-235 whilst light water reactors (the most common type) require fuel with 3-5 % U-235. Therefore, the mined uranium ore has to undergo enrichment to increase the relative proportion of U-235, leaving depleted uranium as a by-product. Once the fuel has been fissioned inside the reactor it will follow one of two paths: the spent nuclear fuel (SNF) will either be stored for disposal as SNF, or it will be reprocessed to retrieve the remaining fissile material which is fed back into the fuel fabrication cycle once again.

![Figure 2-2 Contributions to the UK radioactive waste inventory by existing activities. Reproduced from the 2013 UK Radioactive Waste Inventory (Pöyry Energy & Amec, 2013a). Spent fuel reprocessing includes all wastes from Sellafield, encompassing large waste volumes from legacy defence programmes in addition to those from commercial fuel reprocessing.](image)

Radioactive wastes are generated at all stages of the nuclear fuel cycle. Uranium mine tailings present a significant contaminated land legacy at numerous sites across the globe, e.g. Old Rifle, Colorado (Campbell et al., 2011a, 2011b). Figure 2-2 illustrates the percentage contributions by activity to the total UK inventory forecast from existing nuclear operations in the UK. Uranium enrichment and fuel fabrication operations, conducted at the Capenhurst and Springfields sites respectively, are forecast to produce 243,000 m³ of waste. The majority of the waste will be produced as part of spent fuel reprocessing at Sellafield, which includes not only the HLW arising from the reprocessed SNF, but also decommissioning wastes from the reprocessing plants themselves. Decommissioning of the NPPs only accounts for 16.4 % of the total waste inventory by volume.
Figure 2-3 Contributions to the UK radioactive waste inventory from the different waste categories by volume (A) and activity (B). Reproduced from the 2013 UK Radioactive Waste Inventory (Pöyry Energy & Amec, 2013a, 2013b).

Figure 2-3 shows that in the UK, the VLLW and LLW categories constitute almost 95% of the waste by volume but significantly less than 1% of the total activity. By comparison, HLW accounts for just 0.02% of the total volume but 95% of the total activity (Pöyry Energy & Amec, 2013b). The ILW and HLW categories, collectively termed higher activity wastes (HAW), comprise virtually all of the activity and government policy is that they will be disposed in a GDF. LLW is currently disposed of at the LLW Repository (LLWR), near Drigg in West Cumbria, with VLLW going to licensed landfill.

In addition to the wastes outlined above, nuclear licensed sites are authorised to discharge limited quantities of radioactive material to the environment under The Environmental Permitting (England and Wales) Regulations 2010 (SI 2010/675). Sellafield’s discharge authorisation for release of radioactive materials to the Irish Sea allows for 10 TBq of Tc-99 and 2000 kg of uranium, per year (Sellafield Ltd., 2012). In 2012, the most recent reporting period available, 0.93 TBq of Tc-99 and 340 kg of uranium were discharged. The peak annual discharge of Tc-99 to the sea was in excess of 190 TBq (Sellafield Ltd., 2012). These and various other radionuclides, including americium and plutonium, have been discharged from Sellafield, and their environmental impact is still the subject of much research (Malcolm et al., 1990; McCubbin et al., 2000, 2004; Morris et al., 2000, 2001; Keith-Roach et al., 2003). Further to the authorised discharges of radioactive materials, there have been numerous uncontrolled and unauthorised discharges, from beyond-design incidents such as the accidents at Chernobyl (1986) and Fukushima (2011), leading to radioactive material being dispersed in the environment.
2.2 Radionuclide Geochemistry

Once released into the environment, the mobility of contaminants is governed by their geochemical behaviour and interactions with other aqueous species or mineral surfaces through various processes, such as adsorption, which are influenced by the prevailing geochemical conditions (e.g. pH, ionic strength, redox potential).

Adsorption is the process through which aqueous species accumulate onto the surface of a mineral phase in the same system (Krauskopf & Bird, 1995). There are two modes of adsorption: outer- and inner-sphere. In outer-sphere adsorption, the adsorbing ion is surrounded by a hydration sphere, meaning that water molecules are present between the charged ion and the functional group(s) on the oppositely charged surface, with the mode of sequestration being electrostatic attraction. However, inner-sphere adsorption involves the formation of a chemical bond between the adsorbing species and the surface itself, with no hydration sphere between the two (Krauskopf & Bird, 1995). Since outer-sphere adsorption is an electrostatic attraction, which is typically weak, species that are associated with surfaces through this mechanism are readily displaced to solution. However, species which undergo inner-sphere adsorption are less sensitive to changes in the prevailing geochemical conditions owing to the greater strength of the direct bond to surface.

2.2.1 Uranium Geochemistry

Uranium (U-238 half-life 4.5 x10⁹ years) is a key alpha-emitting radionuclide presenting a risk of release of radioactivity in the long-term (10⁶ years) management and disposal of radioactive waste (Pöyry Energy & Amec, 2013b). Therefore the behaviour of uranium in the environment is of significant interest during performance assessment of a geological disposal facility.

Uranium exists predominantly in two oxidation states in natural environmental systems; as oxidised U(VI) or reduced U(IV). Uranium may also exist as U(V), but the stability field of U(V) is small and it tends to disproportionate (Ekstrom, 1974; Steele & Taylor, 2007). However, recent work suggests that U(V) may be stabilised through incorporation into iron oxide mineral phases, which constrains the structure and prevents disproportionation (Ilton et al., 2012; Boland et al., 2014). U(VI) dominates in oxidising environments (Clark et al., 1995), forming aqueous uranyl complexes (Figure 2-4). Additionally, in aqueous environments with lower pH (<5) and with low carbonate concentrations, in the range 10⁻⁴ – 10⁻³ M, UO₂²⁺ is the dominant aqueous species (Allard et al., 1984; Grenthe et al., 1992), whereas in the near neutral pH range and typical carbonate concentrations, [UO₂(μ₂-OH)₂]³⁻ becomes the dominant species (Grenthe et al., 1992; Palaban, Roberto & Turner, 1997).
Under anoxic conditions U(IV), which is highly insoluble, dominates (Lloyd & Renshaw, 2005) and so aqueous U(IV) tends to precipitate, usually as uraninite (UO$_2$) or coffinite (U(SiO$_4$)$_{1.4}$(OH)$_{0.6}$) (Murphy & Shock, 1999). U(VI) species tend to be more soluble and as such are considered mobile in aqueous systems. Additionally, the carbonate anion (CO$_3^{2-}$) has a strong affinity for uranyl species in aqueous solution, forming strong uranyl-carbonato complexes, e.g. UO$_2$(CO$_3$)$_{4-x}$ or UO$_2$(CO$_3$)$_{2-x}$ (Murphy & Shock, 1999; Reeder et al., 2000). These are able to compete effectively with surface sites such that sorption of charged uranyl-carbonato complexes is limited (Murphy & Shock, 1999), which serves to maintain U(VI) in solution. In low-carbonate environments U(VI), as the UO$_2^{2+}$ ion, exhibits extensive sorption to a range of geological materials (Payne et al., 1994; Waite et al., 1994; Barnett et al., 2000; Sylwester et al., 2000; Jeon et al., 2005; Begg et al., 2011).

![Figure 2-4 Pourbaix diagram of the U-O$_2$-H$_2$O system showing the aqueous stability fields in pure water at 25 °C. Produced in v-MINTEQ.](image)

Aqueous U(VI), when uncomplexed, is present as the uranyl anion, UO$_2^{2+}$, and U(V) as UO$_2^+$ although the latter readily disproportionates through interaction of two U(V) anions to produce a single U(IV) and U(VI) (Cotton & Wilkinson, 1966). The dioxo ions, UO$_2^{2+}$ and UO$_2^+$, are remarkably stable and form linear moieties in both solution and crystalline compounds, and may have four, five or six additional ligand atoms in their equatorial planes (Cotton & Wilkinson, 1966). Inclusion of other metals in a uranium oxide creates mixed oxides, generally referred to as uranates (Cotton & Wilkinson, 1966). In some instances in the literature, the term ‘uranate-like’ is used to refer to uranium, typically U(VI) in 6-fold coordination, with U-O
bond lengths which are all equivalent (e.g. Duff et al., 2002), however, U(VI) or U(V) uranates tend to retain the short axial bonds, with the remaining O atoms forming the equatorial plane (Cotton & Wilkinson, 1966; Katz et al., 1986). In contrast to this, when in the reduced U(IV) state, the U-O bond lengths are all equivalent, taking the cubic structure of fluorite. Typically, the axial U-O bond length in U(VI) and U(V) complexes/compounds is ~1.8 Å and ~1.9 - 2.0 Å, respectively (Burns et al., 1997; Docrat et al., 1999; Huber et al., 2012), with equatorial U-O bonds in the range 2.2 – 2.4 Å (Farges et al., 1992). The U-O bond lengths in UO₂ are all 2.36 Å (Wasserstein, 1951).

2.2.2 Technetium Geochemistry

Technetium (Tc-99 half-life 2.1 x10⁵ years) is a long-lived, beta-emitting fission product present in spent fuel and reprocessing wastes (Pöyry Energy & Amec, 2013b). The long half-life and environmental mobility of technetium in oxidised environments mean that it is a contaminant of concern and as such its behaviour in both natural and engineered environments is well studied (Aarkrog et al., 1997; Lukens et al., 2004; McBeth et al., 2007; Icenhower et al., 2011; Liu et al., 2012b; Peretyazhko et al., 2012; Sellafield Ltd., 2012; Thorpe et al., 2014).

Figure 2-5 Pourbaix diagram of the Tc-O₂-H₂O system showing the aqueous stability fields in pure water at 25 °C. Produced in v-MINTEQ.

Technetium can exist in two oxidation states; oxidised Tc(VII), and reduced Tc(IV). In aqueous systems across the whole pH range, Tc(VII) exists as the pertechnetate anion (TcO₄⁻) (Figure 2-5). The pertechnetate anion is highly soluble and, due to electrostatic repulsion to surfaces
which are typically negatively charged, it exhibits weak sorption behaviour (Icenhower et al., 2011). Therefore, technetium is highly mobile in oxidised environments. Generally Tc(IV) precipitates as sparingly soluble Tc(IV)-hydroxide phases \( (10^{-8} – 10^{-9} \text{ M}) \) (Eriksen et al., 1992; Kunze et al., 1996; Baston et al., 2002) or adsorbs to mineral surfaces below this limit (Burke et al., 2010; Lear et al., 2010; Hallam et al., 2011; Corkhill et al., 2013). In contrast to Tc(VII), sorption coefficients for Tc(IV) tend to be larger, although still relatively low (< 2 mL/g), even at low Eh values (-230 mV) (Baston et al., 2002).

### 2.3 Aqueous Iron Geochemistry

In general, the solubility of both Fe(III) and Fe(II) oxides is low. However, at the extremes of pH, the solubility of both Fe(II) and Fe(III) oxides increases (Cornell & Schwertmann, 2003). Assuming a detection limit for iron in solution of 0.05 ppm, and equilibrium with respect to the oxyhydroxides, the aqueous concentrations of Fe(III) complexes will be at or below detection between pH 5 – 10 (Langmuir, 1996), as shown in Figure 2-6, with the minimum solubility close to the point of zero charge between pH 7-8.

![Figure 2-6](image)

**Figure 2-6** Solubility of ferrihydrite and goethite as a function of pH at 25 °C. Also shown are fields of dominance of Fe³⁺ and Fe³⁺-OH complexes. After Langmuir (1996).

In most natural waters, dissolved Fe(III) forms strong inner sphere complexes with most ligands, particularly the hydroxyl ion, whereas Fe(II) is usually uncomplexed (Langmuir, 1996). To understand the pH dependence of the solubility of the hydroxyl complexes of both Fe(II) and Fe(III), the mass balance of the all iron hydroxyl complexes must first be considered:

\[
\sum \text{Fe}^{(\text{II})}_{\text{aq}} = \text{Fe}^{2+} + \text{Fe(OH)}^{+} + \text{Fe(OH)}_{2}^{+} + \text{Fe(OH)}_{3}^{-}
\]

\[
\sum \text{Fe}^{(\text{III})}_{\text{aq}} = \text{Fe}^{3+} + \text{Fe(OH)}^{2+} + \text{Fe(OH)}_{2}^{+} + \text{Fe(OH)}_{3}^{+} + \text{Fe(OH)}_{4}^{-}
\]
By substitution and elimination, it is possible to solve these two equations in terms of the Fe ion and H+ concentration and hence to plot the dependence of the aqueous Fe ions upon pH (Figure 2-7).

**Figure 2-7** Mole fraction of total dissolved Fe(II)- and Fe(III)-OH complexes as a function of pH in pure water at 25 °C. Fe(II) complexes are shown in green; Fe(III) complexes are shown in orange. Redrawn from Langmuir (1996).

In the ferrous system, the only significant species are Fe$^{2+}$ and Fe(OH)$_3^-$. The cross-over pH at which both species are equal in solution is 9.8, above which Fe(II) is present in solution as Fe(OH)$_3^-$. In the ferric system, Fe$^{3+}$ is only dominant in solution below pH 2 and is absent above
pH 4, with Fe(OH)$_4^-$ the dominant species under hyperalkaline conditions. It is possible to plot a Pourbaix diagram for aqueous iron species using Figure 2-7 to determine which species are the dominant species at particular Eh and pH, forming separate stability fields (Figure 2-8).

**Figure 2-9** The solubility of Fe(II) and Fe(III) as a function of pH. Fe(II) complexes are shown in green; Fe(III) complexes are shown in orange. Redrawn from Cornell & Schwertmann (2003).

Under acidic to near-neutral conditions, reducing conditions have the effect of enhancing the solubility of Fe(III) oxides through reductive dissolution, promoting Fe(II) in solution and increasing the overall activity of Fe in solution. Reducing conditions can enhance the activity of Fe in solution by 4 orders of magnitude in the acid/neutral pH range (Cornell & Schwertmann, 2003). However, under alkaline conditions this trend is reversed, and Fe(III) becomes more soluble than Fe(II), as shown in Figure 2-9 (Cornell & Schwertmann, 2003). Therefore, reduction of iron oxides at alkaline pH does not induce an increase in solubility and hence dissolution.

The physical properties of the iron solid phase present will affect its solubility, with the most important property being the particle size (Cornell & Schwertmann, 2003). At very low particle sizes (< 1 µm), the surface free energy, which for iron oxides is relatively high, governs the dissolution behaviour and hence the solubility (Cornell & Schwertmann, 2003). The higher solubility of smaller particles may lead to the process of Ostwald ripening (Kahlweit, 1975), where larger particles grow at the expense of smaller particles. Aged particles tend to have lower solubilities than freshly precipitated equivalents (Cornell & Schwertmann, 2003).

The iron oxides have various isostructural equivalents where the place of iron within the structure is occupied by another metal ion. This then raises the possibility of formation of solid solution series between end-members via isomorphous substitution of Fe(III) or Fe(II) within
the structure by other metal ions. Iron oxides are known to accommodate substituted metal ions into their structures (e.g. Al, Ti, V, Cr, Mn, Co, Ni (Singh et al., 2000; Cornell & Schwertmann, 2003; Liu et al., 2012a; Rivera et al., 2012)), particularly in natural samples. These substituted iron oxides tend to have lower solubilities, explaining their formation and prevalence in nature (Fey, 1983; Trolard & Tardy, 1987; Cornell & Schwertmann, 2003).

2.4 Iron Oxide Mineralogy

Iron oxides and oxyhydroxides are ubiquitous minerals in sediments at Earth’s surface and also as rock forming minerals (Deer et al., 1992). They are formed through diagenetic weathering processes as well as directly crystallising from solution or magmatic melts. They are typically minor components in igneous and metamorphic rocks but can contribute significant proportions in sedimentary units (e.g. Banded Iron Formations (Katsuta et al., 2012) or laterites (Tardy, 1997)). Here the mineralogy and formation pathway of the key iron (oxyhydr)oxide phases investigated are discussed.

2.4.1 Ferrihydrite

Ferric oxyhydroxides will buffer the concentrations of aqueous iron in groundwater. The poorly ordered Fe(III) oxyhydroxide ferrihydrite is usually the first phase to precipitate from ferric iron rich solutions (Combes et al., 1988; Cornell & Schwertmann, 2003). In aqueous solution, iron cations form hexa-coordinated complexes in which the cationic size and charge control polarisation of the water molecules (Jolivet et al., 2004). Ferric complexes are therefore more acidic than ferrous, and hydroxylation occurs over very specific pH ranges, as indicated by Figure 2-7. Jolivet et al. (2004) discuss the two basic mechanisms by which hydroxylated complexes condense, which depend upon the nature of the coordination sphere of the central cation. Aquohydroxo complexes (i.e. H₂O–M–OH) condense via olation and elimination of water to form hydroxo bridges. However, oxohydroxo complexes (i.e. –M–OH) contain no water molecule in the coordination sphere and therefore condensation proceeds via a two-step process involving an associative mechanism which leads to the formation of oxo bridges. Formation of the zero-charged aquohydroxo complex is the precursor to formation of the solid phase (Jolivet, 2000); however, Fe²⁺ and Fe³⁺ behave very differently. Under anaerobic conditions, the ferrous cation is hydroxylated above pH 6 – 7 and forms an iron hydroxide with a brucite type structure (white rust, Fe(OH)₂). This phase is very sensitive to oxidation and, depending upon the prevailing conditions, may undergo transformation to a wide variety of mineral phases (Jolivet et al., 2004). Hydroxylation of the ferric cation leads to a virtually instantaneous precipitate of the poorly ordered hydrated phase ferrihydrite.
Ferrihydrite is nanocrystalline and hence determination of its structure is not straightforward since most structural determination techniques rely on long-range order. Typically, ferrihydrite is an amorphous nanoparticulate aggregate (Figure 2-10), often termed ‘iron gel’. Ferrihydrite is designated as either 2-line or 6-line from the number of broad maxima in the XRD pattern (Figure 2-11). 2-line ferrihydrite forms at pH $>3$, whilst 6-line forms at lower pH and temperatures nearing 100 °C (Cornell & Schwertmann, 2003).

There is no widespread agreement on the chemical formula of ferrihydrite owing to the lack of a known structure, and variable water content (Jambor & Dutrizac, 1998). Michel et al. (2007) used modelling of the pair distribution function to determine their ferrihydrite structure. They
proposed a central tetrahedrally coordinated Fe atom is connected to 12 octahedrally coordinated Fe atoms arranged in edge sharing groups of three. Michel et al. (2010) proposed a chemical composition of disordered (2-line) ferrihydrite of Fe$_{8.2}$O$_{8.5}$(OH)$_{7.4}$·3H$_2$O.

Ferrihydrite is thermodynamically unstable in aqueous solutions (Das et al., 2011) and over time will undergo transformation into either of the crystalline phases goethite or hematite (Cornell & Schwertmann, 2003) via two distinct pathways discussed below. Schwertmann and Murad (1983) investigated the effect of pH upon the transformation of ferrihydrite to the crystalline iron oxide phases goethite and hematite, after the work of Böhm (1925). They report maximum hematite formation between pH 7 – 8 whilst maximum goethite formation occurred at pH 4 and 12.

2.4.2 Hematite – α-Fe$_2$O$_3$

Hematite has the same structure as corundum (α-Al$_2$O$_3$), with alternating layers of oxygen and iron ions, where the oxygen ions are in a (slightly distorted) hexagonal close-packed arrangement and the iron ions are in six-fold coordination (Deer et al., 1992). The hematite structure is trigonal (space group R$\overline{3}$c, No. 167) with unit cell dimensions are: $a = 5.034$ Å, and $c = 13.75$ Å (Blake et al., 1966). According to the structure of Blake et al. (1966), there are four sharing relationships between iron octahedra, face (Fe$_F$, 1), edge (Fe$_E$, 3) and two corner sharing relationships (Fe$_C_1$ and Fe$_C_2$, 6 each). The interatomic distances of each polygonal sharing relationship are shown in Figure 2-12.

![Figure 2-12 Polygonal sharing relationship between Fe octahedra in the hematite structure of Blake et al. (1966). Redrawn after Cornell and Schwertmann (2003).](image)

The major reflections in the hematite XRD pattern are indexed in Figure 2-13. The most intense peak is the reflection from the (104) direction at 33.1 °2θ, corresponding to a d-spacing of 2.70
Å, and the second most intense peak is from the (110) direction at 35.6 °2θ, which corresponds to a d-spacing of 2.52 Å.

Figure 2-13 Hematite XRD pattern. Data are Cu Kα1 taken from ICSD entry 15840 (Blake et al., 1966).

Hematite is thought to form via a process of solid-state transformation from ferrihydrite by dehydration and internal recrystallisation (Fischer & Schwertmann, 1975; Schwertmann & Murad, 1983; Combes et al., 1990). The process begins with ferrihydrite particle aggregation (Fischer & Schwertmann, 1975) and continues with an increase in the number of face-sharing octahedra within the ferrihydrite structure as a result of particle rotation, which is possibly aided by Brownian motion (Combes et al., 1990). Hematite recrystallisation involves dehydration of the aggregated ferrihydrite particles, accompanied by deprotonation of hydroxyl groups, forming oxy-linkages, and a redistribution of cation vacancies within the new crystal lattice (Shaw, 2005). It has been noted that the major step is the appearance of the face-sharing octahedra, a so-called transient phase, which has an original local structure preventing the formation of goethite due to the necessity to hydrolyse or hydroxylate chemical bonds and destroy three oxo-bridges within the face-sharing octahedra (Combes et al., 1990). Under alkaline conditions, hematite forms from ferrihydrite through a two-stage process involving initial formation of goethite as an intermediary phase, confirmed from time-resolved energy dispersive XRD (Vu et al., 2010). However, at the hyperalkaline pHs relevant to some experimental scenarios explored in this thesis (pH > 12), monovalent Fe(III) is present in solution as the Fe(OH)$_4^{2-}$ ion (Figure 2-7) which strongly favours the formation of goethite over hematite (Schwertmann & Murad, 1983).
2.4.3 Goethite – α-FeOOH

Goethite is isostructural with diaspore (α-AlOOH) with an orthorhombic unit cell (space group Pnma, No. 62) of dimensions: \(a = 9.956 \text{ Å}, \ b = 3.0215 \text{ Å}, \text{ and } c = 4.608 \text{ Å}\) (Szytula et al., 1968). The \(\text{O}^2-\) and \(\text{OH}^-\) anions form a hexagonal close-packed array stacked in the [010] direction with half of the octahedral interstices in each layer occupied by Fe(III) where the Fe(III) are arranged in alternating double rows of occupied and unoccupied sites (Cornell & Schwertmann, 2003). Each Fe(III) is coordinated by 3 \(\text{O}^2-\) and 3 \(\text{OH}^-\), and the structure consists of double chains of edge-sharing octahedra aligned in the (100) direction. According to the structure of Szytula et al. (1968), there are three sharing relationships between iron octahedra, two edge (\(\text{Fe}_{E1}\) and \(\text{Fe}_{E2}\), 2 each) and one corner sharing relationship (\(\text{Fe}_{C}, 4\)). The atomic distances of each polygonal sharing relationship are shown in Figure 2-14.

The major reflections in the goethite XRD pattern are indexed in Figure 2-15. The most intense peak is the reflection from the (101) direction at 21.2 °2θ, corresponding to a d-spacing of 4.18 Å, and the second most intense peak is from the (111) direction at 36.7 °2θ, which corresponds to a d-spacing of 2.45 Å.

![Figure 2-14 Polygonal sharing relationship between Fe octahedra in the goethite structure of Szytula et al. (1968). Redrawn after Cornell and Schwertmann (2003).](image)

At the extremes of pH (pH < 4 or pH > 8) ferrihydrite is more soluble, allowing a dissolution and recrystallisation transformation pathway to proceed; as ferrihydrite dissolves, the solution concentration of Fe(III) increases leading to the formation of goethite (Schwertmann & Murad, 1983). Condensation by olation of a planar tetramer leads to the formation of embryonic octahedral double chains, which have the characteristic structure of goethite. These double chains connect through the formation of oxo-bridges to induce crystallographic growth (Jolivet et al., 2004). In alkaline solutions, ferrihydrite transforms to goethite rapidly (Lewis & Schwertmann, 1980; Schwertmann & Murad, 1983) with crystals elongated along the c axis, forming needles. Silicate ions present in solution modify the solubility of ferrihydrite,
stabilising it and inhibiting the transformation to hematite or goethite through formation of an immobile network (Cornell et al., 1987).

Figure 2-15 Goethite XRD pattern. Data are Cu Kα1 taken from ICSD entry 109041 (Szytula et al., 1968).

2.4.4 Magnetite – Fe₃O₄

The structure of magnetite is that of the inverse spinel structure (cubic, space group Fd3m, No. 227), with two octahedral and one tetrahedral site per oxide unit, occupied by Fe(II) and Fe(III) cations (Fleet, 1981). In pure stoichiometric magnetite, the Fe(II) to Fe(III) ratio is 1:2, or 0.5 expressed as a decimal fraction. All the Fe(II) plus half of the Fe(III) cations reside in the octahedral sites, with the other half of the Fe(III) cations residing in the tetrahedral sites. Magnetite has a face-centred cubic unit cell, of dimension \( a = 8.394 \) Å (Deer et al., 1992), based on 32 O²⁻ cations arranged in a regular cubic close-packed fashion in the (111) direction (Cornell & Schwertmann, 2003).

The major reflections in the magnetite XRD pattern are indexed in Figure 2-16. The most intense peak is the reflection from the (311) direction at 35.4°2θ, corresponding to a d-spacing of 2.54 Å, and the second most intense peak is from the (440) direction at 62.5°2θ, which corresponds to a d-spacing of 1.48 Å.
Magnetite forms during anaerobic oxidation of ferrous hydroxide (Fe(OH)$_2$) through reduction of water molecules which also produce hydrogen and more water, as per the Schikorr Reaction (Schikorr, 1933):

$$3\text{Fe(OH)}_2 \xrightarrow{2\text{H}_2\text{O}} \text{Fe}_3\text{O}_4 + \text{H}_2 + 2\text{H}_2\text{O}$$

Magnetite may also form from ferric oxyhydroxides, ferrihydrite or goethite, via addition of Fe(II) under anaerobic conditions (Cornell & Schwertmann, 2003). Indeed, formation of magnetite from ferrihydrite through addition of aqueous Fe(II) and induced via addition of a base follows a crystallisation pathway through a goethite intermediary (Ahn et al., 2012). Crystallisation of ferrihydrite to magnetite proceeds via sorption of Fe(II) onto ferrihydrite followed by a solid-state transformation, and additional growth of already nucleated magnetite particles (Tronc et al., 1992; Hansel et al., 2003, 2005). At low solution Fe(II) concentrations (<0.03 mmol/L) only goethite precipitates; nucleation of magnetite increases with increasing Fe(II) concentration, with magnetite crystallisation eventually proceeding at the expense of goethite (Tronc et al., 1992; Hansel et al., 2003, 2005). Microbial activity has been shown to induce magnetite crystallisation through the use of Fe(III) as an electron acceptor during the respiration process to produce Fe(II) (Cutting et al., 2009), a pathway favoured at high pH (Williamson et al., 2013). Magnetite has been shown to form as a corrosion product of steel under anoxic aqueous conditions (Musić et al., 1993; Dodge et al., 2002; Duro et al., 2008) with the associated production of hydrogen gas as per the following reaction (Duro et al., 2008):
Fe + 4H₂O → Fe₃O₄ + 4H₂

Magnetite oxidation is influenced by the particle size, its water content and the temperature at which oxidation occurs (Gilkes & Suddhiprakarn, 1979a; Swaddle & Oltmann, 1980). Particle size not only has a bearing upon the rate of oxidation but also the final oxidation product; coarsely crystalline, stoichiometric magnetites undergo slow oxidation to hematite, whilst finer-grained magnetite particles oxidise rapidly to maghemite (Swaddle & Oltmann, 1980), with an inverse relationship between particle size and oxidation rate (He & Traina, 2007), i.e. as particle size decreases, oxidation rate increases. Temperature also has an influence upon the oxidation rate and final product, with maghemite being the dominant product at ambient temperatures (He & Traina, 2007). The experimental studies in this project are generally concerned with fine-grained magnetite particles at ambient temperature; hence the dominant mode of oxidation is via a topotactic transformation to maghemite. This process proceeds with migration of Fe outwards to form a rind of pure Fe(III) maghemite (Sidhu et al., 1977). The exact mechanism of oxidation is not agreed upon. However, it is agreed that oxygen is unlikely to be diffusing into the structure: the oxygen lattice is largely unaffected by oxidation, which is not expected if oxygen were to be diffusing inwardly, plus oxygen is relatively large (crystal radius, 1.40 Å) to be able to migrate through the lattice. Sidhu et al. (1977) suggested that the Fe species migrating during oxidation is Fe(III) driven by charge imbalance and facilitated by its smaller size compared to Fe(II) (crystal radii, 0.65 Å versus 0.74 Å, respectively). However, the authors do concede that migration of Fe(III) plus the excess electrons created by in situ oxidation is effectively the same as migration of Fe(II). Gorski et al. (2010) point out that the favoured model is the outward diffusion of Fe(II) with oxidation at or near the surface. There is no discrete boundary between ‘magnetite’ and ‘maghemite’ layers and instead a solid solution is formed through the oxidising particle with preservation of local electrical neutrality as per the local Fe(II)/Fe(III) stoichiometry (Tang et al., 2003).

Magnetite is frequently non-stoichiometric, not only with respect to the Fe(II)/Fe(III) ratio but also with respect to trace metal substitution. A wide range of cations are able to substitute into the structure because of the presence of both tetrahedral and octahedral sites. Additionally, the oxygen lattice is flexible and able to expand or contract to accommodate cations with radii which differ from Fe(II) or Fe(III) (Cornell & Schwertmann, 2003). Various trace element (Co, Ni, Zn, Cu, Mn, and Cd) substituted magnetites were synthesised by Sidhu et al. (1978). Through digestion of their substituted-magnetites they obtained the distribution of the trace metals owing to the isotropic dissolution behaviour of magnetite (i.e. the lattice dissolves equally in all directions). They found that Co, Ni and Zn were randomly and evenly distributed within the magnetite, but that Cu, Mn and Cd were preferentially located near the
magnetite surface. Further to this, titanomagnetites are well studied in the literature and most recently, focussed on the presence of titanomagnetite phases in the subsurface at the Hanford nuclear facility (Forster & Hall, 1965; Moskowitz et al., 1998; Pearce et al., 2006, 2012; Liu et al., 2013). In titanomagnetite, substitution of Ti(IV) in place of Fe(III) induces reduction of one remaining Fe(III) in the unit cell to Fe(II) to maintain charge balance (Pearce et al., 2006), and a complete solid-solution exists between magnetite and pure ulvöspinel (TiFe$_2$O$_4$).

### 2.4.5 Maghemite – γ-Fe$_2$O$_3$

Maghemite has a similar structure to that of magnetite (isometric, space group P4$_1$32, No. 213), except that in pure maghemite all of the Fe(II) is oxidised to Fe(III), with creation of 2 $\frac{2}{3}$ vacancies per unit cell to balance the charge. This has the effect of contracting the unit cell dimension from $a = 8.396$ Å to $a = 8.340$ Å (Deer et al., 1992; Cornell & Schwertmann, 2003). Eight of the 21 $\frac{1}{3}$ Fe(III) cations in the unit cell are located in the tetrahedral sites, with the remaining Fe(III) cations being randomly distributed among the octahedral sites (Waychunas, 1991).

The maghemite XRD pattern (Figure 2-17) is almost identical to that of magnetite reflecting their almost identical structures. However, in maghemite the peaks corresponding to the (511) and (440) reflections are shifted to higher angles (from 57.0 °2θ to 57.3 °2θ and 62.5 °2θ to 62.9 °2θ, respectively). Also, additional characteristic peaks are observed from the (210) and (211) reflections (at 23.8 °2θ and 26.1 °2θ, respectively) (Kim et al., 2012), created by the development of vacancies within the unit cell.

![Figure 2-17 Maghemite XRD pattern. Data are Cu Kα1 taken from ICSD entry 79196 (Shmakov et al., 1995).](image-url)
Sidhu et al. (1978) synthesised various trace-metal substituted magnetites and determined the distribution of the trace-metals within the magnetite particles via isotropic dissolution. The same authors replicated these experiments and determined the effect of oxidation on the trace-metal distribution (Sidhu et al., 1980). In each case, after oxidation of the substituted magnetite to maghemite, they observed formation of an Fe(III) rich rind in the mineral deficient in trace-metals, with respect to the magnetite, owing to the outward diffusion of Fe during oxidation. Assuming no migration of the substituted trace metal, the Fe(III) rind would be expected to equate to 11% (owing to creation of $2^2/3$ vacancies per unit cell through outwards migration of one in nine Fe atoms), by weight or volume, of the magnetite/maghemite particle, and contain no trace metal, with a corresponding increase in the trace metal to Fe ratio in the particle core. This behaviour was observed for Co, Ni, Zn and Cr; although there were still quantities of trace metal present in the outer 11% of the particle, their concentrations were lower than in the corresponding magnetite (Sidhu et al., 1980). In contrast, Cu and Mn, which were preferentially located in the magnetite surface, remained preferentially located near the surface of the maghemite, although again there was a reduction in their concentrations relative to the substituted magnetite due to the outward migration of Fe (Sidhu et al., 1980). These data show that substituted trace metals are not ejected from the structure during oxidation. Similarly, studies of oxidation of titanomagnetites in natural systems also reveal that the substituted Ti(IV) remains within the oxidised structure and is not ejected (Collyer et al., 1988; Xu et al., 1997; Zhou et al., 1999, 2001). Xu et al. (1997) reported that the process of oxidation of titanomagnetites follows a slow, two-stage process: initial oxidation and loss of Fe creating disordered vacancies, followed by cation and vacancy ordering in the octahedral sites.

### 2.5 Radionuclide – Iron (Oxyhydr)Oxide Interactions

Iron (oxyhydr)oxides tend to exist as small crystals on the micron to nanometre scale and as such have large surface to volume ratios (Cornell & Schwertmann, 2003). This results in the potential for significant surface reactions governing their crystallisation and dissolution behaviour and interactions with aqueous cations (Cornell & Schwertmann, 2003). Iron (oxyhydr)oxides are amphoteric, meaning that they maintain surface reactivity in acidic as well as alkaline conditions, due to surface hydroxyl groups present either as structural OH or through adsorbed water (Cornell & Schwertmann, 2003). They are therefore important phases when considering contaminated environmental systems (Stipp et al., 2002) and have received much attention in the literature with respect to acid mine drainage scenarios (Johnson & Hallberg, 2005; Fu & Wang, 2011) and migration of radionuclides in the environment (Waite et al., 1994; Dodge et al., 2002; O’Loughlin et al., 2003a; Powell et al., 2004, 2005; Novikov et al.,
The key literature reporting uranium and technetium interactions with the major iron (oxyhydr)oxides, goethite, hematite and magnetite, are summarised here.

### 2.5.1 Uranium – Iron (Oxyhydr)Oxide Interactions

The sorption isotherms for hematite and goethite are similar to that reported for ferrihydrite, with no sorption below pH 3 and near complete uptake between pH 5 – 6 and 10 (Hsi & Langmuir, 1985; Waite et al., 1994; Liger et al., 1999; Bargar et al., 2000; Moyes et al., 2000; Missana et al., 2003b; Jang et al., 2007; Sherman et al., 2008; Zeng et al., 2009; Yusan & Erenturk, 2011). U(VI) adsorbs to the surface of ferrihydrite, forming a mononuclear bidentate surface complex along the edge of iron octahedra (Waite et al., 1994). The presence of CO$_3^{2-}$ will result in formation uranyl-carbonato complexes (e.g. UO$_2$(CO$_3$)$_2^{2-}$ or UO$_2$(CO$_3$)$_3^{4-}$) which are unlikely to adsorb strongly to the iron (oxyhydr)oxide surface due to steric and coordination effects, and because of their stability may even induce U(VI) desorption at pH > 8 where these complexes predominate in solution (Waite et al., 1994; Barnett et al., 2000; Stewart et al., 2010). Hematite and goethite have substantially lower capacity to adsorb U(VI) compared to ferrihydrite (Payne et al., 1994), most likely due to a reduction in surface area with increasing crystallinity: ferrihydrite 200 – 500 m$^2$g$^{-1}$ (Childs, 1992; Zhao et al., 1994; Larsen & Postma, 2001; Cornell & Schwertmann, 2003; Das et al., 2011; Marshall et al., 2014a), hematite 28 – 30 m$^2$g$^{-1}$ (Cornell & Schwertmann, 2003; Song et al., 2009; Das et al., 2011; Marshall et al., 2014a), goethite 20 – 27 m$^2$g$^{-1}$ (Trivedi & Axe, 1999; Cornell & Schwertmann, 2003; Das et al., 2011).

Sato et al. (1997) reported scavenging of uranium downstream from the Koongarra uranium ore deposit, Australia, by iron oxides present as fracture fillings, coatings and nodules. The initial uptake of uranium was attributed to sorption by the iron oxides, with subsequent mineralisation to form discrete copper uranyl phosphate phases, evidenced by strong U correlation with Cu and P in SEM-EDX analyses, which were then incorporated as inclusions in the growing iron nodules (Sato et al., 1997). Uranium adsorption onto goethite, amongst other iron bearing mineral phases, is reported by Moyes et al. (2000) to have a similar binding structure as the model of Waite et al. (1994) for uranium adsorbed to ferrihydrite. However, Sherman et al. (2008) argued that the bidentate edge-sharing complex could not account for the entire sorption capacity of goethite, and in addition to this, that the EXAFS signal routinely attributed to the edge-sharing complex could be accounted for by multiple scattering from the uranyl dioxygenyl. The authors instead proposed that a bidentate corner-sharing complex was the dominant adsorption binding site present in the dominant (101) direction of goethite (Sherman et al., 2008). The presence of Fe(II) in solution in contact with U(VI) sorbed iron oxides promotes reduction of the U(VI) to U(IV) and formation of UO$_2$ on the oxide surface.
(Jeon et al., 2005; Jang et al., 2008). However, it has been demonstrated that high U(VI) surface adsorption density results in decreased reduction to U(IV), potentially due to a requirement for proximal adsorption of Fe(II) and U(VI) (Jeon et al., 2005). Exposure of U(VI) to the mixed Fe(II)/Fe(III) oxide magnetite results in reduction of U(VI) to U(IV) on the mineral surface (Grambow et al., 1996; Missana et al., 2003a, 2003c), with coupled oxidation of structural Fe(II) to Fe(III) (Dodge et al., 2002; Scott et al., 2005; Latta et al., 2012a; Singer et al., 2012a). The degree of oxidation of the magnetite to maghemite, i.e. the Fe(II)/Fe(III) ratio of the mineral, has a direct influence on the capacity for U(VI) reduction (Huber et al., 2012; Latta et al., 2012a, 2012b). Commonly, there is incomplete reduction of the U(VI) and consequently there are mixed valence uranium complexes on the magnetite surface (El Aamrani et al., 2007; Huber et al., 2012).

Reduction of U(VI) to U(IV) at the magnetite surface leads to precipitation of UO$_2$ on the mineral surface, with defect sites potentially forming nucleation sites due to increased incidence of UO$_2$ nanoprecipitates at these localities on the magnetite (111) surface (Singer et al., 2012b). Additionally, Latta et al. (2012a) observed non-uraninite U(IV) complexes on the magnetite surface. It was later reported that the surface loading of uranium has an effect on the U(IV) species observed, with low loadings resulting in non-uraninite, mononuclear U(IV) surface complexes, whereas higher loadings result in UO$_2$ precipitation (Latta et al., 2014). However, in the presence of CO$_3^{2-}$, the prevalence of ternary U(VI) carbonate complexes results in no reduction of sorbed U(VI) (Duro et al., 2008; Singer et al., 2012b). In contrast to this, Regenspurg et al. (2009) reported an increase in U(VI) uptake by magnetite in the presence of HCO$_3^-$ which they attributed to formation of Fe(II) carbonates at the mineral surface, creating a readily accessible pool of Fe(II) for reduction of U(VI).

Titanomagnetites have a higher Fe(II)/Fe(III) ratio than pure magnetites due to the coupled reduction of Fe(III) to compensate for the excess charge of the substituting Ti(IV) cation, potentially increasing their reductive capacity with respect to magnetite (Latta et al., 2013; Pearce et al., 2014). Latta et al. (2013) reported a direct influence of the Ti(IV) content upon U(VI) reduction to U(IV) with the formation of a Ti-U(IV) complex at available Ti surface sites. This Ti-U(IV) complex was however, dissimilar to the U(IV)-Ti oxide brannerite (U(IV)Ti$_2$O$_8$) (Latta et al., 2013).

Dissimilatory metal-reducing bacteria (DMRB) have been shown to be able to effect reduction of U(VI) to U(IV), forming UO$_2$ by using Fe(III) minerals as electron acceptors (O’Loughlin et al., 2010; Veeramani et al., 2011; Madden et al., 2012). Lovley & Phillips (1992a, 1992b) have shown that DMRB are able to directly enzymatically reduce U(VI) to U(IV). However, the relative roles of enzymatic and abiotic reduction pathways for U(VI) is a topic for debate.
(Fredrickson et al., 2000; Finneran et al., 2002; Anderson et al., 2003; Behrends & Van Cappellen, 2005; Liu et al., 2005; Lloyd & Renshaw, 2005; Begg et al., 2011). Reduction of U(VI) in pure culture experiments has been shown to produce ‘non-uraninite’ U(IV) (Bernier-Latmani et al., 2010), which is thought to be polymeric and coordinated by carboxyl and/or phosphoryl groups on biomass (Williamson et al., 2013). Law et al. (2011) demonstrated that enzymatic processes dominated reduction of U(VI) in heterogeneous systems, noting the complexity of geomicrobial interactions on the fate of U(VI) in such systems. Williamson et al. (2013) demonstrated the ability of DMRB to operate at extreme pH (>10) and induce reduction of Fe(III) to Fe(II), proving that these processes will be relevant to the hyperalkaline conditions expected around a cementitious GDF, and in fact promoted magnetite formation. Additionally, geomicrobial processes are currently being explored as potential remediation techniques for radiologically contaminated land (Lloyd & Renshaw, 2005; Campbell et al., 2011a, 2011b). This area of research is growing rapidly and is deserving of great attention in discussion of the fate of radionuclides in natural systems; however, since the nature of this thesis is only concerned with abiotic processes, the role of bacterial processes on uranium interactions with iron oxides is not discussed further.

The extractability of U(VI) from iron (oxyhydr)oxides decreases with increasing crystallinity, indicating a process of incorporation of adsorbed U-species during crystal growth (Payne et al., 1994; Giammar & Hering, 2001; Smith et al., 2009). Indeed, XAS has been used to show U(VI) may be substituted into an octahedral site in place of Fe(III) in the goethite structure during Fe(II) mediated crystallisation of ferrihydrite (Nico et al., 2009). In contrast to previous work (e.g. Sato et al. (1997)) which reported entrapment of discrete U phases, Nico et al. (2009) assert that the U(VI) is directly substituted into the goethite lattice. Stewart et al. (2009) performed similar experiments to obtain uranium-incorporated goethite before subjecting their samples to successive oxidation/reduction cycles (up to 3 cycles) to assess the remobilisation potential of incorporated uranium. They reported that the ‘rebound’ uranium concentration observed during oxidation phases was inversely related to the concentration of Fe(II) added during the reduction phases, implying a greater retention of uranium in experiments with a greater reductive (and potentially greater mineralisation) capacity. The authors propose that adsorbed U(VI) was incorporated into the goethite during mineralisation, with additional adsorbed U(VI) reduced to U(IV) and resulting in crystallisation of UO₂. It is then the UO₂ is oxidised and remobilised back into solution as U(VI). Boland et al. (2011) tested the impact of silicate upon the uptake of uranium during Fe(II) mediated crystallisation of ferrihydrite to goethite. Silicate is known to inhibit the crystallisation of ferrihydrite (Cornell et al., 1987) and indeed the authors reported no goethite formation in experiments with silicate. However, they did notice a degree of recalcitrance of uranium adsorbed to the silicate-
Duff et al. (2002) performed coprecipitation experiments to investigate the uranium atomic level bonding of uranium incorporated into hematite. They reported that uranium is incorporated into the octahedral site as U(VI) in place of Fe(III), but that the characteristic uranyl bonds are lost and instead the uranium takes up a ‘uranate-like’ structure. Their model is, however, under coordinated with respect to the U-O bonds expected for U(VI) incorporated into an iron oxide structure. Ilton et al. (2012) doped hematite with U(VI) following the method of Duff et al. (2002) prior to exposing the U(VI)-doped hematite to various reducing agents. They reported that surface-adsorbed U(VI) was reduced to U(IV) as expected but that the structurally incorporated U(VI) was reduced to U(V). Interestingly, when the authors applied the Duff et al. (2002) incorporation model to their unreacted U(VI)-doped hematite they were unable to account for the presence of a uranyl component in the EXAFS. Their assumption was that the uranyl component was attributable to surface-adsorbed U(VI). However, they were unable to desorb any U(VI) using a carbonate solution leaching method (carbonate solutions are effective at removing U(VI) from geological media (Fredrickson et al., 2000)) suggesting the recalcitrant uranyl component belongs to the incorporated U species, be that U(VI) or U(V).

Several authors have suggested incorporation of U(IV) into the magnetite structure (Nico et al., 2009; O’Loughlin et al., 2010; Veeramani et al., 2011; Huber et al., 2012), which appears to be supported by atomistic simulations of uranium incorporation into various iron oxide structures (Kerisit et al., 2011). However, the model simulations do not replicate the available experimental data perfectly (Kerisit et al., 2011), highlighting the complexity of these systems with very limited direct evidence for U(IV), or U(V), incorporation into the magnetite structure (Ilton et al., 2010; Skomurski et al., 2011; Madden et al., 2012).

### 2.5.2 Technetium – Iron (Oxyhydr)Oxide Interactions

The pertechnetate anion (TcO$_4^-$) does not undergo significant sorption to Fe(III) iron (oxyhydr)oxides (Walton et al., 1986). Therefore, pertechnetate interactions with iron oxides are dominated by redox reactions involving Fe(II), either adsorbed or structural, resulting in production of Tc(IV) (Cui & Eriksen, 1996a, 1996b; Keith-Roach et al., 2003; Pepper et al., 2003; Burke et al., 2005, 2010; McBeth et al., 2007; Peretyazhko et al., 2008, 2009; Jaisi et al., 2009; Li & Kaplan, 2012; Kobayashi et al., 2013). Sorption of aqueous Tc(IV) onto the surface of Fe(III) oxides such as hematite and goethite occurs with maximum adsorption in the near-neutral pH range between pH 5.5 – 9 (Hallam et al., 2011). Adsorption onto both hematite and goethite
was also observed in the hyperalkaline range (pH >13), surmised to be due to formation of anionic TcO(OH)₃⁻ (Hallam et al., 2011).

Typically, reports of reduction of Tc(VII) suggest precipitation of hydrous TcO₂, where the proposed mechanism involves polymerisation of Tc(IV) into soluble Tc₄O₆⁽⁴n₂y⁺ chains which precipitate TcO₂·nH₂O when a critical cluster size is reached (Vichot et al., 2002; Maes et al., 2004; Peretyazhko et al., 2012). EXAFS investigations of the nature of the Tc(IV) species’ relationship to the iron oxide report Tc(IV) monomers and dimers bound in a bidentate arrangement with FeO₆ octahedra, forming a technetium containing ferrihydrite-like phase on the surface of the primary iron oxides, goethite, hematite and magnetite (Heald et al., 2007, 2012; Zachara et al., 2007). Heald et al. (2012) only observed a single FeO₆ contribution to the EXAFS from corroded steel coupons reacted with Tc(VII) and so concluded that Tc(IV) was present on the iron oxide corrosion product surface as chains of two to three Tc(IV) octahedra. In contrast to this, Peretyazhko et al. (2009) reacted Tc(VII) with Fe(II)-adsorbed to hematite and goethite and observed significant contributions from Fe in the second EXAFS shell, indicating potential incorporation into a goethite-like structure.

Um et al. (2011, 2012) investigated the potential for incorporation of Tc(IV) into goethite as a stable wasteform for immobilisation of Tc(VII) present in Hanford waste streams. In their experiments they reacted goethite with aqueous Fe(II) and Tc(VII) and successfully removed Tc(VII) as Tc(IV) associated with their iron oxide products, found to be both goethite and magnetite via XRD. Fitting of their EXAFS showed that Tc(IV) was in octahedral coordination with significant FeO₆ neighbours, indeed suggesting incorporation and interpreted as incorporation into goethite by the authors. They also reported limited release of the Tc(IV) into solution upon oxidation. However, the authors did not address the possibility of incorporation of Tc(IV) into magnetite despite the mineral being present in measurable quantities in their system. In their later experiments, the same authors armoured their Tc(IV)-doped goethite through a second stage of goethite crystallisation without Tc(VII) present, overgrowing the Tc(IV)-doped goethite to create a fresh goethite coating (Um et al., 2012). After extensive oxidation, the technetium remained as Tc(IV) with very limited release of technetium to solution indicating the oxidation of Tc(IV) was diffusion controlled and kinetically slow (Um et al., 2012).

The potential for incorporation of technetium into the hematite structure has been investigated through computational simulations (Skomurski et al., 2010). The authors tested two methods of incorporation: substitution of Tc(IV) into the lattice with associated reduction of Fe(III) to Fe(II) to maintain charge balance; or incorporation of TcO₄⁻ into interstitial vacancies. Their findings showed that, whilst pertechnetate incorporation was unfavourable,
up to 2.6 wt% Tc(IV) could be incorporated into the hematite structure, with clustering of the Tc(IV) and Fe(II) in proximity to one another aided by a lower coulombic repulsion compared to Fe(III)-Fe(III) interactions. Walton et al. (1986) suggested that, over a short period time, a small fraction of sorbed Tc(IV) could become incorporated into the hematite lattice but no other experimental evidence has been reported for Tc(IV) incorporation into hematite.

The ability of structural Fe(II) to reduce Tc(VII) to Tc(IV) has been exploited in numerous studies focussing on immobilisation of Tc(VII) by magnetite (and natural sediments), either abiotically (Cui & Eriksen, 1996b; Farrell et al., 1999; McBeth et al., 2011; Liu et al., 2012b; Peretyazhko et al., 2012; Kobayashi et al., 2013) or through microbially induced processes (Lloyd et al., 2000; Keith-Roach et al., 2003; Fredrickson et al., 2004; Istok et al., 2004; Burke et al., 2005, 2006, 2010; McBeth et al., 2007, 2011; Begg et al., 2008; Morris et al., 2008; Cutting et al., 2009; Law et al., 2010; Lear et al., 2010; Thorpe et al., 2014). In microbially active systems, the DMRB may induce Tc(VII) reduction to Tc(IV) either through direct enzymatic action at the cell periphery or indirectly through production of Fe(II) (Lloyd et al., 2000). In situ bioremediation has been tested at Oak Ridge, Tennessee, USA, and proven effective at removing Tc(VII) from contaminated groundwaters (Istok et al., 2004).

Farrell et al. (1999) used magnetite to act as a polarised anode to remove Tc(VII) from solution under anoxic conditions, noting that the technetium was retained by the magnetite when the polarisation was removed. Additionally, they found that, under oxidising conditions, the magnetite was preferentially oxidised rather than the Tc(IV). Further to this, they reported that the amount of Tc(VII) removed from solution could not be explained by formation of TcO₂ alone, indicating that a solid solution was formed between the magnetite and TcO₂ and suggesting some incorporation of the Tc(IV) into the magnetite (Farrell et al., 1999). A similar process appears to have been observed in many systems where Tc(IV) displays a degree of recalcitrance to oxidation implying a mechanism for isolating the Tc(IV) from the oxidising agent, possibly incorporation into the magnetite (Fredrickson et al., 2009; Burke et al., 2010; McBeth et al., 2011; Kobayashi et al., 2013). Many studies report that the choice of oxidising agent has implications for the amount of technetium released upon oxidation, with nitrate proving to be a poor oxidising agent compared to oxygen (Burke et al., 2006; McBeth et al., 2007; Begg et al., 2008; Morris et al., 2008).

The Fe(II)/Fe(III) ratio of the magnetite appears to have an effect upon the reduction rate of Tc(VII) to Tc(IV), most readily observed in titanomagnetites (Liu et al., 2012b). Incorporation of Ti(IV) into the magnetite structure results in reduction of Fe(III) to Fe(II) as a charge compensation mechanism, thereby increasing the Fe(II)/Fe(III) ratio. Liu et al. (2012b) reported a positive correlation between the Tc(VII) reduction rate and the Fe(II)/Fe(III) ratio induced by
altering the Ti(IV) concentration in their titanomagnetites. The authors postulated a mechanistic model of Tc(VII) reduction at the titanomagnetite surface forming Tc(IV)-Fe(III) solids through oxidation of Fe(II) in the particle surface (Liu et al., 2012b), with the reaction propagated through outward migration of Fe(II) to the surface and concurrent inward migration of charge balancing cationic vacancies (Pearce et al., 2012).

Both sulphate- and carbonate-green rusts (layered Fe(II) and Fe(III) hydrous oxides with interlayer anions) have also been shown to be effective at reducing Tc(VII) to produce TcO₂. Under oxidising conditions green rust transforms into a goethite-like structure but the Tc(IV) is retained as TcO₂ (Pepper et al., 2003). Nanoparticulate zero valent iron (NZVI) is able to reduce Tc(VII) to Tc(IV) or Tc(V) on the oxide surface (Darab et al., 2007). Sulphidated NZVI is similarly able to reduce Tc(VII), although this leads to production of a Tc(IV)-sulphide phase with FeS (Fan et al., 2013) which is remobilised during oxidation (Fan et al., 2014). Interaction of pertechnetate with mackinawite (tetragonal FeS) results in production of TcS₂ which, when exposed to oxidising conditions, undergoes transformation into TcO₂ rather than back to Tc(VII) (Wharton et al., 2000).

2.6 Biotite Mineralogy

Biotite has been chosen as a model iron-bearing silicate mineral due to its presence in a great variety of geological environments (Deer et al., 1992). Biotite has a 2:1 sheet silicate structure (monoclinic, space group C2/m, No. 12) (Figure 2-18), with two layers of Si⁴⁺ and Al³⁺ tetrahedra (T) sandwiching a layer of Mg²⁺ and Fe²⁺ octahedra (O). The T-O-T layers have a net negative charge due to Al³⁺ in the tetrahedral layer, which is balanced by K⁺ in the interlayer (Bailey, 1984). The resultant macro-scale crystal structure of biotite ‘books’ formed of close-packed ‘leaves’ with cleavage planes along the (001) plane. Biotite is usually black to brown in colour.

The Commission on New Minerals and Mineral Names (CNMMN) Subcommittee on Nomenclature of the Micas (1998, 1999) recommended that the name biotite be used for a series including phlogopite, siderophyllite, annite and eastonite, and is therefore no longer to be regarded as a species name. However, biotite still receives recognition in the literature with reference to phlogopite for Mg rich species, and hence herein biotite is used to refer to the group as a whole, unless a specific species is mentioned for discussion.
Phlogopite (\(K_2Mg_6[Si_6Al_2O_{20}](OH)_4\)) and annite (\(K_2Fe_6[Si_6Al_2O_{20}](OH)_4\)) are the magnesium- and iron-rich end-members respectively, but pure annite does not occur naturally. However, in most natural biotites there is appreciable substitution of \(Al^{3+}\) for \((Mg^{2+}, Fe^{2+})\), balanced by \(Al^{3+}\) for \(Si^{4+}\) in tetrahedral sites (Tschermak’s substitution), which leads to the end-members siderophyllite (\(K_2Fe_4Al_2[Si_4Al_4O_{20}](OH)_4\)) and eastonite (\(K_2Mg_4Al_2[Si_4Al_4O_{20}](OH)_4\)) (Deer et al., 1992). Ideally, in biotite, the octahedral sites are completely filled but vacancies do occur. The occupation of the octahedral sites by \(Fe^{3+}\) and \(Mg^{2+}\) appears to be random, as is the occupation of the tetrahedral sites by \(Si^{4+}\) and \(Al^{3+}\). However, Mössbauer spectroscopy indicates that \(Fe^{3+}\) preferentially enters the smaller octahedral sites (Deer et al., 1992).

### 2.7 Alkaline Degradation of Biotite

Various authors have studied the weathering products of biotite and published accounts under a range of environmental conditions (Gilkes & Suddhiprakarn, 1979b; Meunier & Velde, 1979; Banfield & Eggleton, 1988; Dong et al., 1998). They report end products that are consistent (e.g. kaolinite) but the observed intermediate assemblages (interstratified biotite and vermiculite, chlorite, kaolin group minerals, iron oxides, gibbsite) differ owing to differences in the chemical environment and fluid composition during breakdown. The dissolution of biotite in alkaline solutions releases \(K^+\) from the interlayer along with the major framework cations \((Al^{3+}, Si^{4+}, Mg^{2+}, Fe^{3+})\) (Murakami et al., 2004; Samson et al., 2005; Sugimori et al., 2008), leading to alteration of the biotite to vermiculite \((Mg(Mg^{2+},Fe^{3+})_6[Si_4Al_4O_{20}](OH)_4\cdot nH_2O)\) – a mineral similar in structure to phlogopite. However, replacement of \(Si^{4+}\) by \(Al^{3+}\) in tetrahedral sites is only partially compensated by \(Al^{3+}\) or \(Fe^{3+}\) substitution for \(Mg^{2+}\) in octahedral sites, resulting in a net negative charge which is balanced by replacement of \(K^+\) in the interlayer by \(Mg^{2+}\).
Figure 2-19 Idealised structure of vermiculite, viewed parallel to the (001) plane.

Water molecules are also present in the interlayer (Figure 2-19). The interlayer cations and water molecules are held in specific locations with respect to neighbouring tetrahedral oxygens, with the water molecules forming two layers of distorted hexagonal networks. Not all available interlayer sites are occupied by cations/water molecules (Deer et al., 1992). Vermiculite is identified by injection of glycol or glycerol to vary the interlayer spacing, or by line broadening of the biotite XRD pattern.

A TEM study of biotite weathering profiles in granite (Banfield & Eggleton, 1988) suggested that transformation of biotite to vermiculite occurred via a direct structural modification process. They found that a single sheet of biotite transforms to vermiculite over only a few angstroms with little disruption to the surrounding structure and that the 2:1 layering was continuous from the 10 Å biotite to the 14 Å vermiculite (Figure 2-20).

Figure 2-20 Lattice fringe image showing conversion of single biotite layer (10 Å) to vermiculite (14 Å) by direct modification of the existing sheet (Banfield & Eggleton, 1988).

The process proceeds at a constant budget of Al$^{3+}$ but releases K$^+$, Si$^{4+}$ and any Ti$^{4+}$ present (which cannot be readily accommodated in the vermiculite structure) and requires small
additional quantities of iron and magnesium. However, no magnesium or iron is required from external sources due to dissolution of the silicate framework elsewhere. The first stage is exchange of K\(^+\) for H\(_3\)O\(^+\) which opens up the interlayer spacing and allows access of oxygen to octahedral Fe\(^{2+}\), promoting oxidation to Fe\(^{3+}\) (Banfield & Eggleton, 1988). A second and relatively uncommon mechanism was also observed, whereby redistribution of the components from two biotite sheets formed a single sheet of vermiculite (20 Å → 14 Å).

Sediments from Hanford have been reacted with highly basic solutions to investigate the release of iron into solution (Qafoku et al., 2007). Base-induced dissolution of iron-bearing minerals (biotite and chlorite were constituents of the sediment) resulted in aluminosilicate secondary phases. X-ray diffraction and electron microscopy techniques were used to provide evidence of secondary iron oxide formation, as both hematite and goethite. A similar study of biotite dissolution in solutions with increasing NaOH concentration, up to 2 mol l\(^{-1}\), observed a corresponding increase in the release of K\(^+\), Fe\(^{2+}\), Si\(^{4+}\) and Al\(^{3+}\) (He et al., 2005). However, the dissolved Fe concentration was approximately an order of magnitude lower than the other cations, which the authors postulate as potentially a result of formation of green rust \((\text{Fe}^{2+}_6\text{Fe}^{3+}_2\text{OH})_{18}\) or white rust (Fe(OH)\(_2\)). They postulated the following breakdown reaction for biotite under alkaline conditions:

\[
\text{K(Mg,Fe)}_3\text{(Si}_3\text{Al})\text{O}_{10}(\text{OH})_2 + \text{OH}^- + \text{H}_2\text{O} \\
\rightarrow \text{K}^+ + \text{Mg(OH)}_2 + \text{Fe(OH)}_2 + \text{Al(OH)}^{4-} + \text{H}_4\text{SiO}_4
\]

followed by

\[
\text{Al(OH)}^{4-} + \text{H}_4\text{SiO}_4 \rightarrow \text{Al(OH)}_3\text{[SiO}_2\text{]}_x + \text{OH}^- + x\text{H}_2\text{O}
\]

When the solution concentration of Na\(^+\) was increased, through the addition of sodium nitrate (NaNO\(_3\)), the release of K\(^+\) was even greater but there was no significant increase in pH. It has been reported that release of K\(^+\) during biotite dissolution was only weakly dependent upon solution pH (Acker & Bricker, 1992), and it has been suggested that the increased solution K\(^+\) concentration is a result of increased substitution by Na\(^+\) in the biotite interlayer (He et al., 2005). This would serve to increase the interlayer spacing, due to the higher charge density on the Na\(^+\) cation, which in turn should lead to greater dissolution of the biotite and associated release of Fe\(^{2+}\) to solution. Biotite crystals, pre-conditioned in pH 8 solutions, and then exposed to solutions in the pH range 10 – 14, exhibit fast preferential release of K\(^+\) from the interlayer followed by near stoichiometric release of Si\(^{4+}\), Al\(^{3+}\) and Mg\(^{2+}\) (Samson et al., 2005). Release of Fe\(^{2+}\) is reported as much slower than the other framework cations. The observed transient increases of cation release with each pH are attributed to dissolution of iron or aluminium oxyhydroxide phases (e.g. FeOOH, AlOOH). When micaceous subsurface sediments from
Hanford were reacted with base solutions (up to 3 mol l\(^{-1}\) NaOH), dissolution of biotite was observed to occur predominantly at the edge structures and not on the basal plane (Ainsworth et al., 2005). With increasing NaOH solution strength and exposure time, the biotite crystals develop crenulated surfaces with curling at the edges of leaves and increasing amounts of secondary precipitated phases, which are overwhelmingly found at the crystal edges and rarely on the biotite basal plane (Ainsworth et al., 2005; Samson et al., 2005).

### 2.8 Summary

The UK has significant quantities of legacy radioactive wastes, of which the higher activity wastes will be disposed of in a deep geological disposal facility, in accordance with government policy. It is therefore imperative from a scientific, but also regulatory, standpoint to understand the behaviour of the waste once it is emplaced within a GDF. There has been a significant body of research produced over several decades in support of geological disposal of radioactive waste. This work has focussed on the behaviour of radionuclides in such an environment as can be expected to prevail in the various disposal concepts considered (e.g. hyperalkaline conditions around a cementitious repository), particularly in respect of the mobility of radionuclides released from the wastes. To date, studies have tended to investigate surface processes that may promote or inhibit radionuclide transport (e.g. adsorption or complexation).

However, it is also known that the extreme geochemical conditions expected in most disposal concepts will affect not only the waste within the GDF, but also the mineralogy of the host rock in which the GDF is built. Therefore the potential exists for these reactions to also have an impact upon radionuclide transport. Numerous studies have indicated that radionuclides may become incorporated into relevant mineral phases, such as iron oxides, and that this is a potentially a significant mechanism for radionuclide immobilisation. However, there is limited direct evidence to conclusively determine the mechanism of incorporation since there have been relatively few targeted studies of dynamic single mineral systems of the type presented in this thesis.
Chapter 3 Research Methods

In this chapter, the research methods (both experimental and analytical) that have been used to obtain data for this thesis will be described and discussed critically.

3.1 Solution pH and Eh

Solution pH was measured using a Thermo Orion 710A+ meter with a PHE1062 combination pH electrode, calibrated using three buffers (from pH 4, 7, 10 and 12), depending upon the expected sample pH range. The electrode was fully inserted into solution and the solution agitated until the reading was stable (typically 30 seconds) before the measurement was taken. pH measurements were recorded to 2 decimal places but only quoted to 1 decimal place, with an error of ± 0.1 pH unit.

Solution Eh was measured using a Thermo Orion 710A+ meter with a PHE1080 combination ORP electrode. The Eh of Zobell’s solution (<6 months old) was measured (+234 mV) as a check on the accuracy of the electrode prior to each use. The electrode was fully inserted into solution and the solution agitated until the reading was stable (typically 60 seconds) before the measurement was taken. Eh measurements were recorded to the nearest multiple of 5 mV, with an error of ± 5 mV.

3.2 Iron (oxyhydr)oxide Syntheses

All iron(oxyhydr)oxides were synthesised as per the methods of Cornell and Schwertmann (2003) which are detailed below.

3.2.1 Ferrihydrite Synthesis

A 1 M potassium hydroxide (KOH) stock solution was prepared from potassium hydroxide (KOH) pellets using deionised water. A 0.2 M iron(III) nitrate (Fe(NO₃)₃) stock solution was prepared from Fe(NO₃)₃·9H₂O powder. In a beaker, placed on a magnetic stirrer, approximately 330 ml of the KOH was added to 500 ml of the Fe(NO₃)₃ to bring the pH to between 7 and 8. The pH was constantly monitored during addition of the KOH to avoid overshooting the target pH range. Once the pH had stabilised at between 7 and 8, the stirrer was switched off, the beaker covered with parafilm, and the suspension allowed to settle for ~1 – 2 hours. After this period, the supernatant was removed and discarded to drain. The remaining suspension was transferred to centrifuge tubes/bottles and centrifuged at 4000 rpm for 5 minutes (1700 g). The supernatant was again discarded. The paste was re-suspended in 18 MΩ Milli-Q deionised...
water (MQ) and centrifuged as before. This washing step was performed three times. The wet paste was stored at 5 °C for no more than one week prior to use in experiments. X-ray diffraction of the product confirmed formation of 2-line ferrihydrite. The solid content of the wet paste was determined via dissolution of a known mass of paste in 1 M HCl and analysing the subsequent solution for Fe(III) by the ferrozine assay (Chapter 3.7.3). Using the mass of Fe(III) per gram of paste, the mass of solid per gram of paste was then calculated using the chemical formula for disordered 2-line ferrihydrite: Fe₈.₂O₈.₅(OH)₇.₄·3H₂O (Michel et al., 2010).

### 3.2.2 Hematite Formation

Ferrihydrite paste was accurately weighed into an HDPE reaction vessel of suitable volume to give an experimental solid-solution ratio of 0.40 g L⁻¹, to give approximately 0.34 g L⁻¹ of final hematite (Fe₂O₃) product as calculated from the Fe(III) content of the ferrihydrite paste. The vessel was transferred into an anaerobic chamber (5 % H₂, balance N₂, maintained at <1 ppm O₂ and CO₂) and an appropriate volume of the reaction solution (pH 10.5) added. The pH was adjusted to pH 10.5 using appropriate strength KOH. The vessel was sealed and shaken vigorously to ensure complete mixing. The vessel was removed from the anaerobic chamber to the bench top and the headspace purged with CO₂-free laboratory air. An equilibration period of 24 hours at room temperature occurred, during which the pH was measured at regular intervals, under CO₂-free air, and re-adjusted as necessary. After the 24 hour equilibration period, the vessel was transferred to a temperature-controlled oven, set to 60 °C for up to 10 weeks, with pH adjustments undertaken as required. Each time the vessel was opened, the headspace was purged with CO₂-free laboratory air. After the desired incubation period, the vessel was removed from the oven and placed into a cold water bath. The suspension was allowed to settle and the supernatant was removed and discarded to drain. The remaining suspension was transferred to a centrifuge tube and centrifuged at 4000 rpm for 5 minutes (1700 g). The supernatant was again discarded. The paste was re-suspended in MQ and centrifuged. This washing step was performed three times. The resulting paste was dried in an oven at 40 °C to obtain a red powder, and stored in a desiccator. X-ray diffraction of the product after 4 weeks reaction at 60 °C confirmed formation of 55 % hematite with 45 % goethite. However, the same experimental procedure with incubation at 105 °C for 10 weeks resulted in a product of > 90% hematite.

### 3.2.3 Goethite Formation

Ferrihydrite paste was accurately weighed into a suitable vessel to give an experimental solid-solution ratio of 0.40 g L⁻¹, to give approximately 0.36 g L⁻¹ of final goethite (FeOOH) product as calculated from the Fe(III) content of the ferrihydrite paste. The vessel was transferred into the
anaerobic chamber and an appropriate volume of the reaction solution (pH 13.1) added. The pH was measured and adjusted to the initial solution pH using appropriate strength KOH. The vessel was sealed and shaken vigorously to entrain all solids and ensure complete mixing. The vessel was removed from the anaerobic chamber to the bench top and the headspace purged with CO₂-free laboratory air. An equilibration period of 24 hours at room temperature was observed, during which the pH was measured at regular intervals and re-adjusted as necessary. After the 24 hour equilibration period, the vessel was transferred to a temperature controlled oven, set to 60°C for up to 4 weeks, with continued pH adjustments as required. Each time the vessel was opened, the headspace was purged with CO₂-free laboratory air. After the desired incubation period, the vessel was removed from the oven and placed into a cold water bath. The suspension was allowed to settle and the supernatant was removed and discarded to drain. The remaining suspension was transferred to a centrifuge tube and centrifuged at 4000 rpm for 5 minutes (1700 g). The supernatant was again discarded. The paste was re-suspended in MQ and centrifuged as before. This washing step was performed three times. The resulting paste was dried in an oven at 40 °C to obtain a yellow powder, and stored in a desiccator. X-ray diffraction of the product after 4 weeks reaction confirmed goethite was the dominant phase produced.

### 3.2.4 Magnetite Formation

Ferrihydrite paste was accurately weighed into a suitable vessel to give an experimental solid-solution ratio of approximately 3 g L⁻¹ ferrihydrite, 2 g L⁻¹ Fe(III). In the anaerobic chamber, an appropriate volume of solution (pH 10.5 – 13.1) was added. The pH was measured and adjusted to the initial solution pH using appropriate strength KOH and allowed to equilibrate for >2 hours. The equivalent molarity of Fe(II) supplied by 0.1 M ferrous chloride (FeCl₂) was then added to give an Fe(II)/Fe(III) ratio of stoichiometric magnetite (i.e. 1/2). The pH was readjusted to the initial solution pH via addition of appropriate strength KOH. The method of addition of the FeCl₂ and associated KOH was dependent on the nature of the radiological risk associated with the experiment: experiments containing technetium were conducted in the anaerobic chamber and additions were via manual pipette; experiments with uranium or no radionuclide were conducted using a chemostat and all additions were automated, with the rate of FeCl₂ addition set to ~0.1 mL s⁻¹ to allow effective automatic pH control. The magnetite was allowed to age under a reducing, CO₂-controlled atmosphere (either zero-grade N₂ or 95 % N₂/5 % H₂) for >2 days prior to sampling or exchange into an oxygenating atmosphere for oxidation experiments. For sampling, the suspension was centrifuged at 4000 rpm for 5 minutes (1700 g), and the supernatant discarded to waste. The paste was re-suspended in MQ and centrifuged as before. This washing step was performed three times. The paste was stored...
in the -80 °C freezer without drying. X-ray diffraction of the product confirmed >98 % magnetite was formed at pH 10.5, with trace goethite. At pH 12.5 and 13.1, up to ~25 % goethite was formed.

### 3.3 Batch Experiments

Batch experiments have been used as the primary experimental method where a series of experiments are set up under the same conditions to obtain replicate experiments or to investigate the effect of varying certain conditions or experimental parameters. Batch experiments have limitations but these are generally outweighed by the ability to work safely with radionuclides, obtain large experimental matrices and generate multi-variable datasets concurrently.

When working with batch experiments, certain assumptions must be made to allow comparisons to be drawn between, and within, experimental batches. The assumptions to be made and their relative importance depend upon the focus of the experiment but, in general, experimental batches must be treated in exactly the same way, and it has to be assumed that they will each react in the same way to the same conditions. Experimental variability is inevitable and must be quantified through replicates, sampling, analysis and effective recording of experimental parameters and conditions.

One criticism frequently levelled at batch experiments, particularly in environmental sciences, is that they tend not to accurately reflect the natural environment they are designed to investigate, e.g. through lower solid-solution ratios than observed in reality. However, these are generally accepted and batch experiments have proven to be a valuable technique to probe simple, well defined and controlled model systems.

Here, batch experiments have been used to investigate effects arising out of changes to redox potential (through atmospheric control) and pH (through solution chemistry control) on the interaction between different solid phases and radionuclides.

### 3.4 Chemostat Experiments

Some experiments (e.g. magnetite formation) required automated control and logging of certain experimental parameters (e.g. pH) which was done using a Labfors Infors reactor system (Figure 3-1). The automated control was primarily utilised to control the pH during automated addition of reagents and maintaining the pH through the reaction, whilst logging pH, Eh, acid/base addition and rate of stirring as a function of time. The reactor also had the ability to be set up with a controlled atmosphere to allow oxygenating or reducing conditions
to be maintained. The reactor vessel was suitable for experiments of up to 1.5 L but required a minimum experimental volume of ~250 mL. Monitoring of pH and Eh was achieved through integrated electrodes connected to the system control unit. pH calibration was via two buffers and tolerance was controllable to ± 0.1 unit. Control of pH was via addition of appropriate user-selected acid and base via automated peristaltic pumps, calibrated prior to each batch run. Eh was logged but not calibrated nor controllable from the reactor; however, the Eh was checked against Zobell’s solution for accuracy prior to each experimental run and was found always to be within ± 10 mV of the desired value (+234 mV). Data logging was set to sample at 5 second intervals and was displayed in real time via connection to a laptop computer on the bench. Atmospheric control was achieved via purging of the reactor headspace with either CO₂-free laboratory air (oxygenating conditions) or zero-grade nitrogen (reducing conditions), which vented through a water trap to prevent pressurisation of the reactor vessel and ensure a closed system in the event of loss of gas supply.

Figure 3-1 Annotated chemostat setup.

### 3.5 Synthetic Cement Leachates

Three synthetic cement leachates have been used to mimic groundwater compositions in and around a cementitious geological disposal facility (GDF) at three points during post-closure of such a facility. These reflect the chemistry of the dominant buffering phases and represent the early-, middle- and late-stage post-closure environment (Berner, 1992; Moyce et al., 2014).
3.5.1 Young Cement Leachate (YCL, pH 13.1)

The young cement leachate (YCL) represents the early-stage post closure groundwater and is dominated by potassium hydroxide and sodium hydroxide (KOH and NaOH, respectively) dissolution. The solution was prepared by first sparging MQ with oxygen-free nitrogen (OFN) for >1 hour per litre before addition of the reagents. Whilst sparging and stirring the MQ with a magnetic stir bar, 5.2 gL\(^{-1}\) potassium hydroxide, 3.8 gL\(^{-1}\) sodium hydroxide and 0.1 gL\(^{-1}\) calcium hydroxide (Ca(OH)\(_2\)) were added. The solution was sealed and left on the stir plate for 24 hours, after which it was stored in an anaerobic chamber maintained at <1 ppm O\(_2\) and CO\(_2\).

3.5.2 Intermediate Cement Leachate (ICL, pH 12.5)

The intermediate cement leachate (ICL) represents the middle-stage post closure groundwater and is dominated by calcium hydroxide (Ca(OH)\(_2\)) dissolution. The solution was prepared by first sparging MQ with OFN for >1 hour per litre before addition of the reagent. Whilst sparging and stirring the MQ with a magnetic stir bar, 1.2 gL\(^{-1}\) calcium hydroxide (Ca(OH)\(_2\)) was added. The solution was sealed and left on the stir plate for 24 hours, after which it was stored in an anaerobic chamber maintained at <1 ppm O\(_2\) and CO\(_2\).

3.5.3 Old Cement Leachate (OCL, pH 10.5)

The old cement leachate (OCL) represents the late-stage post closure groundwater and is dominated by calcium-silicate-hydrate (C-S-H) phase dissolution. The solution was prepared by first sparging MQ with OFN for >1 hour per litre before addition of the reagent. Whilst sparging and stirring the MQ with a magnetic stir bar, 15 mgL\(^{-1}\) calcium hydroxide (Ca(OH)\(_2\)) was added. The solution was sealed and left on the stir plate for 24 hours, after which it was stored in an anaerobic chamber maintained at <1 ppm O\(_2\) and CO\(_2\).

3.6 Chemical Extractions

Chemical extractions are routinely used to quantify relative proportions of metal ions associated with different extraction lixiviants. They are operationally defined techniques which are unable to determine associations with specific mineral assemblages but they can provide (typically) reproducible generic information regarding total metal ion concentrations in broad fractions, i.e. adsorbed, associated with poorly crystalline oxides, associated with reducible oxides (Tessier et al., 1979; Poulton & Canfield, 2005). Here, chemical extractions were used to estimate e.g. adsorbed U or to selectively quantify various pools of Fe during alkaline breakdown of iron-bearing silicates. The resulting solutions were then analysed using one of the solution analytical techniques, as outlined in Chapter 3.7.
3.6.1 Surface Desorption

To quantify the pool of an adsorbed ion, surface desorption extractions were utilised following the method of Vu et al. (2010). This technique was primarily utilised to assess surface-adsorbed uranium in Chapter 4, to differentiate between adsorbed and incorporated uranium species. A series of sacrificial batch experiments were set up to allow for collection of time-resolved data. At the point of sampling, the solution was sampled for uranium to quantify the uranium associated with the solid. The solution was then titrated from the starting pH (10.5) to pH 2-2.5 using nitric acid of appropriate strength and placed onto an orbital shaker table for 2 hours, after which time the solution was again sampled for uranium. The difference between the two solution samples equates to the surface-adsorbed uranium pool. All solution samples were analysed for U-238 using ICP-MS (Chapter 3.7.1). A mass balance calculation, knowing the initial total uranium spiked to solution, gives the size of the incorporated uranium pool as follows:

\[ U_{\text{INCORPORATED}} = U_{\text{TOTAL}} - U_{\text{ADSORBED}} - U_{\text{SOLUTION}} \]

Desorption experiments such as this may lead to overestimates of the adsorbed pool through dissolution of some of the solid material due to the increased solubility at lower pH of iron oxides, and subsequent release from the incorporated pool. In future work, it should be advocated that the user additionally analyses all solution samples for Fe (or the major cation in the solid matrix) to detect changes during the titration which may indicate dissolution. An alternative non-destructive technique would be to use an isotopic tracer (e.g. U-232) to determine the size of the exchangeable (adsorbed) pool after a period of equilibration.

3.6.2 Sequential Extractions of Reducible Iron Oxides

Various published sequential extraction methods for quantification of relative proportions of iron oxides exist and focus on application of progressively stronger lixiviants to target increasingly more resistant phases. The methods used here have been adapted from Phillips and Lovley (1987), Poulton and Canfield (2005) and Raiswell et al. (2010) to create a three-step process tailored to the specific needs of the experiment.

The first step is a citrate-ascorbate extraction (Raiswell et al., 2010) that is highly selective for ferrihydrite, with very limited effect on the remaining iron oxides or iron-bearing clays present. The second step is an oxalate extraction (Phillips & Lovley, 1987) which provides a good estimate of the quantity of poorly crystalline iron oxides present, including goethite and nanomagnetite. The final step is a dithionite extraction (Poulton & Canfield, 2005) which
estimates the total iron oxides remaining, namely hematite. The procedure was undertaken as follows:

Sufficient ascorbate extraction solution was prepared by dissolving 50 g L\(^{-1}\) sodium citrate (0.17 M), 50 g L\(^{-1}\) sodium bicarbonate (0.6 M) and 10 g L\(^{-1}\) L-ascorbic acid (0.057 M) into deoxygenated MQ and the pH adjusted to 7.5 by adding more L-ascorbic acid as necessary. Approximately 0.1 g of wet sample paste was accurately weighed into a 15 mL centrifuge tube. 10 mL of the ascorbate extraction solution was added to the centrifuge tube and the sealed tube placed onto an end-over-end rotator at 20 rpm, for 24 hours at room temperature. Post-extraction, the tube was centrifuged, the supernatant removed for solution analysis, and the remaining wet paste washed in MQ. After further centrifugation, the supernatant was removed to waste and the paste ready for the next extraction.

Sufficient oxalate extraction solution was prepared by dissolving 28 g L\(^{-1}\) ammonium oxalate (0.2 M) and 15 g L\(^{-1}\) oxalic acid (0.17 M) in deoxygenated MQ. 10 mL of the oxalate extraction solution was added to the wet paste. The sealed tube was wrapped in aluminium foil to exclude light and placed onto the rotator at 20 rpm, for 16 hours at room temperature. Post-extraction, the tube was centrifuged, the supernatant removed for solution analysis, and the remaining wet paste washed in MQ. After further centrifugation, the supernatant was removed to waste and the paste ready for the next extraction.

A buffer solution was prepared by dissolving 58.82 g L\(^{-1}\) tri-sodium citrate (0.2 M) into deoxygenated MQ and adding 20 mL L\(^{-1}\) acetic acid (0.35 M). Sufficient dithionite extraction solution was prepared by dissolving 50 g L\(^{-1}\) sodium dithionite (0.29 M) in MQ, the pH adjusted to 4.8 using the buffer solution, and the volume made up with MQ. 10 mL of the dithionite extraction solution was added to the wet paste and placed onto the rotator at 20 rpm, for 2 hours at room temperature. Post-extraction, the tube was centrifuged, the supernatant removed for solution analysis, and the remaining wet paste discarded.

Sequential extractions are not completely selective and struggle to distinguish between certain phases owing to similar solubilities, which may be influenced by their surface area, crystallinity and crystal chemistry, forming overlapping solubility continuums. As such, no chemical extractant can be expected or considered to dissolve one component or phase completely whilst leaving other similar components/phases unaffected (Reyes & Torrent, 1997). Tessier et al. (1979) determined the standard deviation on sequential extraction techniques employed for various trace metal ions to be no better than ± 10 % whilst Raiswell et al. (2010) report a precision of ~8 %.
3.6.3 Acid Digestion

To determine the total mass of U associated with a solid, a total acid digestion was utilised. Many authors have used acid digestions (Malcolm et al., 1990; Payne et al., 1994; Amonette & Templeton, 1998; Handler et al., 2009; Kenna, 2009; Um et al., 2009, 2011; Law et al., 2010) and a brief outline of the procedure used here is given below.

A known mass of sample was added to a clean 100 mL glass beaker and in a fumehood 20 mL concentrated (12N) HCl was added. The beaker was gently swirled to entrain all solids into the acid and then covered with a watch glass and placed onto a hotplate in the fumehood. The temperature was slowly increased whilst the beaker was occasionally gently swirled. Once the solid had dissolved, the solution was brought to the boil and allowed to boil until almost dry. At this point the beaker was removed from the heat and allowed to cool before re-suspension of the sample in 5 mL concentrated (16 N) HNO₃. Appropriate dilutions were then made for analysis for U-238 by ICP-MS (Chapter 3.7.1).

3.7 Solution Elemental Analyses

In general, solution analyses were performed by the author, with the exception of ICP-MS and ICP-AES which were performed by Paul Lythgoe of the Manchester Analytical Geochemistry Unit at The University of Manchester. However, all sample preparations were performed by the author.

For ICP-MS and ICP-AES, at least one sample in 10 was analysed in triplicate and combined errors were calculated for complete datasets, which may include data from more than one analytical batch, with the combined error applied to all values in a set. The formula for calculating the combined error was as follows:

$$\sigma_f = \sqrt{\sum_{i=1}^{n} \left(\frac{\sigma_i}{\bar{x}_i}\right)^2}$$

where \(\sigma_f\) represents the combined error, and \(\sigma_i\) represents the standard deviation of the arithmetic mean of a triplicate set, \(\bar{x}_i\), for \(n\) sets of triplicate measurements.

3.7.1 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) was used to determine the solution concentration of U and Fe in Chapter 4 to Chapter 7. Supernatant samples were removed from the experiments, filtered (0.45 μm) and acidified using HNO₃ as preservative. 100 μl of sample
was made up to 10 ml with 2 % w/v HNO₃, filtered (0.45 μm) and analysed using an Agilent 7500cx ICP-MS (details available from: http://www.seaes.manchester.ac.uk/our-research/facilities/geochemistry/equipmentandfacilities/icp-ms/). Sample batches were run with standards every 10 samples and the limit of detection was 1 – 10 ppb.

3.7.2 Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) was used to determine the solution concentration of a range of determinands in Chapter 7. Supernatant samples were removed from the experiments, filtered (0.45 μm or 0.22 μm, nylon membrane) and acidified using HNO₃ as preservative. 1 ml of sample was made up to 10 ml with 2 % w/v HNO₃, filtered (0.45 μm) and analysed using a Perkin-Elmer Optima 5300 dual view ICP-AES (details available from: http://www.seaes.manchester.ac.uk/our-research/facilities/geochemistry/equipmentandfacilities/icp-aes/). Sample batches were run with standards every 10 samples and the limit of detection was 10 – 100 ppb.

3.7.3 Ferrozine Assay

The ferrozine assay is a photospectrometric technique to determine the solution concentration of Fe(II) (Stookey, 1970; Viollier et al., 2000). The method of Viollier et al. (2000) has been used to determine Fe(II) and total Fe (via reduction of Fe(III)) in solution samples, as well as to determine the total Fe content of ferrihydrite pastes via digestion in 1 M HCl. The ferrozine method relies upon the ferrozine molecule, 3-(2-pyridyl)-5,6-bis(4-phenylsulfonic acid)-1,2,4-triazine, forming a strong-purple coloured complex with aqueous Fe(II) allowing the absorbance to be measured in a photospectrometer using monochromated light at a wavelength of 562.0 nm (Stookey, 1970). Prior to each batch of analyses, the absorbance was reset to zero for a blank cuvette of MQ. The background absorbance of the chelating/reductant/buffer compound(s) was then determined by preparing a cuvette with no sample present. Finally, analyses on samples were performed in triplicate and at a range of dilutions between 10x and 100x. Averaged values at each dilution were calculated and then corrected for dilution, and then these corrected averages were then averaged to give a concentration of aqueous Fe. Fe standards were made up from a 1000 ppm Fe(III) standard to determine the calibration curve and linear response range (typically between absorbance of 0.02 and 2.50). Uncertainties were calculated as the standard deviation on the arithmetic mean of triplicate samples at particular dilutions.
3.7.4 Liquid Scintillation Counting (LSC)

Liquid scintillation counting (LSC) was used to detect the activity of Tc-99, a pure β emitting radionuclide, in solution. The instrument used was a Packard Tri-carb 2100TR liquid scintillation counter. A 100 μl aliquot of sample was added to 5 ml of liquid scintillation cocktail before counting for 30 minutes per sample, recording the activity as counts per minute (cpm) in the energy range 0 – 2000 eV. The cpm was converted to counts per second (cps) by dividing by 60 to give an activity in Bq (disintegrations [or counts] per second) assuming essentially 100 % counting efficiency (as tested with appropriate standards), which was then corrected for sample volume to give an activity in Bq ml⁻¹. The measurements were calibrated by comparison to a sample of known activity. The background radiation in the laboratory was 24.9 ± 1.6 cpm (average of 16 blanks, 10 minute count time) meaning accurate detection of sample counts below 30 cpm or 0.5 Bq (i.e. 3 standard deviation of the background above background) was not possible.

The accuracy of determining radioactivity via LSC is affected by the counting efficiency and quench. Typically, only 4% of the energy from a beta emission is converted to light, and most scintillation detection tubes operate at approximately 25 % efficiency. The efficiency is further reduced since average emission energy is typically 30-40 % of the maximum emission energy (0.294 MeV for Tc-99), reducing the number of photons produced leading to production of fewer scintillations. However, counting efficiency for Tc-99 is generally greater than 90 %, and was monitored throughout this work using calibrated standards.

3.8 Solid Characterisation

Various solid characterisation techniques have been utilised during the project, the details of which are discussed below. In general, the author was trained in the use of each technique and performed the analysis. Exceptions to this are TEM and EELS, which were performed by Mike Ward and Andy Brown of the University of Leeds; and Mössbauer Spectroscopy, which was performed by Paul Wincott of the University of Manchester. Assistance with quantification of XRD patterns was provided by Pieter Bots.

3.8.1 Specific Surface Area Analysis

The specific surface area (SSA) of powdered samples was analysed via the Brunauer–Emmett–Teller (BET) method (Brunauer et al., 1938). The method measures the adsorption of an inert gas over a range of negative pressures at liquid nitrogen temperatures, to assess the surface area per unit mass of solid. The powdered sample was dried under flowing nitrogen for longer
than 19 hours using a Micromeritics FlowPrep 060 sample degas system prior to analysis with a Micromeritics Gemini V BET surface area analyser. The purged samples were evacuated and cooled using liquid nitrogen, before nitrogen gas was admitted to the sample vial and an identical empty vial. A differential pressure transducer measures the imbalance in pressure between the sample and blank vials, caused by the adsorption of gas onto the sample surface. The system uses this data to calculate the number of molecules of nitrogen required to form a monolayer on the sample surface and, since the molecular dimensions of nitrogen are known, calculates the surface area of the sample in square metres per gram.

### 3.8.2 Powder X-Ray Diffraction (XRD)

Solid samples were washed in MQ and dried in a desiccator or an oven at 40 °C. A small mass of dried sample was lightly crushed in a mortar with a few ml of isopropanol. The sample was then transferred to a silicon slide by dropping pipette and allowed to dry in air. The slide was then placed into the diffractometer to be analysed. Air-sensitive samples were dried and prepared in an anaerobic chamber (95 % N₂ / 5 % H₂), and the dried powders analysed in air. No oxidative change was observed during analysis. A small mass of silicon powder was added during crushing to allow for calibration of patterns. Samples have been analysed on three diffractometers: a Bruker D8 (λ = Cu K-α₁) and Phillips PW1050 (λ = Cu Kα) at Leeds University and a Bruker D8 (λ = Cu K-α₁) at Manchester University.

XRD patterns were collated and background subtracted in EVA (Bruker AXS, 2013) and peak matched using the International Centre for Diffraction Data (ICDD) Powder Diffraction File (PDF) database.

Preferred orientation bias is a factor when analysing samples containing minerals of particular morphologies, e.g. acicular goethite needles or planar biotite flakes. However, the sample preparation technique employed aids in alleviating this bias, although some preferred orientation may still be apparent. No preferred orientation analysis was deemed necessary; however, a polar plot of the peak intensities may be used to determine if there is any bias present.

A consequence of using a copper target to generate the x-rays in the XRD diffractometers is that of fluorescence from the iron-containing samples. The iron in the sample absorbs the incident x-rays, reducing the diffracted signal, whilst fluorescence from the excited iron atoms increases the background noise. To counteract this issue for the high iron-content samples studied here, non-standard settings for the LynxEye detector were used; the Low Level was increased from 0.11 to 0.19 and the window width was reduced from 0.14 to 0.08.
3.8.2.1 Quantitative Refinement of XRD Patterns

To quantify the proportions of phases in XRD patterns, Rietveld refinements were performed using Topas v4-2 (Bruker AXS, 2009). Topas uses the integrated intensity of the diffraction peaks and the crystal structure to calculate the relative mass of each of the phases identified in a solid sample.

3.8.3 Electron Microprobe

Chemical mapping of polished thin sections was performed using a JEOL 8230 electron microprobe (working at 15 kV / 15 nA) by Eric Condliffe at the Leeds Electron Microscopy and Spectroscopy Centre at the University of Leeds. A linear transect across a thin section was automated for 20 discreet sampling localities, spaced equally along the transect. Elemental analyses were performed for the major rock-forming cations (e.g. Si, Al, Mg, Na, etc) as weight percent of their respective oxides (e.g. SiO$_2$, Al$_2$O$_3$, MgO, Na$_2$O, etc). The weight percent was then converted to a ‘mole number’ through division by the molecular weight of the oxide. This was then multiplied by the oxygen stoichiometry in the oxide (e.g. 2 for SiO$_2$) to give the ‘oxygen number’ which is normalised to the total ‘oxygen number’ for all elements. Finally, the ‘cation number’ is obtained by multiplication by the ratio of metal cation to oxygen in the oxide (e.g. 0.5 for SiO$_2$). The ‘cation number’ is then averaged for all 20 locations and used as the stoichiometric value of that element in the chemical formula of the mineral. Bound water and/or hydroxide have to be assumed to be present in stoichiometric quantities for the relevant mineral phase in question as these are too light to be analysed by the probe.

3.8.4 Electron Microscopy

Electron microscopy was used to image materials, to obtain chemical information via energy-dispersive X-ray spectroscopy (EDX), and to obtain crystallographic information through selected area electron diffraction (SAED). All electron microscopy was undertaken at The University of Leeds in the Leeds Electron Microscopy and Spectroscopy Centre.

Due to the small quantity of sample required for an electron microscopy sample (typically < 100 mg for SEM and < 1 mg for TEM) there exists the potential for misrepresentation of the sample due to sampling effects. These effects are minimised by homogenisation of the sample during preparation of TEM grids. No homogenisation process was deemed to be required for SEM.
3.8.4.1 Scanning Electron Microscopy (SEM)

Specimens were prepared by adhering < 100 mg of sample to a carbon pad on 1 cm diameter aluminium stubs. The stubs were blown gently using compressed air to remove any material not directly adhered to the carbon pad before sputter coating with 10 nm of platinum to enhance electron conductivity and decrease charging effects. Specimens were analysed using an FEI Quanta 650 field emission gun environmental scanning electron microscope (FEGESEM) fitted with an Oxford Instruments INCA 350 EDX system/80 mm X-Max silicon drift detector, and KE Centaurus electron backscatter diffraction system.

3.8.4.2 Transmission Electron Microscopy (TEM)

Specimens were prepared by immersing < 100 mg of sample into 1 mL of isopropanol which was then sonicated in a sonic bath for > 10 minutes to disaggregate the solid material and homogenise the sample. To emplace the sample onto a TEM grid, 0.1 mL of the suspension was pipetted onto a copper-coated grid with holey-carbon film and the isopropanol allowed to evaporate. The dried sample adhered to the grid through electrostatic attraction.

Specimens were primarily analysed using a Philips CM200 field emission gun TEM/STEM (FEGTEM) with Supertwin Objective lens, cryoshielding, Oxford Instruments INCA EDX system and Gatan Imaging Filter. However, some samples were analysed using an FEI Tecnai TF20 field emission gun TEM/STEM (FEGTEM) fitted with high-angle annular dark-field (HAADF) detector, Oxford Instruments INCA 350 EDX system/80mm X-Max silicon drift detector and Gatan Orius SC600A charge-coupled device camera. All TEM analyses were performed by Andy Brown and Mike Ward, of The University of Leeds.

3.8.4.3 Energy Dispersive X-Ray Spectroscopy (EDX)

Energy-Dispersive X-Ray Spectroscopy (EDX) was performed on both the SEM and TEM using an Oxford Instruments INCA 350 EDX system/80mm X-Max silicon drift detector. The principle of EDX involves excitation of the sample in the electron beam and detection of the emitted x-rays as the excited electrons relax to their ground states. The energies of the emitted x-rays are characteristic of the transitions in each chemical element, permitting the chemical signature of the sample in the electron beam to be determined.

3.8.4.4 Selected Area Electron Diffraction (SAED)

Selected Area Electron Diffraction (SAED) can only be performed in the TEM. The wavelength of the high-energy electrons in the electron beam is on the order of $10^{-3}$ nm, which is well
below the typical atomic spacing in solid materials. Therefore, the atoms act as a diffraction grating and scatter some of the electrons as the beam passes through the sample, creating a diffraction pattern of the selected area illuminated by the beam.

If a single crystal, or a single orientation of a sample, is illuminated, the SAED pattern will appear as a series of dots, each corresponding to a particular reflection in the crystal’s structure. If however, as in most natural samples, multiple crystals are arrayed in a random fashion, a series of circular lines are produced. The spacing between these lines corresponds to the lattice spacing between the reflection planes in the crystal. By measuring the radii of each line, and knowing the focal length of the camera which obtained the patterns and the wavelength of the electron beam, it is possible to calculate the d-spacings using the Bragg equation:

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

where \( n \) is an integer, \( \lambda \) is the wavelength of the incident beam, \( d \) is lattice spacing, and \( \theta \) is the angle between the lattice planes and the incident beam.

Since the incident angle \( \theta \) is small, \( sin\theta \approx \theta \), the Bragg equation may be rewritten as:

\[ \lambda = 2d\theta \]

A right angled triangle is created between the transmitted beam, the diffracted beam (which forms the hypotenuse) and the back focal plane (where the diffraction pattern is viewed). The distance between the sample and the back focal plane is the camera focal length, \( L \). The angle between the transmitted beam and the diffracted beam (the hypotenuse) is \( 2\theta \). The distance on the back focal plane between the incidence of the transmitted and diffracted beams, i.e. the side opposite \( 2\theta \), is \( R \). Trigonometry dictates that:

\[ tan2\theta = \frac{R}{L} \]

And since \( \theta \) is small, \( tan2\theta \approx 2\theta \), therefore the Bragg equation can be rewritten again as:

\[ d = \frac{\lambda L}{R} \]

Therefore, knowing the camera focal length, \( L \), and the wavelength of the incident electron beam, \( \lambda \), the d spacings can be calculated by measuring the radii of the diffraction lines, \( R \), on the diffraction pattern.
3.8.4.5 Electron Energy Loss Spectroscopy (EELS)

Electron energy loss spectroscopy (EELS) was utilised to determine the Fe oxidation state and Fe:O ratio in magnetite samples. Samples were analysed by EELS on the Philips CM200 FEGTEM. O K-edge spectra were aligned to the main peak at 540 eV and Fe L_{2,3}-edge to the Fe(III) peak at 709.5 eV (Brown et al., 2001). Spectra were processed using the Gatan DigitalMicrograph software by Dr Andy Brown of The University of Leeds, with Hartree-Slater cross-sections and 40 eV integration windows.

The energy resolution of the probe at the time of data collection was 0.8-0.9 eV, which prevented determination of the Fe(II):Fe(III) ratio in the samples owing to the 0.5 eV split between the two respective peaks. Therefore, it was necessary to determine the stoichiometry of the samples via their Fe:O ratio to give a measure of oxidation. Three spectra were collected for each sample and the average Fe:O ratio calculated, with an associated uncertainty conservatively estimated at approximately ± 0.1.

3.8.5 Mössbauer Spectroscopy

Mössbauer Spectroscopy makes use of the ‘Mössbauer effect’ whereby atoms in a crystal lattice are able to experience recoil-less gamma ray emission, meaning that resonant emission and absorption can be measured. These emissions/absorptions are influenced by the electronic and magnetic environment which enables extraction of information regarding the chemical environment, including the oxidation state and magnetic environment. Here, Mössbauer spectroscopy was used to determine the degree of oxidation, or maghematisation, of magnetite samples before and after exposure to oxidising conditions. Spectra were collected using a Fastcomtec MCA-3 Mössbauer Spectrometer, with a 925 MBq Co-57 source, at 293 K and 118 K. The commercial software Recoil was used to fit the data using Lorentzian site analysis. Fitting was performed by Dr Paul Wincott. Mössbauer Spectroscopy of magnetite samples is complicated by effects associated with the Verwey Transition and particle size. A distinct change in the magnetic properties of magnetite occurs at the Verwey transition, typically at 121 K (Walz, 2002; Garcia & Subias, 2004) although the cause for these changes is a controversial subject in the literature. Particle size has an effect on the magnetic behaviour of magnetic particles: as the particle size decreases, so too do the magnetic domains giving rise to superparamagnetic effects (Gorski & Scherer, 2010).
3.9 X-Ray Absorption Spectroscopy (XAS)

X-ray absorption spectroscopy (XAS) is an element specific tool for probing atomic structure and chemical state of the absorbing atom. The incident x-ray beam excites a core electron into the continuum state (i.e. unbound), leaving a vacancy in the core shell resulting in relaxation of an outer electron to fill the vacancy. Each electron orbital for each element has a characteristic binding energy, thus by tuning the energy of the incident x-ray beam it is possible to target specific electron transitions, giving the technique element specificity. As the energy of the incident beam approaches the energy required to eject the core electron to continuum, the measured absorption intensity increases dramatically, giving rise to a strong peak termed the absorption edge. The absorption edge is named for the principal quantum number of the electron orbital; for example, excitation of a 1s electron occurs at the K-edge, whilst that of a 2s or 2p electron occurs at the L-edge, and excitation of a 3s, 3p, or 3d electron occurs at the M-edge.

The kinetic energy of the excited electron determines the subset of XAS used to analyse the data. If the excited electron has insufficient energy to reach the continuum, it may be promoted to a higher, unoccupied orbital, giving rise to features in the pre-edge such as that for the 1s→4d transition characteristic of Tc(VII) compounds (Figure 3-3). Electrons that reach the continuum with low kinetic energy contribute to the near-edge structure, or XANES, and those with high kinetic energy produce the extended fine structure, or EXAFS. The XANES region usually refers to up to ~50 eV beyond the absorption edge, with the EXAFS region extending from the XANES region to up to over 1000 eV beyond the absorption edge.

The EXAFS equation is given here:

\[
\chi(k) = \sum_j N_j S_0^2 f_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2\sigma_j^2} \sin[2kR_j + \delta_j(k)]
\]

where the sum is over multiple ‘shells’ or ‘scattering paths’ of the photoelectron. \(N\) is the coordination number of the scattering atoms in a shell; \(R\) is the average interatomic distance between those atoms and the central absorber; \(\sigma^2\) is the mean-square disorder of the interatomic distance, also termed the Debye-Waller factor; \(S_0^2\) is an amplitude reduction term due to the relaxation of electrons to the core hole; \(f(k)\) is the scattering amplitude; \(\delta(k)\) is the phase shift due to the photoelectron passing the potential of the absorbing and scattering atoms; and \(\lambda(k)\) is the mean-free-path length.

The scattering amplitude, \(f(k)\), and phase shift, \(\delta(k)\), are dependent on the atomic number of the scattering atom, and can be calculated using computational methods (e.g. FEFF) along with
the mean-free-path length, $\lambda(k)$, for a particular ‘shell’ or ‘scattering path’. However, it is not possible to distinguish elements with atomic numbers within ~5 mass units of one another, e.g. Fe and Mn or O and N. It is possible to obtain very accurate determinations for interatomic distance, $R$ ($\pm 0.01$ Å for nearest neighbour atoms); however, the coordination number, $N$, is typically much less well defined ($\pm 1$) owing to correlative effects between $N$, the amplitude dampening factor, $S_0^2$ and the Debye-Waller factor, $\sigma^2$.

XAS spectra were collected at DIAMOND synchrotron at room temperature on beamline B18 in fluorescence mode using a 9-element germanium detector (Dent et al., 2009). U L_{III}-edge and Tc K-edge spectra were collected with absorption edges at 17166 eV and 21044 eV, respectively. Reference spectra from U(VI) and U(IV) standards (schoepite ($\text{(UO}_2\text{)}_8\text{O}_2\text{(OH)}_{22}\cdot12\text{(H}_2\text{O)}$) and uraninite ($\text{UO}_2$) respectively) were collected in transmission mode. In-line Y-foil reference spectra were also collected for each U sample for purposes of energy alignment. For Tc, no in line reference was possible owing to the lack of a suitable foil with an edge close to that of the Tc K-edge. Background subtraction, data normalisation and fitting to the EXAFS spectra was performed using Athena and Artemis (Ravel & Newville, 2005).

3.9.1 X-Ray Absorption Near-Edge Structure (XANES)

The XANES spectrum is sensitive to the oxidation state of the central atom owing to the fact that the absorption edge energy increases with increasing oxidation state (Kirby et al., 1981). There are two interpretations of the phenomenon. The first, and more simplistic, explanation is that as the oxidation state increases, the nucleus of the central atom is less well shielded thus having a higher effective charge and resulting in an electron requiring more energy to overcome the electrostatic attraction of the nucleus to escape to the continuum. However, the second explanation is more suitable and requires that the edge features are treated as ‘continuum resonances’, which are short-lived excitation processes where a core electron is placed into an energy state higher than the continuum (Natoli, 1983). A commonly cited example is the potential well between the central absorber and the nearest neighbouring atoms. As this distance, $R$, gets shorter, the energy of the continuum state increases according to the inverse square rule, i.e. $1/R^2$. This explains increasing absorption energy with increasing oxidation state because, in general, the bond distances between the central atom and nearest neighbours get shorter with increasing oxidation state (Penner-Hahn, 2003, 2005). Through careful alignment of experimental XANES spectra to reference spectra which do not have multiple oxidation states (e.g. Y-foil), it is possible to follow changes in oxidation state through a reaction or under different experimental conditions. In this way, XANES may be used as a fingerprinting technique to match unknown spectra to spectra of known oxidation state, with
mixed oxidation states determined through linear combination analysis (Chapter 3.9.3.2). In addition to the edge position, oxidation state also has an influence on the position of the white line maximum (Denecke, 2006). However, the white line maximum is also influenced by a number of other properties of the material, such as the covalency of the bonding between the central absorber and its nearest neighbours, their local symmetry, the electronegativity of the bonding partner and the long-range structure of the material (Antonio & Soderholm, 2006).

Multiple scattering, where the photoelectron wave scatters off more than one atom, is particularly important in the XANES region, meaning that the potential exists to determine the three-dimensional structure of the central absorbing atom. This is due in part to variations in the geometrical arrangement altering the multiple scattering pathways which in turn affects the detailed structure in the XANES region. For example, resonance features in the XANES region of U(VI) containing samples exhibit a resonance feature that is due to multiple scattering from the short, co-linear uranyl bonds (Farges et al., 1992; Antonio & Soderholm, 2006). The position of such resonance features in the energy spectrum is inversely proportional to the bond length (Farges et al., 1992).

### 3.9.1.1 Uranium XANES

The most common absorption edge analysed during uranium XAS studies is the L_{III}-edge, corresponding to excitation of a 2p electron at approximately 17,166 eV (Thompson et al., 1997). The XANES spectra of reference compounds for the two most environmentally relevant oxidation states of uranium – schoepite (U(VI); (UO_2)_8O_2(OH)_{12}.12(H_2O)) and uraninite (U(IV); UO_2) – are shown in Figure 3-2. It is clear that the spectra from the two compounds have different morphologies and that their edge energies are also different. U(VI) compounds typically have an absorption edge 1.3 - ~8 eV higher than for U(IV) compounds (Farges et al., 1992; Kelly et al., 2002; Joseph et al., 2014). The position of the white line maximum may also be used to distinguish oxidation states in uranium XANES, which shifts to higher energies with increasing U oxidation state (Denecke, 2006).

It is difficult to distinguish U(V) from U(VI) since their edge energies are similar, however, the U(VI) white line is shifted to higher energies than the U(V). Additionally, U(V) compounds have a characteristic shoulder on the low energy side of the white line (Soldatov et al., 2007). The shape of the spectra in the XANES post-edge region is influenced by the atomic arrangement of the nearest neighbour atoms; the resonance features visible in Figure 3-2 are evidence of this. In the schoepite spectrum, two features are visible, A and B, whilst only B is visible in the uraninite spectrum. These resonance features correspond to multiple scattering from the axial (A) and equatorial (B) O atoms surrounding the central U atom (Farges et al., 1992; Antonio &
Feature A is absent from the UO$_2$ spectrum since no uranyl bonds are present. Further to this, their location in the energy spectrum is related their bond length, and a change in bond length produces a shift in the position of the corresponding resonance feature that is inversely proportional to the change in bond length (Farges et al., 1992). Therefore, it is possible to track changes in the nearest neighbour atomic arrangement through a reaction by following the position of the resonance features in the XANES spectrum (Marshall et al., 2014a).

![Uranium L$_{III}$-edge XANES spectra of schoepite (U(VI); (UO$_2$)$_8$O$_2$(OH)$_{12}$·12(H$_2$O)) and uraninite (U(IV); UO$_2$). Data from Marshall et al. (2014a). Black lines indicate approximate $E_0$ positions.](image)

**Figure 3-2** Uranium L$_{III}$-edge XANES spectra of schoepite (U(VI); (UO$_2$)$_8$O$_2$(OH)$_{12}$·12(H$_2$O)) and uraninite (U(IV); UO$_2$). Data from Marshall et al. (2014a). Black lines indicate approximate $E_0$ positions.

### 3.9.1.2 Technetium XANES

The most common absorption edge analysed during technetium XAS studies is the K-edge, corresponding to excitation of a 1s electron at approximately 21,044 eV (Almahamid et al., 1995). The XANES spectra of reference compounds for the two most environmentally relevant oxidation states of technetium – pertechnetate (Tc(VII); TcO$_4^-$) and amorphous TcO$_2$ (Tc(IV); TcO$_2$·nH$_2$O) (Hess et al., 2004) – are shown in Figure 3-3. It is clear that the two spectra have different morphologies and that their edge energies are also different. Tc(IV) compounds typically have an absorption edge ~7 eV lower than for pertechnetate (Almahamid et al., 1995).

The Tc(VII) spectrum has a distinct pre-edge feature (Figure 3-3) which is characteristic of the forbidden 1s → 4d transition (Maes et al., 2004). The presence of this pre-edge feature has
been used to determine the presence of Tc(VII), both qualitatively and quantitatively, in potentially mixed valence samples (Morris et al., 2008). Particularly for Tc(IV) compounds, the shape of the XANES spectrum has been used to determine structural information around the central Tc atom. Tc(IV) XANES spectra, typically when measured in iron oxide containing samples, often have a split white line (e.g. Figure 3-3). This morphology has been attributed to the presence of short Tc(IV)-Fe bonds, indicating Tc(IV) incorporation into the iron oxide (Heald et al., 2012). However, this same morphology has also been attributed to multiple scattering from the trans-oxygen ligands of the Tc-coordination sphere, indicating Tc(IV) is in an environment octahedrally coordinated by O (correspondence between Wayne Lukens and Fred Mosselmans, Ifeffit Mail Archive, 6th Aug 2013).

![Technetium K-edge XANES spectra of pertechnetate (Tc(VII); TcO$_4^-$) and amorphous TcO$_2$ (Tc(IV); TcO$_2$.nH$_2$O). Pertechnetate data from Marshall et al. (2014b), TcO$_2$ data from Hess et al. (2004). Black lines indicate approximate E$_0$ positions.](image)

**Figure 3-3**

3.9.2 **Extended X-Ray Absorption Fine-Structure (EXAFS)**

After the absorption edge, a series of oscillations are observed which correspond to wave interactions from the ejected electron and the other electrons around the central atom, and also from backscattered waves from surrounding atoms. Interference between these waves creates maxima and minima where they are either in phase or out of phase (i.e. they constructively or destructively interfere). The backscattered wave from a single cluster of scattering atoms will give rise to sinusoidal oscillations when plotted in terms of photoelectron wavenumber, $k$ (Å$^{-1}$). The amplitude of the oscillations is reduced as wavenumber increases
but there is still information to be gained at high $k$, particularly for heavier elements such as uranium, and so a weighting, typically $k^3$, is applied to amplify the high $k$ oscillations. Viewing the EXAFS data in $k$-space, it is not particularly easy to visualise the information contained within the spectrum, thus a Fourier transform is applied to the data to decompose the signal into its component sinusoidal frequencies, giving a pseudo-radial distribution function. Peaks in the Fourier transform correspond to the frequencies of oscillations contained in the EXAFS in $k$-space and are hence related to the interatomic distance between absorber and scatterers.

Structural information of the scatters is evident in the appearance of the oscillations; the amplitude is proportional to the number of scattering atoms, the frequency is inversely proportional to the interatomic distance between the absorber and scattering atoms, and the shape is dependent on the chemical identity of the scattering atoms. Therefore, it is possible to obtain structural information regarding the position and identity of atoms surrounding the absorbing atom by refining a structural model in a non-linear least-squares fitting procedure. Care must be taken when choosing fitting parameters to avoid false minima leading to a misleading fit of the data. Attention should also be paid to the values assigned to the variables during the minimisation to ensure that they remain within physically relevant ranges.

Multiple scattering is highly angle dependent and is important to consider when the angle is $>150^\circ$. It is particularly strong for co-linear atoms at or near 180°, e.g. $\text{UO}_2^{2+}$ (Stern & Heald, 1983; Koningsberger & Prins, 1988; Newville, 2005; Bunker, 2010)

The ‘goodness of fit’ parameter $R$, is a measure of the residual between the fit and the data, and in general, the lower the value of $R$, the better the fit. However, on its own, $R$ is not a reliable measure of the validity of a fit. The reduced chi-squared, $\chi^2_\nu$, which takes into account the degrees of freedom of the fit (the number of independent data points ($n$) in the data (Stern, 1993) minus the number of variables) however, reveals whether the new parameters have indeed statistically improved the fit. Further to this, by performing an F-test (Downward et al., 2007) on a pair of fits, it is possible to determine if they are statistically distinct at a given confidence level, providing a robust argument for or against improvement in the fitting model applied to the data.

Often there is not a unique answer and judgement as to the most realistic model must be made from information gained by complimentary analytical techniques and by critical analysis of the refined variables and their correlated effects to ensure a physically realistic and defensible model is obtained.
3.9.3 XAS Data Analysis

3.9.3.1 Initial Data Processing

Initial processing of the XAS data constituted merging multiple scans, background subtraction and normalisation, all of which was performed in Athena (Ravel & Newville, 2005). The individual scan files were imported into Athena, with the relevant reference spectra if present, as simply the fluorescence as a function of energy. Each individual scan typically has a low signal to noise ratio; however, through summation of a sufficiently large number of individual scans, the noise can be reduced significantly, following the central limit theorem. All scans were merged in \( \mu(E) \) to give a single spectrum for each sample. All further data processing was performed on this merged spectrum. First, the absorption edge energy position, \( E_0 \), was chosen; this is taken as energy at the point approximately half way up the absorption edge. Choosing the correct point on the absorption edge is very difficult; however, by using the 1\textsuperscript{st} and 2\textsuperscript{nd} derivative of the absorption energy function, it becomes much easier. The derivative of a function is a measure of the gradient of that function. Moving up the edge, the gradient of the absorption energy increases until the point at the edge energy, decreasing thereafter towards the top of the absorption edge (the white line).

\[ D(\mu(E)) \]

\[ D'(\mu(E)) \]

![Figure 3-4](image)

**Figure 3-4** Location of the absorption edge energy (\( E_0 \)) in the 1\textsuperscript{st} (A) and 2\textsuperscript{nd} (B) derivatives of the absorption energy spectrum of schoepite.

Therefore, the plot of the 1\textsuperscript{st} derivative will increase towards a peak at the edge energy and fall thereafter (Figure 3-4A). The 2\textsuperscript{nd} derivative is the derivative of the 1\textsuperscript{st}, and is a measure of the rate of change in the 1\textsuperscript{st} derivative. Therefore, as the 1\textsuperscript{st} derivative approaches its peak, the 2\textsuperscript{nd} derivative approaches zero, hence the position of \( E_0 \) on the 2\textsuperscript{nd} derivative is the zero crossing.
Often, one or other of these two functions is ambiguous and so, by combining both tests, it is possible to accurately define the experimental $E_0$.

Following this, a linear regression is fitted to the pre-edge region to remove the inherent instrument background and any other absorption edges that may be present (e.g. yttrium K-edge in the case of the uranium L-edge). Two points are chosen in the pre-edge region as the start and end points of the regression so that the gradient of the resulting function is close to the gradient of the post-edge region. The next step is to fit a smooth spline to the post-edge region to remove the low frequency components of $\mu(E)$. Again, two points are chosen as the limits to the range of the spline, to produce a post-edge spline that should bisect the oscillations in the data evenly. The spline is least well-defined at the extremities of the range; hence the two points should not simply be the limits of the data in the post-edge. The exact choice of points is important but not critical as the regression is applied to all points in the range. However, the post-edge spline does not approximate the background effectively in the near post-edge region ($< \sim 100$ eV) and so this region should be ignored when choosing the normalisation range. Once this range has been defined, the background curve can be compared to the data; this should be a smooth line running through the data. The data is normalised using the ‘edge-step’ ($\mu_0(E)$), calculated as the difference between the pre- and post-edge lines at the absorption energy, which should produce a spectrum that oscillates evenly around $\mu(E) = 1$. If there are remaining low frequency oscillations about $\mu(E) = 1$ then the pre- and post-edge lines may require redefining. The background subtraction procedures outlined above are illustrated in Figure 3-5.

![Figure 3-5](image.png)  
**Figure 3-5** Background subtraction of non-normalised EXAFS data from schoepite.
When plotted in k space, the data should form a smooth envelope, symmetrical about $\chi(k) = 0$. A k-weighting, usually $k^3$, is applied to enhance the contributions from higher $k$ oscillations. If the data does not plot as a smooth envelope in $k$-space, particularly at high $k$, then the background subtraction splines should be redefined. Additionally, the spline range may be reduced to exclude the end of the data, where the noise to signal ratio may still be significant. At this point the Fourier transform (FT) of the background-subtracted data should be viewed.

Since the FT can be viewed as pseudo-radial distribution function, it is possible to discount peaks in the FT below a distance of 1 Å since this cannot be physical and therefore must be noise. This noise is removed by increasing the ‘Rbkg’ value, which effectively excludes data below this value. However, the ‘Rbkg’ value should be altered with caution, and not at the expense of the signal from the real data. Additionally, the ‘Rbkg’ value should not exceed approximately half of the interatomic distance between the central atom and its nearest neighbour.

### 3.9.3.2 XANES Data Analysis

Linear combination analysis (LCA) is a method of determining the relative contributions to an XAS dataset from other XAS datasets, typically standards of known composition. For example, it is possible to determine the relative proportions of two (or more) compounds present in a mixture of those compounds. LCA is performed using the data analysis tool in *Athena* (Ravel & Newville, 2005) and may be performed in either E-space or k-space, that is to say on the absorption energy profile or the extracted EXAFS signal. The user must specify at least one ‘standard’ to which the ‘experimental’ spectra are compared. The user may also specify the limits, in E or k depending upon the LCA space, between which the datasets are to be compared. If the ‘experimental’ datasets can only consist of one or more defined standards then the combined weights of all standards should be set to equal 1. If there are potentially other contributions from a component for which no standard exists then the combined weights should not be set to equal 1 to allow for the unknown contributions.

### 3.9.3.3 EXAFS Data Modelling

Once the background subtraction has been satisfactorily performed in *Athena*, the data can be imported into *Artemis* (Ravel & Newville, 2005) to perform EXAFS data modelling to obtain chemical and structural information about the bonding environment of the central absorber using IFEFFIT. The approach to modelling EXAFS data in *Artemis* utilises crystallographic information from known compounds as a starting point for FEFF to calculate the potentials and phase shifts that are then used to calculate the theoretical scattering paths. FEFF6 was used in
all cases for work presented in this thesis (Zabinsky et al., 1995). These theoretical scattering paths are then iteratively refined in the model to produce a best fit to the data. Crystallographic Information Files (CIF) are obtained from the Inorganic Crystal Structures Database (ICSC). It is possible to combine theoretical scattering paths from numerous CIF to create a composite model that is representative of the structure of the sample in question. When importing the CIF using the Atoms (Ravel & Newville, 2005) interface it may be necessary to alter some of the information contained in the CIF to reflect the final structure that the CIF is being used to approximate. For example, when attempting to model uranium incorporation into hematite (Chapter 4), the hematite CIF (Blake et al., 1966) was used to obtain the atomic structure. However, it was necessary to change the central atom from Fe-26 to U-92, and also to change the size of the core hole created by the excited electron escaping to the continuum, to model a uranium atom substituting for an iron atom in the hematite structure. In the case of a CIF where the central atom is already of the correct element (e.g. uraninite, UO$_2$), these amendments are not required.

Each scattering path selected for use in the fitting model must be parameterised with variables which the model will refine to obtain the least-squares residual fit to the data. These include the interatomic distance, $R$; the DWF, $\sigma^2$; the amplitude reduction factor, $S_0^2$; and the absorption edge energy, $E_0$. All of these variables are evaluated as a change from a defined value, e.g. $R = R_T + \Delta R$: where $R$ is the refined scattering path length, $R_T$ is the theoretical scattering path length; and $\Delta R$ is the evaluated difference between $R$ and $R_T$. Coordination number, $N$, is set to an integer value during refinement of the model.

In a sample with a single environment for the central atom, e.g. pure UO$_2$, the edge energy, $E_0$, and amplitude reduction factor, $S_0^2$, will be the same for each scattering path included in the model, whilst each path will have its own values for interatomic distance, $R$, and DWF, $\sigma^2$. In general, the refined $\Delta E_0$ should be close to zero, i.e. close to the value chosen during the initial data processing; however, $\Delta E_0$ values of up to $\pm 10$ eV are acceptable. The amplitude reduction factor should refine to approximately 1, with acceptable values in the range $0.8 \sim 1.1$. However, due to the large number of parameters that can affect the amplitude, the accuracy to which it can be obtained is approximately $20 \sim 25$ % (Denecke, 2006). In addition, systematic errors, such as: thickness of concentrated samples (Parratt et al., 1957); self-absorption effects (in fluorescence experiments) (Tröger et al., 1992); detector dead time; or over-fitting or the polynomial spline function (post-edge); may contribute to the inaccuracy in determining $S_0^2$ (Denecke, 2006).

In simple terms, due to correlative effects between the amplitude reduction factor and coordination number, the product of the two may be taken as the refined coordination. An $S_0^2$...
of ~1 means that the defined coordination is approximately equal to the actual coordination, however, an $S_0^2$ that greatly differs from ~1 suggests that the defined coordination of that scattering path is incorrect. Usually, $S_0^2$ is determined from analysis of a standard whose structure is well known, and this value is then applied as a fixed parameter to all other unknown spectra analysed at the same time, under the same beamline conditions. However, this is not always possible given samples may be analysed over several beamtimes and possibly at different beamlines. $S_0^2$ may also be influenced by factors such as sample geometry meaning it may not be practical to apply a single $S_0^2$ to a suite of samples. Given that $S_0^2$ and $N$ are correlated, care must be taken if allowing both the refine. However, the amplitude of the first shell, i.e. from the nearest neighbour atoms, is usually the strongest and so has the greatest influence over $S_0^2$. Hence, it may be valid to refine $S_0^2$ on the basis of a known coordination of the first shell, e.g. the axial U-O bonds in uranyl containing compounds, whilst allowing the coordination of the other shells to float in the fit.

In instances where there are two potential bonding environments occupied by the central absorbing atom, it is possible to obtain an estimate of the relative proportions through conditional parameterisation of the amplitude reduction factor. For instance, if $S_0^2$ of environment A is parameterised by ‘$x \times \text{amp}$’, then environment B would be ‘$(1 - x) \times \text{amp}$’, where $x$ and amp are independent variables, with $x$ constrained to between 0 and 1, for the relative proportions of A and B, and the amplitude reduction factor, respectively.

The DWF in Artemis is usually between 0.003 Å$^2$ and 0.010 Å$^2$, although a DWF of 0.020 Å$^2$ is acceptable for a distant shell of scattering atoms (> ~3.5 Å). Generally the DWF would be expected to be lowest for the closest shell of scattering atoms and increasing with increasing interatomic distance. However, in some instances the DWF for closer shells may be higher than for more distant shells due to, for example, static disorder owing to non-symmetry of the bonding environment. The DWF is also correlated to the coordination, meaning that an extreme DWF indicates an issue with the chosen scattering path. For instance, a very small (<0.001 Å$^2$) or even negative DWF is a result of the model attempting to reduce the amplitude from the particular scattering path to effectively zero, i.e. non-existent. It is therefore extremely important to pay close attention to refined values of the DWF to ensure that they are physically realistic values.

The refined values of R would normally be expected to be reasonably close to the theoretical value ($\pm 0.2$ – 0.3 Å); large values of $\Delta R$ would suggest that the chosen theoretical path is potentially a poor representation of the real structure and an alternative should be sought.
The number of independent data points \( n \) within the selected \( k \)- and \( R \)-ranges is defined by Stern’s rule (Stern, 1993), as modified in *Artemis*:

\[
 n = \left( \frac{2 \delta k \delta R}{\pi} \right) + 1
\]

where \( \delta k \) is the range in \( k \) space; and \( \delta R \) is the range in \( R \) space.

When parameterising the scattering paths chosen for a particular model, the permitted number of independent variables is limited by the number of independent data points. That is to say the degrees of freedom in the fit must be positive. Additionally, as the degrees of freedom tends towards zero, the reliability of the fit also reduces. In general, of two similar fits, the fit with the greater degrees of freedom is more reliable and considered ‘better’. This can be evaluated statistically using the fitting metrics calculated during refinement of competing models by way of an F-Test (Downward et al., 2007).

The goodness of fit parameter, \( R \), is a measure of how well the fit matches the data between the limits specified in the fit, and is evaluated as follows:

\[
 R = \frac{\sum (\text{data} - \text{fit})^2}{\sum \text{data}^2}
\]

In general \( R \) should be less than approximately 0.02 for the fit to be considered ‘good’, with values up to 0.05 acceptable but indicating that there are some minor flaws in the model applied or that the data is of poor quality. Values for \( R \) in excess of 0.05 indicate that the model is seriously flawed. \( R \), however, is unable to provide any statistical information on the validity of the model applied; it is simply a measure of how well the two lines (data and fit) match one another. Therefore attention should be turned to the reduced chi square, \( \chi^2 \), which is calculated as follows:

\[
 \chi^2_{\nu} = \frac{1}{\text{degrees of freedom}} \sum_i \frac{(\text{data} - \text{fit}_i)^2}{\varepsilon_i^2}
\]

where \( \varepsilon_i \) is the measurement uncertainty calculated by *Artemis*.

Unfortunately, it is difficult for *Artemis* to measure the uncertainty in the fit and so the reduced chi square taken in isolation is almost no different to the \( R \) value. However, since it incorporates a measure of the goodness of fit and the degrees of freedom, comparison of the reduced chi square between fits is a reliable tool for assessing their comparative validity.
An F-test is a standard statistical method for assessing whether the standard deviations of two populations are equal. Following on from Hamilton (Hamilton, 1965), Downward et al. (2007) define the F-test for use in EXAFS as follows:

\[
F = \left( \frac{R_1}{R_0} \right) - 1 \left( \frac{n-m}{b} \right)
\]

where \(R_0\) and \(R_1\) are the R-factors of the two fits being compared; \(n\) is the number of independent data points used in \(R_1\); \(m\) is the number of independent variables used in \(R_1\) (i.e. \((n-m)\) is the degrees of freedom in \(R_1\)); and \(b\) is the dimension of the hypothesis which is the difference between the degrees of freedom in \(R_1\) and \(R_0\) or in the case where these are equal, \(b\) is the number of variables that have changed between \(R_1\) and \(R_0\).

The confidence level, \(\alpha\), that the fit which yields \(R_0\) is a better fit than that which yields \(R_1\), is calculated by:

\[
\alpha = 1 - I_x \left[ \left( \frac{n-m}{2} \right), \left( \frac{b}{2} \right) \right]
\]

where \(I_x \left[ \left( \frac{n-m}{2} \right), \left( \frac{b}{2} \right) \right]\) is the incomplete beta distribution function of \(x\) where \(x = \left( \frac{n-m}{n-m+bF} \right) = \left( \frac{R_0}{R_1} \right)^2\).

Downward et al. (2007) assert that for the fit yielding \(R_0\) to be considered a significantly better fit, \(\alpha\) must be in excess of 67 % (1 sigma confidence level) and more preferably above 95 % (2 sigma confidence level). In this thesis, for a fit to be considered ‘a better fit’ statistically speaking, then \(\alpha\) must be in excess of 95 %.
Chapter 4  Incorporation of Uranium into Hematite during Crystallisation from Ferrihydrite

This chapter is a manuscript published in the journal Environmental Science and Technology in March 2014. Supporting Information published with this manuscript is included in Appendix 1.

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Incorporation of Uranium into Hematite during Crystallization from Ferrihydrite

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Supporting Information

ABSTRACT: Ferrihydrite was exposed to U(VI)-containing cement leachate (pH 10.5) and aged to induce crystallization of hematite. A combination of chemical extractions, TEM, and XAS techniques provided the first evidence that adsorbed U(VI) (∼3000 ppm) was incorporated into hematite during ferrihydrite aggregation and the early stages of crystallization, with continued uptake occurring during hematite ripening. Analysis of EXAFS and XANES data indicated that the U(VI) was incorporated into a distorted, octahedrally coordinated site replacing Fe(III). Fitting of the EXAFS showed the uranyl bonds lengthened from 1.81 to 1.87 Å, in contrast to previous studies that have suggested that the uranyl bond is lost altogether upon incorporation into hematite. The results of this study both provide a new mechanistic understanding of uranium incorporation into hematite and define the nature of the bonding environment of uranium within the mineral structure. Immobilization of U(VI) by incorporation into hematite has clear and important implications for limiting uranium migration in natural and engineered environments.

INTRODUCTION

Uranium is an environmental contaminant that arises as a result of authorized and accidental releases at various stages in the nuclear fuel cycle, including from uranium ore mining activities and post-reactor operations. Additionally, in many countries, uranium-containing radioactive wastes, including spent nuclear fuel and intermediate-level waste, are likely to be disposed in deep geological disposal facilities (GDF). Here, uranium will typically be the most significant radionuclide by mass in the waste inventory. After deep disposal has been implemented, it is inevitable that, on geological time scales, uranium (and other radionuclides) will be released from within the waste containers and, importantly, due to its long half-life (4.5 Ga), the behavior of uranium and of its resultant decay chain will be important to any safety case for geological disposal over extended time frames. It is, therefore, crucial that we understand the fate of uranium in these natural and engineered environments to be able to both predict and constrain its environmental impact.

Iron (oxyhydroxides) (e.g., hematite α-Fe₂O₃) are ubiquitous and are known to be effective at reducing the mobility of U(VI) through either their high sorption capacity (e.g., surface adsorption) or, where Fe(II) is present, via reductive precipitation to poorly soluble U(IV) phases. Studies of uranium retardation mechanisms in the environment have tended to focus on adsorption of U(VI) to various mineral phases or reduction of U(VI) to U(IV) either directly or indirectly as a result of microbial or abiotic pathways. However, a change in the geochemical conditions may reverse these processes (e.g., reduction in pH leading to desorption or reoxidation of U(IV)) and cause remobilization of the contaminant. Incorporation of uranium into stable mineral phases, such as iron (oxyhydroxides), offers a pathway for sequestration with the potential for long-term immobilization. It has been shown that goethite and hematite are able to accommodate various impurities (e.g., Si, Ti, Mn, Ni) into their structure. Specifically, U(VI) and reportedly even U(V) may be incorporated into goethite (α-FeOOH) during Fe(II)-catalyzed crystallization of ferrihydrite and evidence for U(VI) incorporation into hematite during coprecipitation has been reported. Notably, Duff et al. precipitated ferrihydrite from a solution containing U(VI) and Fe(II) and induced hematite formation by aging at pH 11

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and 60 °C. Here, they reported incorporation of U(VI) into hematite in a uranate-like coordination environment with the resultant loss of the short uranyl bonds. Ilton et al.16 followed the method of Duff et al.18 and reported a similar structure for incorporated U(VI). Atomic simulations of U(IV), U(V), and U(VI) incorporation into hematite using various different charge compensation mechanisms, based on the Duff et al.18 incorporation model, indicated that U(VI) maintained octahedral coordination in most cases but that the predicted interatomic distances differed from the experimental data.20 Furthermore, in a similar study, chemical extractions on U(VI) associated with ferrihydrite showed a decrease in leachable uranium as the solid phase aged and the formation of U(VI)-labeled crystalline goethite and hematite occurred, suggesting a change in speciation during crystallization.21 The lack of agreement between the spectroscopic and atomistic modeling approaches in the literature to date indicates that the mechanism of uranium incorporation, and the details of the molecular-level bonding environment within the hematite structure warrant further investigation.

In addition to forming in soil and sediments, predominantly as a weathering product of iron-bearing minerals, iron (oxyhydr)oxides form as corrosion products of steel22 and are present in intermediate level radioactive wastes.23 They are also reported to form in deep geological systems on tunnel walls due to biological oxidation of Fe(II).24 Many geological disposal concepts utilize cementitious materials (often within the wasteform itself or in the engineered barrier system) and many contaminated soils at nuclear facilities will be in contact with cements and concrete construction materials. Leaching of the cementitious materials will buffer the pH to hyperalkaline conditions, creating a chemically disturbed zone (CDZ) in the host rock or local environment.25,26 Thus, understanding the changes in speciation (i.e., adsorbed versus incorporated) of actinides during crystallization of iron (oxyhydr)oxides under these geochemical conditions is key to predicting their long-term stability and mobility in natural and engineered environments. Ferrihydrite crystallizes to hematite or goethite depending upon solution conditions, with pH, ionic strength, and temperature all having an influence.26 Hematite formation is favored under near-neutral conditions and higher temperature and ionic strength, whereas goethite forms under extremes of pH (less than 4, greater than 10) and at lower temperature and ionic strength.28,29 The hematite formation process begins with ferrihydrite particle aggregation,30 followed by recrystallization within the aggregate via dissolution and reprecipitation processes that occur at the nanoscale.31 This crystallization involves a variety of processes including dehydration of the ferrihydrite particles, deprotonation of hydroxyl groups, creation of oxy-linkages, and redistribution of cation vacancies.32 During this process, adsorbed uranium has the potential to become incorporated into the structure of the hematite. However, the mechanism of this reaction is poorly constrained, and how much of the adsorbed uranium is incorporated, at which stage in the crystallization process uranium is incorporated, and what the final site of uranium is within the hematite structure are all worthy of attention.

In this contribution, we provide a detailed insight into the mechanism(s) of uranium incorporation during hematite formation under conditions relevant to both geological disposal and contaminated land to determine whether significant amounts of uranium could be sequestered into this phase in the long term. We have combined aqueous chemical data with X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray absorption spectroscopy (XAS) to characterize the solid phase crystallization at elevated pH (10.5). Throughout, we have focused on the fate of uranium during ferrihydrite transformation to hematite to determine the mechanism(s) of uranium incorporation, and our aim was to define the atomic scale bonding environment of uranium within this environmentally important phase.

**Experiments and Analyses.** Batch experiments were used to follow the crystallization of U(VI)-adsorbed ferrihydrite in a synthetic cement leachate (0.015 g L⁻¹ Ca(OH)₂; pH 10.5) system. Full experimental setup and sampling and analysis details are given in Supporting Information. Briefly, batch experiments were set up at a solid solution concentration of 0.4 g L⁻¹ and spiked with U(IV) to give an initial U(III) concentration of 1 ppm (4.2 × 10⁻⁶ mol L⁻¹), which was thermodynamically modeled (PHREEQC) to be below the solubility of any U(VI) phase in the synthetic leachate. The experiments were placed in an oven at 60 °C for up to 70 days. Some experiments were also placed into an oven at 105 °C for up to 45 days to suppress the formation of goethite and favor hematite formation. All experiments were maintained between pH 10.3−10.7 and were purged with CO₂-free air throughout. Partitioning of uranium between the solid and the solution was determined by analysis of uranium in solution (U(solid)). Chemical extractions were performed to assess the partitioning of uranium to the solid phase.33 The surface-bound uranium (U(surface)) was determined by titration of the iron (oxyhydr)oxide suspension to pH 2.5, below the U adsorption edge,34 using HCl. The resulting supernatant was analyzed for uranium, and U(surface) was calculated by subtracting U(liquid). The nonleachable uranium (U(total)) was then calculated from the mass balance according to

\[
U_{(total)} = U_{(surface)} - U_{(ads)} - U_{(aq)}
\]

Aqueous samples were analyzed for ²³⁸U by ICP-MS, and solids were characterized by powder XRD and surface area using the BET method. Particle morphologies were characterized via TEM. Uranium L₃-edge XAS spectra were collected on beamline B18, Diamond Light Source, at room temperature in fluorescence mode using a nine-element Ge detector.35 Reference spectra from U(VI) and U(IV) standards (schoepite \((\mathrm{UO}_2)_2\mathrm{O}(\mathrm{OH})_2\cdot12\mathrm{(H}_2\mathrm{O})\)) and uraninite \((\mathrm{UO}_2)\), respectively) were collected in transmission mode. In-line yttrium foil reference spectra were also collected for each sample for energy calibration. Background subtraction, data normalization, and fitting to the EXAFS spectra were performed using the software packages Athena and Artemis.36

**RESULTS AND DISCUSSION**

**Characterization of Experimental Products.** XRD patterns for the products from the 60 °C crystallization experiment show hematite formed rapidly from 2-line ferrihydrite over the first 24−48 h of aging (Figure 1). Quantitative analysis of the XRD patterns (X2RDX) (Supporting Information Table S1) reveals that greater than 80% of the 24 h sample was hematite, decreasing to 55% hematite with the remaining phase 45% goethite after 30 days. Hematite formation is favored over goethite with increasing temperature,27 therefore, to obtain a high purity end-member hematite sample, a 105 °C crystallization at pH 10.5 was performed. Quantitative analysis of the XRD patterns from the high temperature experiment confirmed that the sample was greater than 90% hematite after 45 days aging.
TEM photomicrographs of the solid samples (Supporting Information Figure S1-1) illustrate the crystallization pathway of hematite and goethite from ferrihydrite at 60 °C. At 0 h, the ferrihydrite nanoparticles were 3–5 nm and had no visible structure within the particles. After 24 h at 60 °C, the ferrihydrite had aggregated and clumps of nanocrystalline hematite and acicular goethite became evident (Supporting Information Figure S1-1). Thereafter, the amount of ferrihydrite rapidly decreased and the size of the hematite/goethite crystals gradually increased. Over the first 48 h of crystallization, there was a rapid decrease in surface area from 164 ± 3 to 21 ± 1 m² g⁻¹, followed by a slow continued decrease to 17 ± 1 m² g⁻¹ after 30 days (Figure 2). The XRD and QXRD, TEM, and BET data indicated that during the first 24–48 h, there was rapid aggregation of ferrihydrite and crystallization of hematite/goethite, causing a large and rapid decrease in surface area. This was followed by a stage of crystal ripening, with some transformation of hematite to goethite (Supporting Information Table S1-1). No evidence for discrete uranium phases was detected using XRD or TEM, as expected from PHREEQC modeling of the system.

The majority of the uranium (91.9 ± 0.2%) was instantaneously adsorbed to the solid phase on its addition to the ferrihydrite slurry (Figure 2). During the aggregation and initial crystallization phase, Uₐ(ads) rapidly decreased to 79.6 ± 3.2% at 1 h and 51.3 ± 2.1% at 48 h, with a continued decrease to 23.2 ± 0.9% after 70 days of aging. On the basis of the uranium mass balance, this shows an increase in Uₐ(ads) from 20.2 ± 2.6% at 1 h to 75.0 ± 9.6% after 70 days (Figure 2). Thus, the chemical extraction data strongly suggest that a significant proportion of the uranium is becoming increasingly strongly associated with, and possibly structurally incorporated into, hematite/goethite during crystallization. Reflecting this, we suggest that uranium adsorbed to the surface of the ferrihydrite particles is trapped within the solid phase during the aggregation process at the early stages of the crystallization process, consistent with the incorporation mechanism of Pb into hematite during hydrothermal crystallization of ferrihydrite. The gradual increase in Uₐ(ads) during crystallization and ripening indicates that U(VI) then continues to be incorporated as the iron (oxyhydr)oxide crystals form and grow. This is in contrast to the behavior observed for Pb, where the contaminant was slowly released from the hematite structure during ripening because of its incompatibility (i.e., located within defect sites) with the mineral structure. This does not occur with uranium, suggesting that it may become located within a stable crystallographic site within the newly formed mineral, in agreement with modeling simulations.

X-ray Absorption Spectroscopy. XANES spectra from a time series of samples spanning the crystallization of ferrihydrite at 60 and 105 °C, along with U(VI) and U(IV) reference spectra are shown in Figure 3.

The edge positions of all XANES spectra from the four iron (oxyhydr)oxide samples aligned to the U(VI) schoepite standard (~17 172 eV) indicating that uranium remained as U(VI) during crystallization. Two prominent resonance features are visible in the XANES spectra of uranyl-containing compounds (A and B, Figure 3) and are due to resonance from the different U=O bonds. Feature A (~17 190 eV) is attributable to the short axial U=O bonds in the dioxygenyl species, and feature B (~17 210–17 215 eV) is attributable to the longer U=O equatorial bonds. Feature A is absent from the XANES spectra of compounds that do not have the axial U=O bonds, such as uraninite, but is clearly present in all our U-bearing Fe sample spectra (Figure 3). The XANES spectrum of the 0 h solid associated sample is very similar to that of schoepite, indicating uranyl coordination. However, during the experiment the resonance features migrate in energy with time indicating a change in the local bonding environment of uranium throughout crystallization. Here, feature A migrates to a lower energy (17 188 to 17 182 eV), whereas feature B migrates to a higher energy (17 211 to 17 228 eV) over time (Figure 3). Changes in the energy of these resonance features in the XANES region are reportedly inversely proportional to the changes in the corresponding bond length. The time series
XANES data, therefore, suggest that during reaction, the axial uranyl oxygen bond elongates while the average bond length in the equatorial plane shortens. The XANES spectra of the 60 °C, 30 day sample and the 105 °C, 45 day sample are very similar to reported XANES for alkali metal uranate compounds. This indicates that the U(VI) associated with the crystalline iron (oxyhydr)oxide is likely in a uranate-like coordination and presumably relates to the uranium becoming structurally incorporated. It is important to note that feature A remains during incorporation, indicating retention of the uranyl bonds, albeit with an increase in the bond distance inferred from its migration to lower energy. The XANES spectra from previous studies of U(VI) incorporation into hematite are also very similar to our data, suggesting the same U(VI) local environment is favored in several experimental systems.

Further information on the bonding environment of the uranium can be determined from analysis of the EXAFS spectra and their Fourier transform (Figure 4a and b respectively). The model of Waite et al. for U(VI) adsorption to ferrhydrite in a mononuclear bidentate complex was applied to the 0 h data and provided a good fit (Figure 4, Table 1). To test our hypothesis of uranium incorporation into hematite during crystallization, fitting was performed using the hematite structure with U(VI) substituted for Fe(III) in the mineral structure. The model was then applied to the 105 °C, 45 day data first because this was 90.8 ± 0.8% hematite and had only limited potential contributions from goethite (Figure 1). The refined fit model from the 105 °C system was then applied to the 60 °C, 30 day data (55% hematite) to assess the goodness of fit to hematite- incorporated uranium in a more environmentally relevant system.

In the hematite structure (Table 1), each Fe is octahedrally coordinated by oxygen and is surrounded by Fe—O octahedra which are face, edge, or corner sharing (Table 1, Figure 5). We assumed an octahedral U—O coordination for our EXAFS fits based on our XANES, previous modeling, and the working hypothesis that the Fe(III) that was replaced by U(VI) was octahedrally coordinated. The best fit to the EXAFS data showed that the optimal coordination was a fit with three separate U—O shells, each with a coordination of 2 at U—O distances of 1.87 Å, 2.07 Å, and 2.23 Å. These U—O distances are similar to those in barium uranate (BaUO₆), in which uranium is also octahedrally coordinated with oxygen, with 2 at U—O distances of 1.89 Å and 4 at 2.20 Å. We were then able to fit all of the four closest neighboring Fe shells expected from the hematite structure with a good level of statistical significance (Supporting Information Table S1-7). The U—Fe bond distances for face sharing Fe (Fe₅) and the nearer corner sharing Fe (Fe₆) are at approximately the same distance as the Fe—Fe distance in hematite, whereas an increased atomic distance to the other two Fe shells (Fe₇ and Fe₈) is observed.
suggested some strain in the structure (Table 1). U(VI) has a larger crystal radius than Fe(III) (0.870 Å versus 0.785 Å), and thus, upon incorporation, it would be expected to cause expansion and distortion to the host octahedral site.

The usual shell-by-shell approach to EXAFS fitting was not possible because the Fe scatterers mostly contribute to the EXAFS spectrum in the low to middle k range (4–10 Å⁻¹) (Supporting Information Figure SI-2); hence, any model that excludes these contributions will be unsatisfactory. Additionally, we found that having data with good signal-to-noise ratio in the high k range (>10 Å⁻¹) was essential to adequately fit the U–O shells (Supporting Information Figure SI-2). Therefore, with our incorporation hypothesis in mind, we iteratively refined the U–O shells and U–Fe shells simultaneously. Once the U–O shells had been satisfactorily resolved, we then constructed a model from a single Fe shell to the full model including four Fe shells refining the model each time and assessing the statistical relevance of each additional shell by way of an F-test (Supporting Information Table SI-7). The F-test results confirmed that the addition of each subsequent Fe shell significantly improved the fit of the model to the data and was statistically valid.

The Debye–Waller factor of the shortest U–O distance, the axial oxygens, is the highest of the three oxygen shells, when normally it would be expected that they would be the tightest bound and, thus, have the lowest Debye–Waller factors. This may be due to static disorder, possibly related to the averaged nature of the EXAFS spectrum and the complexity of the structure with U–O octahedra potential in different orientations, resulting in a range of U–O axial oxygen distances that are averaged in the fit. Additionally, the outermost Fe shell has a comparatively large Debye–Waller factor, ~0.02 Å⁻². Again, this is likely to be due to the relative increase in static disorder in the spectrum as the distance from the central uranium atom increases. Overall, these data, coupled to TEM and XRD show that the U(VI) within the 105 °C, 45 day aged samples was incorporated into the hematite structure by replacing Fe(III).

### Application of the 105 °C Data
The fit model from the 105 °C data can be fitted to the 60 °C data but requires the removal of the outer two Fe shells from the model. This may be due to the reduced accessible k range of the 60 °C data or to the heterogeneity of the uranium location (e.g., an adsorbed and incorporated component) in this sample compared to the high temperature experiment. The fit parameters for the two closest Fe shells (Table 1) were statistically valid and were essentially the same as the 105 °C fit. Quantitative analysis of the XRD revealed up to 45% goethite present in this sample (Supporting Information Table SI-1). The Fe–Fe distances in goethite are similar to those in hematite, although the hematite face-sharing octahedra at 2.90 Å is absent in goethite. However, amplitude at this distinctive distance was clearly present in our data, meaning that the majority of the U(VI) must reside within the hematite, although it was not possible to eliminate some fraction of uranium residing within the goethite. The fit parameters for the O shells in the 60 °C fit did not remain the same as in the 105 °C fit. The U–O₅ bond distance (1.84 Å) in this sample was

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**Table 1. Details of EXAFS Fit Parameters from Uranium Adsorbed to Ferricyanide (t = 0 h) and Uranium Associated with Crystalline Hematite (t = 30 days, 60 °C; t = 45 days, 105 °C)**

**Notes:**
- CN denotes coordination number; R denotes atomic distance; σ² denotes Debye–Waller factor; ΔE₀ denotes the shift in energy from the calculated Fermi level; S₀² denotes the amplitude factor which was constrained to between 0.85 and 1.05; X₀² denotes the reduced χ² square value; R denotes the “goodness of fit” factor; the subscript MS denotes multiple scattering paths in the axial O–U–O unit. The multiple scattering paths considered were linear paths and their ΔR and σ parameters were evaluated as multiples of the corresponding single scattering path parameter. Numbers in parentheses are the standard deviation on the last decimal place.
close to that of the adsorbed model (1.81 Å), and both the equatorial shells have longer U–O atomic distances than the 105 °C fit. Because the Fe–O octahedra in goethite and hematite are nearly identical, U(VI) present in goethite was unlikely to be the cause for the changed U–O environment between the 105 and 60 °C data sets. However, our chemical extraction data illuminate the differences between the U–O shell fit parameters between the two systems. Approximately 30% of the uranium in the 60 °C sample was acid leachable, indicating a significant portion remains surface bound after 30 days aging. Hence, it seems the bulk EXAFS data contained a significant component of signal from U(VI) in a surface adsorption site, which caused the average U–O bond length in the EXAFS signal to be closer to those of surface bound U(VI). Additionally, the Debye–Waller factors for each U–O shell were >0.008 Å², indicating significant disorder: our model did not account for the adsorbed component, and trying to fit two similar U–O environments simultaneously to the 60 °C data set resulted in large disorder in the U–O shells and, thus, was unjustifiable.

Linear combination fitting of the 60 °C, 30 day data, using the 0 h and 105 °C data as end members, indicated a contribution from the adsorbed U(VI) species of approximately 20% (see Supporting Information), which is in agreement with the chemical extraction data (Figure 2). Applying the same linear combination fitting to data taken after 24 h aging at 60 °C indicated approximately 40% U was adsorbed, whereas the chemical extraction suggested closer to 50% was adsorbed. This modest discrepancy may be partially due to an overestimate of the adsorbed fraction by the operationally defined chemical extraction. This is not uncommon for indirect techniques and suggests a small proportion of the partially crystalline iron oxyhydroxide was dissolved at pH 2.5.**

**Uranium Incorporation into Hematite.** For our end-member 105 °C experiment, the EXAFS analysis showed that during hematite crystallization and U(VI) incorporation, the uranyl axial bonds lengthen by 0.06 Å and the average equatorial bonds shorten by 0.17 Å. These changes to the U–O bond lengths are in agreement with our interpretation of the changes in energy of the resonance features in the XANES data. The EXAFS analysis is consistent with 6-fold coordinated U(VI) residing in a distorted uranate-like octahedral site within the hematite structure (Figure 3), although we accept there may be a contribution from minor amounts of U(VI) in goethite.

In earlier work, Duff et al.** formed U(VI)-containing hematite via a coprecipitation method at pH 11 and interpreted their EXAFS as showing incorporation of uranium into the crystal structure, with an oxygen coordination of approximately 4 at radial distances of 2.19 Å (N = 1.4 ± 15%) and 2.36 Å (N = 2.1 ± 20%), with a single Fe atom (N = 1.12 ± 25%) at a distance of 3.19 Å. The implication is that uranium was incorporated into hematite with the loss of the axial U–O bond. Latterly, it has been suggested that the Duff model had an unexpectedly low U–O coordination, suggesting that not all of the U–O bond distances were fully resolved from the EXAFS.** The same approach to uranium incorporation into hematite was followed by Ilkon et al.** who reported a similar uranium environment to Duff et al.** Our EXAFS data analysis showed that these models are incorrect and that U(VI) is fully coordinated by 6 oxygens within a distorted octahedral site in the hematite structure.

Our interpretation is supported by recent work on atomic simulations of uranium incorporation into hematite, which shows that incorporation of octahedrally coordinated U(VI), with reduction of Fe(III) as the charge compensation mechanism, maintains an average U–O bond distance of 2.06 Å. This is identical to the average U–O bond distance obtained from the fit to our data (2.06 ± 0.02 Å). However, the U–Fe atomic distances returned by the simulations were in excess of those obtained from our EXAFS fitting, in particular the calculated single U–Fe distance from the face sharing octahedra was reported at 3.37 Å.** These differences may be due to the simulations assuming a single U–O bond length; this does not take into account the shape of the distorted UO₆ octahedron that we propose. The corresponding simulation that considers incorporation of the U(VI) into an unoccupied interstitial site within the hematite structure returns similar average U–O and U–Fe bond distances to those of our EXAFS fit.** However, the calculated Fe shells in the simulation are doubly overcoordinated compared to our fit and we were unable to reconcile this model with our data, leading us to discount U(VI) incorporation into a vacancy site. We can see no viable mechanism to achieve charge compensation by reduction of Fe(III) to Fe(II) in our fully oxidized system. Similarly, reduction of U(VI) to U(IV) again seems to be improbable in the absence of a suitable reducing agent. Although distinction of U(V) from U(IV) and U(VI) has been shown to be possible with high resolution XAS techniques,** it is not possible to do so for our samples at their low U-loadings. Furthermore, in crystalline materials, reportedly the U(V) cation may occur in octahedral or pentagonal bipyramidal coordination with a near linear O–U–O unit, but the U–O bond length is typically around 2 Å,** which is in vast excess to the 1.87 Å we observed, giving confidence that U(V) was not present in our samples.
Another potential charge compensation mechanism postulated by Kerisit et al.\(^7\) for U(VI) substituting for Fe(III) is via creation of an Fe vacancy in its vicinity. To test for this we refitted the model described above, but with the coordination number of each Fe shell reduced by one, sequentially (Supporting Information Tables S1-3 and S1-4). None of these fits gave a statistical improvement on that presented here, and in fact, the omission of the face-sharing Fe significantly worsened the fit (Supporting Information Table S1-7). This suggests that if the charge compensation is via creation of a Fe(III) vacancy, then the vacancy is (a) located in the edge-sharing or corner-sharing shells and (b) is randomly distributed relative to U(VI) or is undetectable within the constraints of the EXAFS measurements we made.

Overall, in this study, we present clear evidence for U(VI) incorporation into hematite in an octahedrally coordinated environment and via direct substitution for Fe(III). Our model requires retention of the uranyl bonds as evidenced by the XANES and EXAFS analyses, albeit elongated within the structure, which is in direct contrast to previous studies.\(^8,19\) Our data also evidence the importance of high quality spectroscopic data out to high k when attempting to model actinide incorporation into iron oxides.

**Implications for Uranium in the Environment.** Our work highlights that under conditions relevant to both geological disposal and contaminated land, a significant proportion of U(VI) adsorbed to ferricydrate is incorporated into the hematite crystal structure during crystallization. In our experiments, hematite showed the ability to incorporate approximately 3000 ppm U(VI) (0.3 wt %) in the solid. This is relevant to a wide range of nuclear decommissioning and waste management scenarios where iron oxides are ubiquitous. Indeed, the incorporation of uranium into iron oxides, specifically hematite, has implications for reducing the long-term environmental mobility of U(VI), especially given the long-term stability of hematite, which is found in geological settings older than 1 Ga.\(^48\) It is also worth noting that elevated temperatures associated with disposal of heat-yielding radioactive wastes may enhance hematite formation and, thereby, U(VI) immobilization. In addition, under conditions where biogeochemical processes can occur, it is interesting to note that hematite is recalcitrant to microbial reduction due to its crystallinity, with only a thin surface layer of bioavailable Fe(III) present,\(^49\) again suggesting its stability may be significant in, for example, oxic-contaminated land environments. Fe(II)\(_{ox}\) has been shown to enhance the release of iron oxide incorporated trace metals,\(^50\) although interestingly, natural iron oxides substituted with, for example, Al\(^3+\) are less susceptible to Fe(II)-activated recrystallization, and as such, trace metal release may be inhibited in these phases.\(^51\) In particular, the alkaline conditions used in this study show that these processes are directly relevant to the conditions expected around a cementitious disposal facility for radioactive waste\(^52\) as well as alkaline waste management scenarios (e.g., Hanford tanks\(^53\)). Thus, our results show that substantial incorporation of U(VI) into hematite can occur, which is potentially a significant new pathway to immobilize U(VI) and has clear implications for the environmental mobility of this important radionuclide, especially in high pH conditions relevant to engineered waste environments.

**REFERENCES**


This chapter is a manuscript published in the journal Environmental Science and Technology in September 2014. Supporting Information published with this manuscript is included in Appendix 2.

The full citation of the published manuscript is as follows:

Incorporation and Retention of 99-Tc(IV) in Magnetite under High pH Conditions


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2Centre for Radiochemistry Research and Research Centre for Radwaste and Decommissioning, School of Chemistry, The University of Manchester, Manchester, M13 9PL, United Kingdom
3Diamond Light Source Ltd., Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0DE, United Kingdom

Supporting Information

**ABSTRACT:** Technetium incorporation into magnetite and its behavior during subsequent oxidation has been investigated at high pH to determine the technetium retention mechanism(s) on formation and oxidative perturbation of magnetite in systems relevant to radioactive waste disposal. Ferricyanide was exposed to Tc(VII) adsorbed containing cement leachates (pH 10.5–13.1), and crystallization of magnetite was induced via addition of Fe(II) precursors. A combination of X-ray diffraction (XRD), chemical extraction, and X-ray absorption spectroscopy (XAS) techniques provided direct evidence that Tc(VII) was reduced and incorporated into the magnetite structure. Subsequent air oxidation of the magnetite particles for up to 152 days resulted in only limited remobilization of the incorporated Tc(IV). Analysis of both X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) data indicated that the Tc(IV) was predominantly incorporated into the magnetite octahedral site in all systems studied. On reoxidation in air, the incorporated Tc(IV) was recalcitrant to oxidative dissolution with less than 40% remobilization to solution despite significant oxidation of the magnetite to maghemite/goethite: All solid associated Tc remained as Tc(IV). The results of this study provide the first direct evidence for significant Tc(IV) incorporation into the magnetite structure and confirm that magnetite incorporated Tc(IV) is recalcitrant to oxidative dissolution. Immobilization of Tc(VII) by reduction and incorporation into magnetite at high pH and with significant stability upon reoxidation has clear and important implications for limiting technetium migration under conditions where magnetite is formed including in geological disposal of radioactive wastes.

**INTRODUCTION**

Technetium-99 (Tc-99) is a long-lived radioactive fission product (half-life 2.1 × 10^5 years) present in many spent fuel and reprocessing derived radioactive wastes. The environmental mobility of Tc-99 in the subsurface is primarily governed by its oxidation state. Under oxidizing conditions, Tc(VII) is highly soluble (~11 M) and environmentally mobile, existing as the pertechnetate, TcO₄⁻, anion. In contrast, under reducing conditions, Tc(IV) is dominant and generally precipitates as sparingly soluble Tc(IV)-hydroxide phases (10^-9 – 10^-10 M) or adsorbs to mineral surfaces. Due to its high mobility under oxic conditions and its long half-life, Tc-99 is a significant risk driving radionuclide for geological disposal of radioactive wastes, as well as presenting a significant challenge to remediation of radiactively contaminated land in the UK, the USA, and Russia. Past work has shown that Fe(II) bearing oxides and sulfides are effective in removing Tc(VII) from solution via reductive adsorption or precipitation. In addition, Fe(II) adsorbed to mineral surfaces such as iron or aluminum oxides has also been shown to be a highly effective abiotic reductant for Tc(VII). Microbially mediated reduction of Tc(VII) has also been documented, with enzymatic and indirect (via reaction with biogenic Fe(II)) pathways possible but with indirect reduction dominating. Although aqueous Fe(II) is able to reduce Tc(VII), the kinetics of this pathway are relatively slow. In general, the reductive ability of Fe(II) increases from aqueous Fe(II) to structural Fe(II) to adsorbed Fe(II). Reflecting this, transport of Tc-99 in the environment will therefore be significantly controlled by the Tc-99 interactions with Fe(II) bearing solid minerals (e.g., iron oxides, sulfides) through either sorption or surface mediated reduction and precipitation.

Exposure of reduced Tc-99-bearing sediments to oxidizing conditions may induce remobilization of Tc(VII) back into...
solution, although the extent of remobilization will be dependent upon both the binding mechanism and the oxidant. Sediments labeled with Tc-99 from authorized effluent discharges from Sellafield showed evidence that Tc-99 is retained on sediments over periods of decades even in dynamic saltmarsh environments. Laboratory based studies on remobilization of Tc-99 in shallow sediments indicated that, after Fe(III)-reducing conditions had developed and Tc(VII) was reductively scavenged to sediments, upon oxidation a variable fraction of the sediment associated Tc-99 was recalcitrant to oxidative remobilization.\(^{32-35}\) Under certain conditions, oxidative exposure to air caused remobilization of >50% of the sediment associated Tc(IV) over several months.\(^{12,33,36}\) Further, a study on iron minerals by Wharton et al.\(^{19}\) reported Tc-99 remaining as Tc(IV) despite oxidation of associated mackinawite (tetragonal FeS) to goethite in air. In these studies, the potential existed for Tc(IV) to be incorporated within the oxidized secondary mineral phases, potentially contributing to its recalcitrance to oxidative remobilization.

Incorporation of technetium into stable mineral phases, such as iron (oxyhydr)oxides, offers a pathway for Tc sequestration with the potential for immobilization. Indeed, evidence for Tc(IV) incorporation into goethite (\(\alpha-\)FeOOH) during coprecipitation has been reported,\(^{37,38}\) and Tc(IV) incorporation to hematite (\(\alpha-\)Fe₂O₃) has been predicted from modeling.\(^{37}\) Both these studies suggest that Tc(IV) can be octahedrally coordinated within the relevant crystal structure and can directly substitute for Fe(III). Products of steel corrosion (magnetite, maghemite, and goethite) have also been shown to be able to partially reduce Tc(VII) to Tc(IV), with the authors concluding the Tc-99 was incorporated into the corroded steel surface.\(^{40}\) It has also been recently suggested that adsorbed Tc(IV) may, with time, become incorporated into the magnetite (Fe₃O₄) structure.\(^{41}\) It is clear that the redox incorporation of Tc-99 as Tc(IV) into magnetite under environmental conditions relevant to contaminated sites and geodisposal of wastes could significantly reduce the mobility of Tc-99. However, the mechanism of Tc-99 incorporation into the structure of magnetite and the amount and mechanism of release during oxidation remains unknown.

Crystallization of ferrihydrite to magnetite proceeds via sorption of Fe(II) onto ferrihydrite followed by a solid-state transformation between ferrihydrite, goethite, and magnetite and with additional growth of already nucleated magnetite particles.\(^{42-44}\) At low solution Fe(II) concentrations (<0.03 mmol/L), only goethite precipitates, with nucleation of magnetite increasing with increasing Fe(II) concentration and with magnetite crystallization eventually proceeding at the expense of goethite.\(^{45-48}\) Magnetite oxidizes to maghemite (\(\gamma-\)Fe₂O₃) topotactically through outward diffusion of Fe, with no change in the crystal size or shape and the creation of 2.67 cation vacancies per unit cell.\(^{49,50}\) This process initially leads to the formation of a pure Fe(III) surface layer on the magnetite particle which increases in thickness until the entire particle has transformed to maghemite.\(^{51}\) The identity of the Fe species undergoing outward diffusion during this process is not agreed upon in the literature, although Fe(II) is the more favored.\(^{52-54}\) Understanding the potential for incorporation of technetium into magnetite during its formation and oxidation and under conditions relevant to radioactive waste disposal is the focus of this study.

Many geodisposal concepts utilize cementitious materials in the design of a deep geological disposal facility (GDF), for example, as part of the engineered barrier system or as structural materials. Leaching of these materials upon resaturation will buffer the pH to hyperalkaline conditions (pH 10.5–13.1), creating a plume of alkaline fluid in the host rock and/or local environment.\(^{55}\) Furthermore, hyperalkaline conditions can prevail in many contaminated land scenarios, e.g. where cementitious building materials contact subsurface sediments\(^{56,57}\) and at the underground waste storage tanks at the Hanford Site in Washington State, USA, where there has been considerable attention focused on behavior of Tc-99.\(^{31,34,39,51-53}\) Additionally, microbial reduction of Fe(III) leading to the formation of magnetite has recently been shown to occur under alkaline conditions,\(^{31}\) highlighting the importance of biogeochemistry in these processes and lending further significance to the work in this contribution.

The aim of this study was to characterize the mechanism(s) of Tc-99 reaction with magnetite as it crystallizes under alkaline conditions, to determine whether significant amounts of Tc-99 could be incorporated into this environmentally important phase and to explore the effects of oxidative perturbations on Tc-99 speciation and solubility. The system we have explored is crystallization of ferrihydrite as an initial Fe(III) oxohydroxide product to magnetite by addition of aqueous Fe⁴⁺.\(^{52}\) We followed the partitioning of Tc(VII) during this process in three synthetic cement leachates (pH 10.5, 12.5, and 13.1). After a period of aging, the Tc-99 doped magnetite systems were then exposed to oxidizing conditions to test the recalcitrance of any iron oxide associated Tc-99 to reoxidation and thus to explore the stability of the radionuclide. We have combined geochemical data with quantitative powder X-ray diffraction (XQRD), transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX), and X-ray absorption spectroscopy (XAS) to thoroughly characterize the fate of Tc-99 during magnetite crystallization and reoxidation at high pH. Throughout, we have focused on the fate of Tc-99: first, during ferrihydrite crystallization to magnetite, we determined the extent of Tc-99 incorporation and defined its atomic scale bonding environment; we then oxidized the Tc-99-labeled magnetite over several months to determine if incorporation offered protection against oxidative remobilization.

### MATERIALS AND METHODS

Batch experiments were used to follow the Fe(II)-mediated crystallization of ferrihydrite to magnetite in three Tc(VII) amended synthetic cement leachates (CL), chosen to simulate a young (YCL, pH 13.1), intermediate (ICL, pH 12.5), and old (OCL, pH 10.5) postclosure groundwater around a GDF.\(^{49,55}\) Details on preparation of the cement leachates are given in the Supporting Information. Parallel experiments were also set up without Tc(VII) present to allow characterization of the solid products by X-ray diffraction (XRD). The 2-line ferrhydrite used as a starting material was synthesized as per Cornell and Schwertmann, and the Fe(III) content of the resultant paste was determined by dissolution in 1 M HCl and analysis by the ferrozine method.\(^{57}\) A known quantity of ferrihydrite was equilibrated with the cement leachates at a solid/solution ratio of 3.5 g L⁻¹ for 1 h on an orbital shaker at room temperature in an anaerobic chamber (5% H₂, balance N₂, maintained at <1 ppm of O₂ and CO₂). After equilibration with the ferrihydrite, the pH was manually readjusted to the initial leachate pH by
addition of KOH. Tc(VII) was then added to the experiments as ammonium percteinate (NH₃TeO₄) to give an initial solution concentration of 3 ppm (30.3 μM, 2 kbq ml⁻³). Crystallization to magnetite was then induced by addition of Fe(II) as 0.1 M FeCl₂ to give stoichiometric magnetite with an Fe(II)/Fe(III) ratio of 1:2. After Fe(II)-addition, the pH was immediately readjusted to the initial leachate pH using KOH. The alkaline magnetite suspension was then aged for 2 days in the anaerobic chamber. Following this, the experiments were moved to a separate glovebox containing CO₂-free air (Zero grade Air) where they were allowed to oxidize for up to 152 days. A further experiment was set up in the intermediate stage cement leachate (ICL, pH 12.5) as a sorption “control” where the Tc-99 was spiked to preformed magnetite after 1 day. After a further day of reaction, a subsample of the experiment was then transferred to the glovebox containing CO₂-free air for 152 days for oxidation. All experiments were shaken on an orbital shaker (150 rpm) to allow exchange with the relevant atmosphere (i.e., reducing: H₂/N₂ mix; oxidizing: CO₂-free air) but were not purged with the relevant gas. Minor aggregation of particles was observed in all three systems over time. The pH was periodically monitored throughout the experiments, and no further pH adjustment was required after the initial pH was set.

Partitioning of Tc-99 between the solid/solution was determined by analysis of a 1 mL solution aliquot for Tc-99 by liquid scintillation counting (LSC) using a Packard TriCarb 2100TR liquid scintillation analyzer. The distribution of Tc-99 within the magnetite particles and oxidized products was determined by total digestion in 1 M HCl where the relative dissolution rate of Tc-99 versus total Fe in the acidic leachate provided insight into the concentration gradient of Tc-99 through the solid. The mineral sample was allowed to fully dissolve in the acid, with the resultant solution analyzed at selected time points during dissolution. Samples were analyzed for Tc-99 using LSC and Fe by the ferroxine method until no further increase in the concentration of Fe in the acidic solution was observed. Full details of the method are included in the Supporting Information. Where appropriate, selected samples were characterized by XRD using a Bruker D8 diffractometer (λ = Cu K-α). For TEM, solid samples were characterized using an FEI CM200 Field Emission Gun TEM, operating at 197 kV and fitted with a Gatan Imaging Filter (GIF 200) and an Oxford Instruments Silicon Drift Detector EDX spectrometer running AZTEC software. Tc-99 K-edge XAS spectra were collected on Beamline B18, at the Diamond Light Source at room temperature in fluorescence mode using a 9-element Ge detector. Data reduction and fitting of the X-ray absorption fine structure (EXAFS) spectra were performed using the software packages Athena and Artemis.

## RESULTS AND DISCUSSION

Characterization of the Iron Oxide Products. XRD patterns show that, after 2 days of aging, magnetite was the dominant product formed in each of the leachates (Figure SI-1, Supporting Information) but that in the YCL (pH 13.1) and ICL (pH 12.5) experiments goethite was also formed (QXRD analysis suggested up to 20-25%, Table 1). In contrast, the pH 10.5 OCL product was magnetite only (Figure SI-1, Supporting Information, Table 1). During the oxidation experiments, the color of solids changed from black to brown in all leachates suggesting that oxidation of the magnetite had occurred. After 21 days of oxidation in CO₂-free air, the XRD patterns for all experiments were the same as the fully reduced samples within error and with no significant increase in the goethite present in the YCL and ICL systems and no measurable ingrowth of goethite into the OCL system (Figure SI-1, Supporting Information, Table 1). However, after 152 days of oxidation, all three samples contained approximately 50% goethite as evidenced for magnetite oxidation at high pH (Figure SI-1, Supporting Information, Table 1). Oxidative maghemisation was evident from a shift in the peak at (511) and (440) peaks in the XRD pattern to higher 20 in the 152 days of oxidation in both the ICL and OCL experiments, in agreement with the QXRD data (Figure SI-2, Supporting Information). However, the characteristic maghemite (210) and (211) peaks were not observed (Figure SI-2, Supporting Information), indicating only partial maghematisation has occurred. The length of the unit cell a axis dimension has previously been used as a measure of stoichiometry, i.e., Fe(II)/Fe(III) ratio. Stoichiometric magnetite has an Fe(II)/Fe(III) ratio of 0.5 which decreases to zero in maghemite, while the unit cell length decreases from 8.396 to 8.340 Å. In the 152 day samples, a shortening of the unit cell length was observed in all three systems indicating a decrease in the Fe(II)/Fe(III) ratio consistent with oxidation (Table 1). Using the stoichiometric method of Gorski and Scherer, we have calculated the Fe(II)/Fe(III) ratio and, hence, the degree of maghematisation, for our samples (Table 1). After 152 days of oxidation, complete oxidation of the three experiments had not occurred; the lowest Fe(II)/Fe(III) ratio and hence greatest extent of maghematisation was observed in the ICL system (0.12 ± 0.03), while the
least extent of magnetization was in the YCL system (0.39 ± 0.05). Complete oxidation of maghemite nanoparticles in aqueous systems has been observed to occur over approximately three months, suggesting that, in our alkaline systems, magnetite has a degree of recalcitrance to oxidation. Incorporation of trace elements into magnetite (e.g., Co, Ni, Zn, up to 1 wt %) has previously been shown to stabilize Fe(II) and suppress magnetisation through a decrease in electron mobility. The incomplete magnetization observed in our samples despite almost double the oxidation time compared to the past study could potentially indicate incorporation of Tc(IV) and stabilization of Fe(II) within the magnetite structure in the immediate vicinity of Tc(IV) as a charge compensation mechanism and which may inhibit complete oxidation.

TEM images (Figures SI-3 and SI-4, Supporting Information) confirmed the presence of crystalline nanoparticulate magnetite (angular to rounded cubes and rhombs, 5–20 nm in size) and goethite (needles) in the reaction products. Tc-99 was not detected using energy dispersive X-ray spectroscopy (EDX) in any of the samples analyzed, suggesting the Tc-99 was distributed throughout the sample rather than as a discrete phase and/or the Tc-99 concentration was below the limit of detection for this technique.

Technetium removal from solution to the solid during magnetite formation and oxidation is shown in Figure 1.

![Figure 1](image1.png)

**Figure 1.** Removal of Tc-99 from solution (%) during magnetite aging (days 0–2) and subsequent oxidative remobilization of Tc-99 to solution during air oxidation (days 3–154) in young (YCL, pH 13.1), intermediate (ICL, pH 12.5), and old (OCL, pH 10.5) cement leachates. Closed blue diamonds = YCL coprecipitation; closed red diamonds = ICL coprecipitation; open red diamonds = ICL sorption; closed green diamonds = OCL coprecipitation.

Regardless of pH, all Tc-99 was removed from solution to below detection limit (ca. 0.5 Bq m^-3; 0.8 ppb) within minutes after the addition of Fe(II) and with no release back to solution during aging. Upon oxidation in air, there was an initial rapid remobilization of Tc-99 to solution over the first day with a continued slow release over the first 2 weeks; however, the Tc-99 concentration in solution then remained essentially constant. The total amount of oxidative release of Tc-99 was dependent upon the solution composition. The Tc-99 released in the OCL (pH 10.5) and ICL (pH 12.5) systems was similar with ~20% of Tc-99 released after 1 day of oxidation rising to ~30% after 152 days. In the YCL, the release profile was similar, but the total release was higher, at ~30% after 1 day rising to ~40% after 152 days. The greater extent of Tc-99 released to solution in the YCL compared to the ICL and OCL may be due to increased oxidation of the magnetite surface at higher pH. In addition, differential aggregation of the particles could potentially influence the Tc(IV) remobilization behavior. However, the particle aggregation on reoxidation was similar for each leachate and seems not to explain the differential remobilization across the different cement leachates and the persistently greater remobilization in the YCL. In contrast, in the adsorption experiment where Tc-99 was adsorbed to preformed magnetite at pH 12.5 in ICL, greater oxidative remobilization was observed compared to the coprecipitated experiments with ~70% of the Tc-99 oxidatively remobilized to solution after 152 days. In the reoxidation experiment with the adsorbed sample, the remaining ~30% of Tc-99 was in some way recalcitrant to air oxidation and was retained by the solid phase even though Tc(VII) was exposed to the preformed Fe(II)-bearing mineral. Interestingly, similar behavior has been observed for reduction of Tc-99 onto preformed magnetite, where EXAFS analysis suggested some incorporation of Tc-99 into the magnetite after aging.

**Technetium Distribution within the Solids.** Magnetite dissolves isotropically allowing the distribution profile of trace elements within the solid to be assessed by acid digestion. We performed 1 M HCl digestions on the samples from the OCL (pH 10.5) experiment to explore the Tc-99 distribution profile in the solid since these contained negligible goethite implying that all Tc-99 measured would be from magnetite associated Tc-99 (Figure 2). The dissolution profile of Tc-99 vs Fe in the reduced sample had a gradient initially greater than 1 which then fell to less than 1 when more than 50% of the available Fe was dissolved. This indicated that Tc-99 was not uniformly distributed through the magnetite particles and was relatively concentrated at the surface, an effect previously observed for Mn(II) and Cu(II). The OCL oxidized mineral sample from 21 days, which showed no ingrowth of secondary goethite, showed that approximately 10% of the Fe in the sample was dissolved before any Tc-99 was detected in

![Figure 2](image2.png)

**Figure 2.** Tc-99 release to solution from solids versus total Fe release to solution in a 1 M HCl leach of magnetite coprecipitated with Tc-99 in old cement leachate (pH 10.5). Black diamonds = reduced magnetite; orange circles = 21 day air oxidized magnetite.
solution, suggesting the development of an Fe rich/Tc-99 poor rind during oxidation. After this, the Tc-99 and Fe profiles were similar to the magnetite sample with an initial slope greater than 1, and after approximately 50% Fe dissolution, the gradient fell to below 1 reflecting an apparently heterogeneous distribution of Tc-99. From the Tc-99 distribution profile of the reduced OCL magnetite sample, 30% Tc-99 was dissolved in the acetic acid by the time only 10% Fe had dissolved (Figure 2) suggesting that 30% of the Tc-99 released to solution during oxidation (Figure 2) can be explained by release of Tc-99 from the outer 10% of the 1 M HCl leachable magnetite particles.

**X-ray Absorption Spectroscopy.** X-ray absorption near edge structure (XANES) and EXAFS spectra were collected from the reduced magnetite and two oxidized samples (21 and 152 days) from coprecipitation experiments in each cement leachate, along with the sorption sample in ICL (pH 12.5). It was not possible to collect XAS data for the 21 day oxidized sorption sample as it was found that the Tc-99 concentration was too low for analysis. The edge position of all the XANES spectra aligned to the Tc(IV) reference, and there was no evidence in any samples for the distinctive Tc(VII) pre-edge peak at 21045–21050 eV (Figure 3). A linear combination fit between the oxic and reduced reference spectra resulted in no (0%) contribution from Tc(VII) to each of the experimental spectra (Table SI-1, Supporting Information). This indicated that Tc(VII) was fully reduced to Tc(IV) in each system and that, for oxidized samples, any Tc-99 that remained associated with the solid was retained as Tc(IV) throughout air oxidation. The distinct double peak observed in the near edge of each of the sample spectra, which is absent from the TcO₂ reference, has previously been attributed to the presence of Tc–Fe bonds.

The EXAFS spectra collected from samples in the ICL system (pH 12.5) are plotted in Figure 4, along with the nonlinear least-squares fits to the data. It is clear that the Tc-99 in the sorption sample (Figure 4) is in a very different coordination environment when compared to the coprecipitation samples, with a single wave dominating the k-space in the sorption system. The relatively weak second peak in the Fourier transform at approximately 3.5 Å suggests there are few absorbers/scatterers in the second shell suggesting the Tc-99 was predominantly present on the magnetite surface. Interestingly, all of the ICL coprecipitation samples are strikingly similar including the 21 and 152 day oxidized samples (Figure 4). This confirms that air oxidation had very little effect on the Tc-99 local bonding environment in these samples, even after 152 days. In the coprecipitation systems, again there was similarity across the reduced and oxidized samples and it is also clear that in all the samples the second shell of scattering atoms contributed more strongly to the EXAFS compared to the parallel sorption sample. This was confirmed by intense peaks in the phase-shifted Fourier transform of all three coprecipitation samples in the 2.5–4 Å range indicating a large number of backscattering atoms in these shells and suggesting incorporation of Tc(IV) into the magnetite structure.

Previously, Tc(IV) reduced onto environmental surfaces has been fitted using polymeric Tc chain-like phases, and both of these models can be applied to our magnetite sorption data with similar results. In the reduced and oxidized sorption samples, the addition of either Tc-99 or Fe shells beyond the Tc–O shell did not significantly improve the fit, and F-tests confirmed the more complex fits were statistically indistinct from a single Tc–O shell fit (Figure SI-5 and Tables SI-2 to SI-4, Supporting Information). Therefore, the best fit to the sorption sample was an averaged TcO₂ structure, as expected for an amorphous hydrous-TcO₂ precipitate on the magnetite surface. Interestingly, the double peak in the XANES region in all samples suggests the presence of Tc–Fe bonds. The presence of this feature in the magnetite sorption samples may indicate a component of a Tc–Tc chain sorbed to the magnetite surface or indeed some incorporation of Tc(IV) into the magnetite, as postulated previously and supported by the Tc-99 solution data (Figure 1).

The Tc-99 EXAFS from the coprecipitation samples were fitted assuming a model of Tc(IV) incorporation into the magnetite structure where Tc(IV) was substituted solely into the octahedral site and similar to the model for Ti(IV) substitution into magnetite. In our model, the Tc–O coordination was fixed at 6 while the coordination of the two Tc–Fe shells was allowed to vary. This approach achieved a good fit with interatomic distances similar to those for octahedrally coordinated Fe(III) in pure magnetite (Table 2). The Tc–Fe coordination in both shells was lower than, although within error of, the expected coordination of 6, with 4.7 ± 1.3 and 4.4 ± 1.3 in the Tc–Fe shells. In nanoparticulate systems, surface effects may result in lower coordination numbers; atoms residing in the near-surface of a particle will have a lower coordination in the metal–metal shells than those in the particle core. This effect has previously been observed for U–U coordination in uraninite nanoparticles. We have shown that, in our reduced samples, Tc-99 was relatively concentrated in the near-surface of iron oxide nanoparticles, which suggests surface effects may explain the observed low Tc–Fe coordination. The EXAFS data and associated fits from the reduced and oxidized magnetite in the YCL (pH 13.1) and OCL (pH 10.5) systems are within error of those in the ICL (pH 12.5) system (Figure SI-6 and Table SI-5, Supporting Information).
The ionic radii of Tc(IV) and Fe(III) are identical at 0.785 Å. The octahedrally coordinated site in the maghemite structure should accommodate Tc(IV) with little distortion. There is an excess charge associated with Tc(IV) substituting for octahedrally coordinated Fe(III), and this may cause the slightly lengthened Tc–Fe distance (~3.05 Å) observed from the EXAFS fitting in our samples compared to the Fe–Fe distance in maghemite (2.97 Å). The excess charge associated with the Tc(IV) substitution must be balanced through charge compensation. One suitable mechanism to do this would be for coupled substitution of a lower charged ion, but no credible candidate exists in our system. Alternatively, the solid may compensate the charge through creation of a vacancy site or through reduction of Fe(III) to Fe(II) as in the case of Ti(IV) substitution into maghemite, and this is the most likely mechanism here, although the relatively low concentration of Tc-99 in the samples at 0.1 wt % means that direct evidence for this was not available in our systems. Although there is no indication of the presence of a surface Tc(IV) phase in the EXAFS or the dissolution data, destructive interference between potential Tc–Tc and Tc–Fe signals has been reported and we cannot definitively rule out minor contributions from a surface Tc(IV) phase in the reduced coprecipitated sample.

**Tc(IV) Retention during Oxidation.** Comparison of the spectra from the two oxidized samples and their respective fits to the reduced coprecipitation sample revealed that oxidation of Fe(II) to Fe(III), as confirmed from XRD measurements, had no significant effect on the speciation of the Tc-99 remaining in the solid even though significant maghematization and oxidation to goethite had occurred by 152 days. Indeed, in the 152 day sample, Tc-99 remained as Tc(IV) and could be

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**Table 2. Details of EXAFS Fit Parameters of Tc-99 Adsorbed to and Coprecipitated with Maghemite and Subsequent Air Oxidation in the Intermediate Cement Leachate (pH 12.5)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tc-</th>
<th>CN</th>
<th>R + ΔR (Å)</th>
<th>σ² (Å²)</th>
<th>ΔE₀ (eV)</th>
<th>S₀²</th>
<th>X₀²</th>
<th>R</th>
</tr>
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<tr>
<td>ICL sorption</td>
<td>O</td>
<td>6</td>
<td>2.02 (1)</td>
<td>0.004 (0)</td>
<td>−1.5 ± 1.4</td>
<td>0.90²</td>
<td>116.1</td>
<td>0.025</td>
</tr>
<tr>
<td></td>
<td>Tc</td>
<td>6</td>
<td>3.28 (3)</td>
<td>0.016 (3)</td>
<td>−5.0 ± 1.6</td>
<td>0.90²</td>
<td>317.2</td>
<td>0.024</td>
</tr>
<tr>
<td></td>
<td>Fe₁</td>
<td>4.3 ± 1.5</td>
<td>3.04 (2)</td>
<td>0.008 (3)²</td>
<td>−4.7 ± 1.5</td>
<td>0.90²</td>
<td>185.5</td>
<td>0.026</td>
</tr>
<tr>
<td></td>
<td>Fe₂</td>
<td>4.0 ± 1.4</td>
<td>3.48 (2)</td>
<td>0.008 (3)²</td>
<td>−5.0 ± 1.7</td>
<td>0.90²</td>
<td>549.0</td>
<td>0.027</td>
</tr>
<tr>
<td></td>
<td>Oₘ₅</td>
<td>6</td>
<td>4.00 (2)</td>
<td>0.010 (1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ICL coppt, oxidized</td>
<td>O</td>
<td>6</td>
<td>1.99 (1)</td>
<td>0.004 (1)</td>
<td>−4.7 ± 1.5</td>
<td>0.90²</td>
<td>185.5</td>
<td>0.026</td>
</tr>
<tr>
<td></td>
<td>Fe₁</td>
<td>4.3 ± 1.2</td>
<td>3.05 (1)</td>
<td>0.007 (2)²</td>
<td>−5.0 ± 1.7</td>
<td>0.90²</td>
<td>549.0</td>
<td>0.027</td>
</tr>
<tr>
<td></td>
<td>Fe₂</td>
<td>3.6 ± 1.1</td>
<td>3.47 (2)</td>
<td>0.007 (2)²</td>
<td>−5.0 ± 1.7</td>
<td>0.90²</td>
<td>549.0</td>
<td>0.027</td>
</tr>
<tr>
<td></td>
<td>Oₘ₅</td>
<td>6</td>
<td>3.99 (2)</td>
<td>0.008 (1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ICL coppt, oxidized</td>
<td>O</td>
<td>6</td>
<td>1.99 (1)</td>
<td>0.004 (1)</td>
<td>−4.7 ± 1.5</td>
<td>0.90²</td>
<td>185.5</td>
<td>0.026</td>
</tr>
<tr>
<td></td>
<td>Fe₁</td>
<td>4.4 ± 1.3</td>
<td>3.04 (1)</td>
<td>0.006 (2)²</td>
<td>−5.0 ± 1.7</td>
<td>0.90²</td>
<td>549.0</td>
<td>0.027</td>
</tr>
<tr>
<td></td>
<td>Fe₂</td>
<td>3.7 ± 1.2</td>
<td>3.47 (2)</td>
<td>0.006 (2)²</td>
<td>−5.0 ± 1.7</td>
<td>0.90²</td>
<td>549.0</td>
<td>0.027</td>
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<tr>
<td></td>
<td>Oₘ₅</td>
<td>6</td>
<td>3.98 (2)</td>
<td>0.008 (1)</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

- CN denotes coordination number; R + ΔR denotes atomic distance; σ² denotes Debye–Waller factor; ΔE₀ denotes the shift in energy from the calculated Fermi level; S₀² denotes the amplitude factor; X₀² denotes the reduced Chi square value; R denotes the “goodness of fit” factor; the subscript MS denotes multiple scattering paths. Numbers in parentheses are 1 standard deviation on the last decimal place. The multiple scattering paths considered were linear paths, and their ΔR and σ² parameters were evaluated as multiples of the corresponding single scattering path parameter. Parameter was fixed. Parameters were tied in a given fit.

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**Figure 4.** Technetium K-edge XAS spectra from Tc-99 adsorbed to and coprecipitated with magnetite and subsequent air oxidation in the Intermediate Cement Leachate (ICL, pH 12.5). Panel A, k³-weighted EXAFS; panel B, Fourier transform of k³-weighted EXAFS, using a Hanning window function and plotted with phase shift calculated from the Tc–O path. Black lines are data, and red lines represent best fit models for the data.
modeled as being predominantly substituted for Fe(III) in octahedral sites within the magnetite/maghemite structure. The presence of significant (~50%) goethite has little effect on the Tc EXAFS in these systems. Interestingly, the fits to the 21 and 152 day oxidized samples do not perfectly capture features in the EXAFS in the k = 10–12 Å⁻¹ range (Figures 4 and SI-6, Supporting Information) which become more apparent with greater oxidation of the samples. Addition of a Tc=Fe distance that could be indicative of Tc(IV) incorporation into a secondary goethite phase (~3.2 Å) returned physically unrealistic Debye-Waller Factors, and so, this model was discounted. Changes in the host mineral structure could account for these features, for example, creation of vacancies during maghematization, but such effects were challenging to reproduce within the EXAFS model.

Our dissolution data suggest that a Tc-99 poor layer was created in the magnetite upon oxidation, and 1 M HCl extractions suggest ~10 wt % of the particle volume is depleted in Tc. Formation of trace element depleted surface layers following oxidation has previously been observed for a range of trace-metal incorporated magnetites.46 Comparison with this past work suggests that this depleted layer forms due to a mix of oxidative Tc-99 diffusion out of the solid into solution and outward diffusion of Fe during dynamic maghematization.45,66 The Fe(II)/Fe(III) ratio in solids dropped from 0.5 to between 0.12–0.21 in the ICL and OCL oxidation experiments indicating that at least ~40% of the magnetite had been oxidized to maghemite. This equates to a surface layer with a thickness of ~15% of the particle radius. This indicates that a model where there are three “zones” in a cross-section through the oxidized particles, an outer maghemite layer with essentially no Tc-99 (~10%), a maghemite layer containing Tc-99 (~30%), and a magnetite core containing Tc-99 (~60%), could explain the Tc distribution in the samples. This three layer model is an oversimplification of the true system since there will not be a discrete boundary between magnetite and maghemite.46 However, it is clear that, despite significant oxidation of the magnetite, solid associated Tc(IV) remains in the reduced state and resides in regions with complete oxidation of structural Fe(II) to Fe(III) and in a site almost identical to the octahedral site in magnetite (Figure 4, Table 2). This suggests that a significant fraction of Tc(IV) incorporated into iron oxides may be recalcitrant to oxidation even if the iron oxide itself is oxidized, with the suggestion that irreversible binding of Tc-99 is possible in these systems.

It has recently been demonstrated that secondary arming of Tc(IV) incorporated into goethite crystals protects the Tc(IV) from oxidation and decreases the release of Tc-99 from within goethite.37,38 In our systems, it is possible that the maghematization process resulted in arming of the Tc(IV) incorporated magnetite through creation of an Fe(III)-rich rind via outward diffusion of Fe(III).55 Such a rind could serve to limit or even prevent further outward diffusion of Tc-99 to solution, which may account for the observation that, on recrystallization of magnetite, Tc-99 release to solution was restricted and was essentially at steady state after the initial rapid release during the first couple of weeks of oxidation. This suggests that Tc(IV) incorporated into magnetite may be stable over an extended time, even in the event of a shift to oxidizing conditions, and implies that reductively scavenged Tc-99 may be essentially irreversibly bound within magnetite over a wide range of geochemical conditions.

Effect of Solution pH. The EXAFS spectra for all of the coprecipitation samples were broadly similar for each of the three leachates (Figure SI-6 and Table SI-5) Supporting Information. This suggests that the behavior of Tc-99 during maghemite crystallization was pH independent, perhaps unsurprising given the predicted speciation of Tc in solution as TcO₂⁻ over the entire pH range (10.5–13.1).56 The YCL (pH 13.1) and OCL (pH 10.5) fits were the same as the ICL (pH 12.5) fits; the reduced coprecipitation sample data were again best fit with the model of Tc(IV) incorporation into the magnetite octahedral site, as were the data from the oxidized samples. From the analysis of the XRD patterns, up to 20% of goethite crystallized in the YCL (pH 13.1) and ICL (pH 12.5) reduced systems. This however had no measurable impact on the Tc-99 speciation evidenced by the similarity of the EXAFS spectra and best fits to the pure magnetite OCL (pH 10.5) system. The coordination of Fe(III) in goethite is similar to that of Fe(III) in an octahedral site; Fe(III) is octahedrally coordinated by O at ~2 Å, and there are shells of Fe at ~3 and ~3.5 Å with coordination of 2 and 4, respectively; however, there is an additional pair of Fe atoms at ~3.3 Å.74 The total Fe=Fe coordination in goethite of 8 matches the total Fe=Fe coordination in our incorporated iron oxides. This necessitated examination of the possibility that Tc-99 resided in the goethite. Despite recent evidence of Tc(IV) incorporation into goethite,57,58 our data could not be fitted using the published model from this work57,58 and clearly show a coordination environment where Tc-99 was best modeled by incorporation into magnetite/maghemite. However, we cannot rule out the possibility that a small fraction of Tc-99 is residing in goethite present in the YCL (pH 13.1), ICL (pH 12.5), and 152 day oxidized OCL (pH 10.5) systems.

Implications for Tc-99 Behavior in the Environment. The data presented show that Tc(VII) is reduced to Tc(IV) and incorporated into the magnetite structure during crystallization from a ferrhydrite precursor, with 60–70% of the incorporated Tc(IV) retained as Tc(IV) during relatively robust, long-term reoxidation. Counterintuitively, the oxidation process may in fact aid retention of a sizable proportion of Tc(IV) within the magnetite/maghemite via an armorng process with Fe(III), leaving a significant fraction of the Tc(IV) recalcitrant to oxidation. Incorporation of Tc-99 into maghemite may offer a long-term sequestration mechanism for significant quantities of Tc-99 in alkaline environments (pH >10) where magnetite is present and may help to explain previous observed recalcitrance of Tc-99 during reoxidation of reduced, iron oxide-bearing sediments. It is noteworthy that additional geochemical variables not considered in this study, e.g., groundwater chemistry, may have significant impacts on the ability of iron oxides to sequester Tc-99 and merit further investigation. For example, resistance to Tc(IV) has been shown to inhibit ferrhydrite crystallization to goethite and hematite,75 although it does not seem to affect magnetite crystallization at circum-neutral pH.76

Given that Tc(VII) was reduced and incorporated into magnetite over the entire experimental pH range and that magnetite has been shown to be a significant component in the corrosion of iron and steel under anaerobic conditions,77 this study highlights the potential for significant retention of Tc-99 in radioactive waste disposal as a consequence of waste from iron corrosion. The mechanism of Tc(VII) reductive immobilization and incorporation into magnetite could therefore
present a significant sink for Tc(VII) in both waste disposal and contaminated land scenarios.

**ASSOCIATED CONTENT**

- Supporting Information
  Supporting Information includes additional figures and data tables for TEM/XAS analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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Chapter 6  The Fate of Uranium During Crystallisation of Magnetite from Ferrihydrite

6.1  Introduction

Due to its long half-life (U-238; 4.5 x10⁹ years), uranium is predicted to become the dominant contributor to radioactivity (along with its daughter decay products) in a GDF beyond 10⁵ years (Pöyry Energy & Amec, 2013b) and as such represents a key contributor to risk in longer-term performance assessments of geological disposal of radioactive wastes. In addition to this, uranium presents a significant challenge to remediation of radioactively contaminated land.

The mobility of uranium in environmental systems is primarily governed by its oxidation state. Under oxidising conditions U(VI) is the dominant valence state, which is relatively soluble in aqueous solution, particularly in the presence of carbonate, and thus environmentally mobile (Clark et al., 1995). In contrast, under reducing conditions U(IV) dominates which is sparingly soluble and may precipitate as U(IV) oxide phases (Murphy & Shock, 1999; Lloyd & Renshaw, 2005). U(VI) has a strong affinity for the carbonate anion, forming strong aqueous uranyl-carbonate complexes (Murphy & Shock, 1999) which stabilise U(VI) in solution, thereby increasing its mobility. Additionally, formation of stable uranium colloids may also promote migration of uranium in cementitious environments (Bots et al., 2014).

Uranium will adsorb to the surface of a wide range of geological materials under oxic and reducing conditions which may act to retard its environmental mobility (Payne et al., 1994; Waite et al., 1994; Barnett et al., 2000; Jeon et al., 2005; Shuibo et al., 2009; Begg et al., 2011). In addition, both goethite (α-FeOOH) and hematite (α-Fe₂O₃) have been shown to be capable of incorporating uranium, either as U(VI) or U(V), into their structure, offering a pathway for sequestration with the potential for long-term immobilisation (Nico et al., 2009; Boland et al., 2011, 2014; Ilton et al., 2012; Marshall et al., 2014a). Magnetite (Fe₃O₄) is an environmentally relevant mixed Fe(II)/Fe(III) oxide (Fleet, 1981; Cornell & Schwertmann, 2003) and as such has received substantial attention in respect of its interactions with uranium. Previously magnetite has been shown to be effective at removing U(VI) from solution through reduction to U(IV) through coupled oxidation of Fe(II), with precipitation of UO₂ on the magnetite surface (Grambow et al., 1996; Dodge et al., 2002; Missana et al., 2003a, 2003c; Scott et al., 2005; Duro et al., 2008; Latta et al., 2012b; Singer et al., 2012a, 2012b). Recent work has shown that at low uranium loadings, mononuclear U(IV) complexes form on the magnetite surface which then nucleate the precipitation of UO₂ as the surface loading increases (Latta et al., 2014). It has even been suggested that through time, adsorbed uranium may become incorporated into
the magnetite structure (Huber et al., 2012). In this study, the authors observed the presence of both U(IV) and U(V) in the magnetite near surface via XPS measurements, and corroborated these observations with XANES spectra which were interpreted as containing U(IV) and U(V)/U(VI). However, the authors were not able to define the oxidation state of the U species that their EXAFS modelling suggested was incorporated into the magnetite octahedral site. Microbial activity has been shown to play an important role in U(VI) reduction to U(IV) (O’Loughlin et al., 2010; Veeramani et al., 2011; Madden et al., 2012), although it is unclear if direct enzymatic reduction (Lovley & Phillips, 1992a, 1992b; Law et al., 2011) or indirect reduction by biogenic Fe(II) is more important (Fredrickson et al., 2000; Finneran et al., 2002; Anderson et al., 2003; Behrends & Van Cappellen, 2005; Liu et al., 2005; Lloyd & Renshaw, 2005; Begg et al., 2011).

U(IV) associated with iron oxide minerals as UO$_2$ or as non-uraninite U(IV) (Bernier-Latmani et al., 2010) is easily remobilised to solution under oxidising, and potentially even mildly reducing conditions (Senko et al., 2002, 2007; Sani et al., 2005; Ginder-Vogel et al., 2006; Ulrich et al., 2008, 2009; Campbell et al., 2011b). However, if the U(IV) is incorporated within the iron oxide structure, it may be protected from oxidative release, as observed with goethite (Stewart et al., 2009). Indeed, recent work has shown that reduction of U(VI) concurrent with biomagnetite formation resulted in U(IV) associated magnetite which was recalcitrant to oxidative remobilisation (Law et al., 2011).

Many geodesposal concepts utilise cementitious materials in the design of a geological disposal facility (GDF), for example, as part of the engineered barrier system or structural materials. Leaching of these materials will buffer the pH to hyperalkaline conditions in the range 13.1 to 10.5, creating a so-called chemically disturbed zone (CDZ) in the host rock and/or local environment (Berner, 1992). In addition, hyperalkaline conditions prevail in many contaminated land scenarios, for example at Sellafield, UK (Wallace et al., 2012, 2013), and associated with the waste storage tanks at the Hanford Site in Washington State, USA (Catalano et al., 2004; Wan et al., 2009). Most geological disposal concepts and interim storage sites utilise iron and steel in the engineered barrier materials (e.g. steel canisters for the wasteform) or structural materials during construction (e.g. rock bolts). Anaerobic corrosion of steel leads to the formation of magnetite (Musić et al., 1993) which has been shown to be effective at removing uranium from solution through reductive immobilisation (Dodge et al., 2002; Duro et al., 2008). However, there has been relatively little investigation of the structural environment of U incorporated into magnetite and the effect of oxidation of the host mineral. Understanding the changes in uranium speciation during crystallisation of iron (oxyhydr)oxides, and particularly magnetite, under alkaline conditions relevant to disposal of
radioactive waste and contaminated land is important to enable prediction of the long term stability and environmental fate.

In this contribution the incorporation of uranium into magnetite under alkaline conditions was examined to determine the likely speciation of the incorporated U, including oxidation state and bonding environment, the effects of changing pH, the amount of uranium sequestered, and the fate of U following oxidation of the magnetite with air. Ferrihydrite was used as the starting material and magnetite crystallisation was induced by addition of aqueous Fe(II) (Tronc et al., 1992; Hansel et al., 2003). Throughout this process, the partitioning behaviour of U(VI) was followed, in two synthetic cement leachates (pH 10.5 and 13.1). After a period of ageing, the systems were then exposed to oxidising conditions to test the recalcitrance of any iron oxide associated uranium. Solution chemistry data was combined with quantitative powder X-ray diffraction (qXRD), transmission electron microscopy (TEM), and X-ray absorption spectroscopy (XAS) to characterise the fate of uranium during magnetite crystallisation and reoxidation at high pH.

6.2 Materials and Methods

6.2.1 Experimental setup

Batch experiments were used to follow the Fe(II)-induced crystallisation of ferrihydrite to magnetite in two U(VI) amended synthetic cement leachates chosen to simulate early (pH 13.1) and late (pH 10.5) stage evolution of groundwater around a GDF (Berner, 1992; Marshall et al., 2014b; Moyce et al., 2014). The young cement leachate (YCL) reflects the early post-closure stage and is dominated by potassium and sodium hydroxide (KOH and NaOH, respectively) dissolution. By contrast, the old cement leachate (OCL) reflects the late post-closure stage when the aqueous chemistry is dominated by equilibrium with calcium-silicate-hydrate (C-S-H) phases. The leachates were prepared by first degassing MQ with oxygen-free nitrogen (OFN) for over 1 hour per litre before addition of the reagents. The YCL composition was: 5.2 gL\(^{-1}\) potassium hydroxide, 3.8 gL\(^{-1}\) sodium hydroxide and 0.1 gL\(^{-1}\) calcium hydroxide (Ca(OH)\(_2\)); and the OCL composition was: 15 mgL\(^{-1}\) calcium hydroxide (Ca(OH)\(_2\)). After addition of the reagents, during which time the solutions were continuously degassed with oxygen-free nitrogen, each leachate was sealed and left on the stir plate for 24 hours, after which it was stored in an anaerobic chamber (atmosphere of 5 % H\(_2\), balance N\(_2\)) maintained at < 1ppm O\(_2\) and CO\(_2\).

2-line ferrihydrite was synthesised as per Cornell and Schwertmann (Cornell & Schwertmann, 2003) and the Fe(III) content of the resultant paste was determined by dissolution in 1 M HCl.
and analysis by the ferrozine method (Viollier et al., 2000). A known quantity of ferrihydrite was equilibrated with the cement leachates at a solid to solution ratio of 4 gL^{-1} for 1 hour on an orbital shaker at room temperature and in the anaerobic chamber. Hydroxylation of the ferrihydrite surface induced a solution pH drop of approximately 1 – 2 pH units in the OCL over the course of a few hours, but no pH drop was observed in the YCL. The pH of the OCL was manually readjusted to the leachates’ initial pH (10.5) by KOH addition. In the coprecipitation experiments, the ferrihydrite-equilibrated leachates were spiked with U(VI) prior to Fe(II) addition to give an initial solution concentration of 4 ppm (1.7 x 10^{-5} mol L^{-1}). Crystallisation of magnetite was induced by addition of Fe(II) as 0.1 M FeCl_{2} to give a final Fe(II) to Fe(III) ratio of stoichiometric magnetite (1:2). Addition of the FeCl_{2} (pH ~2) resulted in a fall the pH of the OCL and the YCL (~2 pH units) but the pH was immediately re-adjusted using KOH. The magnetite was aged for two days in the anaerobic chamber, after which the experiments were moved to a separate glovebag containing CO_{2}-free air (Zero Grade Air) and the experiments allowed to oxidise for 14 days. Parallel experiments were also set up without U(VI) present for full characterisation of the solid products. A further batch of experiments was setup as a sorption ‘control’ where the U(VI) was spiked to solution after 1 day of magnetite ageing. After 1 further day of ageing, samples of the solution and solid were taken and the experiment transferred to the glovebag containing CO_{2}-free air (Zero Grade Air) and allowed to oxidise for 14 days.

Coprecipitation experiments were also conducted, in both YCL and OCL, where the amount of Fe(II) added to the ferrihydrite suspension was lower than required to form stoichiometric magnetite. Only 28 % of the stoichiometric amount of Fe(II) was added to make an Fe(II):Fe(III) ratio of 0.14, as opposed to 0.5 for stoichiometric magnetite (Jolivet et al., 2004). This equates to an Fe(III):Fe(total) ratio of 0.88 rather than 0.67 of stoichiometric magnetite. These experiments were designed to test the ability of magnetite formed under conditions with low Fe(II) availability to reduce and incorporate U(VI) from solution. Such scenarios may arise during the early stages of steel corrosion in a GDF environment where the Fe(II) flux is limited, or in biologically active systems where Fe(II) flux will be controlled by microbial metabolism.

### 6.2.2 Analyses

Partitioning of uranium between the solid and solution was determined by analysis of the solution U concentration by ICP-MS (Agilent 7500cx). The uranium distribution in the solid phase was determined by dissolution of a time-series of the solid samples in 1 M HCl and the solution analysed for U and Fe by ICP-MS, after the method of Sidhu et al. (1978). The technique exploits the isotropic dissolution behaviour of magnetite, i.e. magnetite dissolves
equally in all crystallographic directions. Therefore, the concentration of Fe in solution is directly proportional to the volume of magnetite dissolved, and hence the relative concentration change in uranium solution concentration allows insight into its distribution within the magnetite particles (Sidhu et al., 1978).

Solids were characterised by XRD using a Bruker D8 diffractometer (λ = Cu K-α1). For TEM, solid samples were characterised using an FEI CM200 FEG-TEM, operating at 197 kV and fitted with a Gatan Imaging Filter (GIF 200) and an Oxford Instruments SDD EDX spectrometer running AZTEC software. Uranium LIII-edge XAS spectra were collected on beamline B18, Diamond Light Source, at room temperature in fluorescence mode using a 9-element Ge detector (Dent et al., 2009). Reference spectra from U(VI) and U(IV) standards (schoepite ((UO₂)₈O₂(OH)₁₂·12(H₂O)) and uraninite (UO₂), respectively) were collected in transmission mode. Data reduction and fitting of the EXAFS spectra were performed using the software packages Athena and Artemis (Ravel & Newville, 2005).

6.3 Results and Discussion

The characterisation of the experimental products in the inactive samples has been discussed in detail in Chapter 5 (Marshall et al., 2014b), but the results will be briefly outlined here also. In the YCL, magnetite was formed rapidly although some goethite (25.8 %) was also present in the aged material. In contrast, in the OCL, only magnetite is present in the aged material (Table 5-1 and Figure A2–1). After 14 days oxidation, in both systems the magnetite had partially oxidised to maghemite, evident by a decrease in the unit cell length (Gorski & Scherer, 2010) which was more pronounced in the OCL (Table 5-1).

All uranium was removed from solution during the crystallisation/ageing stage in both systems (Figure 6-1). After exposure of the aged solids to the oxygenated atmosphere for 14 days, 6 ± 1 % and 21 ± 1 % of the uranium was remobilised to solution in the YCL and OCL, respectively (Figure 6-1). 1 M HCl digestions were performed on the aged and oxidised magnetites, from both systems, to explore the U distribution profile in the solids (Figure 6-2). In the YCL system, the gradient of 1 suggested that U was uniformly distributed through the aged magnetite particles and oxidation of the host mineral had no effect upon the U distribution (Figure 6-2). In the OCL system, U distribution through the aged magnetite particles in the OCL system also shows a uniform concentration throughout the particle. After 14 days oxidation in the OCL system, a similar uniform distribution is observed but with an offset along the y-axis suggesting that approximately 15 % of the uranium associated with the solid was present at the surface (Figure 6-2). This is not altogether unsurprising given that after 14 days oxidation, 21 % of the total U
in the experiment was present in solution so that presumably a significant pool of ‘available’ U could re-adsorb to the oxidised magnetite surface.

![Graph](image)

**Figure 6-1** Concentration of U in solution (%) during magnetite ageing (days 0-2), and subsequent air oxidation (days 2-16) in YCL (red) and OCL (green).

![Graph](image)

**Figure 6-2** Release of U and total Fe during dissolution of magnetites in 1 M HCl in the YCL system (pH 13.1) (left) and OCL system (pH 10.5) (right). Black lines are reduced magnetite experiments, orange lines are oxidised magnetite experiments.

This behaviour was not observed in the YCL system and no pool of adsorbed U was evident in the dissolution data from the oxidised sample. The extent of oxidation in the YCL system after 14 days oxidation is limited, whereas in the OCL there has been appreciable oxidation over the same period (Chapter 5). This difference in oxidation between the leachates may explain the different behaviour of U in the two oxidised systems; the extent of oxidation and hence oxidative release of U to solution is lower in the YCL, but additionally, any remobilised U(VI)
may form colloidal U(VI) phases (Bots et al., 2014) and hence exhibit more limited re-
adsorption behaviour with the magnetite.

Magnetite oxidation to maghemite proceeds via outward migration of Fe(II) (Sidhu et al., 1977; 
Tang et al., 2003; Gorski et al., 2010). U(VI) and U(IV) have crystal radii (in octahedral 
coordination) of 0.87 Å and 1.03 Å, respectively, whilst the crystal radii of Fe(III) and Fe(II) (in 
octahedral coordination, high spin) are 0.785 Å and 0.92 Å, respectively (Shannon, 1976). The 
uniform distribution of U in the oxidised samples, particularly in the OCL system, suggests that 
least some fraction of U is retained during oxidation and it is not completely ejected from 
the structure (Figure 6-2), despite the comparatively large crystal radii of U compared to Fe. In 
magnetite, similar uniform distributions have been observed for Co, Ni and Zn, whereas Cu, 
Mn and Cd have been observed to have a dominantly (near) surface accumulation (Sidhu et al., 
1978). Further to this, Tc was also observed to have a near surface distribution predominance 
(Chapter 5). It has been suggested that the comparative ionic charge, radii and 
electronnegativity all have an influence on the substitution behaviour of different elements 
within host minerals (Sidhu et al., 1978), but it is unclear which characteristic dominates. 
Further to this, the ability of an element to exhibit the Jahn-Teller effect (Jahn & Teller, 1937) 
will affect its substitution behaviour (Sidhu et al., 1978). Simple solution enrichment may 
explain instances of accumulation in the near surface; if substitution of a trace metal is initially 
unfavourable, the concentration in solution will increase with respect to Fe as Fe is depleted 
during crystallisation, resulting in a greater distribution of the trace metal in the solid with 
time (Sidhu et al., 1978).

6.3.1 X-ray Absorption Spectroscopy

U L_{III}-edge XANES and EXAFS spectra were collected on aged magnetite from the YCL (pH 13.1) 
and OCL (pH 10.5) coprecipitation and adsorption experiments, along with an oxidised 
magnetite from the OCL coprecipitation experiment. The XANES spectra are shown in Figure 3 
with the U(VI) and U(IV) reference spectra. It is clear that in all experiments U(VI) reduction 
occurred with an obvious shift in the energy of the adsorption edge of all experimental spectra 
towards that of the U(IV) standard (Figure 6-3). However, the edge position of the three 
coprecipitation experiments’ spectra ((d)-(f)) were approximately 1 eV higher than both the 
U(IV) standard and the parallel adsorption experiments ((a)-(c)). This higher edge energy in the 
coprecipitation experiments could potentially result from either mixed valence U in multiple 
sites within the sample (e.g. incorporated U(IV) and adsorbed (U(VI)) or it could indicate the 
presence of U(V) stabilised through incorporation into the magnetite structure (Huber et al., 
2012), which has also been reported for other iron oxides (Ilton et al., 2010, 2012; Boland et
al., 2014). Additionally, the coprecipitation experiments’ spectra displayed a broad white line with a shoulder on the rising edge (Figure 6-3) that was absent in the sorption samples and which has previously been attributed to U(V) or U(VI) in octahedral uranate coordination (Vanden Berghe et al., 2002; Soldatov et al., 2007). Therefore, both the partial shift to lower absorption edge energy and the shoulder feature in the coprecipitation experiments suggest that U was at least partially present as U(V) in these samples. The YCL adsorption sample also displayed a broad white line, although there was little evidence for a shoulder on the rising edge and the edge position was aligned to the U(IV) reference. In contrast to the coprecipitation experiments, this suggests that the dominant signal was from U(IV), likely to be UO₂. However, the broad white line may indicate a small proportion of the U becoming incorporated into the magnetite surface as a result of dynamic equilibrium or crystal ageing (e.g. Ostwald ripening (Kahlweit, 1975)).

![Figure 6-3 U LIII-edge XANES spectra. (a) uraninite (U(IV) reference); (b) OCL adsorption; (c) YCL adsorption; (d) OCL coprecipitation aged; (e) OCL coprecipitation oxidised; (f) YCL coprecipitation aged; (g) schoepite (U(VI) reference).](image)

The EXAFS data and the respective fits for each sample are shown in Figure 6-4, and the refined fit parameters are given in Table 6-1. The OCL adsorption sample EXAFS is markedly different to the other spectra, lacking a peak in the EXAFS at k = 6 Å⁻¹, and also lacking a peak in the Fourier transform (FT) at 3 Å. It was expected that UO₂ would reductively precipitate on the preformed magnetite surface (Singer et al., 2012a; Latta et al., 2014) and indeed this sample was fit using the uraninite (UO₂) structure with the addition an Fe shell at 2.97 Å (Table
6). The presence of the Fe shell suggests that some component of U(IV) may be adsorbed U(IV) (Latta et al., 2014). Fitting of the aged OCL coprecipitated sample assumed incorporation of U into the magnetite octahedral site. The refined U-Fe distances for the two Fe shells (3.21 Å and 3.46 Å) corresponded well to the Fe-Fe distances for the octahedral site in magnetite structure (2.97 Å and 3.48 Å). The longer U-Fe distance of the first shell (3.21 Å versus 2.97 Å) is due to expansion of the octahedral site to accommodate U in place of Fe, as predicted by a modelling study of uranium incorporation into iron oxides (Kerisit et al., 2011). The crystal radius depends upon the coordination and the oxidation state of the element in question; in six-fold coordination, U(IV), U(V) and U(VI) have crystal radii of 1.03 Å, 0.90 Å and 0.87 Å, respectively (Shannon, 1976); whilst the crystal radii of Fe(II) and Fe(III) in six-fold coordination (high spin) are 0.92 Å and 0.785 Å, respectively (Shannon, 1976). Both Fe(II) and Fe(III) occupy the octahedral sites in the magnetite inverse spinel structure, but substitution of U into the structure is likely to preferentially replace Fe(III) to aid charge balance. Therefore, the expansion of the site is observed, as in other instances of metal incorporation (Dardenne et al., 2002; Walter et al., 2009). The presence of the shoulder on the rising edge in the XANES spectrum was consistent with U(V) in the OCL aged sample. However, the axial U-O distance (1.81 ± 0.01 Å) is short for a U(V) uranyl distance (1.90 – 2.05 Å (Burns et al., 1997; Docrat et al., 1999)) and so may indicate an additional component of adsorbed U(VI) is also present (Singer et al., 2012b). Additionally, a small contribution from a U-U shell was required at 3.95 Å to fit the peak in the FT at around 4 Å. This was attributed to contribution from U(IV) as UO₂ precipitates on the aged magnetite surface. The coordination number of the second Fe shell (3.1 ± 1.5) is lower than expected (6) and is likely due to nanoparticulate effects (Yanina & Rosso, 2008), and as we suggest that some of the U is present as UO₂ this will also decrease the effective coordination numbers. The same model was applied to the OCL oxidised sample. The U-O interatomic distance of the uranyl shell lengthened to 1.87 Å, possibly suggesting a diminished adsorbed U(VI) component and increased incorporated U(V) component due to oxidative recrystallisation of the magnetite. The Debye-Waller factor for this shell is relatively large and indicates a degree of static disorder from a number of overlapping contributions at similar U-O distances. The other U-O shells remain relatively unchanged from the aged model, as does the first Fe shell at ~3.2 Å. However, a second Fe shell cannot be resolved in the fit and the UO₂ component is entirely absent, as can be seen in the FT. This suggests that oxidative dissolution of precipitated UO₂ is the dominant mechanism for the elevated release of U back into solution in this system.

Fitting of the YCL adsorption sample was approached in the same way as the OCL adsorption sample. The EXAFS data from the YCL adsorbed sample, however, share more similarities with the OCL aged and oxidised samples than with the OCL adsorbed sample (e.g. peak at 6 Å⁻¹).
Further to this, a very short U-O distance (1.70 Å) was required to fully fit the U-O peak in the FT and this may reflect the presence of adsorbed U(VI) or uranate phases (e.g. Ca-clarkeite (Bots et al., 2014)) on the surface. Additionally, the U-Fe distance in this adsorbed sample is similar to the U-Fe distance from the OCL aged and oxidised samples, suggesting that some U is incorporated into the magnetite and not solely adsorbed at the surface. Similar behaviour has been observed before where over time, adsorbed radionuclides have become incorporated into magnetite (Huber et al., 2012; Kobayashi et al., 2013). The EXAFS data of the YCL aged sample does not appear to be similar to the OCL aged and oxidised samples, despite the obvious similarities of the XANES spectra. The FT of the YCL adsorbed sample has three distinct peaks which roughly correlate to the three peaks observed in the FT of the OCL aged sample, but the relative magnitude of the peaks was greater in the YCL example, particularly for the U-U shell (3rd peak, ~ 4 Å), indicating the presence of strong U-U bonds. The EXAFS was best fit using similar U-O and U-Fe shells to the OCL aged and oxidised samples (at 2.17 Å and 3.12 Å, respectively) but also with contributions from a calcium-uranate phase comprising; one uranyl U-O distance at 1.69 Å, two Ca at 3.41 Å, and two U-U shells at between 3.8 – 4.2 Å, similar to the structure of Ca-clarkeite (Bots et al., 2014). U(VI) in solution in the YCL (pH 13.1) has been shown to be over 99 % colloidal in systems with and without mineral phases present (Bots et al., 2014; Smith et al., 2014). This suggests that during coprecipitation the U(VI) interaction with the crystallising magnetite was via a nanoparticulate colloidal phase and not via ionic solution species, leading to the possibility of adsorbed nanoparticulates and even potentially entrapped colloidal inclusions.

**Figure 6-4**  U L\textsubscript{III}-edge \(k^2\)-weighted EXAFS spectra (left) and Fourier Transforms plotted without phase shift (right). Black lines are data and colour lines are fits to the data; (a) OCL adsorption; (b) OCL coprecipitation aged; (c) OCL coprecipitation oxidised; (d) YCL adsorption (e) YCL coprecipitation aged.
Table 6-1 Details of EXAFS fit parameters of U adsorbed to, and coprecipitated with magnetite and subsequent air oxidation

<table>
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<th>σ² (Å²)</th>
<th>ΔE₀ (eV)</th>
<th>S₀²</th>
<th>χ²</th>
<th>R</th>
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<td>U-O₁</td>
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<td>2.33 (1)</td>
<td>0.013 (1)</td>
<td>2.8 ± 0.8</td>
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<tr>
<td></td>
<td></td>
<td>U-Fe₁</td>
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<td>0.014 (3)</td>
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<td></td>
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<td>0.034 (4)</td>
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<td></td>
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</tr>
<tr>
<td>(b)</td>
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<td>14.4 ± 1.3</td>
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<td></td>
<td></td>
<td>U-Fe₁</td>
<td>6.1 (24)</td>
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<td>0.018 (4)ᵇ</td>
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<td>U-Fe₂</td>
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<td>U-U₁</td>
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<td>0.007 (3)</td>
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<td>(c)</td>
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<td>0.014 (3)</td>
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<td></td>
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<td>U-U₁</td>
<td>3ᵃ</td>
<td>3.90 (2)</td>
<td>0.006 (2)ᵇ</td>
<td></td>
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<td>4.20 (8)</td>
<td>0.006 (2)ᵇ</td>
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CN denotes coordination number; R+ΔR denotes atomic distance; σ² denotes Debye-Waller factor; ΔE₀ denotes the shift in energy from the calculated Fermi level; S₀² denotes the amplitude factor; χ² denotes the reduced Chi square value; R denotes the ‘goodness of fit’ factor. ⁺Parameter was fixed. ⁃Parameters were tied in a given fit. S₀² was restrained to a value between 0.8 – 1.0. Numbers in parentheses are 1 standard deviation on the last decimal place.

Incorporation of uranium into magnetite has been modelled using atomistic (Kerisit et al., 2011) and quantum-mechanical (Shuller-Nickles et al., 2014) approaches. Kerisit et al. (2011) refined the structure around incorporated U(IV), U(V) and U(VI) atoms, in both octahedral and tetrahedral sites, with various charge compensation mechanisms to balance the excess charge imposed by the substituting U species. By contrast, Shuller-Nickles et al. (2014) targeted
specific incorporation modes including: U(VI) incorporation into an octahedral site coupled with either octahedral or tetrahedral vacancies; and U(IV) incorporation into an octahedral site with either creation of an octahedral vacancy or Fe(III) reduction to Fe(II) to maintain charge balance. They determined that incorporation of U(VI) in an octahedral site in place of an Fe(III), with coupled creation of an octahedral Fe(III) site vacancy in the immediate vicinity was the most energetically favourable. Furthermore, they reported U-Fe coordination of 4 rather than 6 for charge compensation purposes. With this arrangement, the U-Fe$_1$ atomic distances refined to 3.08 Å, whilst the equatorial U-O$_2$ distances were 2.13 Å. These are in close agreement with the refined interatomic distances and coordination numbers in the model presented here (Table 6-1). However, the axial U-O$_1$ distance was 2.26 Å, longer than their equatorial U-O$_2$ distance, and significantly longer than the 1.8 – 1.9 Å observed here and suggesting a component of adsorbed U(VI) in the current study. The equivalent model from atomistic simulations (Kerisit et al., 2011) does not distinguish between axial and equatorial O, however, the U-O distance reported (2.13 Å) corresponds well with the average distance reported here (2.11 – 2.22 Å) and from quantum-mechanical modelling (2.17 Å) (Shuller-Nickles et al., 2014). The Fe coordination observed here agrees well with quantum-mechanical modelling (Shuller-Nickles et al., 2014), but was in excess of that observed experimentally elsewhere (Huber et al., 2012). However, in contrast to the study of Huber et al. (2012), here U was present during magnetite formation indicating that U incorporation occurs dominantly during the rapid crystallisation phase, but continues during ageing.

### 6.3.2 Non-Stoichiometric Magnetite

XRD patterns from the non-active stoichiometric samples (Table 5-1 and Figure A2–1) coupled with a visual colour change (red brown to black/brown) during the ageing phase suggested that magnetite/maghemite was the dominant product. A previous study of spinel formation through Fe(II) adsorption to ferrihydrite (Tronc et al., 1992) offers some insight into the likely mineral product of the non-stoichiometric coprecipitation experiments here. They found that for an Fe(II):Fe(III) ratio of 0.10 – 0.15, two families of spinel particles formed, one small (25 – 30 Å) and one large (~130 Å), in addition to Fe(II)-ferrihydrite. During ageing, the Fe(II)-ferrihydrite disappears to the benefit of the small spinel particles. Chemical analyses determined that the small spinel particles were relatively Fe(II)-deficient (Fe(II):Fe(III) ≈ 0.05 – 0.07), whilst the larger spinel particles were relatively Fe(II)-rich (Fe(II):Fe(III) ≈ 0.30). Therefore, it is likely that non-stoichiometric magnetite is indeed the dominant mineral product formed during the experiments here. Due to the mechanism of magnetite oxidation, where Fe(II) migrates outwards towards the surface where it is oxidised (Sidhu et al., 1977), these non-stoichiometric magnetites also offer additional insight into the fate of U associated
with oxidised magnetites, although these samples were never exposed to oxidising conditions. The behaviour of U in solution during the crystallisation follows the same trend as the stoichiometric experiments under anoxic conditions, whereby all U is removed instantaneously from solution and is associated with the solid phase throughout.

Figure 6-5 U L_{III}-edge $k^3$-weighted EXAFS spectra (left) and Fourier Transforms plotted without phase shift (right). Black lines are data and colour lines are fits to the data; (a) YCL non-stoichiometric coprecipitation; (b) OCL non-stoichiometric coprecipitation.

Table 6-2 Details of EXAFS fit parameters of non-stoichiometric magnetite coprecipitation samples

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<th>$σ^2$ (Å²)</th>
<th>ΔE₀ (eV)</th>
<th>S0²</th>
<th>$Χ^2_v$</th>
<th>R</th>
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<tbody>
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<td>(a)</td>
<td>YCL</td>
<td>U-O₁</td>
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<td>1.68 (2)</td>
<td>0.006 (3)</td>
<td>10.5 ± 1.1</td>
<td>0.80 (7)</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>U-O₂</td>
<td>5</td>
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<tr>
<td></td>
<td></td>
<td>U-Fe₁</td>
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<td>0.010 (1)</td>
<td></td>
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<td>U-Ca₁</td>
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<td>0.005 (3)</td>
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<td></td>
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<td>U-U₁</td>
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<td>3.90 (2)</td>
<td>0.004 (1)</td>
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<td>U-U₂</td>
<td>1</td>
<td>4.22 (7)</td>
<td>0.004 (1)</td>
<td></td>
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<td></td>
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<tr>
<td>(b)</td>
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<td>1</td>
<td>1.74 (2)</td>
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<td>13.8 ± 1.1</td>
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<td></td>
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<td>U-Fe₁</td>
<td>3</td>
<td>3.19 (2)</td>
<td>0.010 (2)</td>
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<td>3.37 (3)</td>
<td>0.010 (2)</td>
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CN denotes coordination number; R+ΔR denotes atomic distance; $σ^2$ denotes Debye-Waller factor; ΔE₀ denotes the shift in energy from the calculated Fermi level; S0² denotes the amplitude factor; $Χ^2_v$ denotes the reduced Chi square value; R denotes the ‘goodness of fit’ factor. Parameter was fixed. Parameters were tied in a given fit. S0² was restrained to a value between 0.8 – 1.0. Numbers in parentheses are 1 standard deviation on the last decimal place.

U L_{III}-edge EXAFS were collected on non-stoichiometric magnetites aged for 2 days in the YCL and OCL (Figure 6-5). Comparison of these spectra with the stoichiometric magnetite spectra
reveals clear similarities. The YCL and OCL non-stoichiometric data are very similar to the stoichiometric YCL aged data (Figure 6-4) and OCL oxidised data, respectively. Therefore, the same models were applied to the non-stoichiometric data as used to fit their complimentary stoichiometric data sets (Table 6-2). In each case, fits to the non-stoichiometric data were obtained with excellent agreement to the model. In the YCL system the same mixture of incorporated U and a Ca-uranate phase is obtained, whilst in the OCL system, U is purely incorporated into the magnetite.

6.4 Conclusions

The chemical dissolution data clearly suggest that uranium is incorporated into the reduced magnetite phase in both cement leachates (pH 10.5 – 13.1). Partial oxidation results in reordering of the magnetite structure to accommodate charge balancing vacancies as Fe(II) is oxidised to Fe(III), however it would appear that during this reordering a significant fraction of incorporated uranium was retained within the structure (Figure 6-2). XANES data suggest that U was present as U(V), although contributions from both U(IV) and U(VI) cannot be excluded. Fitting of the EXAFS data suggests that U, likely to be U(V), is incorporated into an expanded octahedral site within the magnetite structure in place of Fe; likely to be Fe(III) to aid charge balance. The short axial U-O interatomic distances resolved in the EXAFS may indicate contributions from U(VI), although these contributions may be from adsorbed rather than incorporated U(VI). Some U may have been present as U(IV), either as incorporated U(IV) or as surface UO$_2^-$, however the data suggested they were minor components.

In the YCL coprecipitation sample, in addition to U(IV), some of the U appears to be present as a U(VI)-Ca-uranate phase. This is due to the formation of U(VI) colloids in the YCL as opposed to U(VI) being present as an aqueous species as predicted by PHREEQC modelling (Bots et al., 2014). Despite the formation of U(VI) colloids at high pH, magnetite appears to have the ability to reductively immobilise U(VI) from solution through incorporation.

Magnetite is a common corrosion product of steel (Musić et al., 1993; Dodge et al., 2002), and may therefore potentially provide a pathway for significant incorporation and immobilisation of uranium derived from radioactive waste contained within a geological disposal facility, which is also, to a large extent, resistant to oxidative remobilisation.
Chapter 7 Long-term Alkaline Alteration of Biotite and the Fate of Uranium(VI)

7.1 Introduction

Biotite is an example of an Fe-bearing sheet silicate mineral, typically found in crustal rocks expected at depths considered for a GDF for radioactive wastes (200-1000 m (Defra, 2008)). Use of cementitious materials in a GDF, as either construction materials (e.g. cavern wall strengthening) or as part of the engineered barrier (e.g. wasteform grout or vault backfill) will lead to formation of a hyperalkaline plume as the re-saturating groundwater begins to dissolve these materials (Berner, 1992). The host rock mineralogy exposed to this hyperalkaline plume will begin to react; due to the dissociation of silicic acid at alkaline pH, the solubility of silicate minerals rapidly increases above pH 8-10 (Langmuir, 1996). Biotite and chlorite have been shown to be susceptible to hydroxyl attack and release of cations to solution (Malmstrom & Banwart, 1997; Gustafsson & Puigdomenech, 2003; He et al., 2005; Samson et al., 2005). The dissolution of the cementitious materials will result in formation of secondary calcium-silicate-hydrate (C-S-H) phases (Shaw et al., 2000). The release of cations to solution from mineral breakdown will drive formation of secondary minerals such as aluminium or magnesium containing silicate hydrates (Hong & Glasser, 2002). Further to these phases, released Fe has been inferred to form secondary iron oxides (He et al., 2005; Samson et al., 2005). Iron oxides have been shown to be important phases for limiting radionuclide mobility (Nico et al., 2009; Stewart et al., 2009; Ilton et al., 2010; Um et al., 2011; Marshall et al., 2014a, 2014b). Therefore, it is possible that breakdown of Fe-bearing silicate minerals in a GDF near-field hyperalkaline chemically disturbed zone (CDZ) may induce secondary Fe-(oxyhydr)oxide mineralisation which may interact with radionuclides to reduce their environmental mobility.

The single mineral Fe-oxide-radionuclide systems presented in Chapters 4-6 have successfully shown the ability of Fe-oxides to incorporate uranium and technetium. The experiments discussed in this chapter attempted to reproduce these results in a dynamic and heterogeneous system. Here, biotite has been exposed to a synthetic cement leachate (YCL, pH 13.1) to mimic the early stage of groundwater evolution around a GDF, first qualitatively to assess biotite breakdown and second to quantify the impact upon uranium dissolved in the cement leachate.
7.2 Initial Solid Characterisation

![Secondary electron micrographs of (a) fresh platy biotite grains and (b) a single grain viewed parallel to the (001) cleavage plane.](image)

Figure 7-1 Secondary electron micrographs of (a) fresh platy biotite grains and (b) a single grain viewed parallel to the (001) cleavage plane.

Biotite specimens, from the Silver Crater Mine near Cardiff, Ontario, Canada, were purchased from the Excalibur Mineral Company. The biotite was crushed using a mechanical ceramic ball mill and sieved to obtain the 125 – 250 µm size fraction for use in the experiments. The sieved material was then washed by sonication in isopropanol with removal of the supernatant containing any ultrafine material. This washing step was repeated three times in total prior to drying of the solid in an oven at 60 °C for 24 hours. Morphological characterisation was conducted via SEM. Samples were prepared on standard 1 cm aluminium stubs with an adhesive carbon pad and coated with 10 nm of platinum/palladium prior to imaging. Figure 7-1 shows the fresh, unaltered biotite displaying characteristic platy morphology of biotite with straight-edged, close-packed leaves. The specific surface area (SSA) of the crushed material was determined via the BET method and determined to be 0.69 ± 0.1 m² g⁻¹. Compositional analysis of the fresh material was performed using XRD and electron microprobe. Figure 7-2 shows the indexed XRD pattern of the fresh biotite along with the published pattern of Takeda and Ross (1975). The pattern from the fresh biotite displays preferred orientation and hence only the {001} planes are apparent. Two polished thin sections were made from representative hand specimens that were then analysed on the electron microprobe at 20 equally spaced points along a transect across the centre of the sections shown in Figure 7-3. An average composition was then calculated from the 40 individual analyses (Table A3–1 to Table A3–4) to give the following compositional formula:

\[
K_{1.80}Na_{0.15}(Mg_{3.15}Fe^{2+}_{2.34}Ti_{0.25}Mn_{0.11})(Si_{5.99}Al_{1.96}O_{20})(OH)_4
\]

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Trace amounts of Ca and Cr were detected in approximately half the points analysed on the microprobe, but these were omitted from the calculations of the biotite formula.

Figure 7-2 XRD patterns of fresh, crushed biotite (top) and biotite of Takeda and Ross (1975) (bottom).

Figure 7-3 Secondary electron micrographs of biotite specimens (a) 65190 and (b) 65191, analysed using electron microprobe.

7.3 Phase 1 Experiments

A test experiment (Phase 1) was devised to determine the ability to induce mineralogical alteration in the laboratory and the most suitable analytical techniques to follow the reaction. The Phase 1 experiment utilised a chemostat reactor to automatically control the experimental conditions, as described below.
7.3.1 Experimental Setup

An Infors Labfors 4 bio-incubator fitted with an integral redox potential electrode capable of monitoring and maintaining the system pH was used for the experiment. The pH was maintained within user-defined limits (pH 13.1 ± 0.1) by the addition of acid and base via calibrated automated peristaltic pumps. An integrated motorised stirrer was located on the PEEK reaction vessel head-plate which enabled mixing within the sealed reaction vessel. A further user-controlled peristaltic pump allowed dosing of experimental reagents into the reaction vessel. The atmosphere inside the reaction vessel headspace was controlled through purging with either nitrogen or laboratory air, depending upon the desired redox environment. The input gas was passed through a series of scrubbers to remove CO$_2$ to eliminate potential uranium carbonate complexation reactions. The scrubbers consisted of four sequential dreschel bottles: the first two contained 4 M NaOH; the third, water; and the fourth was empty, to prevent condensation input from the saturated gas into the reaction vessel. Nitrogen gas was of zero-grade quality and certified CO$_2$-free so was not required to pass through the trap, however, this was still performed to ensure equal conditions (e.g. gas vapour saturation) were maintained between reducing (N$_2$) and oxidising (air) stages. Laboratory air was pumped through the system with the pump placed after the NaOH traps to avoid overpressurisation in the setup. The reaction vessel outlet was passed through a water trap to maintain a closed system in the event of a pump failure. A schematic diagram of the chemostat setup is shown in Figure 7-4. Sampling of the experiment was performed using a syringe, purged with zero grade N$_2$ three times.

The chemostat was controlled from a laptop interface which also logged the real-time data fed back from the chemostat. The pH was maintained at 13.1 ± 0.1 through the addition of a base solution at 10 times the ionic strength of the experimental solution. This ensured that the overall ratio of the different components was not altered during pH control. The total volume of base added and the volume of reagent added were also logged, as was the stirring rate and the redox potential.
Samples were removed from solution and filtered to 0.45 µm to track the total Fe in solution, via the ferrozine method (Viollier et al., 2000), as a measure of silicate breakdown. No samples were taken for major cation analysis by ICP-AES from Phase 1. Solid samples were removed, washed in isopropanol and dried in a desiccator. The solid samples were characterised via SEM and the SSA determined by the BET method.

### 7.3.2 Phase 1 Results

The SSA rose rapidly to approximately double (1.5 m$^2$g$^{-1}$) that of the freshly prepared biotite (0.7 m$^2$g$^{-1}$) over the first few days of reaction, remaining at 1.5 m$^2$g$^{-1}$ after three weeks. However, after eleven weeks of exposure to the YCL, the SSA had fallen to 0.9 m$^2$g$^{-1}$, although this still represented a 30% increase over the fresh biotite SSA. There was no detectable change in the total Fe in solution as measured by the ferrozine method (Viollier et al., 2000), with all data within error (0.46 ± 0.05 ppm).

Figure 7-5a illustrates a biotite crystal edge after 78 days contact with the YCL. There appeared to be extensive vermiculitisation, manifest as crenulation of the biotite sheets due to an expansion of the interlayer spacing as H$_2$O replaces K. Alteration product and debris had collected between the cleavage planes, however, this was reduced in comparison with the 20 day sample. A possible explanation for this is that with increased breakdown of the biotite and greater separation of the cleavage planes; the rapid stirring of the solution prevented the fine material from collecting between the cleavage planes. This was also evident from the increase in fine-grained material held in suspension which was harvested using a gravity settling column to allow analysis of the fine-grained material separately.
Figure 7-5 SEM evidence for vermiculitisation and secondary iron (oxyhydr)oxide crystallisation. (a) secondary electron image of crenulated biotite grain, typical of vermiculitisation; (b) high magnification secondary electron image of point marked in (a) showing secondary mineralisation that has acicular habit, possibly goethite; (c) mixed secondary and backscattered electron image showing high density (bright) coating of biotite grain; (d) EDX spectrum taken at point marked in (c) showing bright region is rich in Fe.

Figure 7-5b illustrates a cluster of goethite needles amongst the detrital material between the cleavage planes of the biotite grain in Figure 7-5a. Analysis by EDX and imaging with backscattered electrons was not possible on this cluster because it was sitting deep between the cleavage planes, preventing clear line of sight to the detectors. However, the needle-like morphology is indicative of goethite, which is the stable iron oxide phase at pH 13 (Langmuir, 1996). Figure 7-5c is a mixed secondary and backscattered electron image taken on the fine fraction of the solid sample harvested on 78 days through gravity-settling the bulk solid. This image shows an Fe rich coating, on a small detrital biotite grain. The coating shows up as a bright region due to the higher electron density and is confirmed by the EDX spectrum given in Figure 7-5d.
7.3.3 Lessons Learnt from Phase 1

Characterisation of the solids through SEM confirmed that alkaline breakdown was occurring at an appreciable rate to be observed in the laboratory. However, it was suspected that the rapid rate of stirring was contributing to the breakdown through mechanical abrasion. This was evident from the analysis of much of the detrital material proving to be fragments of biotite with only minor amounts of secondary mineralisation apparent. It was therefore decided that the Phase 2 experiments should not be continuously agitated, with only occasional mixing to prevent cementation of the solid material.

It was decided that release of Fe to solution needed to be quantified using a more sensitive technique than the ferrozine method, which was also capable of quantifying the other major cations released to solution, such as K, Na, Al and Si. Therefore, in the Phase 2 experiments, solution samples were analysed by ICP-AES.

7.4 Phase 2 Experiments

Long-term batch experiments (Phase 2) were setup with a number of alterations to the basic experimental conditions. A batch experimental setup was utilised to allow investigation of a number of variables simultaneously and hence over a greater timescale than was possible using the chemostat setup. All batch experiments were incubated at 40 °C to mimic the elevated temperatures expected in a GDF environment as a result of the geothermal gradient (Busby et al., 2011).

7.4.1 Experimental Setup

Four batches were set up to accomplish a 2x2 experimental matrix where the variables were headspace atmosphere (reducing; oxidising) and radioactivity (inactive; 10 ppm U-238). Reducing batches were maintained with a CO₂-free nitrogen headspace, whilst oxidising batches were purged with CO₂-free air. The same apparatus was used for purging the inlet gas of CO₂ in both experiments, as outlined in Phase 1. However, a valved ballast line was installed to enable regulation of the pressure through the system since it was not possible to alter the pump’s flow rate. However, by closing the ballast valve, more flow was forced through the experiment, and conversely, when the ballast line was opened, the flow through the system was reduced.

Calibration of the pH electrode was undertaken with buffers maintained at 40 °C to eliminate introduction of potential temperature effects which may induce bias between the calibration and experiment measurements. Calibration was always undertaken with 3 buffers: pH 10, 12
and 13. The oven was maintained at a temperature of 40 °C ± 0.5 °C for the duration of the experiment. However, the experiments were removed from the oven during sampling and pH checking operations which will have resulted in temperature perturbations down to ~ 20 °C although this was not monitored.

### 7.4.1.1 Non-radioactive Batch Experiments

Non-radioactive batch experiments were set up to provide material for characterisation of the solids, to assess the extent of any mineral breakdown and secondary mineralisation. Each batch, reducing and oxidising, was set up in duplicate, with 10 g L\(^{-1}\) of biotite contacted with the YCL. The duplicate bottles were placed in line in a closed system and their headspace was periodically purged with the respective gas. Sampling and pH monitoring required opening each individual bottle; however, these operations were conducted under flowing gas to prevent ingress of O\(_2\) or CO\(_2\) to the system. During the first 6 months of the experiment, the bottles remained connected to the in-line closed system. Thereafter, the bottles were isolated. A schematic of the experimental setup is shown in Figure 7-6.

![Schematic diagram of non-radioactive batch experimental setup](image)

**Figure 7-6** Schematic diagram of non-radioactive batch experimental setup.

Slurry samples were removed from each experiment and phase separated by centrifugation at 4000 rpm (1700 g) for 5 minutes. A portion of unfiltered supernatant was kept as an archive sample, frozen at -80 °C. Solution samples were taken from the remaining supernatant and filtered to 0.45 µm using syringe top filter units with a polyethersulfone (PES) membrane (chemically resistant to extreme base). Samples were then acidified in nitric acid as preservative until preparation for analysis of major cations in solution by ICP-AES. Solid
samples were washed once in DIW to remove any residual salt and dried in a desiccator. All samples were manipulated for subsampling in the anaerobic chamber.

Evaporation from solution was a concern and three steps were taken to minimise and monitor potential mass loss: the input gas was vapour-saturated at room temperature as a result of passing through the CO$_2$ traps; each bottle was weighed before and after sampling; and a known quantity of chloride was added to each bottle. However, monitoring of chloride concentration via ion chromatography proved to be difficult given the high solution OH$^-$ concentration and so this method was subsequently abandoned. The mass lost due to evaporation was below 1%.

7.4.1.2 Radioactive Batch Experiments

Radioactive batch experiments were set up in triplicate along with a blank, containing no solid material. These experiments were scaled down with respect to the non-active experiments to comply with the principle of ALARP (as low as reasonably practicable) regarding the use of radioactive materials. The experiments were run at 10 g L$^{-1}$ of biotite, as per the non-radioactive batches. Each batch was housed in a desiccator fitted with gas inlet/outlet ports to provide a sealed environment with the ability to purge the headspace around the bottles. This arrangement also gave secondary containment to the radioactive materials, providing a safety function to the laboratory users. At each pH checking and sampling point, the batches were removed from the desiccator and transferred into an anaerobic chamber, maintained at <5 ppm O$_2$ and CO$_2$. Each bottle was spiked with uranium as U-238 to provide an initial solution concentration of 10 ppm (4.2 x 10$^{-5}$ mol L$^{-1}$), which was thermodynamically modelled (PHREEQC) to be below the solubility of any U(VI) phase in the synthetic leachate, and confirmed by ultra-filtration of solubility experiments. A schematic diagram of the setup of the radioactive batch experiments is shown in Figure 7-7.

Slurry samples were removed from each experiment and phase separated by centrifugation at 4000 rpm (1700 g) for 5 minutes. A portion of unfiltered supernatant was kept as an archive sample, frozen at -80 °C. Solution samples were taken from the remaining supernatant and filtered to 0.45 µm using syringe top filter units with a polyethersulfone (PES) membrane (chemically resistant to extreme base). Samples were then acidified in nitric acid as preservative until preparation for analysis of major cations in solution by ICP-AES and U-238 by ICP-MS. Solid samples were washed once in isopropanol to remove any residual salt and dried in a desiccator. All samples were manipulated for subsampling in the anaerobic chamber.
7.4.2 Results

7.4.2.1 Solution Chemistry

The solution concentrations of the major elements (K, Na, Al, Si, Ca, and Fe) through time over the first six months of the Phase 2 experiments are shown in Figure 7-8. The concentrations of K and Na were relatively stable throughout and reflected the high background concentrations of the YCL. Hence, it is not possible to determine any release of K or Na from the biotite as a result of vermiculitisation. No differences were observed between the oxic and anoxic experiments. Similarly, Al was relatively stable in solution over the course of the experiments, with no differences observed between oxic and anoxic experiments. The higher Al concentration observed in the experiments containing biotite and uranium was most likely due to differences in the total mass of biotite between the two sets of experiments and not due to any effect from the presence of uranium. The data for Si display a similar artefact. However, the Si data suggested that steady state was not reached since a general increasing trend was evident. Additionally, the experiments containing biotite but no uranium (open diamonds) appeared to be diverging between the oxic and anoxic treatments. This trend was not observed in the experiments which also contained uranium and so no firm conclusions can be drawn regarding preferential breakdown of biotite in the oxic experiments.
Figure 7-8 Solution chemistry data for K, Na, Al, Si, Ca and Fe in solution during Phase 2 batch experiments. Yellow markers = oxic experiments; green markers = anoxic experiments. Diamonds are experiments that contained biotite; crosses are blank experiments that didn’t contain biotite; Open diamonds are experiments that contained no uranium; filled diamonds are experiments that contained uranium. Errors are smaller than the size of the point markers.

There is an initial spike in the Fe solution data, which is more pronounced in the anoxic treatment. However, by 11 weeks, the Fe in solution is close to the detection limit and by 6 months, is below detection. This suggests a rapid release to solution, most likely from residual Fe coatings but potentially from biotite breakdown also, which is then lost through secondary precipitation. It is difficult to quantify the extent of Fe contribution from biotite breakdown. Sequential extractions for the reducible iron oxides and total silicate Fe were inconclusive of any trends in the data. The behaviour of uranium in solution over 3 years in the Phase 2 experiments is shown in Figure 7-9. Uranium was spiked to give an initial solution concentration of 10 ppm; however, the measured initial concentration was below 9 ppm,
suggesting uranium was above the solubility limit, at least locally, and some precipitation occurred. Interestingly, the experiments with biotite present (closed diamonds) remain at steady state with approximately 8 ppm U in solution whilst in the experiments with no biotite present (crosses) a decreasing trend with time is observed. This decreasing U in solution trend is more pronounced in the oxic (yellow) experiment than the anoxic (green).

Figure 7-9 Uranium in solution during Phase 2 experiments.

7.4.2.2 Scanning Electron Microscopy

The Week 6 samples from both the oxic and anoxic experiments have been imaged and reveal no major differences between the two. There is evidence of vermiculitisation with some grains displaying folding and crinkling at their edges. However, there is no abundance of detrital material between cleavage planes, supporting the theory that weathering was accelerated due to mechanical breakdown in the Phase 1 experiment. This has been eliminated by manually agitating the solution and not constantly stirring. Small (<1 µm) spherical particles are observed on the basal plane at, and near to, the grain edges which are rich in calcium (Figure 7-10). These are observed in equal quantities in both the oxic and anoxic sample, as well as in the Phase 1 images, although these were overlooked originally. These are likely to be calcite precipitations, although their exact mineralogy was not determined. It is possible that these were a calcium silicate phase but it is unlikely from preliminary analyses using SEM-EDX. It is not known how quickly these precipitates formed; however, there were similar features visible within approximately 1 week in the Phase 1 experiments.
The same features are also visible after 32 weeks alteration in both the oxic and anoxic experiments (Figure 7-11). Bots et al. (2014) observed formation of uranium colloidal nanoparticles in the YCL within several hours which were stable in solution for greater than 2.5 years. They determined the dominant U phase to be a sodium uranate, clarkeite, but with substitution of K and Ca into the structure. The formation of such colloidal nanoparticles in the Phase 1 and Phase 2 systems investigated here may at least partially explain the observed loss of Ca and U from solution. The Ca phase precipitations visible in Figure 7-10 and Figure 7-11 cannot be clarkeite as these are observed in the non-uranium containing systems. Ingress of CO$_2$ during sampling and/or CO$_3^{2-}$ impurities from the initial chemicals are potential sources of CO$_3^{2-}$ contamination which may lead to calcite formation.

**Figure 7-10** SEM and EDX evidence of Ca phase crystallisation. (a) secondary electron image perpendicular to (001) plane; (b) EDX spectrum taken at location 1; (c) EDX spectrum taken at location 2; (c) secondary electron image parallel to (001) plane.
Figure 7-11 Secondary electron images of Phase 2 experiments (without uranium) after 32 weeks alteration in (a) oxic and (b) anoxic environments. Figure 7-11 reveals limited evidence of vermiculitisation, which is especially visible in the oxic system (Figure 7-11a). However, the extent of reaction in Phase 2 after 32 weeks is much less than was observed in Phase 1 after 20 days, confirming the detrimental effect of the mechanical mixing in Phase 1.

7.5 Conclusions

From these experiments, it is evident that the biotite sheet silicate undergoes destructive alteration with the subsequent release of mineral forming cations, such as Al and Si, as has been previously observed (Murakami et al., 2004; Samson et al., 2005; Sugimori et al., 2008). However, the extent of alteration is limited in our Phase 2 experiments where we have avoided accelerated weathering of the mineral through not actively stirring the experiments. Therefore, it is very difficult to determine the extent of any secondary mineralisation on the timescales presented herein, and what effect that may have on the fate of uranium present in these systems. Goethite and other iron oxides were observed in the Phase 1 experiments and so it can reasonably be expected that, given time, the same secondary mineralisation should occur in the Phase 2 experiments. In Chapter 4, it was shown that uranium can become incorporated into hematite during crystallisation (Marshall et al., 2014a) and other authors have shown similar results for other iron oxides (Nico et al., 2009; Stewart et al., 2009; Boland et al., 2011, 2014). It is therefore reasonable to assume that a proportion of the uranium in the Phase 2 experiments should become associated with the secondary iron oxide products that are expected to form.

Sampling of these experiments continued beyond 6 months although only the uranium solution data are presented here. The solution data for the major cations, along with morphological analyses of the solid products is to be published by Rosie Hibberd and so this
data is not included within this thesis. The experiments have been retained and are ongoing with the hope that future students may continue to sample them to build a very-long term (>5 years) dataset for the fate of uranium during hyperalkaline alteration of biotite.

Formation of uranium colloid nanoparticles, such as clarkeite (Bots et al., 2014), is assumed to account for the observed lower-than-expected initial uranium solution concentration. This was observed in each experimental batch and has been investigated and confirmed by other researchers in the BIGRAD consortium. The formation of such nanoparticles may isolate a fraction of the total uranium pool from interacting with the biotite and its alteration products in the long term. However, 90% of the uranium pool was initially measured as ‘in solution’ and so this effect should be minimal.
Chapter 8  Concluding Remarks

8.1  Conclusions and Evaluation of the Thesis Hypotheses

The key aim of the project was to investigate mineral transformation processes that are likely to occur in and around model GDF and CDZ environments and determine the fate of uranium and technetium during these transformations. Prior to this work, incorporation of radionuclides into iron oxides has been shown to be possible but there is a discord between experimental data and modelling predictions regarding the structure around such substituted radionuclides. Here, a series of experiments were undertaken to understand incorporation of radionuclides into key iron oxide phases (hematite and magnetite) using state-of-the-art techniques to probe the atomic structure of the incorporated radionuclides and thus the mechanisms of reaction for these complex systems. The four hypotheses that this thesis set out to investigate in Chapters 4 – 7, respectively were:

- U(VI) will be incorporated into the structure of hematite as it crystallises from ferrihydrite
- Tc(VII) will be reduced and incorporated into the structure of magnetite as it crystallises from ferrihydrite
- U(VI) will be reduced and incorporated into the structure of magnetite as it crystallises from ferrihydrite
- Hyperalkaline alteration of Fe-bearing silicate minerals (e.g. biotite) will produce secondary iron oxide minerals which will sequester radionuclides from solution

In Chapter 4, through experiments where ferrihydrite was equilibrated with a U(VI)-containing cement leachate (pH 10.5) and incubated at 60 °C and 105 °C, it was shown that U(VI) is incorporated into an octahedrally coordinated environment via direct substitution for Fe(III) in the hematite structure, up to a concentration of 0.3 wt % U. Further to this, evidence from X-ray absorption spectroscopy was presented that showed uranyl bonds were retained upon incorporation to the mineral, albeit elongated from 1.81 Å to 1.87 Å due to steric constraints of the hematite lattice. This was in contrast to previous studies which suggested these uranyl bonds were lost upon incorporation (Duff et al., 2002; Ilton et al., 2012). Given the long-term stability of hematite, which is present in geological settings older than 1 Ga (Hitzman et al., 1992), and that iron oxides are implicated in retention of uranium in sediments (Payne et al., 1994), this mechanism of uranium sequestration may potentially be a significant pathway for immobilisation of U(VI) in selected environments.
In Chapter 5, ferrihydrite was equilibrated with Tc(VII)-containing cement leachates (pH 10.5, 12.5 and 13.1) and crystallisation to magnetite was induced via addition of aqueous Fe(II). X-ray absorption spectroscopy data were presented that showed Tc(VII) was reduced to Tc(IV) in all systems, with near complete incorporation of Tc(IV) into the octahedral site within the magnetite structure in place of Fe(III), and similar to that observed for Ti(IV) in titanomagnetites (Pearce et al., 2012). During oxidation for up to 152 days, 30–40% of Tc was remobilised to solution, but that which remained associated with the mineral product was retained as Tc(IV) in a very similar structural environment to the corresponding reduced sample. Additionally, dissolution of a time series of the solid phase materials during oxidation revealed Tc was preferentially located at the magnetite surface in reduced samples, but that a Tc-deficient, Fe-rich rind developed during oxidation, where the Tc mass balance equated to the Tc lost to solution. This indicates a diffusion controlled loss of Tc during oxidation which was impaired as the rind developed. During oxidation, spectral features appeared in the EXAFS in the k = 10–12 range which could not be satisfactorily fitted using the model for the reduced sample. However, the model for Tc(IV) incorporation into reduced magnetite was unable to account for vacancies which are generated during the topotactic transformation of magnetite to maghemite (Chapter 2.4.5); a possible mechanism for the poor fit observed in this region of the EXAFS for the oxidised samples. The influence of pH appeared to be minimal given the similar behaviour in all three cement leachates, reflecting the expected speciation of Tc in solution (pertechnetate, TcO$_4$$^-$$^-$) across the entire experimental pH range. XRD data revealed that goethite was also present during crystallisation at pH 12.5 and 13.1, but since none was present at pH 10.5 and there was no discernible change in the XAS data between the different leachates, Tc incorporation into goethite was not believed to be significant. Given that Tc(VII) was reduced and incorporated into magnetite over the entire experimental pH range and that magnetite has been shown to be a significant component in the corrosion of steel under anaerobic conditions, this study highlights the potential for significant retention of Tc in both radioactive waste disposal and contaminated land scenarios.

In Chapter 6, ferrihydrite was equilibrated with U(VI)-containing cement leachates (pH 10.5 and 13.1) and crystallisation to magnetite was induced via addition of aqueous Fe(II). Chemical extraction data suggested that U was incorporated throughout the solid phase in both systems and was retained as such after 21 days partial oxidation of magnetite. X-ray absorption spectroscopy data revealed that U chemistry was complicated in both systems; with potential contributions from U(IV), U(V) and U(VI). However, analysis of the XANES data suggested that the dominant species was U(V). Modelling of the EXAFS data supported the view that U was present as U(V), although contributions from U(VI), present either within the magnetite structure or adsorbed to particle surfaces, cannot discounted. Additionally, some U may be
present as surface adsorbed (non-uraninite) U(IV) or more likely as discrete \( \text{UO}_2 \) precipitates. After partial oxidation of the magnetite, 6 – 21% of the U (in YCL and OCL respectively) was present in solution, with a further 15% of the solid associated U in the OCL appearing to be present on the magnetite surface. Modelling of the EXAFS from the oxidised sample (OCL) indicated that the incorporated U remained in a similar environment to the reduced sample. In the reduced YCL system, there appeared to be a component of U(VI) which corresponded well to the structure of U(VI) colloids observed to form in the YCL. Formation of U(VI) colloids accounted for no observed interaction between the partially oxidised solid and the U released to solution during oxidation in the YCL. However, potential entrapment and incorporation of colloidal nanoparticles in the reduced magnetite sample suggested that magnetite was able to sequester highly mobile U(VI) colloids during rapid crystallisation. Again, this study highlights the ability of magnetite to sequester key radionuclides, in this case U(VI), under conditions expected in the CDZ and around some radioactive waste storage sites (e.g. Hanford, USA (McKinley et al., 2007)).

In Chapter 7, crushed biotite (125 – 250 \( \mu \text{m} \) size fraction) was equilibrated with a cement leachate (pH 13.1), with and without U(VI) (10 ppm) for approximately 6 months at 40 °C. SEM imaging revealed evidence of vermiculitisation, manifest as crenulation of the biotite grains, indicating alkaline breakdown of the primary mineral had occurred as expected (Banfield & Eggleton, 1988). Evidence for vermiculitisation was also apparent in the solution chemistry, with release of Al and Si to solution. There was an initial spike in the concentration of Fe in solution which may be derived from biotite breakdown but there may also have been contributions from amorphous iron (oxyhydr)oxide coatings not removed from the crushed seed material during the washing process. Fe solubility at pH 13.1 is low and so any Fe in solution was likely to re-precipitate as iron (oxyhydr)oxides, although no evidence for secondary mineralisation was detected in the XRD. There was, however, limited evidence for secondary goethite needles observed in detrital material that had collected between the crenulated cleavage planes. Unfortunately these secondary iron oxides were observed in experiments not containing uranium and so no correlative associations could be determined, although given the previous chapters in conjunction with other published literature, it is reasonable to expect that similar phases would have formed in the uranium containing experiments and that uranium would be at least partially associated with these phases. Further to this, small (<1 \( \mu \text{m} \)) spherical particles were observed on the biotite basal plane, with SEM-EDX spectroscopy identifying these as Ca-rich. Investigations of the uranium solubility in the pH 13.1 cement leachate revealed that the uranium was present as a nanoparticulate colloidal phase, clarkeite, a sodium uranate (Bots et al., 2014). The observed decrease in solution concentrations of Ca and U may be attributable to formation of a similar phase in
these experiments. More equilibration time of the system is required to allow for greater primary mineral breakdown before it is likely that any secondary mineralisation is able to significantly impact upon the uranium speciation in solution, and crucially, to be detectable. These experiments have been allowed to continue for a further 2 years and are ongoing. The data presented here (months 0 – 6) will be combined with the longer-term data as part of a wider study into the behaviour of uranium in the presence of a number of mineral phases (including biotite, orthoclase, illite, and quartz).

In summary, the work presented here highlights the importance of mineral reactions within the CDZ, particularly those involving iron (oxyhydr)oxides, in determining the fate of key redox sensitive radionuclides within radioactive wastes disposed of in a GDF. Crystallisation of iron (oxyhydr)oxides presents a significant pathway for sequestering both U(VI) and Tc(VII) through incorporation into their structures in place of Fe. Furthermore, this work highlights that radionuclides immobilised through incorporation are recalcitrant to oxidative remobilisation. This is in contrast to previous studies purely involving surface adsorption or precipitation and implies that incorporation will immobilise radionuclides within the CDZ on the long-term, and provides further insight into and confidence with the concept of deep geological disposal of radioactive waste.

8.2 Future Research Directions

In future studies of the kind presented here, where quantification of adsorbed and incorporated pools of uranium is desired, then a non-destructive approach should be adopted, in contrast to the approach utilised here. Uranium has many isotopes which can be readily distinguished with advanced mass spectrometry techniques, leading to the possibility of accurately measuring isotopic signatures of uranium isotopes present in a sample. Hence, a uranium tracer of a different isotope (e.g. U-232) to the main experimental isotope (e.g. U-238) could be used to quantify the exchangeable pool of uranium on the solid without compromising the solid itself and introducing the possibility of dissolution-induced overestimation of the adsorbed pool.

Incorporation of radionuclides into iron oxides is now a very active area of research with numerous groups working on a range of iron oxides and various radionuclide contaminants. However, the transuranic elements remain relatively under-studied owing to the complexity and difficulties associated with working with such radioelements. Therefore, a systematic approach to a batch of experiments designed to mimic the experimental setup utilised in the research presented in this thesis is proposed, targeting neptunium and plutonium in the first instance since their behaviour is similar to uranium (and so it is reasonable to expect successful
incorporation), followed by americium and curium. Two major contributors to long-lived activity in ILW besides uranium are zirconium-93 and nickel-59 (Pöyry Energy & Amec, 2013b). Therefore, investigations of the behaviour of these two elements would also be interesting, even though magnetite has previously been shown to have the ability to incorporate Ni into the structure (Sidhu et al., 1980, 1981). In addition, it would interesting to assess the impact of Si and Al upon crystallisation of iron (oxyhydr)oxides and incorporation of radionuclides.

Further to this, metal oxides such as manganese oxides (e.g. birnessite \((\text{Na}_{0.3}\text{Ca}_{0.1}\text{K}_{0.1})(\text{Mn}^{4+},\text{Mn}^{3+})_2\text{O}_4\cdot1.5(\text{H}_2\text{O}))\), hausmannite \((\text{Mn}^{2+}\text{Mn}^{3+})_2\text{O}_4\)) are also environmentally important, reactive mineral phases which have generally not been well studied in the context of potentially retarding radionuclide mobility in the geosphere. Similar to iron, manganese has more than one redox state which could aid reductive immobilisation of redox active radionuclides.

Finally, it is hoped that the biotite alteration experiments set up during this project can continue to be sampled on a periodic basis to build a very long term (5 – 10 year) dataset for the hyperalkaline breakdown of Fe-bearing silicate minerals and the fate of uranium during this process.
List of References


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Appendix 1

A1  Supporting Information for Chapter 4 Incorporation of Uranium into Hematite during Crystallisation from Ferrihydrite

A1.1  Materials and Methods

All reagents used were of analytical grade and 18.2 MΩ deionised water (DIW) was used throughout. Two-line ferrihydrite was synthesised as per Cornell and Schwertmann (2003). In brief, 1 M KOH was added to 0.2 M Fe(NO₃)₃·9H₂O whilst stirring to bring the pH to ~7. The suspension was centrifuged and the supernatant discarded. The solids were washed three times in DIW and stored at 5 °C for no more than a week before use. The Fe(III) content of each batch of ferrihydrite slurry was determined using the ferrozine assay (Viollier et al., 2000) after digestion in 4 M HCl. A synthetic cement leachate (pH 10.5) was used to represent groundwater conditions during evolution of the chemically disturbed zone (CDZ) around a cementitious repository (Nuclear Decommissioning Authority, 2011). The leachate was prepared by adding 0.015 g L⁻¹ analytical grade calcium hydroxide (Ca(OH)₂) to DIW whilst stirring and sparging with zero grade N₂. The solutions were stored in an anaerobic chamber (~ 5 % H₂, balance N₂) maintained at < 1 ppm O₂ and CO₂ throughout sample manipulations.

Ferrihydrite was equilibrated with the cement leachate at a solid to solution ratio of 0.4 g L⁻¹ for 1 hour on an orbital shaker at room temperature, and the pH manually adjusted to 10.5 by addition of KOH. The headspace of each experiment was flushed with CO₂-free air to avoid complexation of U(VI) with dissolved CO₃²⁻. Experiments were spiked with U(VI) to give an initial U(aq) concentration of 1 ppm (4.2 x 10⁻⁶ mol L⁻¹), which was thermodynamically modelled (PHREEQC) to be below the solubility of any U(VI) phase in the synthetic leachate, and left to equilibrate for 24 hours. After this equilibration, the 0 hours sample was taken, and the remaining experiments placed into an oven at 60 °C for up to 70 days to induce crystallisation to hematite. Parallel experiments were also set up without U(VI) present for BET surface area and XRD analysis. The experiments were agitated daily with pH regularly monitored and adjusted as necessary to maintain the starting pH (± 0.2). Samples were removed from each experiment under flowing CO₂-free air. Solid samples were obtained by centrifugation (4000 rpm, 1700 g, 5 minutes) of the suspension and removal of the supernatant. The resulting wet paste was treated in one of two ways: samples for XRD, BET and TEM were washed three times in DIW to remove any surface salt and stored in a desiccator under CO₂-free conditions;
samples for XAS were immediately frozen at -80 °C without washing so as not to risk leaching any adsorbed U.

For U analysis, aqueous samples were 0.45 µm filtered (nylon membrane), preserved in 4 M HNO₃, and analysed for ²³⁸U by ICP-MS on an Agilent 7500cx. Combined errors have been calculated for each data series. Solids were characterised by XRD using Bruker D8 (λ = Cu K-α1) and Phillips PW1050 (λ = Cu Kα) diffractometers. Topas v4-2 (Bruker AXS, 2009) was used for quantitative analysis of the XRD patterns. Surface area was measured using the BET method on a Micromeritics Gemini V analyser. Particle morphologies were characterised via TEM using an FEI Tecnai TF20 TEM and a Phillips CM200 TEM.
A1.2 TEM Imaging

Figure A1–1 TEM images of hematite/goethite crystallisation at 60 °C: (a) 0 hours; (b) 24 hours; (c) 7 days; (d) 30 days. H and G indicate hematite and goethite respectively.
A1.3 Quantitative Analysis of XRD Patterns

To quantify the proportions of goethite and hematite in the solid samples, Rietveld refinements were performed using Topas v4.2 (Bruker AXS, 2009). Topas uses the integrated intensity of the diffraction peaks and the crystal structure to calculate the relative mass of each of the phases identified in a solid sample (Rietveld, 1969; Hill & Howard, 1987). However, distinct Bragg peaks in diffraction patterns were absent for ferrihydrite, due to the nanocrystalline nature of this phase. Two very broad peaks were visible in the diffraction patterns when ferrihydrite was present. The amount of ferrihydrite was calculated using the structure for ferrihydrite derived by Michel et al. (2007) with fixed unit cell parameters, and assuming the particle size was constant throughout the experiments. A particle size of approximately 2.5 nm was determined which corresponds well with the collected TEM images.

Table A1–1 Quantitative refinement of XRD patterns

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<tr>
<th>Time point</th>
<th>Hematite</th>
<th>Goethite</th>
<th>Ferrihydrite</th>
<th>Total</th>
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<td>wt%</td>
<td>error (wt%)</td>
<td>wt%</td>
<td>error (wt%)</td>
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<td></td>
<td></td>
<td></td>
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<td>0H</td>
<td>100.0 ± 0.0</td>
<td>100.0</td>
<td>100.0 ± 0.0</td>
<td>100.0</td>
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<tr>
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<td>94.3 ± 0.6</td>
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<td>5.5 ± 0.4</td>
<td>78.4 ± 0.9</td>
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<tr>
<td>12H</td>
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<td>9.6 ± 0.3</td>
<td>57.6 ± 0.8</td>
<td>100.0</td>
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<tr>
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<td>82.1 ± 0.5</td>
<td>17.9 ± 0.3</td>
<td></td>
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<tr>
<td>2D</td>
<td>74.2 ± 0.5</td>
<td>25.8 ± 0.5</td>
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<tr>
<td>4D</td>
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<td>28.0 ± 0.6</td>
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<tr>
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<tr>
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<td>9.2 ± 0.8</td>
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Blank cell indicates structure not included in refinement
A1.4 EXAFS Fitting

A1.4.1 Shell by Shell Contributions to EXAFS Fit

Figure A1–2 Uranium LIII-edge $k^3$ EXAFS spectra and corresponding Fourier transform of the 105 °C data (black line) and model fit of U(VI) incorporation into hematite via substitution for Fe(III) (red line), with theoretical spectral contributions from each modelled path as calculated by Feff6.0 (Zabinsky et al., 1995). The Fourier Transform is plotted with a phase correction calculated from $O_{ax}$. 
A1.4.2 105 °C Data; Oxygen Shell Fitting

The results of iterative fits to the 105 °C data are presented below. The coordination of the shells is shown in Table A1–2 and the fit plots are shown in Figure A1–3. Details of the fit parameters are given in Table A1–5.

Table A1–2 Coordination numbers for Fe/O shells for iterative oxygen shell fitting models applied to the 105 °C data

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<th>(c)</th>
<th>(d)</th>
<th>(e)</th>
<th>(f)</th>
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Blank cell indicates shell was omitted from the fitting model. MS denotes multiple scattering paths.

Figure A1–3 Iterative oxygen shell EXAFS fits (red) to 105 °C data (black). Details of fit and fit parameters are given in Table A1–5. The Fourier Transforms are plotted with a phase correction calculated from O_{ax} in each case.
A1.4.3  105 °C Data; Effect of Additional Iron Shells and Uncoordinated Iron Shells

The results of iterative fits to the 105 °C data are presented below. The coordination of the shells is shown in Table A1–3 and the fit plots are shown in Figure A1–4. Details of the fit parameters are given in Table A1–5.

Table A1–3 Coordination numbers for Fe/O shells for additional iron shell fitting models applied to the 105 °C data

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<th>(g)</th>
<th>(h)</th>
<th>(i)</th>
<th>(j)</th>
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Blank cell indicates shell was omitted from the fitting model. MS denotes multiple scattering paths.
Figure A1–4 Additional iron shell EXAFS fits (red) to 105 °C data (black). Details of fit and fit parameters are given in Table A1–5. The Fourier Transforms are plotted with a phase correction calculated from $O_{ax}$ in each case.
A1.4.4  60 °C Data; Effect of Additional Iron Shells and Uncoordinated Iron Shells

The results of iterative fits to the 60 °C data are presented below. The coordination number of the shells is shown in Table A1–4 and the fit plots are shown in Figure A1–5. Details of the fit parameters are given in Table A1–5.

Table A1–4 Coordination numbers for Fe/O shells for additional iron shell fitting models applied to the 60 °C data

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</table>

Blank cell indicates shell was omitted from the fitting model. MS denotes multiple scattering paths.

Figure A1–5 Additional iron shell EXAFS fits (red) to 60 °C data (black). Details of fit and fit parameters are given in Table A1–5. The Fourier Transforms are plotted with a phase correction calculated from \( O_{ax} \) in each case.
### Table A1-5 EXAFS fit parameters for fits (a) to (k)

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<th>$\sigma^2$ (Å²)</th>
<th>$\Delta E_0$ (eV)</th>
<th>$S_0^2$</th>
<th>$\chi^2$</th>
<th>$R$</th>
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<td>Fe$_E$</td>
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<td>0.010 (3)</td>
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<td>0.011 (3)</td>
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| (m) | \( O_{ax} \) | 2 | 1.87 (2) | 0.007 (2) | \(-4.0 \pm 5.7\) | 0.85 (10) | 27.3 | 0.017 |
|     | \( O_{eq1} \) | 2 | 2.07 (2) | 0.003 (1) |
|     | \( O_{eq2} \) | 2 | 2.23 (3) | 0.005 (2) |
|     | \( \text{Fe}_F \) | 1 | 2.87 (3) | 0.007 (2) |
|     | \( \text{Fe}_E \) | 3 | 3.11 (2) | 0.010 (2) |
|     | \( \text{Fe}_{C1} \) | 3 | 3.46 (6) | 0.016 (7) |
|     | \( \text{Fe}_{C2} \) | 5 | 4.01 (6) | 0.022 (6) |
|     | \( O_{ax MS} \) | 2 | 3.74 (4) | 0.015 (4) |

| (n) | \( O_{ax} \) | 2 | 1.80 (6) | 0.006 (4) | \(-10.0 \pm 12.0\) | 0.85 (10) | 230.8 | 0.193 |
|     | \( O_{eq1} \) | 2 | 2.06 (9) | 0.003 (6) |
|     | \( O_{eq2} \) | 2 | 2.21 (9) | 0.002 (5) |
|     | \( \text{Fe}_F \) | 1 | 2.81 (18) | 0.019 (18) |
|     | \( O_{ax MS} \) | 2 | 3.60 (12) | 0.012 (9) |

| (o) | \( O_{ax} \) | 2 | 1.84 (1) | 0.009 (1) | 6.5 ± 2.9 | 0.85 (3) | 30.7 | 0.013 |
|     | \( O_{eq1} \) | 2 | 2.17 (4) | 0.008 (4) |
|     | \( O_{eq2} \) | 2 | 2.31 (6) | 0.012 (9) |
|     | \( \text{Fe}_F \) | 1 | 2.91 (2) | 0.006 (2) |
|     | \( \text{Fe}_E \) | 3 | 3.16 (2) | 0.011 (1) |
|     | \( O_{ax MS} \) | 2 | 3.68 (3) | 0.017 (3) |

<p>| (p) | ( O_{ax} ) | 2 | 1.83 (2) | 0.008 (2) | 2.8 ± 5.8 | 0.85 (8) | 62.9 | 0.012 |
|     | ( O_{eq1} ) | 2 | 2.14 (5) | 0.007 (6) |
|     | ( O_{eq2} ) | 2 | 2.28 (5) | 0.008 (9) |
|     | ( \text{Fe}<em>F ) | 1 | 2.89 (4) | 0.006 (2) |
|     | ( \text{Fe}<em>E ) | 3 | 3.14 (3) | 0.011 (2) |
|     | ( \text{Fe}</em>{C1} ) | 3 | 3.53 (14) | 0.029 (25) |
|     | ( O</em>{ax MS} ) | 2 | 3.66 (4) | 0.017 (4) |</p>
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CN denotes coordination number; R denotes atomic distance; $\sigma^2$ denotes Debye-Waller factor; $\Delta E_0$ denotes the shift in energy from the calculated Fermi level; $S_0^2$ denotes the amplitude factor which was constrained to between 0.85 and 1.05; $\chi^2_v$ denotes the reduced Chi square value; R denotes the 'goodness of fit' factor; MS denotes multiple scattering paths in the axial O-U-O unit. * the multiple scattering paths considered were linear paths and their $\Delta R$ and $\sigma^2$ parameters were evaluated as multiples of the corresponding single scattering path parameter. Numbers in parentheses are errors on the last significant figure(s).
A1.4.5   F-Test Analysis of EXAFS Fits

Following the methods of Downward et al. (2007) we have performed a series of F-tests to determine if two fits are statistically significantly different, as a way of assessing if a change to the model has improved the fit (e.g. addition of a shell). The data used in the F-test calculations are presented in Table A1–6 and the results of the various F-tests performed are presented in Table A1–7. The parameter $\alpha$ is the statistical significance level that the null hypothesis can be rejected, i.e. a large $\alpha$ means that the two fits are indeed significantly different.

Table A1–6 EXAFS fit data used in F-test calculations for fits (a) to (s)

<table>
<thead>
<tr>
<th>Fit</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
<th>(e)</th>
<th>(f)</th>
<th>(g)</th>
<th>(h)</th>
<th>(i)</th>
<th>(j)</th>
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<td>105 °C</td>
<td>105 °C</td>
<td>105 °C</td>
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<td>df</td>
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<td>363.5</td>
<td>103.8</td>
<td>71.1</td>
<td>680.0</td>
<td>220.6</td>
<td>133.8</td>
<td>342.7</td>
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<td>$\chi_v^2$</td>
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<td>57.6</td>
<td>27.5</td>
<td>85.2</td>
<td>45.8</td>
<td>711.3</td>
<td>82.3</td>
<td>35.2</td>
<td>31.4</td>
<td>80.3</td>
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<td>$R$</td>
<td>0.257</td>
<td>0.088</td>
<td>0.018</td>
<td>0.125</td>
<td>0.030</td>
<td>0.066</td>
<td>0.185</td>
<td>0.058</td>
<td>0.037</td>
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<td>$\sqrt{R}$</td>
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<td>0.297</td>
<td>0.134</td>
<td>0.354</td>
<td>0.174</td>
<td>0.257</td>
<td>0.430</td>
<td>0.241</td>
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<tr>
<th>Fit</th>
<th>(k)</th>
<th>(l)</th>
<th>(m)</th>
<th>(n)</th>
<th>(o)</th>
<th>(p)</th>
<th>(q)</th>
<th>(r)</th>
<th>(s)</th>
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<td>105 °C</td>
<td>105 °C</td>
<td>60 °C</td>
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<td>3.6</td>
<td>1.6</td>
<td>5.6</td>
<td>3.6</td>
<td>3.6</td>
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<tr>
<td>$\chi^2$</td>
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<td>64.8</td>
<td>62.0</td>
<td>1282.7</td>
<td>109.4</td>
<td>97.9</td>
<td>794.7</td>
<td>456.5</td>
<td>112.0</td>
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<td>$\chi_v^2$</td>
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<td>28.6</td>
<td>27.3</td>
<td>230.8</td>
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<td>143.0</td>
<td>128.3</td>
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<td>$R$</td>
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<td>0.019</td>
<td>0.018</td>
<td>0.193</td>
<td>0.013</td>
<td>0.012</td>
<td>0.114</td>
<td>0.069</td>
<td>0.013</td>
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<tr>
<td>$\sqrt{R}$</td>
<td>0.136</td>
<td>0.137</td>
<td>0.133</td>
<td>0.439</td>
<td>0.115</td>
<td>0.108</td>
<td>0.338</td>
<td>0.262</td>
<td>0.114</td>
</tr>
</tbody>
</table>

$T$ denotes experimental temperature; df denotes the degrees of freedom; $\chi^2$ denotes the chi square value; $\chi_v^2$ denotes the reduced chi square value; $R$ denotes the ‘goodness of fit’ factor; $\sqrt{R}$ denotes the square-root of $R$. 

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<table>
<thead>
<tr>
<th>F Test</th>
<th>α (%)</th>
<th>Comment</th>
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</thead>
<tbody>
<tr>
<td>105 °C Data</td>
<td></td>
<td></td>
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<tr>
<td>(a) vs (b)</td>
<td>96.5</td>
<td>Addition of U-Oax significantly improves fit</td>
</tr>
<tr>
<td>(b) vs (c)</td>
<td>96.7</td>
<td>Splitting the U-Oeq shell into two significantly improves fit</td>
</tr>
<tr>
<td>(c) vs (d)</td>
<td>98.4</td>
<td>Changing total U-O coordination from 6 to 4 significantly worsens fit</td>
</tr>
<tr>
<td>(c) vs (e)</td>
<td>31.9</td>
<td>Changing total U-O coordination from 6 to 8 worsens fit</td>
</tr>
<tr>
<td>(c) vs (f)</td>
<td>98.8</td>
<td>Excluding the Fe shells significantly worsens fit</td>
</tr>
<tr>
<td>(g) vs (h)</td>
<td>99.2</td>
<td>Addition of FeE significantly improves fit</td>
</tr>
<tr>
<td>(h) vs (i)</td>
<td>76.3</td>
<td>Addition of FeC1 greatly improves fit</td>
</tr>
<tr>
<td>(i) vs (c)</td>
<td>78.7</td>
<td>Addition of FeC2 greatly improves fit</td>
</tr>
<tr>
<td>(c) vs (j)</td>
<td>97.6</td>
<td>Omission of FeE significantly worsens fit</td>
</tr>
<tr>
<td>(c) vs (k)</td>
<td>0.0</td>
<td>Under co-ordination of FeE as charge compensation does not change the fit</td>
</tr>
<tr>
<td>(c) vs (l)</td>
<td>0.0</td>
<td>Under co-ordination of FeC1 as charge compensation does not change the fit</td>
</tr>
<tr>
<td>(c) vs (m)</td>
<td>0.0</td>
<td>Under co-ordination of FeC2 as charge compensation does not change the fit</td>
</tr>
<tr>
<td>60 °C Data</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(n) vs (o)</td>
<td>99.9</td>
<td>Addition of FeE significantly improves fit</td>
</tr>
<tr>
<td>(o) vs (p)</td>
<td>22.2</td>
<td>Addition of FeC1 does not change the fit</td>
</tr>
<tr>
<td>(o) vs (q)</td>
<td>99.7</td>
<td>Omission of FeE significantly worsens fit</td>
</tr>
<tr>
<td>(o) vs (r)</td>
<td>99.9</td>
<td>Omission of FeE but addition of FeC1 significantly worsens the fit</td>
</tr>
<tr>
<td>(o) vs (s)</td>
<td>0.0</td>
<td>Under co-ordination of FeE as charge compensation does not change the fit</td>
</tr>
</tbody>
</table>
A1.4.6  Linear Combination Fitting of 60 °C Data

Linear combination fitting was performed in Athena (Ravel & Newville, 2005) on two sets of EXAFS data collected at different time points from the 60 °C hematite ageing experiment; after 24 hours and after 30 days. Two end member standards were used, these being the 0 hour (adsorbed) and 105 °C 45 day (incorporated) datasets. The fits were performed in both normalised μ(E) space and k space, with both standards required in each fit. The weights of the standards were forced to between 0 and 1 and also to sum to 1. The fit results from the two fitting spaces for each sample are within error, providing confidence in the results. The relative proportions of the two end-members are similar to the results of the chemical extractions (24 hours = 48 % incorporated; 30 days = 69 % incorporated) but the chemical extractions underestimate the incorporated U pool by approximately 10 % versus the linear combination fits. The results of the linear combination fitting are given in Table A1–8 and plotted in Figure A1–6 to Figure A1–9.

Table A1–8  Linear combination fitting results for 24 hours and 30 days samples aged at 60°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>24 hours</th>
<th>30 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fitting space</td>
<td>normalised μ(E)</td>
<td>χ(k)</td>
</tr>
<tr>
<td>Fit range</td>
<td>-50 to 100 eV</td>
<td>3.0 – 12.0</td>
</tr>
<tr>
<td>R</td>
<td>0.00056</td>
<td>0.25</td>
</tr>
<tr>
<td>χ²</td>
<td>0.0179</td>
<td>82.5</td>
</tr>
<tr>
<td>χ²v</td>
<td>0.00012</td>
<td>0.46</td>
</tr>
<tr>
<td>Standard</td>
<td>0 hour</td>
<td>105 °C</td>
</tr>
<tr>
<td>Weight (%)</td>
<td>38 (2)</td>
<td>62 (2)</td>
</tr>
<tr>
<td>E₀</td>
<td>0.1 (20)</td>
<td>-0.3 (1)</td>
</tr>
</tbody>
</table>

In a given fit: both standards were required in the fit; all weights were forced to between 0 and 1; all weights were forced to sum to 1. Numbers in parentheses are standard deviation on last significant figure.
**Figure A1–6** Linear combination fit to 24 hour data in E-space. Black line is the data. Red line is the fit to the data. Green line is the residual. Purple line is the scaled contribution from the 105°C ‘standard’. Blue line is the scaled contribution from the 0 hour ‘standard’.

**Figure A1–7** Linear combination fit to 30 day data in E-space. Black line is the data. Red line is the fit to the data. Green line is the residual. Purple line is the scaled contribution from the 105°C ‘standard’. Blue line is the scaled contribution from the 0 hour ‘standard’.
Figure A1–8 Linear combination fit to 24 hour data in $k$-space. Black line is the data. Red line is the fit to the data. Green line is the residual. Purple line is the scaled contribution from the 105°C ‘standard’. Blue line is the scaled contribution from the 0 hour ‘standard’.

Figure A1–9 Linear combination fit to 30 day data in $k$-space. Black line is the data. Red line is the fit to the data. Green line is the residual. Purple line is the scaled contribution from the 105°C ‘standard’. Blue line is the scaled contribution from the 0 hour ‘standard’.
Appendix 2

A2  Supporting Information for Chapter 5 Incorporation and Retention of 99-Tc(IV) into Magnetite Under High pH Conditions

A2.1  Synthetic Cement Leachate Preparation

Three synthetic cement leachates have been used to mimic groundwater compositions in and around a cementitious geological disposal facility (GDF) at three points during post-closure of such a facility. These reflect the chemistry of the dominant buffering phases and represent the early-, intermediate- and late-stage post closure environment (Berner, 1992; Moyce et al., 2014).

Young Cement Leachate (YCL, pH 13.1). The young cement leachate (YCL) represents the early-stage post closure groundwater and is dominated by potassium and sodium hydroxide (KOH and NaOH respectively) dissolution. The solution was prepared by first sparging 18 MΩ Milli-Q water (MQ) with oxygen-free nitrogen (OFN) for 1 hour per litre before addition of the reagents. Whilst sparging and stirring the water with a magnetic stir bar, 5.2 gL⁻¹ potassium hydroxide, 3.8 gL⁻¹ sodium hydroxide and 0.1 gL⁻¹ calcium hydroxide (Ca(OH)₂) were added. The solution was sealed and left on the stir plate for 24 hours, after which it was stored in an anaerobic chamber (5 % H₂, balance N₂, maintained at < 1 ppm O₂ and CO₂).

Intermediate Cement Leachate (ICL, pH 12.5). The intermediate cement leachate (ICL) represents the middle-stage post closure groundwater and is dominated by calcium hydroxide (Ca(OH)₂) dissolution. The solution was prepared by first sparging MQ with oxygen-free nitrogen (OFN) for 1 hour per litre before addition of the reagent. Whilst sparging and stirring the water with a magnetic stir bar, 1.2 gL⁻¹ calcium hydroxide (Ca(OH)₂) was added. The solution was sealed and left on the stir plate for 24 hours, after which it was stored in an anaerobic chamber (5 % H₂, balance N₂, maintained at < 1 ppm O₂ and CO₂).

Old Cement Leachate (OCL, pH 10.5). The old cement leachate (OCL) represents the late-stage post closure groundwater and is dominated by calcium-silicate-hydrate (C-S-H) phase dissolution. The solution was prepared by first sparging MQ with oxygen-free nitrogen (OFN) for 1 hour per litre before addition of the reagent. Whilst sparging and stirring the water with a magnetic stir bar, 15 mgL⁻¹ calcium hydroxide (Ca(OH)₂) was added. Dissolved silica was not included in the OCL since PHREEQC modelling predicted solubility of silica in equilibrium with tobermorite-14 Å to be low (0.03 mmol). Although silica has been shown to have an inhibitory
effect on the crystallisation of ferrihydrite to goethite and hematite (Cornell et al., 1987), this
does not appear to be the case with crystallisation to magnetite (Kukkadapu et al., 2004). The
solution was sealed and left on the stir plate for 24 hours, after which it was stored in an
anaerobic chamber (5 % H₂, balance N₂, maintained at < 1 ppm O₂ and CO₂).
A2.2 Tc-99 Distribution Profile in Magnetite Particles

Magnetite dissolves isotropically which allows the distribution of Tc-99 within the magnetite particles to be determined by total digestion in 1 M HCl (Sidhu et al., 1978, 1980). Digestions were performed on the samples from the OCL system because potential contributions from Tc-99 possibly incorporated into goethite could be discounted with certainty since XRD confirmed these to be 100% magnetite. A mass of solid (< 0.1 g) was allowed to fully dissolve in 40 mL 1 M HCl in centrifuge tubes placed onto an end-over-end rotator at 30 rpm to ensure complete mixing. Solution samples were removed periodically and filtered using syringe-top filter units with 0.22 µm polyethersulfone (PES) membrane filters to remove any suspended particles. The resultant solution was analysed for Tc-99 by LSC and for total Fe by the ferrozine method (Viollier et al., 2000) until no further increase in the solution concentration of Fe was observed, taken as 3 consecutive concentrations within error of each other. At this point the solid was deemed to have completely dissolved and the experiment ended. The Tc-99 and Fe in solution data were normalised to the maximum solution concentrations and plotted as Tc-99 versus Fe, providing a concentration gradient of Tc-99 through the solid.

The Tc-99 distribution in the oxidised magnetite particles revealed formation of a Tc-99 deficient layer equating to 10 wt. % Fe. Since the observed morphologies of the nanoparticulate magnetite are typically rounded (Figure A2–3 and Figure A2–4), a spherical particle can be assumed. In this geometry, 10 wt. % of the Fe is contained in a surface layer with a thickness of 3.5 % of the radius of the particle. In a 30 nm particle, this equates to a surface layer 0.5 nm thick which is approximately one unit cell.
Figure A2–1 XRD patterns of reduced and air oxidised from each of the three synthetic cement leachates: YCL (pH 13.1), ICL (pH 12.5), and OCL (pH 10.5). (a) YCL reduced; (b) YCL 21 day oxidised; (c) YCL 152 day oxidised; (d) ICL reduced; (e) ICL 21 day oxidised; and (f) ICL 152 day oxidised; (g) OCL reduced; (h) OCL 21 day oxidised; and (i) OCL 152 day oxidised. Observable peaks are indexed, with M and G signifying magnetite and goethite, respectively.
A2.4 Evidence of Maghemisation from X-Ray Diffraction

Evidence of maghemisation of air oxidised samples is seen as a shift in the magnetite (511) (A) and (440) (B) peaks, however, only partial maghematisation has occurred since the characteristic (210) and (211) peaks are absent (C).

Figure A2–2 Expanded XRD patterns of reduced and air oxidised samples from each of the three synthetic cement leachates: YCL (pH 13.1), ICL (pH12.5), and OCL (pH 10.5). (a) YCL reduced; (b) YCL 21 day oxidised; (c) YCL 152 day oxidised; (d) ICL reduced; (e) ICL 21 day oxidised; and (f) ICL 152 day oxidised; (g) OCL reduced; (h) OCL 21 day oxidised; and (i) OCL 152 day oxidised.
Figure A2–3 Reduced magnetite TEM data. A–C – TEM images from reduced magnetite crystallised in ICL (pH 12.5); D – Selected area electron diffraction pattern from image C, with index for magnetite overlaying the pattern; E – stack of energy dispersive X-ray spectra taken from various magnetite clusters, with expanded sections on the right showing absence of Tc-99 peaks due to the concentration of Tc-99 being below the technique limit of detection in the sample as presented.
A2.6 TEM Data from Oxidised Magnetite

Figure A2–4 Oxidised magnetite TEM data. A-C – TEM images from oxidised magnetite crystallised in ICL (pH 12.5); D – Selected area electron diffraction pattern from image B, with index for maghemite overlaying the pattern; E – stack of energy dispersive X-ray spectra taken from various magnetite clusters, with expanded sections on the right showing absence of Tc-99 peaks due to the concentration of Tc-99 being below the technique limit of detection in the sample as presented.
A2.7 XANES Linear Combination Fitting

Linear combination fitting was performed in *Athena* (Ravel & Newville, 2005) on all XANES data collected from the sorption and coprecipitation experiments, in each of the three synthetic cement leachates. Two reference standards were used: the Tc(IV) reference being the TcO₂·xH₂O reference from Hess et. al. (2004) and a pertechnetate (Tc(VII), TcO₄⁻) reference collected on the same beamtime as the experimental spectra. The fits were performed in normalised μ(E) space between -30 and +40 eV. Neither standard was stipulated as required in the fit but the weights of the standards were forced to between 0 and 1, and also to sum to 1. The results of the linear combination fitting are given in Table A2–1 below.

**Table A2–1** Linear combination fitting results for all XANES Spectra

<table>
<thead>
<tr>
<th>Sample</th>
<th>R</th>
<th>X²</th>
<th>Xᵥ²</th>
<th>Reference Weighting</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TcO₂</td>
</tr>
<tr>
<td>YCL Sorption</td>
<td>0.008</td>
<td>0.137</td>
<td>1.94E-03</td>
<td>1.00 (0)</td>
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<tr>
<td>Co-ppt reduced</td>
<td>0.009</td>
<td>0.148</td>
<td>2.09E-03</td>
<td>1.00 (0)</td>
</tr>
<tr>
<td>Co-ppt oxidised 21 day</td>
<td>0.011</td>
<td>0.433</td>
<td>2.39E-03</td>
<td>1.00 (0)</td>
</tr>
<tr>
<td>Co-ppt oxidised 152 day</td>
<td>0.012</td>
<td>0.177</td>
<td>2.49E-03</td>
<td>1.00 (0)</td>
</tr>
<tr>
<td>ICL Sorption</td>
<td>0.009</td>
<td>0.386</td>
<td>2.13E-03</td>
<td>1.00 (0)</td>
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<tr>
<td>Co-ppt reduced</td>
<td>0.009</td>
<td>0.146</td>
<td>2.02E-03</td>
<td>1.00 (0)</td>
</tr>
<tr>
<td>Co-ppt oxidised 21 day</td>
<td>0.012</td>
<td>0.502</td>
<td>2.76E-03</td>
<td>1.00 (0)</td>
</tr>
<tr>
<td>Co-ppt oxidised 152 day</td>
<td>0.011</td>
<td>0.172</td>
<td>2.43E-03</td>
<td>1.00 (0)</td>
</tr>
<tr>
<td>OCL Sorption</td>
<td>0.009</td>
<td>0.136</td>
<td>1.91E-03</td>
<td>1.00 (0)</td>
</tr>
<tr>
<td>Co-ppt reduced</td>
<td>0.009</td>
<td>0.147</td>
<td>2.07E-03</td>
<td>1.00 (0)</td>
</tr>
<tr>
<td>Co-ppt oxidised 21 day</td>
<td>0.012</td>
<td>0.504</td>
<td>2.78E-03</td>
<td>1.00 (0)</td>
</tr>
<tr>
<td>Co-ppt oxidised 152 day</td>
<td>0.010</td>
<td>0.172</td>
<td>2.33E-03</td>
<td>1.00 (0)</td>
</tr>
</tbody>
</table>

*R* denotes the ‘goodness of fit’ factor; *X²* denotes the Chi square value; *Xᵥ²* denotes the reduced Chi square value. Numbers in parentheses are standard deviation on the last decimal place.
A2.8 EXAFS Fitting – ICL Reduced Sorption Sample Fits

The results of fits to the ICL sorption reduced data are presented below. The rationale behind fitting models (a)-(g) are given in Table A2–2. The fits are plotted in Figure A2–5 and coordination of the shells in each fit along with key fit metrics are given in Table A2–3. Results of F-test comparisons (Downward et al., 2007) are given in Table A2–4.

**Figure A2–5** Technetium K-edge XAS spectra from Tc-99 adsorbed to magnetite in the intermediate stage cement leachate (ICL, pH 12.5) showing different fitting models outlined in Table A2–2. Panel A – $k^2$-weighted EXAFS; panel B – Fourier transform of $k^2$-weighted EXAFS, using a Hanning Window function and plotted with phase shift calculated from Tc-O path. Black lines are data and red lines are fits to the data.

**Table A2–2** Rationale of fitting models (a)-(g) applied to ICL sorption reduced data

<table>
<thead>
<tr>
<th>Fit</th>
<th>Rationale</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>Tc(IV) octahedrally coordinated with a with a single shell of 6 O at ~2 Å</td>
</tr>
<tr>
<td>(b)</td>
<td>Disordered TcO$_2$ structure (Rogers et al., 1969) modelled with a single shell of 6 Tc at ~3.3 Å in addition to 6 O at 2 Å</td>
</tr>
<tr>
<td>(c)</td>
<td>Mono-dentate adsorbed Tc(IV) species</td>
</tr>
<tr>
<td>(d)</td>
<td>Bi-dentate adsorbed Tc(VI) species</td>
</tr>
<tr>
<td>(e)</td>
<td>Mono-dentate adsorbed Tc(IV) species with Tc-Tc polymeric chain</td>
</tr>
<tr>
<td>(f)</td>
<td>Partial incorporation into magnetite</td>
</tr>
<tr>
<td>(g)</td>
<td>Polymeric Tc-Tc chain</td>
</tr>
</tbody>
</table>
Table A2–3 Coordination numbers for shells within the fitting models applied to the ICL reduced sorption data, as plotted in Figure A2–5 with key fit metrics for F-test comparison

<table>
<thead>
<tr>
<th>Fit</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
<th>(e)</th>
<th>(f)</th>
<th>(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tc-O</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
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<td>$\chi^2_v$</td>
<td>418.2</td>
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<tr>
<td>$R$</td>
<td>0.027</td>
<td>0.030</td>
<td>0.046</td>
<td>0.048</td>
<td>0.036</td>
<td>0.036</td>
<td>0.039</td>
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Blank cell indicates shell was omitted from the fitting model; df denotes the degrees of freedom in the fit; $\chi^2_v$ denotes the reduced Chi square value; $R$ denotes the ‘goodness of fit’ factor.

Table A2–4 F-test results from comparison of pairs of fits applied to ICL reduced sorption sample, as outlined in Table A2–2

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<th>F Test</th>
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<th>Comment</th>
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<tr>
<td>(a) vs (b)</td>
<td>0.1</td>
<td>Addition of a single shell of 6 Tc atoms at ~3.3 Å does not significantly improve the fit</td>
</tr>
<tr>
<td>(a) vs (c)</td>
<td>39.8</td>
<td>Monodentate adsorption does not significantly improve the fit</td>
</tr>
<tr>
<td>(a) vs (d)</td>
<td>47.4</td>
<td>Bidentate adsorption does not significantly improve the fit</td>
</tr>
<tr>
<td>(a) vs (e)</td>
<td>10.5</td>
<td>Monodentate adsorption of Tc-Tc chain does not significantly improve the fit</td>
</tr>
<tr>
<td>(a) vs (f)</td>
<td>10.7</td>
<td>Partial incorporation into magnetite does not significantly improve the fit</td>
</tr>
<tr>
<td>(a) vs (g)</td>
<td>15.6</td>
<td>Polymeric Tc-Tc chain does not significantly improve the fit</td>
</tr>
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$\alpha$ denotes the probability that the two fits are statistically distinct from one another.
A2.9 Full EXAFS Dataset

Figure A2–6 Technetium K-edge XAS spectra from Tc-99 adsorbed to, and coprecipitated with magnetite and subsequent air oxidation in all cement leachates. Panel A – $k^3$-weighted EXAFS; panel B – Fourier transform of $k^3$-weighted EXAFS, using a Hanning Window function and plotted with phase shift calculated from Tc-O path. Black lines are data and coloured lines are fits to the data. (a) YCL coprecipitation reduced; (b) YCL coprecipitation oxidised 21 days; (c) YCL coprecipitation oxidised 152 days; (d) ICL adsorption reduced; (e) ICL coprecipitation reduced; (f) ICL coprecipitation oxidised 21 days; (g) ICL coprecipitation oxidised 152 days; (h) OCL coprecipitation reduced; (i) OCL coprecipitation oxidised 21 days; (j) OCL coprecipitation oxidised 152 days.
Table A2–5 Details of EXAFS fit parameters of Tc-99 adsorbed to, and coprecipitated with magnetite and subsequent air oxidation in all cement leachates, as presented in Figure A2–6.

(a) YCL coprecipitation reduced; (b) YCL coprecipitation oxidised 21 days; (c) YCL coprecipitation oxidised 152 days; (d) ICL adsorption reduced; (e) ICL coprecipitation reduced; (f) ICL coprecipitation oxidised 21 days; (g) ICL coprecipitation oxidised 152 days; (h) OCL coprecipitation reduced; (i) OCL coprecipitation oxidised 21 days; (j) OCL coprecipitation oxidised 152 days

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<tr>
<th>Fit</th>
<th>Path</th>
<th>CN</th>
<th>R (Å)</th>
<th>σ² (Å²)</th>
<th>ΔE₀ (eV)</th>
<th>S₀²</th>
<th>χ₀²</th>
<th>R</th>
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<td>(a) YCL co-ppt, reduced</td>
<td>O 6†</td>
<td>2.02 (1)</td>
<td>0.004 (0)</td>
<td>-6.4 ± 1.0</td>
<td>0.90 c</td>
<td>102.9</td>
<td>0.018</td>
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<tr>
<td></td>
<td>Fe₁</td>
<td>2.8 ± 0.7</td>
<td>3.06 (1)</td>
<td>0.006 (2)‡</td>
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<tr>
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<td>Fe₂</td>
<td>3.5 ± 0.8</td>
<td>3.51 (1)</td>
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<tr>
<td></td>
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<td>6†</td>
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<td>0.011 (1)‡</td>
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<tr>
<td></td>
<td>O₇MS †</td>
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<td>(c) YCL co-ppt, oxidised 152 days</td>
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<td>0.005 (1)</td>
<td>-7.4 ± 2.2</td>
<td>0.90 c</td>
<td>8.6</td>
<td>0.030</td>
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<td>Fe₁</td>
<td>6.0 ± 0.0</td>
<td>3.06 (2)</td>
<td>0.011 (1)‡</td>
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<tr>
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<td>3.97 (3)</td>
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<td>(d) ICL sorption</td>
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<td>-1.5 ± 1.4</td>
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<td>(e) ICL co-ppt, reduced</td>
<td>O 6 c</td>
<td>2.00 (1)</td>
<td>0.005 (1)</td>
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<td>0.90 c</td>
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<td>0.008 (3)‡</td>
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<td>O₇MS †</td>
<td>6 c</td>
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<td>0.010 (1)</td>
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<td>0.90 c</td>
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<td>3.6 ± 1.1</td>
<td>3.47 (2)</td>
<td>0.007 (2)‡</td>
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<td>O₇MS †</td>
<td>6 c</td>
<td>3.99 (2)</td>
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<td>0.006 (2)‡</td>
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<td>(h) OCL co-ppt, reduced</td>
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<td>2.01 (1)</td>
<td>0.004 (0)</td>
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<td>0.004 (1)</td>
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<td>0.90 c</td>
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<td>4.8 ± 1.3</td>
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<td>0.007 (2)‡</td>
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<td>21 days</td>
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<td>3.7 ± 1.2</td>
<td>3.47 (2)</td>
<td>0.007 (2)‡</td>
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<td>0.008 (1)</td>
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<td>3.98 (1)</td>
<td>0.008 (1)</td>
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CN denotes coordination number; R denotes atomic distance; $\sigma^2$ denotes Debye-Waller factor; $\Delta E_0$ denotes the shift in energy from the calculated Fermi level; $S_0^2$ denotes the amplitude factor; $\chi^2_v$ denotes the reduced Chi square value; $R$ denotes the ‘goodness of fit’ factor; MS denotes multiple scattering paths. * the multiple scattering paths considered were linear paths and their $\Delta R$ and $\sigma^2$ parameters were evaluated as multiples of the corresponding single scattering path parameter. Numbers in parentheses are standard deviation on the last decimal place. ‡ denotes parameters were tied in a given fit. † denotes parameters were fixed.

The fits presented in Table SI-5 were constrained through tying the Debye Waller factors (DWF) of the two Fe shells. If this constraint is removed and all parameters are allowed to vary independently, the resultant fit was statistically indistinct from the constrained fit, yet physically unrealistic: the DWF for the outer Fe shell was half the DWF of the nearer shell (0.009 and 0.004 respectively) and coupled to this, the coordination of the outer shell decreases from ~4 to ~2.5. The coordination and DWF are correlated and so it is unsurprising to observe a decrease in both parameters, however, the refined values are physically unrealistic and hence justify imposing the constraint on Fe shells’ DWF.
A2.10 Electron Energy Loss Spectroscopy Data

Figure A2–7 EELS O K and Fe L$_{2,3}$-edge spectra of reduced (black) and 21 day air oxidised (orange) magnetite in the ICL (pH 12.5) system. A – full spectra; B – expanded O K edge; C – expanded Fe L$_{2,3}$-edge. The decrease in the Fe:O ratio during oxidation is visible as an increase in intensity in the O K edge coupled to a decrease in the Fe L$_{2,3}$-edge intensity, reflecting the change in the magnetite structure during maghematisation as vacancies are generated to compensate the increase in charge as Fe(II) is oxidised to Fe(III).

After comments from two of the four reviewers questioned the strength of the data, and therefore their validity, it was decided that these data would not be included in the published material. As has previously been discussed (Chapter 3.8.4.5), the energy resolution of the detector at the time of data acquisition was approximately 0.8 – 0.9 eV, whilst the split between the Fe(II) and Fe(III) L-edges is 0.5 eV. Therefore, it was not possible to distinguish between the two Fe oxidation states. However, due to the change in Fe:O ratio during oxidation of magnetite to maghemite, the two phases have characteristic, but different, ratios between their characteristic Fe L$_{2,3}$ and O K edge ratios of 0.75 ± 0.1 and 0.65 to 0.68 ± 0.1 respectively, and it is possible to use this ratio to determine the stoichiometry of an unknown sample (Colliex et al., 1991; Brown et al., 2001). In the ICL (pH 12.5) system the Fe:O ratios of the magnetite were found to be 0.77 ± 0.1 and 0.69 ± 0.1 for the reduced and oxidised samples respectively (Figure A2–7). The uncertainties on the Fe:O ratios quantified by EELS are large, and hence both samples are close to within error of each other, meaning it is not possible to reliably state that these are statistically different from each other.
A2.11 Mössbauer Spectroscopy Data

Figure A2–8 Mössbauer spectra from the reduced and 21 day oxidised magnetite samples from the OCL (pH 10.5) system at 118 K and 293 K

Table A2–6 Fitting data for Mössbauer spectra from the reduced and 21 day oxidised magnetite samples from the OCL (pH 10.5) system at 118 K and 293 K

<table>
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<tr>
<th>T (K)</th>
<th>Samples</th>
<th>Doublet (D1)</th>
<th>Sextet (S1)</th>
<th>Sextet (S2)</th>
<th>$\chi^2$</th>
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<td>118 K</td>
<td>Reduced</td>
<td>4.76 ± 0.14</td>
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<td>32.84 ± 0.91</td>
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<td>Oxidised</td>
<td>3.72 ± 0.05</td>
<td>64.42 ± 0.33</td>
<td>31.86 ± 0.38</td>
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<tr>
<td>293 K</td>
<td>Reduced</td>
<td>5.25 ± 0.07</td>
<td>37.44 ± 0.35</td>
<td>57.30 ± 0.46</td>
<td>105.4</td>
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<tr>
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<td>Oxidised</td>
<td>6.56 ± 0.13</td>
<td>35.27 ± 0.54</td>
<td>58.17 ± 0.70</td>
<td>42.4</td>
</tr>
</tbody>
</table>

These data were not included in the published Supporting Information. As has been previously discussed (Chapter 3.8.5), Mössbauer spectroscopy of magnetite samples of unknown stoichiometry is complicated. Data collection was performed at 118 K, as this was the only cooled temperature available, and at 293 K, to avoid superparamagnetic effects associated with being close to the Verwey Transition (121 K (Walz, 2002; Garcia & Subias, 2004)). As can be seen in Figure A2–8 and Table A2–6, at both temperatures, there are very few differences...
between the reduced and 21-day oxidised samples. The first sextet (S1) is a good match for magnetite in all samples. However, the second sextet (S2) could be interpreted as either maghemite or nanoparticulate magnetite. The doublet is certainly not goethite (goethite exhibits a sextet which is not present) and this is in agreement with the qXRD data. The doublet could be explained by either an unknown contaminant in the sample, or more likely, a fitting error inherent to the fit due to complexities introduced by temperature effects that cannot be resolved. Therefore, with the current data it was not possible to distinguish between the reduced and 21-day oxidised samples at either 118 K or 293 K.
## Appendix 3

### A3 Supporting Information for Chapter 7 Long-term Alkaline Alteration of Biotite and the Fate of Uranium(VI)

#### A3.1 Electron Microprobe Data Tables

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<th>FeO</th>
<th>TiO₂</th>
<th>MnO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
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<td>18.13</td>
<td>2.12</td>
<td>0.90</td>
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<td>3.93</td>
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<td>0.44</td>
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Data omitted for Cr₂O₃ and CaO. F not considered during analysis.
### Table A3–2 Electron microprobe analysis for biotite section 65191: oxide weight %

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Data omitted for Cr$_2$O$_3$ and CaO. F not considered during analysis.
Table A3–3 Electron microprobe analysis for biotite section 65190: cation numbers scaled to total oxygen number of 24

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Data omitted for Cr₂O₃ and CaO. F not considered during analysis.
Table A3–4 Electron microprobe analysis for biotite section 65191: cation numbers scaled to total oxygen number of 24

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Data omitted for Cr$_2$O$_3$ and CaO. F not considered during analysis.
Appendix 4

A4 Travel Bursaries and List of Conference Presentations

The following is a list of travel bursaries granted to the author for attendance at various international conferences, followed by a list of all 1st author presentations given at conferences during the course of the PhD, split into oral and poster presentations, along with a copy of each poster.

A4.1 Travel Bursaries

- Postgraduate Student Bursary, Mineralogical Society of Great Britain and Ireland, 2012 (£350) to attend Goldschmidt 2012.
- Postgraduate Student Travel Grant, Geological Society Geochemistry Group, 2012 (£250) to attend Goldschmidt 2012.
- Young Researchers’ Fund, RSC Radiochemistry Group, 2012 (£500) to attend Goldschmidt 2012.
- TALISMAN Training and Education 1st call, 2013 (£1000) to attend Actinides 2013.
- Young Researchers’ Fund, RSC Radiochemistry Group, 2013 (£500) to attend Migration 2013.

A4.2 Oral Presentations


The fate of technetium and uranium during iron oxide crystallisation from ferrihydrite. Timothy A. Marshall, Katherine Morris, Gareth T.W. Law, J. Frederick. W. Mosselmans, Pieter Bots, and


**A4.3 Poster Presentations**


Evolution of the Geochemical Environment Surrounding a Radioactive Waste Repository: Mineral Alteration in the Chemically Disturbed Zone

Timothy A. Marshall, Samuel Shaw, Katherine Morris

1. Earth Surface Science Institute, School of Earth and Environment, University of Leeds, Leeds, West Yorkshire, LS2 9JT, UK. 2. Research Centre for Radioactive Waste, North West Centre for Environmental Sciences, University of Manchester, Manchester, M13 9PL, UK.

The UK concept for disposal of ILW
The UK has 364,000 m\(^3\) of radioactive waste designated as Intermediate-Level Waste (ILW). In 2008, the UK Government accepted an independent committee's recommendation and set out a framework for deep geological disposal for higher activity wastes.

Why biotite?
Biotite is an Fe-bearing 2:1 sheet silicate mineral, ubiquitous in many types of crustal rocks. Biotite contains reduced Fe\(^{2+}\), which when released during alkaline breakdown may interact with radionuclides to reduce their mobility.

Owing to its structure, biotite has perfect cleavage and forms books with flat, parallel, close-packed cleaves.

Our research hypothesis
Biotite alteration in the Chemically Disturbed Zone
This will create a hydraulically plume which will react with the geological barrier, forming a Chemically Disturbed Zone (CDZ). With time, the chemical and physical properties of the Chemically Disturbed Zone will evolve as leaching of the cementitious material becomes more extensive (pH drop from pH 12 to 10) and primary minerals react to form secondary phases.

The next step
A series of long-term biotite alteration batch experiments have been designed to build upon the results from the 1st experiment.

Parallel experiments will be run under two atmospheric conditions, one anoxic and one oxic, and either in the presence of a radionuclide (uranium or technetium) or without.

These experiments have been designed to determine the ability of the Fes(II)/Fe(II) redox couple to reduce environmentally mobile radionuclides.

The bonding environment of the radionuclides will be analysed using synchrotron-based X-ray spectroscopic techniques (e.g. XAS, EXAFS) to determine whether mineral phases they are preferentially associated with.

Schematics of the experimental set-up are shown opposite.

What have we learnt?
Only limited alteration occurs at ambient temperature, which is difficult to quantify using bulk analytical techniques.

Analysed techniques used so far cannot conclusively identify secondary alteration phases.

The solution pH was unaffected by the alteration reaction.

References


Special thanks to Dr. Eric Condiffe for his assistance with the SEM imaging work, Dr. Samuel Shaw for his advice and assistance with the experimental set-up and Miss Lesley Neve for her assistance with the IED.

This work has been conducted as part of the UK NERC funded SHIFT consortium (www.nerc.ac.uk).

Presented at the Environmental Mineralogy Group Research in Progress Meeting, 6th May 2011, Edinburgh University, UK.
The UK concept for disposal of ILW

The UK has 364,000 m$^3$ of radioactive waste designated as Intermediate Level Waste (ILW)\(^1\).

In 2008 the UK Government accepted an independent committee’s recommendation and set out a framework for deep geological disposal for high activity wastes\(^2\).

The Nuclear Decommissioning Authority’s concept for disposal of Intermediate Level Waste is based on the multi-barrier principle, involving a series of engineered barriers to complement the natural geological barrier\(^3\).

The concept utilises cementitious materials for the wasteform and backfill to chemically engineer the repository environment.

The multi-barrier concept for ILW disposal is shown in Fig. 1.

Our research hypothesis

Biotite alteration in the Chemically Disturbed Zone

Once the repository is sealed, groundwater will redistribute the repository and begin leaching the cementitious barrier.

This will create a high alkaline plume which will react with the geological barrier, forming a Chemically Disturbed Zone (CDZ). With time, the chemical and physical properties of the Chemically Disturbed Zone will evolve as leaching of the cementitious material becomes more extensive (pH drop from $>12$ to $10$) and primary minerals react to form secondary phases.

It is critical that we understand this geochemical evolution, and its impact upon the geological barrier, so that we can predict the long term performance and safety of a repository for radioactive waste.

Why biotite?

Biotite is an Fe-bearing 2:1 sheet silicate mineral, ubiquitous in many types of crustal rocks.

Biotite contains reduced Fe\(^2\) which when released during alkalis breakdown may interact with radionuclides to reduce them, and their environmental mobility.

Owing to its structure, biotite has perfect cleavage and forms books with flat, parallel, close-packed leaves.

Evolution of the Geochemical Environment Surrounding a Radioactive Waste Repository: Mineral Alteration in the Chemically Disturbed Zone

Timothy A. Marshall\(^1\), Samuel Shaw\(^1\), Katherine Morris\(^1\)

\(^1\)Earth Surface Science Institute, School of Earth and Environment, University of Leeds, Leeds, West Yorkshire, LS2 9JT, UK. * tatmar@leeds.ac.uk

\(^2\)Research Centre for Radioactive Waste disposal, School of Earth, Atmospheric and Environmental Sciences, University of Manchester, Manchester, M13 9PL, UK.

Alteration of biotite in a young cement leachate (pH 13.1) for 78 days at ambient temperature

Hydrolysis attack causes the cleavage planes to separate and induces exfoliation of the biotite crystal.

Secondary alteration minerals, such as these potential goethite needles, form on clusters of cleavage biotite grains which collect in the crevices between cleavage planes.

Our research hypothesis

Backscattered electron imaging reveals bright coatings, which are indicative of compositional differences on dehydrated biotite grains.

Energy dispersive X-ray spectroscopy taken at the point marked by the cross in the above image reveals the coatings to be Fe-oxides.

The next step

A series of long-term biotite alteration batch experiments have been designed to build upon the results from the first experiment.

Parallel experiments will be run under two atmospheric conditions, one oxic and one anoxic, and either in the presence of a radionuclide (uranium or technetium) or without.

These experiments have been designed to determine the ability of the Fe(ii)/(Fe(iii)) redox couple to reduce environmentally mobile radionuclides.

The bonding environment of the radionuclides will be analysed using synchrotron based X-ray spectrometric techniques (e.g. XAS, EXAFS) to determine which mineral phases they are preferentially associated with.

Schematics of the experimental set-up are shown opposite.

References


This work has been conducted as part of the UK NERC funded SYNCLUS consortium: www.synclus.org

What have we learnt?

Only limited alteration occurs at ambient temperature, which is difficult to quantify using bulk analytical techniques.

Analytical techniques used so far cannot conclusively identify secondary alteration phases.

The solution pH was unaffected by the alteration reaction.

How will this feed into our plans?

Experiments will be run at $50\degree\text{C}$ which will give an $8\times$ fold increase reaction rate.

Make use of TEM to provide greater resolution imaging and EDX, plus perform chemical extractions to determine what Fe-oxides are forming.

Move to manual pH control which will allow more batch reactions to be run simultaneously.

191
The UK concept for disposal of ILW

The UK has 364,000 m$^3$ of radioactive waste designated as Intermediate Level Waste (ILW)\(^1\). In 2008 the UK Government accepted an independent committee’s recommendation and set out a framework for deep geological disposal for higher activity wastes\(^2\).

The Nuclear Decommissioning Authority’s concept for disposal of Intermediate Level Waste is based on the multi-barrier principle, involving a series of engineered barriers to compartmentalize the natural geological barrier\(^3\). The concept utilizes cementitious materials for the wasteform and backfill to chemically engineer the repository environment.

Our research hypothesis

Biottite alteration in the Chemically Disturbed Zone

Once the repository is sealed, groundwater will recondition the repository and begin leaching the cementitious barrier.

This will create a hydraulically plausible which will react with the geological barrier, forming a Chemically Disturbed Zone (CDZ). With time, the chemical and physical properties of the Chemically Disturbed Zone will evolve as leaching of the cementitious material becomes more extensive (pH drop from pH 13 to 10) and primary minerals react to form secondary phases.

It is critical that we understand this geochanical evolution, and its impact upon the geologic barrier, so that we can predict the long term performance and safety of a repository for radioactive waste.

What have we learnt?

- Only limited alteration occurs at ambient temperature, which is difficult to quantify using bulk analysis techniques.
- Analytical techniques used so far cannot conclusively identify secondary alteration phases.
- The solution pH was unaffected by the alteration reaction.

How will this feed into our plans?

- Experiments will be run at 50°C which will give an 8 fold increase reaction rate.
- Make use of TEM to provide greater resolution imaging and EDS, plus perform chemical extractions to determine what Fe-oxides are forming.
- Move to manual pH control which will allow more batch reactions to be run simultaneously.

The next step

A series of long-term biotite alteration batch experiments have been designed to build upon the results from the first experiment.

Parallel experiments will be run under two atmospheric conditions, one oxidising and one anoxic, and either in the presence of a radionuclide (uranium or technetium) or without.

These experiments have been designed to determine the ability of the Fe(III)/Fe(II) redox couple to reduce environmentally mobile radionuclides.

The bonding environment of the radionuclides will be analysed using synchrotron based x-ray spectroscopic techniques (e.g. XAS, EXAFS) to determine which mineral phases they are preferentially associated with.

Schematics of the experimental set-ups are shown opposite.

References


2. The UK concept for disposal of ILW: The UK has 364,000 m$^3$ of radioactive waste designated as Intermediate Level Waste (ILW). In 2008 the UK Government accepted an independent committee’s recommendation and set out a framework for deep geological disposal for higher activity wastes.

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This work has been conducted as part of the UK NERC funded BIGRAD consortium: www.bigrad.org.uk

Special thanks go Dr. Samuel Althorn for his advice and assistance with the experimental set-up, to Dr. Eric Coddiffe for his assistance with the SEM imaging work, and Miss Lesley Hove for her assistance with the ICP.
Our research hypothesis

The current ILW concept is for a cementitious GDF®. Groundwater flow through the GDF® post-closure will leach the cementitious backfill producing a high alkaline plume. This will react with the geological barrier, creating a Chemically Disturbed Zone (CDZ).

It is critical that we understand this geochemical evolution, and its impact upon the geological barrier, so that we can predict the long term performance and safety of a repository for radioactive waste.

Ambient weathering of non-bearing silicate minerals, e.g. biotite, releases the major framework cations, resulting in an altered primary silicate mineral and formation of secondary iron (hydr)oxides and aluminium silicates. The breakdown mechanism and kinetics of these minerals under hyperalkaline conditions are poorly understood. However, it is likely that iron (hydr)oxides and aluminium silicates will form rapidly. The highly reactive nature of these phases, and the presence of Fe(III) may lead to reduction of redox-active radionuclides to less environmentally mobile forms within the CDZ.

We have chosen to work with biotite, an Fe(III)-bearing triothedral 2:1 sheet silicate mineral common in many types of crustal rocks, as it may be an important source of iron in the CDZ. Our single mineral experiments will characterise the potential alteration pathways for Fe(III)-bearing silicate minerals in the CDZ, and key radionuclide-mineral associations.

Alteration of biotite under hyperalkaline conditions relevant to a cementitious ILW repository

The alkaline alteration of biotite can be written as:

\[ K_Mg_2Fe_2[Si_3Al_2(OH)_10]_2\cdot2H_2O + OH^- + H_2O \rightarrow K_Mg_2Fe_2[Si_3Al_2(OH)_10]_2 \cdot 2H_2O + OH^- + H_2O \]

The secondary alteration products will depend upon the fluid the primary mineral is subjected to, meaning that the evolution of the CDZ will control which secondary alteration products are formed and have an impact on the long-term fate of key radionuclides.

Current batch experiments

Long-term weathering experiments on limited samples will be focused on pyrophilic hydrous ferric oxides and on the minerals found in the CDZ. The experiments will include soaking the biotite in hyperalkaline and reducing fluids and the analysis of the alteration products.

Results to date

The pH has remained stable at 13.5 ± 0.1 in all systems. No change in dissolved K or Na is observed against the high ionic strength of the YGL. However, both dissolved Si and Al have increased through time, an effect which is more marked in the presence of uranium. Dissolved Fe is at or close to the limit of detection. Uranium is remaining in solution at approximately 8 ppm. CaO-rich precipitates have been observed in both the calcitic and aragonitic systems. In the absence of uranium, the dissolved CaO concentration has remained stable and equilibrated with respect to the blank. However, in the presence of uranium, dissolved CaO is decreasing through time with respect to the blank. A peak in extractable Fe(II) and Fe(III) from the altered solid by 0.5N HCl is observed in Figure 5. After this, there is a decrease in Fe(II) extracted, but there is an increase in the percentage extracted as Fe(III), which is stable at ~90% over the first three weeks but rises to ~95% thereafter.

Conclusions

Uranium remains in solution above pH 13 and is not substantially removed by biotite or any secondary phases formed due to hyperalkaline alteration.

Some dissolution and reprecipitation of calcite impurities in the original biotite has occurred. Although calcium is being removed from solution in the uranium experiments, this does not appear to be due to formation of a calcium uranate phase since the concentration of uranium in solution has remained stable. The peak in extractable iron is likely to be due to dissolution of Fe(III) oxides not removed from the biotite surface during the initial washing process.

After approximately three months, only a limited amount of reaction has occurred. Further in lies (12 months) to fully characterise hyperalkaline alteration of biotite.

References


Edward Surface Science Institute, School of Earth and Environment, University of Leeds, Leeds, West Yorkshire, LS2 9JT, UK. * metam@leeds.ac.uk
1 Research Centre for Radiative and Decommissioning, School of Earth, Atmospheric and Environmental Sciences, University of Manchester, Manchester, M13 MPL, UK.
2 Centre for Radiochemistry Research, School of Chemistry, University of Manchester, Manchester, M13 MPL, UK.
The fate of uranium and technetium during magnetite crystallisation at hyperalkaline pH

Timothy A. Marshall*, Katherine Morris†, Gareth T.W. Law‡, J. Frederick W. Mosseimans§, Samuel Shaw

*Research Centre for Radioactive Waste Management and Williamson Research Centre, School of Earth, Atmospheric and Environmental Sciences, The University of Manchester, M13 9PL, UK.
†Centre for Radiotechnology Research and Research Centre for Radioactive Waste Management, School of Chemistry, The University of Manchester, M13 9PL, UK.
§Diamond Light Source Ltd., Diamond House, Harwell Science and Innovation Campus, Didcot, Oxfordshire, OX11 0DE, UK.

Waste is encapsulated in cement grout inside steel containers...

...which are stacked on top of each other by a cementitious backfill...

...inside a vault excavated in a suitable and stable host rock...

...at a depth of 300 - 1000m to provide geological confinement...

Groundwater ingress will leach the cementitious backfill creating a hyperalkaline plume at the Chemically Disturbed Zone (CDZ).

What is the fate of radionuclides, leached from the waste, in the CDZ?

Both uranium and technetium are highly mobile in their oxidised state, but are highly insoluble in their reduced state, rendering them immobile.

It has been shown that magnetite is able to reduce U(VI) to U(IV) and Tc(VII) to Tc(IV), but these phases are highly susceptible to oxidative remobilisation.

However, we have shown incorporation into magnetite offers a viable long-term sequestration mechanism for U and Tc.

Uranium
- All U is removed from solution during crystallisation
- U is reduced and incorporated into magnetite at both pH 13.1 and 10.5
- Some U is present as surface species in mixed oxidation states
- Major fraction of U is recalcitrant to oxidation at pH 10.5, remaining in the iron oxide as U(IV)

Technetium
- All Tc is removed from solution during crystallisation, with limited remobilisation during oxidation
- Major fraction of Tc is recalcitrant to oxidation and remains sequestered within the iron oxide as Tc(IV)

We thank Dr. Steve Parry and Richard Douil for assistance at Diamond, Mr. Paul Lyngbye for ICP-MS analysis (data not shown) and Dr. John Waters for assistance with collection of XRD patterns.

This work has been funded as part of the UK NERC BIGRAD consortium grant NE/I007766/1. Experiments at beamline 12B was funded by the Diamond Light Source through grants SP7367, SP7393 and SP8670.

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Uranium and technetium form highly mobile aqueous species in their oxidised states, but form insoluble species in their reduced states.

Iron will be present in geological disposal facilities, leading to formation of various iron oxides. Magnetite, a mixed Fe(III)/Fe(II) oxide, is able to reduce U(VI) to U(IV) and Tc(IV) to Tc(III), however, the fate of radionuclides is poorly determined at high pH.

EXAFS and chemical extraction techniques, suggest both U(IV) and Tc(IV) may become incorporated into the magnetite structure, and that a significant proportion is retained during oxidation.

We thank Dr Steve Parny and Mr Richard Claff for assistance at Diamond. Mr Philip Lingard for XAS/RAND data collection. Dr. S. Caffrey for assistance with collection of XRD patterns. Dr. A. J. Bevan for assistance with sample preparation. Dr. M. Subramaniam and Dr. N. C. Derbyshire for TED imaging (EDR, XRD and EELS data not shown).

This work has been funded as part of the UK NERC BIGRAD consortium grant NE/F000797/1. beamsline at Diamond B18 was hosted by the Diamond Light Source through grant G015737. The experiments were funded by TANET (R) and Diamond Light Source (TANET R) to allow Tim Marshall to attend Actinides 2013.

* tim.marshall@manchester.ac.uk
Presented at Migration 2013, 14th International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere, 8th – 13th September 2013, Brighton, UK.

Uranium and technetium form highly mobile aqueous species in their oxidised states, but form insoluble species in their reduced states. Iron will be present in geological disposal facilities, leading to formation of various iron oxides. Magnetite, a mixed Fe(II)/Fe(III) oxide, is able to reduce U(VI) to U(V) and Tc(VII) to Tc(VI), however, the fate of radionuclides is poorly determined at high pH. EXAFS and chemical extraction techniques suggest both U(IV) and Tc(IV) may become incorporated into the magnetite structure, and that a significant proportion is retained during oxidation.

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We thank Dr. Steve Panay and Mr. Richard Dayll for assistance at Diamond, UPPL500 for IC-679 analyses (data not shown). Dr. J. Price for assistance with collection of HPO acidity. XPS and photoelectron spectroscopy (XPS) data collected at the Diamond Light Source in collaboration with Dr. T. Shaw and RSC Radiochemistry Group to allow attention to migration.

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Geological disposal of radioactive wastes is the internationally accepted management pathway for these materials. Many disposal concepts utilise cementitious materials as part of the engineered barrier or during construction. The geological time scales required for containment of wastes will exceed the lifetime of the engineered barrier with continued containment provided by the natural barrier - the host geology. It is therefore vital to understand how the natural barrier will react to the changing geothermal conditions and how this will affect the behaviour of radionuclides released from a geological disposal facility (GDF).

Iron oxides will be ubiquitous in disposal with corrosion products, wastes and host rock contributions. For example, Fe-bearing silicate minerals in the host rock will undergo alteration to form iron oxides (left, 3). The fate of radionuclides during interactions with iron oxides is poorly constrained (4,5). Here we have studied the fate of U(VI) and Tc(VII) during crystallisation of ferrihydrite to hematite and magnetite in terms of sorption, precipitation and incorporation.

U(VI) incorporation into hematite

Ferrhydrite was heated to induce hematite crystallisation in U(VI) spiked cement leachate (pH 10.5). Shifts in features A and B in the XANES reveal changes to the U-O bond lengths during hematite crystallisation as adsorbed U(VI) is incorporated into the structure.

EXAFS fitting confirmed that U(VI) was incorporated into a distorted octahedral site via substitution for Fe(III) within the hematite structure (6).

Tc(VI) incorporation into magnetite: limited oxidative remobilisation

Ferrithydate was crystallised to magnetite via addition of Fe(III) in Tc(VII) spiked cement leachates (pH 10.5 - pH 13.1). All Tc(VII) was reduced and removed from solution to the magnetite as Tc(V). Chemical extractions reveal Tc was predominantly concentrated at the magnetite surfaces. During oxidation, there was limited release of Tc back into solution (30%) with formation of an Fe rich/Tc deficient layer at the oxidised magnetite surface.

EXAFS fitting shows Tc(V) is incorporated into an octahedral site via substitution for Fe(III) within the magnetite structure (7). The incorporation mechanism and structural environment of Tc(V) is similar to that reported for Tc(VI) substitution into magnetite (8).
Appendix 5

A5 Author’s Contributions to Other Work

The author has made contributions to other bodies of work besides those contained within this thesis. Details of these bodies of work and the contributions from this author are detailed below.

The stability of colloidal U(VI) nanoparticles under GDF conditions when in contact with biotite, quartz, orthoclase, and NRVB. Rosemary Hibberd, Gareth T.W. Law, Pieter Bots, Timothy A. Marshall, Samuel Shaw, Nicholas D.Bryan, Katherine Morris. In preparation for submission to Mineralogical Magazine.

This author contributed to the original experimental setup and provided a large amount of data to compliment similar datasets as part of the wider review paper.

The Fate of Neptunium During Iron (Oxyhydr)Oxide Crystallization. Pieter Bots, Samuel Shaw, Gareth T.W. Law, Timothy A. Marshall, Melissa Denecke, Jörg Rothe, Kathy Dardenne, Katherine Morris. In preparation for submission to Environmental Science and Technology.

This author contributed to the XAS data collection and provided assistance with XAS data analysis.


Transnational Access to Large Infrastructure for a Safe Management of Actinide (TALISMAN) is a European Commission Framework 7 funded network to promote access to actinide research facilities across Europe. This author co-wrote the grant application for a 6-week research secondment to the KIT-INE laboratories in Germany with 3 days of μ-focus synchrotron beamtime at the INE-Beamline at the ANKA synchrotron at KIT. Additionally, this author designed the experimental set up and liaised with INE staff to optimise the set up; organised the logistics of the secondment; undertook the entire experimental programme, with assistance from INE staff for some analytical techniques; led the synchrotron data collection; performed all data analysis and is first author on the manuscript arising from the project, to be submitted to a suitable journal in due course.