Uranium solubility, speciation and complexation at high pH

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Uranium Solubility, Speciation and Complexation at High pH

by

Mark Sutton

A Doctoral Thesis submitted in partial fulfilment of the requirements for the award of

Doctor of Philosophy

of Loughborough University

October 1999

Research Supervisor: Prof. Peter Warwick

Sponsorship by British Nuclear Fuels plc

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ABSTRACT

Low level nuclear waste arising from UK nuclear sites, research establishments, hospitals and industry is currently disposed of at the Drigg Disposal Facility in Cumbria. Waste is packed into steel canisters before being compacted and grouted into larger steel storage containers. The aqueous chemistry of wastes, especially radionuclides, in the presence of grout material is of major interest. The grout used at the Drigg site is a mixture of Ordinary Portland Cement and Pulverised Fly Ash additive, from which ingressing water will leach high levels of calcium, sodium and potassium and produce waters of a high pH. Aerobic environments are expected to dominate over the early period of the vault life, after which the combined effect of canister corrosion and microbial activity will lead to anaerobic conditions. After a much longer period (100,000 years) anaerobic conditions may cease and yield once again an aerobic environment where migration of radionuclides may be sorption-controlled rather than on hydroxide precipitation at high pH.

Work has been performed under both aerobic and anaerobic conditions to study uranium solubility in the presence of complexing ligands that may be present in the waters of the nearfield of a low-level waste disposal vault. Eleven ligands have been investigated: carbonate, phosphate, chloride, sulphate, acetate, citrate, EDTA, NTA and organic matter- humic acid, fulvic acid and iso-saccharinic acid.

Anaerobic conditions were achieved by two different procedures; the first used ferrous ions in hydroxide solution and the second used dithionite in hydroxide solution. Both methods produce reducing electrode potentials and high pH.

Computer software has been used to model experimental results, thereby predicting uranium solubilities and speciation, and to propose new formation constants to fit the experimental results more closely.

Studies have also been performed to measure uranium sorption by grout material at high pH in the presence of the above ligands.

This work makes a significant contribution to the understanding of uranium solubility and speciation in waters at high pH and under conditions relevant to low level nuclear waste disposal.
Dedicated to my parents, without whom I would not be where I am today,
and to the memory of Bill Armstrong.
ACKNOWLEDGEMENTS

I would like to thank British Nuclear Fuels plc for sponsoring my research and providing me with the opportunity to work towards a PhD. I would like to thank Professor Peter Warwick for his advice and support during my research. Thank you to Carwyn Jones, Eugene Kelly, Matt Randal and Paul Humphreys at British Nuclear Fuels plc for their help and support. Thank you to Dr Tony Hall for his introduction to modelling and for his enthusiasm and help throughout the course of my PhD.

Thank you to Jim Robson at BNFL-Geoffrey Schofield Laboratories for analysis of grout leachate solutions, to Professor John Patrick at Loughborough University for analysis of grout material by XRF analysis and to Dr Alex Slawin at Loughborough University for help with XRPD analysis.

Thanks to the Environmental Radiochemistry Research Group, past and present at Loughborough: Linda for bad hair days and late night chats, Vanessa for mints and squash games, Helen for her motivation and making me work at weekends, Sam, Sarah (and Hannah), Karen and finally to Linda Sands for being ‘Lab-Mother’ and looking after us all.

Thanks to the staff of the Glenn T. Seaborg Institute for Transactinium Science at Lawrence Livermore National Laboratory- California, for their hospitality, friendship and encouragement, especially Maureen, Cindy, Brian, Lou, Phil and Joanne. Thank you to Karyn for her friendship and for giving me belief in myself.

Finally, thank you to all my friends and family for all the support they have given me over many years. Thank you to Linda and Lee for their friendship and kindness, to Louise for always being no more than a phone-call away and to Donna for her love and friendship.
“The most incomprehensible thing about the world is that it is comprehensible.”

Albert Einstein
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<td>Frumkin Adsorption Coefficient</td>
</tr>
<tr>
<td>K_{adF}</td>
<td>Freundlich Adsorption Coefficient</td>
</tr>
<tr>
<td>K_{adL}</td>
<td>Langmuir Adsorption Coefficient</td>
</tr>
<tr>
<td>K_d</td>
<td>Distribution Coefficient</td>
</tr>
<tr>
<td>K^o</td>
<td>Retention Factor</td>
</tr>
<tr>
<td>K_e</td>
<td>Dielectric Constant</td>
</tr>
<tr>
<td>K_f</td>
<td>Formation Constant</td>
</tr>
<tr>
<td>k_J</td>
<td>Kilo-Joule</td>
</tr>
<tr>
<td>K_{sp}</td>
<td>Solubility Product</td>
</tr>
<tr>
<td>k_s</td>
<td>Sorption Rate Constant</td>
</tr>
<tr>
<td>l</td>
<td>Litre</td>
</tr>
<tr>
<td>l</td>
<td>Path Length</td>
</tr>
<tr>
<td>l_0</td>
<td>Distance of Separation</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------------------------</td>
</tr>
<tr>
<td>LLW</td>
<td>Low Level Waste</td>
</tr>
<tr>
<td>LOI</td>
<td>Loss On Ignition</td>
</tr>
<tr>
<td>LSC</td>
<td>Liquid Scintillation Counting</td>
</tr>
<tr>
<td>M</td>
<td>Molar</td>
</tr>
<tr>
<td>m</td>
<td>Metre</td>
</tr>
<tr>
<td>mg</td>
<td>Milli-Gram ($10^{-3}$)</td>
</tr>
<tr>
<td>min</td>
<td>Minute</td>
</tr>
<tr>
<td>ml</td>
<td>Milli-Litre</td>
</tr>
<tr>
<td>mM</td>
<td>Milli-Molar ($10^{-3}$)</td>
</tr>
<tr>
<td>mV</td>
<td>Milli-Volt ($10^{-3}$)</td>
</tr>
<tr>
<td>N</td>
<td>Number of Atoms</td>
</tr>
<tr>
<td>n</td>
<td>Number of Electrons</td>
</tr>
<tr>
<td>NEA</td>
<td>Nuclear Energy Authority</td>
</tr>
<tr>
<td>NRVB</td>
<td>Nirex Reference Vault Backfill</td>
</tr>
<tr>
<td>NTA</td>
<td>Nitrilotriacetic Acid</td>
</tr>
<tr>
<td>OPC</td>
<td>Ordinary Portland Cement</td>
</tr>
<tr>
<td>PFA</td>
<td>Pulverised Fuel Ash</td>
</tr>
<tr>
<td>pH</td>
<td>-log$_{10}$ [$H^+$]</td>
</tr>
<tr>
<td>pH$_{pzc}$</td>
<td>Point of Zero Charge</td>
</tr>
<tr>
<td>Qe</td>
<td>Effective Charge</td>
</tr>
<tr>
<td>R</td>
<td>Molar Gas Constant</td>
</tr>
<tr>
<td>r</td>
<td>Radius</td>
</tr>
<tr>
<td>R$_d$</td>
<td>Linear Adsorption Coefficient</td>
</tr>
<tr>
<td>s</td>
<td>Seconds</td>
</tr>
<tr>
<td>SI</td>
<td>Saturation Index</td>
</tr>
<tr>
<td>S$_l$</td>
<td>Solubility Limit</td>
</tr>
<tr>
<td>T</td>
<td>Temperature (Kelvin)</td>
</tr>
<tr>
<td>t</td>
<td>Time</td>
</tr>
<tr>
<td>t$_{1/2}$</td>
<td>Half-Life</td>
</tr>
<tr>
<td>TIC</td>
<td>Total Inorganic Carbon</td>
</tr>
<tr>
<td>TRLFS</td>
<td>Time Resolved Laser Induced-Fluorescence Spectroscopy</td>
</tr>
<tr>
<td>v</td>
<td>Velocity</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>XRF</td>
<td>X-Ray Fluorescence</td>
</tr>
<tr>
<td>XRPD</td>
<td>X-Ray Powder Diffraction</td>
</tr>
<tr>
<td>yr</td>
<td>Year</td>
</tr>
<tr>
<td>$z_i$</td>
<td>Charge on Ion, i</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Alpha Decay</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Beta Decay</td>
</tr>
<tr>
<td>$\beta_{ad}$</td>
<td>Energy of Adsorption</td>
</tr>
<tr>
<td>$\beta_{f}$</td>
<td>Guggenheim Ionic Interaction Coefficient</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>Ion-Water Interaction</td>
</tr>
<tr>
<td>$\gamma_i$</td>
<td>Activity Coefficient for Ion, i</td>
</tr>
<tr>
<td>$\Delta G^*$</td>
<td>Change in Free Energy</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Molar Extinction Coefficient</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength, Decay Constant</td>
</tr>
<tr>
<td>$\mu_e$</td>
<td>Electrophoretic Mobility</td>
</tr>
<tr>
<td>$\mu M$</td>
<td>Micro-Molar ($10^{-6}$)</td>
</tr>
<tr>
<td>$\mu m$</td>
<td>Micro-Metre ($10^{-6}$)</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Viscosity</td>
</tr>
<tr>
<td>$\theta_i$</td>
<td>Angle of Diffraction</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Osmotic Coefficient</td>
</tr>
<tr>
<td>$\Sigma$</td>
<td>Sum</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>Zeta Potential</td>
</tr>
</tbody>
</table>
CHAPTER ONE

Introduction
1. Introduction

1.1 Background

Uranium, as well as being naturally abundant, is used as a nuclear fuel supply in power stations around the world. With the advent of nuclear power came the problem of disposal of the wastes associated with each stage of the nuclear fuel cycle - mining, manufacture, reprocessing, decommissioning and research. While all uranium isotopes are radioactive (nearly all of which decay by alpha particle emission and are long-lived), their half-lives and energies are very different and are all a hazard to the environment and the life which occupies it. The long-term, safe disposal of wastes is clearly of key importance and is being studied in depth as part of an on-going research program into the characterisation and maintenance of the Drigg disposal site. One part of this work is designed to help build a better understanding of the chemistry of uranium in the high pH cementitious environments.

1.2 Aims of the Research

The aims of this work are detailed below:

1. To chemically characterise Drigg grout and grout leachate.
2. To study the solubility of uranium at high pH under both aerobic and anaerobic systems.
3. To characterise the uranium precipitates formed at high pH in the presence of various metal cations and grout leachate.
4. To study the effect of complexing ligands which may be present in the vault waters at Drigg on the solubility of uranium under the conditions described above.
5. To examine sorption phenomena of uranium onto Drigg grout material at high pH and subsequent desorption using complexing ligands.

6. To model the experimental results using geochemical codes and to evaluate the current literature formation constants for each species.

7. To provide a useful addition to the knowledge base of waste disposal and characterisation at the Drigg site for purposes of risk assessment.

1.3 Low Level Radioactive Waste Classification and International Disposal

Waste from nuclear installations can be classified in three categories:

- low level waste, LLW; requires no shielding and contains only trace amounts of radionuclides
- intermediate level waste, ILW; requires shielding and contains short lived radionuclides
- high level waste, HLW; requires heavy shielding and contains long lived radionuclides

Many countries around the world have nuclear installations, all of which will produce radioactive waste. In an era of environmental concern it is recognised that each country should take responsibility for the safe disposal of its own waste. Countries with storage facilities for LLW are listed below, with their storage and disposal facilities in parentheses.

Belgium (prefabricated buildings on site of manufacture)
Canada (Ontario Hydro Bruce Nuclear Power Development site, Chalk River Labs and Whiteshell Labs, concrete-lined trenches, storage buildings, steel containers in concrete-lined bore-holes; planning for Intrusion Resistant Underground Structure at Chalk River Labs)
Finland (Olkiluoto, waste drums in concrete within vertical silo in shotcreted rock)

France (Centre de l'Aube, concrete sealed with a leak-proof cover)

Germany (on site of manufacture and at a salt mine Gorleben)

Italy (on site of manufacture)

Japan (on site; combination of engineered and natural barrier at Rokkasho-Mura)

Korea (on site of manufacture; possible disposal on Guleop Island)

Mexico (on site of manufacture; triple barrier method under design)

Netherlands (on site of manufacture)

Spain (El Cabril, 28 concrete vaults containing waste drums in concrete containers)

Sweden (SFR-Forsmark, caverns in bedrock under Baltic region, backfill, buffer and sealed with concrete)

Switzerland (on site of manufacture; Wellenberg site planned and under review)

UK (Drigg and Dounray sites, trenches and concrete lined vaults)

United States (seven shallow land burial sites with trenches covered by concrete and soil).

The design of these and future sites are of constant interest to scientists, geologists, engineers and the general public alike.

The chemical and physical characteristics of any disposal site can be described in terms of two zones. The near-field zone is described as the region of the containment site itself and may extend some 10-100m outwards from the vault. The near-field is a complex chemical and physical environment, designed to minimise the migration of the radionuclide inventory into the far-field. The characteristics that determine the transport of materials from the near-field is called the source-term. The far-field zone is defined as the area outside the near-field and encompasses the local geology and hydrology (geosphere) and stretches as far as
the biosphere, where the presence of hazardous materials affects the life of plants, animals and humans.

This work is concerned with the chemistry, solubility and transport of uranium within the near-field zone especially within the vault storage facility at Drigg in England. A schematic diagram of the key components of a near-field risk assessment program is shown below in Figure 1.1. Three different uranium systems have been investigated: aerobic solubility, anaerobic solubility and sorption phenomena on Drigg grout material. The effect of complexation of uranium at each stage has also been investigated.

![Figure 1.1 Schematic Diagram of Near-field Risk Assessment for a Waste Disposal Site](image)

Figure 1.1 Schematic Diagram of Near-field Risk Assessment for a Waste Disposal Site
1.4 The Drigg Site

1.4.1 History

Low level waste arising in the UK is currently disposed of at Drigg, situated four miles from the British Nuclear Fuels plc (BNFL) Sellafield site in Cumbria, England. Drigg is owned by BNFL and managed by the Low Level Waste Management Group. The site started operation in 1959 and site closure is predicted to be around the year 2100.

Low level waste arising from Sellafield comprises of some 70% of the total disposed of at Drigg. Waste is also accepted from the operation and decommissioning of other BNFL sites, nuclear power stations, research facilities and hospitals, providing the remainder of the inventory. Items such as clothing, tissue, wood, paper, plastics, PVC, polythene, rubber, metal, building materials, soil, and miscellaneous organics and inorganics are disposed of at Drigg, provided that their associated radioactivity is low enough to be classified as “low-level radioactive”.

Early disposal at Drigg was in seven trenches cut into the native boulder clay and waste was tipped into the trenches. When the trenches were completely filled, a capping was applied in the form of stone and soil, and this was later enhanced by a low water permeable membrane together with further soil.
A typical ground water composition together with the range of values encountered is given in Table 1.1. As for long term, a model ground water composition had to be adopted. The actual chemistry of the ground water will depend on the chemistry of the vault walls and the cap used. Since the cap has not yet been applied and the system has not been sealed, it is very difficult to predict its effect on the water passing through it. Vault 8 at Drigg is approximately half on top of the water table at the Drigg site. Hydrological investigations suggest that the horizontal groundwater flow maybe less important than the rainwater from above. This rainwater will have to pass through the cap if it is to reach the waste within the vault and so will be chemically conditioned as near-surface ground water. The current ground water flow at the site is 240m³/yr.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Typical Drigg Groundwater</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.4</td>
<td>5.9 - 8.1</td>
</tr>
<tr>
<td>Eₘ (mV)</td>
<td>-80</td>
<td>-86 - +46</td>
</tr>
<tr>
<td>Na (mM)</td>
<td>1.270</td>
<td>0.779 - 3.436</td>
</tr>
<tr>
<td>K (mM)</td>
<td>0.087</td>
<td>0.036 - 0.228</td>
</tr>
<tr>
<td>Ca (mM)</td>
<td>1.584</td>
<td>0.414 - 2.153</td>
</tr>
<tr>
<td>Mg (mM)</td>
<td>0.794</td>
<td>0.160 - 0.827</td>
</tr>
<tr>
<td>Fe (mM)</td>
<td>0.192</td>
<td>0.002 - 0.202</td>
</tr>
<tr>
<td>Si (mM)</td>
<td>0.178</td>
<td>0.174 - 0.267</td>
</tr>
<tr>
<td>SiO₂ (mM)</td>
<td>0.161</td>
<td>0.113 - 0.183</td>
</tr>
<tr>
<td>Cl⁻ (mM)</td>
<td>1.340</td>
<td>0.762 - 3.808</td>
</tr>
<tr>
<td>NO₃⁻ (mM)</td>
<td>0.024</td>
<td>0.000 - 0.131</td>
</tr>
<tr>
<td>SO₄²⁻ (mM)</td>
<td>0.396</td>
<td>0.078 - 0.645</td>
</tr>
<tr>
<td>HCO₃⁻ (mM)</td>
<td>4.002</td>
<td>0.539 - 4.716</td>
</tr>
<tr>
<td>Fulvics (mg/l)</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.1 Composition of Drigg Groundwater [1]
1.4.3 Disposal of LLW in Vault 8, Drigg

In 1989 a concrete lined vault was built, “Vault 8”, allowing for the disposal of approximately 700,000m$^3$ (1,500,000 tonnes) of low level waste. A predicted Drigg vault inventory at the time of site closure is detailed in Table 1.2.

The low-level waste is packed into primary containers of either mild steel 200 litre drums or 1m$^3$ boxes. The mild steel used will undergo corrosion much faster than stainless steel. The primary containers undergo high-force compaction at 5000 tonnes of applied force. This minimises the volume of the waste containers. The resulting “pucks” are packed into large iso-freight (secondary) containers, again produced from mild steel. The containers are grouted to fill all void space. Neither the primary nor secondary containers are completely sealed since gas evolution and waste degradation would lead to an undesirable pressure build-up.

<table>
<thead>
<tr>
<th>Component of Vault Waste Inventory</th>
<th>Percentage of Waste (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grout (PFA/OPC)</td>
<td>46.3</td>
</tr>
<tr>
<td>Iron &amp; steel (containment)</td>
<td>27.7</td>
</tr>
<tr>
<td>Infill (silica sand)</td>
<td>8.0</td>
</tr>
<tr>
<td>Cement &amp; concrete (decommissioning)</td>
<td>7.8</td>
</tr>
<tr>
<td>Other metals</td>
<td>3.2</td>
</tr>
<tr>
<td>Polymers / rubbers / plastics</td>
<td>2.3</td>
</tr>
<tr>
<td>Miscellaneous inorganics</td>
<td>2.2</td>
</tr>
<tr>
<td>Cellulosics</td>
<td>2.1</td>
</tr>
<tr>
<td>Miscellaneous organics</td>
<td>0.4</td>
</tr>
<tr>
<td>Total volume</td>
<td>~700,000 m$^3$</td>
</tr>
<tr>
<td>Total Mass</td>
<td>~1,500,000 tonnes</td>
</tr>
<tr>
<td>Total Density</td>
<td>2.0 tonnes / m$^3$</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.2 - 0.3 litres / m$^3$</td>
</tr>
</tbody>
</table>

Table 1.2 Predicted Drigg vault inventory at the time of site closure [1]
The grout used at Drigg is a cement composite material made from a 3:1 ratio of pulverised fly ash (PFA) and ordinary Portland cement (OPC). The chemical analysis of the grout used is described in chapter 2. The grout is designed specifically to facilitate the complete filling of each iso-freight container, making use of high-flow properties of the wetted grout. The overhead pressure exerted on the containers from stacking and capping could lead to the collapse of waste into void spaces. This would result in a possible subsidence, observed as cracks and fractures in the applied cap, providing easy and unacceptable routes for the release of radionuclides.

Drigg grout was not designed with the intent of chemical conditioning of the waste to retard radionuclide transport. But this work will show that the grout material has beneficial properties with regard to high pH, leading to the precipitation and sorption of uranium.

The ISO-freight containers are stacked in the vault and the space between is filled with an inert filler such as silica sand. Items too large to be packed into either primary or secondary containers are placed in the vault and grouted in situ.

Once full, the vault will be capped with soil, gravel and a low permeability plastic membrane to minimise water ingress.

1.4.4 Vault Pore-water

Vault pore-water is the term used for the waters inside the vault which have come to equilibrium with the main contents of the vault, namely the concrete walls of the vault, and the mild steel ISO-freight containers. The modelled chemical analysis of vault pore-water [1] is described in Table 1.3, below.
### Table 1.3  Modelled Chemical Analysis of Drigg Vault Pore-water

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Vault Pore-water (Modelled)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>9.8</td>
</tr>
<tr>
<td>$E_h$ (mV)</td>
<td>-300</td>
</tr>
<tr>
<td>Na (mM)</td>
<td>0.5</td>
</tr>
<tr>
<td>K  (mM)</td>
<td>0</td>
</tr>
<tr>
<td>Ca (mM)</td>
<td>0.1</td>
</tr>
<tr>
<td>Mg (mM)</td>
<td>0.2</td>
</tr>
<tr>
<td>Fe (mM)</td>
<td>0.003-100</td>
</tr>
<tr>
<td>Cl (mM)</td>
<td>0.6</td>
</tr>
<tr>
<td>NO₃ (mM)</td>
<td>0</td>
</tr>
<tr>
<td>SO₄ (mM)</td>
<td>0.2</td>
</tr>
<tr>
<td>TIC (mM)</td>
<td>0.25</td>
</tr>
<tr>
<td>Acetate (mM)</td>
<td>0</td>
</tr>
<tr>
<td>Humics/Fulvics (mM)</td>
<td>0</td>
</tr>
<tr>
<td>ISA (mM)</td>
<td>0</td>
</tr>
</tbody>
</table>

1.4.5 Vault Evolution and Risk Assessment

For the purpose of safety, licensing and risk assessment, it must be shown without reasonable doubt that the Drigg site will constitute negligible risk to the environment. The risk assessment for the Drigg site should cover at least 100,000 years. All factors must be investigated, studying the three main pathways of risk to the environment: water pathways, gaseous diffusion and human intrusion. Although this task is the duty of the operator, its determination and application is not an easy matter. Every eventuality must be accounted for: climate change, political and social stability and geological processes.
When the timescale required is put into perspective, it is easy to see that this is no mean feat: in the last 100,000 years there have been four ice ages to sweep over the UK [2]. An ice age could clearly glaciate out a landfill site and carry its contents hundreds of miles. Interspersed between ice ages are the interglacial periods with times of global warming and rising sea-levels. Such natural phenomena could swallow miles of coastline and dissolve landfill sites into the ocean. Man himself has evolved dramatically over the last 100,000 years, from Neanderthal and anatomically modern Africans, to Cro Magnon Man and finally to our lifestyles today [3].

The task of prediction is made more difficult in that the Drigg disposal site is not yet completed. Site closure will only take place once all the available space is used to accommodate waste. For this reason, models are used to predict the chemical and physical changes within the life of the disposal site. It is, however, important to investigate every possibility and it is with this in mind that this study was undertaken, to study a specific set of physical and chemical conditions which may have an impact on the solubility, speciation and transport of uranium. While the work presented here may be a reasonable assumption of vault behaviour, it should be noted that there are many conceptual models as to the long-term vault characteristics.

The study specifically takes into account the probable evolution of pH and $E_{h}$, which are examined in sections 1.5.5 and 1.6.3.

### 1.4.6 Uranium Inventory Within Vault 8

At the time of writing, only an estimate of the uranium inventory of Vault 8 at site closure is available. The total uranium estimated content is 219 tonnes by the year 2100, based on predictions of future LLW arising from UK nuclear installations. The majority of the uranium (some 99% by mass) will be the naturally occurring
238U isotope, 1% 235U and negligible amounts of other uranium isotopes. If the volume and porosity of the vault and its waste are taken into account and assuming that all the uranium present is available to vault pore water, the uranium concentration in the vault leachate could reach a maximum of $5 \times 10^{-3}$ M.

1.5 Chemical and Physical Properties of Cement and Grout

The grout used at the Drigg site and in this study is a composite of ordinary portland cement and pulverised fuel ash (mixed in a 1:3 proportion), chosen for its flow properties (rheology) to minimise the void space in the ISO-freight containers used to dispose of LLW. This property is due to the physical nature of the particulates associated with fuel ash, which are mostly smooth, spherical particles of an aluminosilicate glassy material.

1.5.1 Ordinary Portland Cement, OPC

Although there are controls on the quality of cement and its production, in terms of analytical chemistry there are wide variations in the constituents. The industrial characterisation of cement is considered adequate for large scale use and includes the chemical composition, physical particle size, strength, porosity and setting time. The chemical composition is defined in terms of key components which change the physical properties of the cement. An excess of magnesium and calcium oxides leads to ‘delayed’ expansion of the cement when reacted slowly with water.

OPC is produced on a large scale by a high temperature reaction of limestone with clay (illite and kaolinite) and gypsum. Addition of iron ore and sand may also be required to increase the Fe, Al and Si content and therefore change the physical properties of the cement. The mixture is crushed to a fine powder before being transferred to a rotary kiln which reaches around 1400°C at certain points. At this
temperature the raw materials are intermixed in a melt. Although at these temperatures most of the unwanted components such as sodium, potassium, chloride and sulfur are volatilised, some impurities remain throughout the process. These impurities do however help to decrease the temperature required to create a melt. On cooling, the impurities are trapped into the crystallising lattice.

OPC consists of varying phases of several mineral compounds, including:
- Alite: $3\text{CaO}.\text{SiO}_2$
- Belite: $2\text{CaO}.\text{SiO}_2$
- Aluminate: $3\text{CaO}.\text{Al}_2\text{O}_3$
- Ferrite: $4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$

together with oxides of sodium, potassium, magnesium, sulfur and trace titanium and manganese amongst others. A typical OPC composition is shown in Table 1.4 [4].

The addition of other inorganic minerals can dramatically change the properties of the cement. Two such types of additive are pulverised fuel ash and blast furnace slag, both used to create a composite cement for specific usage. Addition can be made either at the primary stage in the kiln (termed 'intergrinding') or at the blending stage.

1.5.2 Pulversied Fuel Ash, PFA

As the name suggests, PFA is a by-product of the burning of fossil fuels such as coal. When coal is burnt, associated minerals such as $\text{SiO}_2$, clay and feldspars (aluminium silicates) are disintergrated and are seen as waste. While the heavier particles are left behind, some of the finer particles are lost in flue gas. With the onset of environmental concern, fossil-fuel power stations were required to trap the harmful emissions. Techniques such as electrostatic precipitators, filters and
cyclone separators are employed to minimise the environmental impact. A typical PFA composition is detailed in Table 1.4 [4].

It was later realised that the ash was similar to volcanic ash and would therefore possess pozzolanic properties, i.e. the reaction between SiO$_2$ and CaO in water to form an insoluble, cement-like mixture which is discussed below.

<table>
<thead>
<tr>
<th>Component</th>
<th>% Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>67</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>21</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>7</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>3</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0</td>
</tr>
<tr>
<td>MgO</td>
<td>0</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>2</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0</td>
</tr>
<tr>
<td>Cl</td>
<td>0</td>
</tr>
</tbody>
</table>

Current classification of PFA in the UK is defined by Type-I and Type-II additions of PFA to cement. A Type-I addition is one which is used to improve or achieve certain properties of the mixture, one in which the pozzolanic nature of the PFA is not utilised and is not self-cementitious. A Type-II addition is one which does utilise the pozzolanic properties of PFA to create a faster setting, more durable and self-cementitious mixture.
In the UK, the guidelines for use of PFA are based on the British Standards BS6610 and BS3892 parts 1, 2 and 3; “Specifications for Pozzolanic PFA Cement (1996)”, “Specifications for PFA for Use With OPC (1997)”, “Specifications for PFA to be Used As a Type I Addition (1996)” and “Specifications for PFA for Use in Cementitious Grouts (1997)” respectively. BS3892 parts 2 and 3 are for use of PFA as a Type-I admixture while BS3892 part 1 and BS6610 are for PFA use as a Type-II admixture. The difference in the requirements is reflected in the allowed composition of PFA for each standard, each with increasing amounts of calcium carbonate composition allowed. This limits the availability of calcium oxide (and therefore calcium hydroxide) to act as a pozzolan.

1.5.3 Pozzolanic Reaction

Pozzolanic materials are not in themselves cementitious, but form insoluble cement-like products in the presence of water and calcium hydroxide. Calcium oxide in water will form calcium hydroxide. At high pH, the bridging between silica groups in the cement structure is attacked due to an excess of free hydroxide ions in solution and the presence of calcium hydroxide in the pore waters.

The -Si-O-Si- linkages broken are replaced by -Si-O-Si-OH groups. Once this process has occurred several times, SiO₄²⁻ is broken from the cement framework and is transferred to the pore water. The counter ions for this silicate ion are in the form of Na⁺, K⁺ (both present in the cement) and H⁺ from the dissociated water molecules. This yields rapid precipitation of amorphous alkali silicates. However, due to the greater abundance of calcium in the cement, this effect is only short-lived, and eventually leads to the formation of less soluble calcium silicate hydrates (C-S-H, discussed in chapter 1.5.4) and hydrated calcium aluminate phases.
1.5.4 Cement Hydration and Pore Water

Hydrous silica reacts initially with CaO and water as follows:

$$\text{SiO}_2\cdot\text{H}_2\text{O} + 3\text{CaO} + \text{H}_2\text{O} \rightarrow 3\text{CaO}\cdot\text{SiO}_2\cdot x\text{H}_2\text{O}$$

This hydrated calcium-silicate then undergoes a rearrangement in which a CaO moiety is lost to yield $2\text{CaO}\cdot\text{SiO}_2\cdot x\text{H}_2\text{O}$ and a transient equilibrium is established. However, the Ca:Si ratio continually changes to reach a more stable structure. The presence of other ions, such as $\text{K}^+$ or $\text{Na}^+$, reduces the free Ca concentration and the free SiO$_2$ must therefore increase to satisfy the equilibrium ratio.

These clearly defined calcium-silicate phases give way to less clearly defined structures of mixed stoichiometry, known as C-S-H gels, where the dashes indicate a range of Ca:Si:H,O ratios. These C-S-H phases can be likened to minerals such as tobermorite (Ca$_2$Si$_6$O$_{17-9}$H$_9$O) or jennite (Ca$_6$Si$_6$O$_{21-11}$H$_9$O).

After a long period of time, the C-S-H gel degrades to form calcite (CaCO$_3$) and silica. The presence of free carbonate can lead to carbonation, in which carbonate leaches calcium from the C-S-H gel to form more calcite and calcium-aluminate phases.

Reactions and rearrangements also occur in the Al$_2$O$_3$-Fe$_2$O$_3$-SiO$_2$-CaO-H$_2$O system, with a large variation in mineral structures being produced to provide a strongly bound material that we know as cement.

The use of an additive such as PFA leads to the formation of more C-S-H by reaction of the added SiO$_2$ in the PFA with free Ca(OH)$_2$ in the OPC. Natural zeolites (aluminium silicates with open cage-like structures) may also be present in the PFA material and these act as cation exchangers, ‘mopping-up’ any free Ca(OH)$_2$ before breaking down to form C-S-H and hydrated alumina.
Cement pore water (referred to as grout leachate in this work) is water which has been in intimate contact with the cementitious material. High concentrations of Ca\(^{2+}\), K\(^+\), Na\(^+\), SO\(_4\)\(^{2-}\) and OH\(^-\) are obtained after only a few hours of contact with water [5]. In practice, little variation was observed for 12 hours since an equilibrium was set up between the dissolution of the cement and the precipitation of new products of hydration. However, after 12-16 hours of contact time, a decrease in the Ca\(^{2+}\) and SO\(_4\)\(^{2-}\) concentrations in the leachate was observed, due to the formation and renewed growth of ettringite (Ca\(_6\)Al(OH)\(_{16}\)(SO\(_4\)\(_3\)).3H\(_2\)O). After this stage, the concentrations of each component may rise in the leachate to reach a maximum after perhaps 28 days.

1.5.5 pH Evolution at Drigg

It is assumed that the grout material will not interact with the waste until that time when it comes into contact with ground water. The pH of the waters will be greatly affected and dependent on the contact material.

Before the vault water reaches the waste, it will have been conditioned by the concrete walls of the vault to a pH of 9.8. Once the waters reach the waste, immediate leaching of NaOH and KOH from the grout lead to a sharp increase in pH to between pH 10 and 12. This pH is maintained for as long as there is potassium and sodium available to the pore water. Afterwards, the pH reduces slightly to between pH 10 and 11, controlled by the dissolution of calcium oxides (CaO) leading to Ca(OH)\(_2\) and CaCO\(_3\). After many thousand years, calcium silicate hydrate (CSH) gels control the pH to around pH 10. This is a long-term pH controlling phase and is itself expected to last for many tens of thousands of years. However, the degradation of organic material in the waste matrix may cause a significant pH decrease over a short period of time.
1.6 Chemical and Physical Properties of Mild Steel and Corrosion

As noted earlier, the low-level waste material at the Drigg site is packed into mild steel containers which then undergo high-force compaction. The following section is a brief overview of the chemistry of mild steel and its possible corrosion mechanisms.

1.6.1 Mild Steel

Mild steel is one in which the carbon content and other impurities are kept low, with the main component being iron. A typical composition of mild steel [6] is shown below in Table 1.5.

Impurities are added to alter the characteristics of the steel, but the impurities can also be problematic. Carbon, molybdenum, copper, nickel, manganese and chromium all increase the strength of the steel, while the latter two also help to maintain iron in a low oxidation state during manufacture. Phosphorus aids the machinability and stiffens mild steel. Sulphur lowers the mechanical properties of the steel and silicon is added to protect the refractories in manufacture and to balance any lime added during the desulfurisation and dephosphorisation stages.
### Table 1.5  Typical Composition of Mild Steel [6]

<table>
<thead>
<tr>
<th>Component</th>
<th>% Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.1-0.2</td>
</tr>
<tr>
<td>Cr</td>
<td>0.25 max</td>
</tr>
<tr>
<td>Cu</td>
<td>0.3 max</td>
</tr>
<tr>
<td>Mn</td>
<td>0.6-1.0</td>
</tr>
<tr>
<td>Ni</td>
<td>0.4 max</td>
</tr>
<tr>
<td>P</td>
<td>0.05</td>
</tr>
<tr>
<td>S</td>
<td>0.05</td>
</tr>
<tr>
<td>Si</td>
<td>0.6</td>
</tr>
<tr>
<td>Mo</td>
<td>0.15 max</td>
</tr>
<tr>
<td>Fe</td>
<td>97</td>
</tr>
</tbody>
</table>

The key characteristic of mild steel is that it is fairly malleable and is therefore ideal for use in a high-force compactor.

#### 1.6.2 Steel Corrosion

Corrosion is defined as the degradation or destruction of a material by reaction with its environment. There are eight general forms of corrosion [7]:

---

19
1. **Uniform Attack:** The most common form of corrosion, especially in mild steels; reaction of the material with a medium by chemical or electrochemical processes over the surface.

2. **Galvanic Corrosion:** Important in stainless/alloyed steels; electrochemical reaction between two metals present in the steel when immersed in a conducting solution, due to the difference in potential difference between the two metals, resulting in the enhanced corrosion of the least corrosion-resistant metal and decreased corrosion of the other metal.

3. **Crevice Corrosion:** Important in stainless steels; localised corrosion in any crevices available to corrosive material.

4. **Pitting:** The most destructive form of corrosion; chloride attack usually results in autocatalytic-pitting in which the anodic dissolution of the metal causes chloride ions to migrate towards the pit forming soluble metal chloride which may then hydrolyse to yield free acid to re-attack the prone steel surface.

5. **Intergranular Corrosion:** Characteristic of stainless/alloyed steels; under certain conditions the grain boundary becomes very reactive compared to the grains themselves.

6. **Selective Leaching:** Characteristic of stainless/alloyed steels; the selective removal of one of the metals from an alloy over other metals, depending on the corrosive solution.

7. **Erosion Corrosion:** Important only where relative movement of material and corrosive occur; a secondary type of corrosion which increases the rate of corrosion when one of the above mechanisms has commenced.

8. **Stress Corrosion:** Cracking of the material due to the application of tensile stress while in the presence of a corrosive.
Under aerobic environments, an oxide film is deposited over the surface which passivates the steel and results in negligible ‘uniform’ corrosion. The main type of corrosion under aerobic environments is therefore localised corrosion: for mild steel, pitting is the main ‘localised’ form of corrosion; while for stainless steels, ‘crevice’ corrosion is more likely (enhanced by any chloride or thiosulfate available) as well as stress corrosion. In the presence of cement and chloride, a 3mm pit depth was reported over 4 years by [8].

The effect of pH on the corrosion of steels shows little difference between pH 4.5 and 9.5 [9], where the products of steel corrosion buffer the pH at 9.5 at the steel-solution interface. When the corrosion of a steel sample is studied with pH variation, hydrogen gas is evolved when the pH is decreased below pH 4 and the rate of corrosion greatly increases. If a weak acid such as carbonic acid is present, the minimum pH at which hydrogen gas evolution begins is raised to pH 6. Above pH 9.5 the rate of steel corrosion decreases and the presence of carbonate in this pH region inhibits corrosion.

The presence of soil or soil-equilibrated water may affect the corrosion of steel. Soil may be present in the form of waste compacted into the LLW canisters at Drigg. A study by Romanoff [10] showed that a number of carbon steels were all subject to corrosion when in contact with a wide range of soil types. The presence of microbes can cause corrosion of steels also, with nearly half of all failures of subterranean metals due to microbial action [9]. Microbes can either thrive on aerobic or anaerobic atmospheres; aerobes can produce sulphuric acid from sulphur oxidation, while anaerobes can produce hydrogen sulphide from sulphate reduction.

The passivity of the steel may only pertain to time-scales over which oxygen is available. Once oxygen has expired, the system becomes anaerobic and leads to uniform corrosion of the steel in which the surface of the steel reacts with water to form metal oxides and hydroxides together with the evolution of hydrogen gas, which in turn can react with the metal structure and cause mechanical failure. The
dissolution rate is very low at high pH: 0.1-0.5\(\mu\text{m/yr}\) for mild steel, <0.1\(\mu\text{m/yr}\) for stainless steel [8]. However, Marsh [11] reports that aerobic localised corrosion would not be significant, but that anaerobic corrosion will completely consume steel in 1000 years.

1.6.3 \(E_h\) Evolution at Drigg

The oxidising or reducing capability of a system is measured in terms of \(E_h\), the standard potential with respect to the normal hydrogen electrode. Using the Nernst equation, it is possible to relate the measured redox potential to the proton concentration and therefore the pH of the system,

\[
E_h = E^\circ - \frac{RT}{nF} \ln \frac{\{H_2O\}}{\{H^+\}}
\]

in which \(E_h\) is the measured potential, \(R\) is the molar gas constant, \(n\) is the number of electrons transferred, \(F\) is the Faraday constant, \(\{H_2O\}\) is the activity of water (taken as unity) and \(\{H^+\}\) is the proton activity.

The redox potential can also be defined by thermodynamics if a chemical equilibrium is established between each solution and an electrode, since the term \(\{\text{oxidant}\}/\{\text{reductant}\}\) can be substituted by an equilibrium constant, \(K_f\)

\[
E_h = \frac{2.303RT}{nF} \log K_f
\]

and since \(\Delta G^\circ = -RT\log K_f\), the following relationship can be stated

\[
\frac{-\Delta G^\circ}{nF} = \frac{2.303RT}{nF} \log K_f = E_h
\]
It can then be stated that if an $E_h$ is positive, a spontaneous reaction occurs which favours the formation of the oxidised species.

The equilibrated $E_h$ of the ground water at Drigg ranges from -86 to +46 mV. During the initial stages of vault life, the vault waters will be aerobic.

The corrosion of iron in the mild steel containers will lead to reducing potentials being induced, due to the following oxidation reactions

$$Fe = Fe^{2+} + 2e^- \quad E^o = -0.447V$$

and

$$Fe^{2+} = Fe^{3+} + e^- E^o = 0.771V.$$ 

Therefore, as soon as the steel begins to corrode, the vault waters will become increasingly reducing, until a potential defined by the ferric/ferrous pair, together with other redox couples present in the waste matrix and leachate, reach equilibrium. Cellulose degradation will lead to microbial activity and this will also aid the production of anaerobic potentials in the waste matrix.

The anaerobic stage of the vault life is expected to last for possibly many thousands of years. Once the iron in the steel has been completely consumed by corrosion, aerobic environments may again be re-established.

The redox behaviour of uranium is examined in chapter 1.8.1 of this work.

1.7 Solubility and Complexation Theory

As part of the research undertaken to assess the solubility and chemistry of uranium at high pH, thermodynamic modelling of uranium solubility was performed to compare against experimental work. The results from the modelling provided information concerning the aqueous speciation and precipitated phases of uranium,
together with an approximate composition of a variety of uranium precipitates at high pH.

A 'model' is a term used to describe the calculated results obtained using a speciation code (such as MINTEQA2) and the raw data used by the code in the form of a database (such as HATCHESv10). It is important to note that a thermodynamic model is not definitive and should be supported with experimental work where possible. The output from a model is only as good as the thermodynamic data it uses. Evidence of this is discussed in chapters 5, 6 and 7 of this thesis.

In order to understand the theory of precipitation and the reasoning behind speciation modelling, an examination of thermodynamic stability in solution is described below.

1.7.1 The Equilibrium Constant

When examining the possible species present in a given system, the constant which largely determines the chemical activity of a species in a system is the thermodynamic equilibrium formation constant, $K_f$.

For an equilibrium process in which species $A^+$ and $B^-$ react to give species $AB$, a formation constant can be derived for their respective activities:

$$aA + bB = A_a^b B_b$$

$$K_f = \frac{\{AB\}}{\{A\}^a \{B\}^b}$$
If species AB is a solid phase, the above equation can be simplified on the basis that the activity of a solid phase is by definition, equal to unity. Thus the formation constant is the reciprocal of the products of the soluble species,

\[ K_f = \frac{1}{{[A]^a [B]^b}} \]

Because the numerical values for these constants vary over such a wide range, a logarithmic scale is used and values are often quoted as \( \log K_f \).

The formation constant of the solid phase can be replaced by a reciprocal for the solubility product, \( K_{sp} \),

\[ K_{sp} = {[A]^a [B]^b} \]

The formation of a precipitate from solution and its subsequent dissolution depends not only on its solubility product, but also on the formation constants of the possible dissolved species.

When modelling aqueous systems with speciation codes such as MINTEQA2 [12] or PHREEQE [13], these formation constants are often adjusted to take into account the ionic strength effects and variations and therefore the variations in activity coefficients. Where a formation constant is listed as \( K_f \), the model then recalculates a new formation constant \( (K'_f) \) based on the effect of the activity coefficient for that species \( (\gamma_i) \), i.e.

\[ K'_{fi} = K_{fi} / \gamma_i \]

This subject of ionic strength calculations is also described in section 1.7.3.
1.7.2 Competing Equilibria

When two slightly soluble salts are in competition for the pairing with a single counter ion, and their solubility products differ, it is possible to precipitate one of the ions with the counter ion whilst leaving the remaining ion in solution.

Again, considering the ions $A'$ and $B^-$, precipitation occurs when $[A'][B^-] > K_{sp}$

If $A'$ and $D^+$ are the ions in competition for the counter ion, $B^-$, leading to the formation of a slightly soluble precipitate; and if $K_{sp}(AB) < K_{sp}(DB)$, a precipitate of AB may be achieved by careful addition of $B^-$ ions to the solution.

The general rule is that the salt with the lower solubility product will precipitate out first.

When more than one solid phase is present and the system is to be modelled, an order of priority is created after the first aqueous equilibration, based on the formation constants and ion-activity-products (IAP) for each solid phase. This leads to a ‘saturation index’ (SI) allowing a quick and easy comparison of solid phases which are most likely to be formed;

$$SI_i = \log\left(\frac{\text{IAP}_i}{K_{fi}}\right)$$

For a SI value of less than zero, a solid phase is said to be undersaturated and will not therefore precipitate. For a SI value greater than zero, a solid phase is oversaturated and may precipitate.

All ionic strengths are then recalculated and the model equilibrates all species and solid phases based on the assumption that, at the final equilibrium, the saturation index is equal to zero. The MINTEQA2 code uses the Newton-Raphson
approximation method for iterative recalculation of the IAP so that the saturation index is equal to zero.

Conversion of one precipitate to another (known as transposition) is another possible process which must be considered when studying solid / solution chemical interactions. It can be induced by changing one of the counter ions and maybe required if one precipitate is too insoluble.

\[
A_aB_b (s) = aA^{b+} (aq) + bB^{a+} (aq) \quad K_{sp} = [A^{b+}]^a[B^{a+}]^b
\]

\[
A_aC_c (s) = aA^{c+} (aq) + cC^{a-} (aq) \quad K_{sp} = [A^{c+}]^a[C^{a-}]^c
\]

where \(K_{sp}(AB) < K_{sp}(AC)\).

By transposing the above chemical equations, the following is obtained:

\[
[B^{a+}]^b / [C^{a-}]^c = k_{sp}(AB) / k_{sp}(AC)
\]

But \(k_{sp}(AB) / k_{sp}(AC)\) is equivalent to \(k\), the equilibrium constant for the system, and so

\[
A_aB_b (s) + cC^{a-} (aq) = A_aC_c (ppt) + bB^{a+} (aq)
\]

However, transposition is often difficult, due to the generation of ‘carried-down’ impurities. The newly formed precipitate forms a layer on top of the first precipitate, leaving it protected from further reactions. Transposition is not a method used by the MINTEQA2 model for predicting solid phases.
1.7.3 Ionic Strength Calculations and Adjustments

Thermodynamic codes such as MINTEQA2 [12], PHREEQE [13], EQ3/6 [14] and CHESS [15] all use almost similar iterative methods to arrive at the final answer. A major difference is the method used for calculating the ionic strength and the corresponding activities of each component in the model. Some use the Debye-Huckel formula, others use the Davies or the Guggenheim equation.

The Gibbs equation is the basis for chemical thermodynamics. This equation requires chemical activities to be used in place of concentration. When experiments are performed in the laboratory, concentrations are measured rather than chemical (or ionic) activities and therefore a conversion factor must be used to relate the chemical concentration to the chemical activity:

\[ C_i = \gamma_i a_i \]

which can also be written \[ [i] = c_i \{i\} \]

where \( C \) is the molal concentration, \( a \) is the chemical activity and \( \gamma \) is the activity coefficient if an ion, \( i \).

In order to determine the activity coefficient the ionic strength, \( I \), is also required:

\[ I = \frac{1}{2} \Sigma c_i z_i^2 \]

where \( z_i \) is the charge on ion \( i \). Note that the calculation of \( I \) requires summation over all ions.

Now that the ionic strength is known, the activity coefficient can be calculated by one of the following equations:

The Debye-Huckel equation accounts for long-range electrostatic contributions \((A_i I^{1.2})\) and the fact that ions in solution are not point charges \((B_i a I^{1.2})\), where \( a \) is
the distance of closest approach of the ions (can be assumed to be the ionic
diameter) and $A_\gamma$ and $B_\gamma$ are coefficients which are dependent on the solution and
ions involved. For concentrated solutions,

$$\log \gamma_i = -|z_i| \left( \frac{A_\gamma I^{1/2}}{1 + B_\gamma \alpha I^{1/2}} \right)$$

For dilute solutions (typically less than $I = 10^{-5}$ M), the limiting form of the Debye-
Huckel equation assumes that the ions are point charges:

$$\log \gamma_i = -|z_i| A_\gamma I^{1/2}$$

However, the Debye-Huckel assumption that the ions have a constant diameter
means that the ions are assumed to be non-deformable spheres. This is not the case
in reality.

The Davies equation is very similar to the Debye-Huckel equation, in which the
term $A_\gamma / B_\gamma a$ is assumed to be equal to unity.

$$\log \gamma_i = -A_\gamma |z_i| \left( \frac{I^{1/2}}{1 + I^{1/2} - 0.24I} \right)$$

A more realistic value for the activity coefficient of an ion is obtained when using
the Guggenheim equation, which takes into account multicomponent electrolytes
which are 'real' with non-electrostatic contributions up to $I = 0.1$ M

$$\log \gamma_i = \frac{-z_i^2 A_\gamma I^{1/2}}{1 + I^{1/2}} + 2 \sum_{i=1}^{\beta_j} \beta_j c_i + \Gamma$$
where $\beta_{ij}$ is the coefficient allowing for interactions between the ion $j$ and other ions in solution, $l$, and $\Gamma = -\log(1 + a_{H_2O} \sum_i c_i)$ where the activity of water is calculated as $a_{H_2O} = \frac{-2c_{mx} \phi}{55.51 \ln 10}$ and the osmotic coefficient, $\phi$ in a background electrolyte solution, $mx$, of much higher ionic strength than the reacting ions, where the molarity of water is taken as 55.51 M.

1.8 A Review of Uranium Solubility and Complexation

Concise reviews of the processes involved in studying the solubility and mobility of radionuclides in the environment are provided by Lieser [16] and Silva [17]. These reviews include description of solubility, complexation, sorption, colloids, redox potential, pH and modelling. For a description of the general chemistry of uranium, and other actinides, “The Chemistry of the Actinide Elements” by Katz, Seaborg and Morss [18] can be consulted.

Key factors in considering solubility and mobility are (a) the speciation of the radionuclides and, (b) the components of the waste, groundwater and near-field. A literature review of uranium(VI) and uranium(IV) complexes relevant to this work is detailed in the following sections, together with a review of the chemistry of uranium in cementitious environments.

A concise examination of the literature of all the available species and formation constants for aqueous uranium is contained in the NEA review [19]. However, although the NEA review is thorough, care must be taken when selecting which species to examine in any one system; a point which is highlighted by the modelling in this study and reported later in chapters 1.8.1, 4.4.2, 5.3 and 7.3.
With the recent development of spectroscopic techniques such as time-resolved laser induced fluorescence (TRFLS), Raman spectroscopy and extended X-ray absorption fine structure (EXAFS), the interpretation of complex stoichiometry has become easier and therefore the knowledge of possible species has increased.

1.8.1 Electrochemical Aspects of Aqueous Uranium

Uranium can exist in several oxidation states in aqueous solutions: III, IV, V and VI. The presence of each state depends on both the $E_h$ and pH of the solution, as shown in Figure 1.2, which is a Pourbaix ($E_h$-pH) diagram based on the electrochemical (reduction potential) and thermodynamic equations for each oxidation state. These redox equations and thermodynamic constants can both be related to the Gibbs free energy changes involved in the reduction and formation of species and solid phases. The formation constants for solid phases used in modelling throughout this work are listed in appendix 1. As defined in section 1.6.3, the standard reduction potential can be related to both the Gibbs free energy of the system and the formation constant using the equation

$$E^\circ = -\frac{\Delta G^\circ}{nF} = \frac{RT}{nF} \ln K$$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\log K$</th>
<th>$\Delta G^\circ$</th>
<th>$E^\circ (V)$ = $-\Delta G/nF$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U^{4+} + e^- = U^{3+}$</td>
<td>-9.35</td>
<td>53.39</td>
<td>-0.553</td>
</tr>
<tr>
<td>$UO_2^{2+} + 4H^+ + 2e^- = U^{4+} + 2H_2O$</td>
<td>9.04</td>
<td>-51.59</td>
<td>0.267</td>
</tr>
<tr>
<td>$UO_2^{2+} + e^- = UO_2^+$</td>
<td>1.48</td>
<td>-8.47</td>
<td>0.088</td>
</tr>
</tbody>
</table>

Table 1.6 Standard Reduction Potential, Free Energy and Formation Constant for Uranium III, IV, V and VI [19]
Also note that in Figure 1.2, the unhydrolysed species are considered, but the limits of the species domain encompass both the unhydrolysed and hydrolysed species.

Aqueous uranium complexes in the lowest oxidation state, uranium(III), are unstable in water and yield H₂ gas and oxidise to U(IV). Uranium(V) complexes are the least stable oxidation state of aqueous uranium and, above pH 3, undergo disproportionation to form aqueous U(IV) and U(VI) species. However, U(V) complexes can still be produced by careful manipulation of pH and Eₘ in polarographic experiments during which the reduction of UO₂²⁺ forms UO₂⁺. At a pH range between 2.5 - 3, the rate of U(V) disproportionation is slow and therefore U(V) compounds can be isolated by rapid precipitation. The IV and VI oxidation states are the most stable of uranium species and are likely to be produced in an environment. For this reason, U(IV) and U(VI) are the only oxidation states that will be considered in this work.

![Figure 1.2 - Eₘ-pH Predominance Diagram for Uranium](image)

1.8.2 Hydroxide Complexes

Hydrolysis of uranium can form either monomeric structures or polymeric structures depending on the uranium concentration and solution conditions such as...
ionic strength, temperature and other ions available for complexation. The typical range of proposed U(VI):OH ratios are 1:1, 1:2, 1:3, 1:4, 1:5, 2:1, 2:2, 2:3, 2:4, 3:1, 3:4, 4:3, 5:2, 5:3, 6:3, 6:4, 7:3, 7:4, 8:3, 8:5, 9:3 and 19:9.

The aqueous chemistry of uranium at high pH has been the subject of debate for many years. The first noticeable papers on the aqueous chemistry of the uranyl ion and its hydrolysis were written by Sutton [20], Ahrland [21] and Hearne & White [22], using titration methods to investigate a variety of hydroxide complexes. Later reviews by Baes & Mesmer [23] and Allard [24] have become literature standards for the hydrolysis of uranium.

In general, hydrolysis follows the equation

\[ xUO_2^{2+} + yH_2O = (UO_2)_x(OH)_{2y-x} + yH^+. \]

Monomeric species including UO\(_2\)(OH)\(^+\), UO\(_2\)(OH)\(_2\), UO\(_2\)(OH)\(_3\)\(^+\) and UO\(_2\)(OH)\(_4\)\(^2-\) depend on both the pH and uranium concentration, as do polymeric species such as (UO\(_2\))\(_2\)(OH)\(_2\)\(^2+\), (UO\(_2\))\(_3\)(OH)\(_5\)\(^+\) and (UO\(_2\))\(_3\)(OH)\(_7\)\(^-\).

However, while monomeric structures are predominantly formed at lower uranium concentrations [19] and polymeric at higher uranium concentrations, there still seems to be an uncertainty as to what is termed low and high uranium concentrations. If Grenthe’s review is to be quoted directly, readers should be drawn to the statement that at lower uranium concentrations, monomeric species are more likely to be present than polymeric species. There is clearly a problem when modelling the solubility and speciation of uranium at high pH, since how is one to decide which species are to be included or excluded? If modelling is performed using monomeric species such as the trihydroxyuranyl ion, UO\(_3\)(OH)\(^+\); and the tetrahydroxyuranyl ion, UO\(_4\)(OH)\(_4\)\(^2-\); the solubility of uranium is predicted to be several orders of magnitude higher than that observed by experiment. This
was highlighted in two recent papers when modelling the solubility of uranium in cementitious environments \[25, 26\] and is also discussed in chapter 5 of this work.

Moulin et al \[27\] showed a clear trend in the speciation of uranium at high pH with varying uranium concentration. Using a combination of modelling and time resolved laser induced fluorescence specroscopy (TRLFS), it was shown that polymeric species become more important at higher uranium concentrations \((4.1 \times 10^{-4} \text{ M})\) and are negligible at lower uranium concentrations \((4.1 \times 10^{-4} \text{ M})\) where the system is undersaturated with respect to uranium. Clark \[28\] identified the structure of tetra- and penta-hydroxyuranyl ions by complexation with the tetramethylammonium counter-cation which suppressed the formation of polyuranate salts at high pH, and suggested that the term ‘high’ uranium concentrations required for the formation of polymeric hydroxide species is in the order of 0.1 mM.

Formation constants used during this work and described in this thesis are shown in appendix I and are, in most cases, taken from the \textit{Harwell/Nirex Thermodynamic Database for Chemical Equilibrium Studies} (HATCHESv10) database \[29\] unless stated otherwise.

The hydrolysis of U(IV) is again reviewed by Baes & Mesmer and Allard and follows the general equation

\[ xU^{4+} + yH_2O = U_x(OH)_{y(x-y)} + yH^+. \]

Formation constants are available in the HATCHES database for the 1:1, 1:2, 1:3, 1:4 and 1:5 complexes with formation constants, \(\log K_f = -0.54\) \[19\], -2.0 \[30\], -5.0 \[31\], -5.3 \[30\] and -17.3 \[30\] respectively. The database also provides details of large variations in formation constants and later excludes the 1:2, 1:3 and 1:5 species based on exclusion from the NEA review \[19\] and modelling of uranium solubility in cementitious environments performed by AEAT \[32\]. There is some
uncertainty in these formation constants which are included in the HATCHES database. Grenthe suggested that the formation constant, logK_f, for the 1:4 hydroxide was -4.53 based on thermodynamic derivation, compared with that of Lemire [30] of -5.3. The HATCHES database is in line with the NEA review chaired by Grenthe, but experimental work performed by AEAT [32] did not follow their model predictions based on the recalculated formation constants. Their experimental work suggested that the formation constant was -10.5. In order to compensate for the difference between experimental and modelled results, the formation constant for UO_2\cdot xH_2O was subsequently changed in the HATCHES database by the same amount that the formation constant proposed by Grenthe changed the 1:4 hydroxide formation constant, i.e. from 4 [33] to -1.97. Whether this practice is justified depends on the interpretation of the reader or modeller. According to Tweed [34], refinements are made to the database and it is generally easiest to justify alteration of solubility products due to varying crystallinity of solid. However, while changing a number by 5.97 may not seem that significant, it should always be remembered that the values given are logarithms and hence changes are made by 10^{5.97} = 933254.

1.8.3 Inorganic Complexes

Much of the recent foundation work on the stoichiometry of a variety of inorganic complexed uranium species has been performed by Nguyen-Trung [35] using Raman spectroscopy to define complexes.

After hydroxide complexation, carbonate complexation is the most intensely reported in the literature, mainly because of the importance of carbonate in the environment and the highly favourable formation of uranylcarbonato complexes. Reviews by Newton and Sullivan [36] and Allard [24] provided a good understanding of carbonate complexation, while more recent studies have fine-tuned formation constants and speciation for many carbonato complexes, by using
a variety of experimental methods such as electro-spectrometry [37], UV-spectrophotometry [38, 39], precipitation [40, 41], laser induced photoacoustic spectroscopy [42], time resolved laser induced fluorescence spectroscopy [43], thermal lensing spectrophotometry [44], potentiometry [45], coulometry [46]. There are also suggestions that mixed uranylhydroxycarbonato species exist [46, 47]. All the uranium carbonate complex formation constants are reviewed in [48] together with some structure determinations.

Uranium(IV) carbonate complexes are far less investigated compared to that of U(VI). Ferri et al [49] studied the reduction of U(VI) to U(IV) in carbonate solutions and derived a number of formation constants using potentiometry.

Phosphate complexation of uranium is one of the most complicated systems, second only to hydroxide complexation. While there appears to be a comprehensive study of phosphate complexation of uranium in acidic solutions, there is very little information on complexation at high pH. Grenthe’s review lists only Sandino [50] as a reliable reference at higher pH, with the formation of UO$_2$PO$_4^-$ and UO$_2$HPO$_4$ with formation constants log$K_f$ = 13.23 and 20.24 respectively. Eliet et al [51] later dismissed the thermodynamic phosphate model proposed by Sandino on the basis of fluorescence studies of hydroxide complexes in the presence of phosphate at high pH. The HATCHES database also include a species UO$_2$(HPO$_4$)$_2^{2-}$, log$K_f$ = 43.7 [31]. There are a number of insoluble uranyl phosphate minerals with a variety of hydration numbers, but these are not of use in this work and are therefore not detailed here.

There are a number of U(IV) phosphate complexes described in the literature, but again these have been studied at low pH. UHPO$_4^{+2}$, U(HPO$_4$)$_2^+$, U(HPO$_4$)$_3^{2-}$, U(HPO$_4$)$_4^4$, UH$_2$PO$_4^{+3}$ having formation constants log$K_f$ = 24.35, 46.70, 68, 88 [31] and 27.5 [19, 29] respectively.
Uranium complexes containing sulphate are not as numerous as the previously considered inorganic uranium complexes. However, there are two uranium(VI) sulphate species quoted in the HATCHES database [19, 29] for both a 1:1 and a 1:2 complex in which \( \log K_f = 2.72 \) [31] and 4.3 [24] respectively. Uranium(IV) sulphate complexes are also given in the HATCHES database. Again, the 1:1 and the 1:2 complexes are detailed with formation constants \( \log K_f = 6.6 \) and 10.5 respectively [19, 29].

Chloride complexes of uranium have been studied to a great degree over the last 50 years. Raman spectroscopy [35] showed evidence of a number of uranyl chloride complexes: \( \text{UO}_2\text{Cl}^+, \text{UO}_2\text{Cl}_2, \text{UO}_2\text{Cl}_3^-, \text{UO}_2\text{Cl}_4^{2-} \) and \( \text{UO}_2\text{Cl}_6^{3-} \). However, the thermodynamics of all species is not fully known and Grenthe [19] does not include species of stoichiometry higher than 1:2 for the chloride system. U(IV) chloride complexes are examined by Grenthe [19] and those included in the HATCHES database are the 1:1 and 1:2 complexes with formation constants, \( \log K_f = 1.72 \) and 1.9 respectively.

1.8.4 Anthropogenic Complexes

Ethylenediaminetetraacetic acid (EDTA, \((\text{CH}_2\text{N(\text{CH}_2\text{COOH}))}_2)\) is a well known anthropogenic complexing agent, widely used for decontamination. Uranium-EDTA complexation is somewhat less understood. Some authors state that such complexes are not stable or favourable [18, 52] leading to the degradation of EDTA. However, formation constants are available in the literature for a number of species and are listed in the HATCHESv10 database [29] together with their original authors: \( \log K_f = 18.28 \) [53] for the 1:1 protonated uranium-EDTA complex and 12.1 [54] for the 1:1 unprotonated uranium-EDTA complex. There are also steric requirements for the multidentate EDTA to form a metal ligand chelate. These requirements are not fulfilled with \( \text{UO}_2^{2+} \) [18] and often polymeric complexes are formed by bridging. Such dimer species are also considered in the
modelling of this work, with formation constants of $\log K_f = 18.54$ and 27.44 [53] for the 2:1 and 2:2 complexes respectively. Mixed species are also considered, especially since the systems under investigation are at high pH. For example, for the species $\text{U:EDTA:OH}$, the formation constants are quoted as $\log K_f = 13.53, 18.14$ [53] and 41.3 [55] for the 2:1:1, 4:2:4 and 6:3:4 species species respectively.

Data for U(IV) complexation with EDTA are not as numerous, with a 1:1 complex having a formation constant of $\log K_f = 29.1$ [56].

Nitrilotriacetic acid (NTA, $\text{N(CH}_2\text{COOH)}_3$) is similar to EDTA in that it can complex as a multidentate ligand. While formation constants are available for a number of metal-NTA species [56, 57], constants could not be found for uranium-NTA complexes. It will be shown in the modelling of experimental complexation in the course of this work, that NTA is capable of complexation of uranium and formation constants are predicted based on a ‘best fit’ between the model and experimental complexation. Results are shown in terms of complexation (dissolution) profiles, in which the uranium solubility is plotted against the concentration of added ligand. The beginning (or termination) of a complexation profile provides a point to determine the numerical value of the formation constant, while the stoichiometry can be estimated by comparing the gradient of modelled and experimental uranium complexation profiles.

There is also evidence of NTA degradation in the presence of uranium [57] similar to that of EDTA.

1.8.5 Simple Organic Complexes

Some of the first major studies of the uranyl-acetate system were performed by Tishkoff [58] and Ahrland [59] suggesting mono- di- and tri- acetato uranyl complexes. Acetate complexes were more recently studied using Raman
Spectroscopy [35] in which the 1:1, 1:2 and 1:3 complexes were observed. A 1:4 complex, previously suggested by Banerjea et al [60], was absent. Formation constants used in this work are in line with the HATCHES database [29] and are logK_f = 3.04, 5.5, 6.9 [61] and 19.6 [62.] for the 1:1, 1:2, 1:3 and 1:4 species respectively. U(IV) acetate complexes are also detailed in the HATCHES database as 1:1, 1:2, 1:3 and 1:4 complexes with logK_f = -0.5, 0.8, 1.1, 0.6 respectively.

As with carbonate, carboxylic functional group ligands (acetate and citrate included), the bonding occurs between the uranium ion and two of the oxygen atoms of the ligand. This leads to a stronger bond being formed than would generally be expected for carboxylate complexes, i.e. less than carbonate, but greater than sulphate.

The complexation of citrate with uranium is not as simple as with acetate. At very dilute concentrations, uranium forms monomeric citrate complexes, while at higher concentrations dimerisation can occur if the ligands possess two or more carboxylic acid groups [63]. For citrate, a dimerisation constant for the 2:2 dimer is quoted as logK_f = 3.95. The literature formation constants used are logK_f = 8.7 for the 1:1 complex [61] and logK_f = 21.18 for the 2:2 complex [61]. U(IV) complexes with citrate also and formation constants are available for the 1:1 and 1:2 species, logK_f = 14.75 and 23.5 respectively [54]. There are two U(IV) citrate complexes listed in the HATCHES database, 1:1 and 1:2 complexes with formation constants logK_f = 14.75 and 23.5 respectively.

1.8.6 Dissolved Organic Matter Complexes

The term organic matter in this work is used to classify three complexing agents: humic acid (HA), fulvic acid (FA) and iso-saccharinic acid (ISA), all of which are produced from biodegradation of organic material.
Humic acid is that component of soil that is insoluble in aqueous acid solution (pH < 2), while fulvic acid is the soluble component of soil at all pH values. Components insoluble in aqueous systems at all pH’s are termed humins and are not considered in this work.

Since the Drigg site is excavated in the local landscape, one could imagine that soluble components of soil were available to the nearfield. They may also be important as there may be some soil deposited at the site as waste. Both humic and fulvic acids are site specific and their exact chemical composition is not known exactly. The humic and fulvic acid matter used in this study was extracted from samples taken from boreholes at the Drigg site and provided by BNFL. Proposed structures of HA [64] and FA [65] are shown in Figure 1.3.

![Figure 1.3 Proposed Structures of (a) Humic Acid and (b) Fulvic Acid](image)

The interest in humic and fulvic complexation of metal ions has grown over the last two decades. A proposed model for HA and FA complexation with metals is the charge neutralisation model described by Kim and Czerwinski [66]. In this model,
the number of protons exchanged from the HA molecule and replaced by the metal ion is determined by the charge on the metal ion after other complexed ligands are taken into account. For example, the formation of a UO$_2$-HA complex at low pH would involve replacing two protons on the HA molecule and forming a bidentate complex, UO$_2$HA$^{2+}$. At a higher pH, the uranyl ion may be hydrolysed and therefore the complex will only require removal of one proton from the HA molecule to yield UO$_2$(OH)HA$^{+}$. A number of studies have been performed to calculate the formation constants of these complexes in the literature and a concise review is given by Moulin et al [67] on the complexation of actinides with HA and FA including studies by [68, 69, 70, 71] with additional constants provided by [72 and 73].

As the formation constants used in modelling are generally in line with those published in the HATCHESv10 thermodynamic database, 1:1 and 1:2 complexes are included with formation constants of 7.6 and 11.5. A mixed UO$_2$(OH)HA complex is also included in this work with a formation constant of 14.7 derived by [74].

U(IV) HA and FA complexes are included in the HATCHES database with formation constants for 1:1 and 1:2 species of log$K_f$ = 7.0 and 11.5 for HA and 6.6 and 11.6 for FA respectively [70].

Isosaccharinic acid (CH$_2$OHCHOHCH$_2$COH(CH$_3$OH)COOH, ISA, 2-C-(hydroxymethyl)-3-deoxy-D-pentonoic acid) is a major product of cellulose degradation [75] and therefore may be at significant concentrations in the LLW disposed of at the Drigg site. ISA is formed by a de-cyclisation of a cellulose molecule at high pH and usually at ambient temperatures. The reaction is shown in Figure 1.4 and summarised by [76].
Relatively little work has been undertaken on the effects of ISA on the solubility and sorption of uranium, with most studies concentrating on plutonium complexes. However, Ilett et al [77] have shown that ISA both increases the solubility of uranium(VI) and uranium(IV) at high pH and decreases the sorption of uranium onto cementitious material. Recent work by Getahun [78] suggests that ISA behaves somewhat similar to that of saccharinates and gluconates in their complexation with metal ions. Formation constants for uranium saccharinates and gluconates are available in the HATCHES database [29]. The formation constants chosen from the database and used in this work are detailed in appendix 1 and discussed in chapters 5, 6 and 7.

1.8.7 Uranium in Cementitious Environments

With several countries around the world researching nuclear waste disposal, there has been a substantial amount of work performed on the solubility and transport of radionuclides in cementitious environments or in groundwater systems. Much work has been performed on the study of radionuclide transport at the Gorleben site in Germany, while in the UK, NIREX have undertaken a great deal of research for the proposed underground repository for ILW and HLW disposal. Of more interest to this work is the cementitious interaction with radionuclides. Again, concise reviews by [16, 17] are the key to the understanding of all the chemical and physical processes involved in the study of radionuclide transport in the environment.
There have been numerous studies into the solubility of uranium in the presence of cement and cement leachates. However, there seems to be much disagreement between authors on the exact nature of the solubility limiting phase in such high pH, Ca rich systems. Atkins et al [79] suggest two phases of $\text{Ca}_6\text{U}_6\text{O}_{19}\cdot 11\text{H}_2\text{O}$ and $\text{Ca}_2\text{UO}_6\cdot x\text{H}_2\text{O}$ where $x$ lies between 1.3 and 1.7. Moroni and Glasser [80] state that the phase lies somewhere between that of $\text{UO}_3\cdot 2\text{H}_2\text{O}$ and $\text{CaO}$. Workers at AEAT have investigated the formation of calcium uranates and suggest calcium diuranate is the solubility limiting phase. This subject will be discussed further in chapter 4.

Under reducing environments, provided by canister corrosion, uranium(VI) will be reduced to uranium(IV). Under these conditions, uranium will be precipitated as the $\text{UO}_2\cdot 2\text{H}_2\text{O}$ phase (chemically equivalent to $\text{U(OH)}_4$). Solubility investigations have more recently been performed on this phase by Ryan & Rai [81, 33] and have shown it to be amorphous. Rai has also undertaken studies into the speciation of U(IV) in high pH, high CO$_2$ system in the presence of sodium and potassium cations. These studies have proposed a mixed hydroxycarbonate species [82].

Sorption of uranium by cement components is also of importance in the transport of radionuclides. Again, much work has been performed by AEAT as part of their assessment with NIREX of the proposed underground repository in the UK. A cementitious material is proposed for the NIREX repository, termed the Nirex Reference Vault Backfill, NRVB, which is specifically designed to chemically buffer the environment and immobilise radionuclides. As noted earlier, the cement used at the Drigg site was not designed to retard the transport of radionuclides. Uranium sorption in a cementitious repository has been investigated by workers at AEAT [e.g.83-87], with and without organic materials such as cellulose and ISA as part of the NIREX research.

Many studies have been undertaken into the sorption of uranium onto a variety of surfaces for example, hydrous oxides [88], multivalent metal hydroxides [89, 90,
91], carbonate-rich sediments and minerals [92], calcite [e.g. 93, 94] and specific cement components such as ettringite and CSH [95, 96].

The subject of sorption onto Drigg grout will be discussed in chapter 7 of this thesis.
CHAPTER TWO

Characterisation Of Grout
And Grout Leachate
2. Characterisation of Grout and Grout Leachate

2.1 Grout Characterisation

2.1.1 X-Ray Fluorescence (XRF)

The use of XRF allows qualitative and quantitative, rapid, non destructive analysis of both liquids and solids [97].

Whilst x-ray diffraction is discussed in chapter 4.2.1 in the characterisation of solid uranium phases, the chemical analysis of the grout material by XRF is described in this section. Whilst the former method utilises the phenomenon of x-ray diffraction by a crystal structure, the latter utilises the photoelectron effect, which is shown schematically in Figure 2.1.

![Figure 2.1: Schematic Diagram of Energy Transitions in X-Ray Fluorescence](image)

As an x-ray interacts with an atom (1), it may contain enough energy to remove the innermost ‘K’ electrons from the target (2), creating an electron deficiency. This electron ‘hole’ is filled by an electron falling from the adjacent high energy electron shells, either ‘L’ or ‘M’ (3). This transition is also accompanied by a photon emission of almost monochromatic wavelength which is of lower energy than the absorbed x-ray and which is characteristic of the target atom (4).
The emitted x-rays can be analysed by two methods. Firstly, by means of wavelength separation at a crystal surface (crystal diffraction spectrometry) and detection with a standard scintillation counter probe. Qualitative analysis is obtained by rotating the diffraction crystal and detector to select characteristic wavelengths, then quantitative analysis is made by fixing the crystal and detector position to measure the intensity of emitted radiation for one analyte at a time. Secondly, by using the difference in energy of the emitted x-rays: the longer the wavelength, the lower the energy of the photon (energy dispersion analysis) and detection with a lithium-doped silicon solid state detector which converts the x-ray photons to an electric charge proportional to the energy of the photon. The signal is amplified, passed through an analogue-to-digital converter, registered on a multi-channel analyser and stored on a personal computer. This method of detection allows multi-element qualitative and quantitative analysis simultaneously.

2.1.2 Grout Analysis

Two samples of grout material were supplied by BNFL plc, Sellafield. Sample BM4 was taken from the grouting facility in 1995 while sample BM14 was taken on 5/2/97.

A sample of the BM4 Drigg grout was characterised by x-ray fluorescence (Professor John Patrick, Chemical Engineering Department, Loughborough University). Loss on ignition (LOI) was determined over 24 hours at 850°C and is a measure of the moisture content of the grout material. The results are shown in Table 2.1.
### Component Oxide

<table>
<thead>
<tr>
<th>Component Oxide</th>
<th>Experimental Percentage by Weight</th>
<th>Theoretical Percentage by Weight [4]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂O</td>
<td>0.52</td>
<td>0.84</td>
</tr>
<tr>
<td>MgO</td>
<td>1.21</td>
<td>1.90</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>27.1</td>
<td>19.57</td>
</tr>
<tr>
<td>SiO₂</td>
<td>42.3</td>
<td>35.48</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.03</td>
<td>2.35</td>
</tr>
<tr>
<td>CaO</td>
<td>7.59</td>
<td>16.50</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.83</td>
<td>0.95</td>
</tr>
<tr>
<td>MnO</td>
<td>0.04</td>
<td>-</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.35</td>
<td>6.45</td>
</tr>
<tr>
<td>LOI (850°C, 24hrs)</td>
<td>13.57</td>
<td>14.00†</td>
</tr>
</tbody>
</table>

Table 2.1: Analysis of Drigg Grout

† Adjusted to account for OPC:PFA mix of 1:3 and 14% LOI
‡ The maximum loss on ignition as defined by BS3892pt3

### 2.2 Grout Leachate Characterisation

Vault waters at a disposal site will be in contact with the waste canisters. In order to reach the waste housed in the canisters these vault waters will not only have to pass through the canister material itself, but also through the grout infill material. It is therefore important that grout equilibrated waters are used in the study of uranium and that the composition of the leachate is known.

#### 2.2.1 Preparation of Grout Leachate

BM4 grout material was sieved through a 90µm test sieve (Endecotts Ltd, London). 25g portions of grout were placed in a glass conical flask together with 250ml of deionised water. The flask was then stoppered and the contents stirred for four days. The pH of a previous sample was monitored for one week, reaching a plateau of pH 11.8 after four days. The grout leachate was then filtered through a 0.45µm filter membrane (Gelman Sciences) and used fresh.
Grout BM14 was equilibrated with water as above, but after one week an equilibrium pH of 9.5 was obtained. This sample was only used as a comparison of grout samples and it will be shown that there is a substantial variation in leachate composition.

2.2.2 Leachate Analysis

A secondary wash leachate was produced by re-equilibrating BM4 grout material with deionised water. Once the grout had been filtered from the first wash, the filter paper was placed in an oven at 50°C over a period of 4 days. The dried grout material was re-suspended in deionised water for a further four days before being filtered as with the first wash.

Both the first and second leachates were analysed for major cations by ICP-MS and major anions by Dionex at BNFL (Jim Robson, Geoffrey Schofield Laboratory).

The analysis of both BM4 grout leachate washings are shown in Table 2.2, together with the percentage of each component leached with respect to the experimentally determined composition of the grout material determined by XRF, chapter 2.1.2. Analysis of BM14 grout leachate is shown in Table 2.3, along with analysis of a leachate from the same BM14 grout sample performed by BNFL [98] after 2 days equilibration time.
### Table 2.2: Analysis of BM4 Drigg Grout Leachate, Primary and Secondary Washings

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration in Leachate BM4, mM</th>
<th>% Leached from Drigg Grout BM4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wash 1</td>
<td>Wash 2</td>
</tr>
<tr>
<td>K</td>
<td>91.282</td>
<td>3.135</td>
</tr>
<tr>
<td>Na</td>
<td>41.130</td>
<td>8.698</td>
</tr>
<tr>
<td>Ca</td>
<td>19.250</td>
<td>7.837</td>
</tr>
<tr>
<td>Mg</td>
<td>0.099</td>
<td>-</td>
</tr>
<tr>
<td>Si</td>
<td>0.217</td>
<td>0.047</td>
</tr>
<tr>
<td>Al</td>
<td>0.033</td>
<td>0.024</td>
</tr>
<tr>
<td>Fe</td>
<td>0.003</td>
<td>0.001</td>
</tr>
<tr>
<td>TIC</td>
<td>0.125</td>
<td>0.092</td>
</tr>
<tr>
<td>SO₄</td>
<td>0.305</td>
<td>0.079</td>
</tr>
<tr>
<td>Cl</td>
<td>0.035</td>
<td>0.014</td>
</tr>
<tr>
<td>pH</td>
<td>11.8</td>
<td>11.1</td>
</tr>
</tbody>
</table>

2.3 Summary

The BM4 Drigg grout material contains a large amount of SiO₂ and Al₂O₃ which constitute a higher proportion of the total weight than for the theoretical grout material shown in Table 2.1. The potassium and sodium contents of the grout material are present in significant amounts (together with calcium) leading to the possible precipitation of uranium by formation of alkali-uranate minerals at high
pH (discussed in chapter 5 of this work). Less Fe$_2$O$_3$ and CaO are present in the ‘real’ sample than in a ‘theoretical’ grout material shown in section 1.5.2 and Table 1.4. This factor could result in the enhanced formation of sodium and potassium uranates rather than of calcium uranate precipitation at high pH, as is shown in chapters 4 and 5.

The British standard, BS3892-Part3 [99], defines grout material as “a fluid suspension containing PFA and cement mixed in water”. Drigg grout conforms to this standard, with LOI < 14% and is used because of the flow properties (rheology) of the grout.

It can be seen from Table 2.2 that the majority of potassium (73%) and sodium (99%) are removed from BM4 grout after just two sequential leachings. Almost 7% of the total calcium available has been removed at the same stage. These facts are reflected in the high pH of both leachates and the reduction in the pH between the first and second leachings. Negligible portions of magnesium, silicon, aluminium and iron oxides are removed.

These findings indicate that a high sodium/potassium ‘plume’ may be expected to develop very early on around the compacted waste material at the Drigg site. Calcium will be leached at a comparatively slower rate, although it will remain soluble enough to buffer the leachate at approximately pH 11. Free calcium will be limited by the high sulphate concentration present in the leachate, which with aluminate can form ettringite (Ca$_3$Al(OH)$_6$(SO$_4$)$_3$.3H$_2$O). A typical pH for cement leachate is in the range of pH 12 - 13 [100, 101], but the final equilibrium pH of the grout material is determined by the specific type grout used and therefore depends on the alkali content and availability, and the ratio of OPC:PFA:water.
The results of the analysis of the leachate from Drigg grout sample BM14 are shown in Table 2.3 and these are compared to the results obtained by BNFL Sellafield (after 2 days equilibration time) [98]. The results show poor agreement in leachate composition apart from the equilibrium pH value and this may be due to equilibration time variation or sample heterogeneity. It should be noted that the ‘as received’ grout samples were a mixture of powder and hard, bulky materials.

Comparisons between leachates from grout samples BM4 and BM14 show significant differences in the compositions of the leachates. Sample BM14 has a lower concentration of calcium, sodium and potassium, with larger concentrations of silicon and aluminium. The variations in total inorganic carbon, chloride and iron are negligible. Of most interest is the difference in pH and sulphate concentration. The equilibrium pH of grout BM14 leachate is only 9.5 compared to pH 11.8 for grout BM4 leachate. This difference is most likely due to the excess alkali metal hydroxides in grout BM4. The findings of this intercomparison are that it is not acceptable to simply assume that the grout material will buffer to a very high pH. The variation in grout leachate composition proves that an investigation into the solubility of uranium over a wide pH range and, in the presence of a variety of metal ions and anions, should be undertaken.
CHAPTER THREE

Uranium Purification
And Determination
3. **Uranium Purification and Determination**

3.1 **Introduction**

The two isotopes used in this work were $^{238}$U and $^{233}$U; their decay schemes are shown below in Figure 3.1 Although the two isotopes differ radiochemically, their aqueous chemistry is exactly the same.

$^{238}$U $\longrightarrow$ $^{234}$Th $\longrightarrow$ $^{234m}$Pa $\longrightarrow$ $^{234}$U $\longrightarrow$ $^{230}$Th...

$^{233}$U $\longrightarrow$ $^{229}$Th $\longrightarrow$ $^{225}$Ra $\longrightarrow$ $^{221}$Fr...

**Figure 3.1** Early Decay Schemes of $^{238}$U (4n+2) and $^{233}$U (4n+1)

For the decay of $^{238}$U, the various daughter products are in secular and transient equilibrium. The half life of $^{238}$U is very large compared to that of $^{234}$Th (4.7 x 10$^9$ years and 24.1 days respectively). We can therefore assume secular equilibrium for these two nuclides, that is, the activity (rate of decay) of both the $^{238}$U and $^{234}$Th are equal, since

$$\frac{dN}{dt} = -\lambda N$$

where $\lambda$, the disintegration constant, equals $ln2 / t_{1/2}$ and $N$ is the number of atoms of each isotope. The relationship between parent and daughter nuclei at secular equilibrium is given by the equation

$$\frac{dN_{Th}}{dt} = \lambda_{U}N_{U} = \lambda_{Th}N_{Th}$$

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The half life of $^{234}$Th and $^{234m}$Pa are of similar orders of magnitude (24.1 days and 1.2 mins respectively) and therefore these nuclides are in transient equilibrium with each other. The relationship between parent and daughter nuclei at transient equilibrium is given by the equations

$$N_{Pa} = [\lambda_{Th}N_{Th} \times \exp(-\lambda_{Th}t)] / (\lambda_{Pa} - \lambda_{Th}).$$

and

$$N_{Pa} / N_{Th} = \lambda_{Th} / (\lambda_{Pa} - \lambda_{Th}).$$

Once a separation of uranium from its daughters is performed, the equilibrium between thorium and uranium is disrupted. Calculations can be made to assess the rate of ingrowth of thorium.

The equation for secular equilibrium as described above can no longer be used. Instead, we have to allow for the growth of thorium and then its subsequent decay.

$$\frac{dN_{Th}}{dt} = \lambda_{U}N_{U} - \lambda_{Th}N_{Th}$$

Integration of this equation, together with the assumption that thorium has been completely removed, allows the modelling of the ingrowth of thorium:

$$N_{Th} = \lambda_{U}N_{U}[\exp(-\lambda_{U}t) - \exp(-\lambda_{Th}t)] / (\lambda_{Th} - \lambda_{U}).$$

The problem of thorium ingrowth and interference is greatly reduced by using a different isotope of uranium. The $^{233}$U isotope decays by alpha emission to $^{229}$Th. The half life of $^{229}$Th is long ($7.2 \times 10^3$ years) compared to that of $^{234}$Th. This means that although the interference in determination still occurs, the rate of in-growth is much slower. Because the half lives of $^{233}$U and $^{229}$Th are of similar orders of magnitude, the $^{233}$U-$^{229}$Th equilibrium is transient.

After chemical separation, the chemical concentration of thorium is negligible but the radiochemical activity is not and leads to inaccurate radioactivity measurement.
of uranium. For this reason, $^{238}\text{U}$ has been used in both the spectrophotometric determination of uranium (aerobic complexation of uranium at moderate ligand concentration) and the phase characterisation of uranium precipitates at high pH. Where the determination of lower concentrations of uranium was required, or where smaller changes in solubility have been studied, $^{233}\text{U}$ has been used.

3.2 Uranium Purification by Separation

Two methods were used to purify the uranium solutions:

- ion exchange for $^{238}\text{U}$ requiring moderate separation of bulk solutions and ideal for ‘chemical’ use, such as spectrophotometric analysis and X-ray diffraction studies.
- extraction chromatography for $^{233}\text{U}$ for high grade separation of small volumes and ideal for ‘radiochemical’ use, such as $^{233}\text{U}$ determination by liquid scintillation counting.

The theory and method of each separation procedure is detailed in this chapter, together with the two methods for the determination of uranium concentration.
3.2.1 Ion Exchange Chromatography

3.2.1.1 Theory

Ion exchange is based on the affinity between cations and anions, i.e., electrostatic charge attraction. Amberlite IR-120 cation exchange resin (BDH) has been used in this work to separate and therefore purify uranium from its daughter decay products.

Amberlite IR-120 is a cation exchange resin consisting of polystyrene beads coated in a polymer of divinylbenzene with a sulphonate acidic group. The polymeric chains are 'crosslinked' by means of methylene bridges, creating 'pockets' which are lined with the $\text{SO}_3^-$ functional group. IR-120 resin has a cross linking factor of 8, i.e., 8% of the divinylbenzene is crosslinked. The more positive the charge on the cation, the stronger it will be attracted (and therefore bound) to the resin and a more positive cation will displace less positive ions, as demonstrated in Tables 3.1 and 3.2, below.

![Molecular Structure of p-Divinylbenzyl Sulphonate used in Amberlite IR-120 Resin](image)

3.2.1.2 Experimental

A glass column of approximately 300mm in length and 20mm in diameter, was packed with Amberlite IR-120 resin (BDH) and washed with 200ml of 5M...
hydrochloric acid followed by copious amounts of deionised water. Uranyl nitrate crystals (BDH) were dissolved in deionised water to yield 250ml of a 0.02 M solution. This stock solution was then added to the column.

The retained protactinium was eluted by the addition of 100ml of 0.5M hydrochloric acid. Afterwards, uranium was eluted with 100ml of 4M hydrochloric acid. During the course of the uranium elution, thorium remained on the column.

<table>
<thead>
<tr>
<th>Eluent</th>
<th>Uranium</th>
<th>Thorium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-Load</td>
<td>UO$_2^{2+}$</td>
<td>Th$^{4+}$</td>
</tr>
<tr>
<td>0.5M HCl</td>
<td>UO$_2^{2+}$.$n$SO$_3$—resin</td>
<td>Th$^{4+}$.$n$SO$_3$—resin</td>
</tr>
<tr>
<td>4M HCl</td>
<td>UO$_2$Cl$_2$</td>
<td>ThCl$_3$$^{+}$.$n$SO$_3$—resin</td>
</tr>
</tbody>
</table>

Table 3.1  
Species of U and Th at Each Elution Stage of the Adopted Ion Exchange Separation Method

The resulting uranium solution was reduced in volume using a rotary evaporator and allowed to crystallise. The resulting crystals were redissolved in 4M nitric acid, and the crystallisation repeated once in 4M nitric acid and twice in deionised water. The purified uranyl nitrate was dissolved in deionised water as required and the concentration was determined by spectrophotometry, as described in section 3.3.2 below.

3.2.2  Extraction Chromatography

3.2.2.1 Theory

The use of extraction in the separation of metals from solution is widely used, especially in radiochemistry and in processing of nuclear waste. Whereas ionic or charged species are highly soluble in water due to its high dielectric constant, neutral species may be highly soluble in organic solvents.
There are two categories of extraction. The first, chelate extraction, requires the solvent to contain groups which act as a Lewis base, such as oxygen or nitrogen, with electron lone pairs. The extraction is based on the formation of a multi-dentate chelate structure between the solvent molecule and the metal. The reaction is similar to that shown by metal complexation with EDTA, but in the case of extraction, the solvent replaces the co-ordinated water molecules around the metal hydration sphere. The second type of extraction is ion association, and, as the name suggests, is a formation of an ionic complex between the solvent and the metal. As discussed above, the metal must be present as a neutral species in order for it to be extracted and this means that the solvent must break and replace one or more of the metal-ligand bonds. There are three main types of ion association: (a) where the metal is incorporated into a very large ion with bulky organic functional group, (b) where anions such as nitrate or chloride are present with the metal and the solvent molecule contains oxygen atoms, and (c) where the metal is present as a salt which forms micelles in the organic solvent.

The partitioning of metal ions, $M^{x+}$ between solvents 1 and 2 can be expressed in terms of a distribution coefficient, $K_d$:

$$K_d = \frac{[M^{x+}]_2}{[M^{x+}]_1} \quad \text{for the equilibrium: } M^{x+}_1 \leftrightarrow M^{x+}_2$$

Of more importance when considering the extraction of a metal from one solvent to another is the distribution ratio, $D$. This accounts for chemical interactions between distributing species in both the organic and aqueous phases:

$$D = \frac{[M^{x+}]_{TOT}^{org}}{[M^{x+}]_{TOT}^{aq}} \quad \text{where } [M^{x+}]_{TOT} \text{ is the total metal ion concentration in each phase}$$
For extraction chromatography performed in columns of resin coated with an organic extractant, this ratio can be further converted into a retention factor. This factor reflects the extent to which the metal will remain on the column, with respect to the volume of aqueous solvent which can be passed through the column before a peak elution and with respect to the effective 'volume' of organic solvent coated onto the resin. It can also be seen as the number of free column volumes before the elution peak maximum is reached, and is illustrated in the equation,

$$K_D' = D \frac{\text{Vol}_{aq}}{\text{Vol}_{org}}$$

The extraction chromatography was performed using U/TEVA resin (EICchrom). The resin is an inert polymeric support (100-150µm in diameter) with a coating of diamylamyl phosphonate (DAAP) extractant. The structure of DAAP is shown in Figure 3.3. It can be seen that the DAAP structure contains three oxygen atoms with lone pairs of electrons and thus the uranium is extracted into DAAP by ion association in the presence of nitric and/or hydrochloric acid, according to the reaction:

$$\text{UO}_2^{2+} (aq) + 2\text{NO}_3^- (aq) + 2\text{DAAP}_{(org)} = \text{UO}_2(\text{NO}_3)_2 . 2\text{DAAP}_{(org)} [102]$$

Bonding between U and DAAP is via the oxygen of the P=O functional group.

![Figure 3.3 Molecular Structure DAAP used in UTEVA Resin](image-url)
The extraction of uranium may also be influenced by chelate formation with DAAP since there is the possibility of forming a multi-dentate chelate structure if steric influences allow. This makes DAAP a very powerful extractant.

### 3.2.2.2 Experimental

The method used was in-line with EIChrom’s published method for the separation of uranium from thorium [103].

Pre-packed 2ml UTEVA solvent extraction resin (EIChrom) columns were washed and activated with 5mls of 3M nitric acid. A 1ml aliquot of $^{233}$U uranyl nitrate (AEAT, 5MBq/5mls) was diluted to 10mls with 3M nitric acid and then slowly loaded onto the column. A 5ml wash of the above acid was performed before 5mls of 9M hydrochloric acid was passed through the column. This was followed by 15ml of 5M hydrochloric acid in order to elute thorium from the column.

<table>
<thead>
<tr>
<th>Eluent</th>
<th>Uranium</th>
<th>Thorium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Species</td>
<td>Approx $K_D$</td>
</tr>
<tr>
<td>Pre-Loading</td>
<td>$UO_2^{2+}$</td>
<td>-</td>
</tr>
<tr>
<td>3M HNO$_3$</td>
<td>$UO_2(\text{NO}_3)_2 \cdot 2\text{DAAP}$</td>
<td>100</td>
</tr>
<tr>
<td>9M HCl</td>
<td>$UO_2\text{Cl}_2 \cdot 2\text{DAAP}$</td>
<td>100</td>
</tr>
<tr>
<td>5M HCl</td>
<td>$UO_2\text{Cl}_2 \cdot 2\text{DAAP}$</td>
<td>100</td>
</tr>
<tr>
<td>0.02M HCl</td>
<td>$UO_2^{2+}$</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 3.2 Approximate $K_D$ Values [104] and Species of U and Th at Each Elution Stage of the Adopted EIChrom-UTEVA Method
Uranium was then eluted in 3mls of 0.02M hydrochloric acid solution. The radioactivity was measured by liquid scintillation counting (described below in section 3.3) and compared to the theoretical activity of the initial stock. A yield of 97.7% of the uranium in a 3ml fraction was achieved. The absence of any excess of unaccountable radioactivity (much greater than 100% of the expected activity) confirmed that thorium had been removed from the uranium solution during the separation.

The number of free column volumes to peak maximum, $K_v'$, for the above procedure of uranium and thorium separation are summarised by Horwitz [104] and are shown in Table 3.2 together with the species present at each stage of the separation.

3.3 Uranium Determination by Spectrophotometry

3.3.1 Theory

The uranium determination was based on the formation of a uranium complex with Arsenazo-III (also termed AA-III; 3,6-bis-[(2-arsonophenyl)azo]-4,5-dihydroxy-2,7-naphthalenedisulphonic acid), which is determined by visible absorption spectrophotometry. The method has been described by Savvin [105].

The metal AA-III complex formed is stable. Bonding is via the nitrogen of the azo groups and the oxygen of both the acid and hydroxide groups. This causes a distortion of the arsenazo molecule and consequently a shift to longer wavelength in the absorbance of the molecule; thus complexed and uncomplexed AA-III can be distinguished.

Within the pH range of 2-3, the azo dye complexes with divalent and trivalent metal ions and can be used to determine the concentration of the uranyl ion, $\text{UO}_2^{+}$.
in solution. In strong acids (typically 6-8M HCl) the dye can be used to determine the concentration of tetravalent metal ions in solution, such as U$^{4+}$ and Th$^{4+}$.

![Molecular Structure of Arsenazo-III](image)

**Figure 3.4 Molecular Structure of Arsenazo-III**

In the determination of UO$_2^{2+}$, several authors have suggested that a 1:1 complex is formed between AA-III and the uranyl ion [106-109]. However some authors suggest a 2:2 complex [107], even though it would be highly sterically hindered. Formation constants are quoted as ($\log K_f$) 5.42 [109] and 7.2 for the 1:1 complex and 20 [107] for the 2:2 complex.

### 3.3.2 Experimental

A stock solution of 2.5mM AA-III was prepared by dissolving 0.2g of the sodium salt of AA-III (Fluka) in 100ml of deionised water containing a few drops of 0.2M nitric acid and 0.5g sodium acetate at pH 2.5. The stock solution was stored in an amber coloured glass bottle.

For each determination, 350µl of AA-III solution were added to each uranium sample before adjusting the pH to 2.5 with small additions of dilute nitric acid and adjusting the volume to 10ml using deionised water. After standing for ten minutes, the absorbances of the U-AAIII complexes were measured at 655nm using a spectrophotometer (Philips Scientific, model PU8730) and compared to the
absorbance of calibration plots produced by addition of known uranium concentrations to AA-III. Figure 3.5 shows a plot of absorbance against the number of mols of uranium present. A regression line through experimental points show that the determination follows the Beer-Lambert law in which the concentration is proportional to the absorbance observed, i.e.

$$\log \left( \frac{\text{Int}_o}{\text{Int}_{\text{obs}}} \right) = \varepsilon \cdot C \cdot l = \text{Absorbance}$$

where Int$_o$ represents the intensity of the incident beam of monochromatic light falling on the sample, Int$_{\text{obs}}$ is the observed intensity after the beam has passed through a sample solution of thickness, l and concentration, C. The term $\varepsilon$ is known as the molar absorption coefficient and is dependent on the molecule of interest in solution and the wavelength used.

![Figure 3.5 Calibration for Uranium(VI) Determination by Spectrophotometry](image)

**Figure 3.5** Calibration for Uranium(VI) Determination by Spectrophotometry
3.4 Uranium Determination by Liquid Scintillation Counting

3.4.1 Theory

A useful method for the determination of radioactivity (α or β decay) and for distinction between radio-isotopes is liquid scintillation counting. The energy carried in an emitted particle as a result of a radioactive decay can be converted into a pulse of light by means of a scintillation fluid. Such fluids usually contain organic molecules which have a number of double bonded carbon, nitrogen and/or oxygen atoms bonded in conjugation, typically aromatic. The molecules have the ability to absorb the energy of emitted particles by shifting electronic energy around the conjugated bond systems which exist in excited electronic states for a very small time-scale (typically nano-seconds or pico-seconds). Molecules then revert to the electronic ground state via the emission of excess energy in the form of a light photons. In practice, thousands of molecules may be electronically excited and when they revert to their ground state, a flash of light is produced which contains a large number of photons.

These photons are detected on a photomultiplier tube or diode array where the light flash is converted to an electronic signal and sent to a multichannel analyser and microprocessor.

3.4.2 Experimental

For each determination, 1ml of sample solution was taken and acidified with dilute nitric acid before adding 10mls of EcoScint-A scintillation fluid (National Diagnostics, USA) together in a 20ml polyethylene vial (Canberra Packard). The vial was shaken by hand and placed in a liquid scintillation counter (LKB-Wallac) to light adapt for 1 hour and samples were then counted automatically for five minutes each.
Figure 3.6  Calibration for Uranium Determination by LSC
(a) $^{238}\text{U}$, (b) $^{238}\text{U}$ Spiked with 1% $^{233}\text{U}$ and (c) $^{233}\text{U}$
The results obtained were compared with calibration plots produced by the addition of known uranium concentrations in the same manner as described here. The calibration plots determined from known additions of uranium are shown in Figure 3.6 and show linear relationships.

3.5 Summary

$^{238}\text{U}$ has a longer half-life than $^{233}\text{U}$ and the half-life of $^{234}\text{Th}$ is much less than that of $^{229}\text{Th}$. Therefore, (a) the specific activity of $^{233}\text{U}$ is higher than that of the $^{238}\text{U}$ isotope and (b) the ingrowth of thorium is less of a problem when uranium is to be determined by virtue of its radioactivity. This means that for the detection of lower uranium concentrations with less interference from the decay of daughter products (namely thorium), $^{233}\text{U}$ should be used.

Uranium can be separated from its daughter products in both the $^{238}\text{U}$ and $^{233}\text{U}$ cases. Separation has been achieved both by ion exchange (Amberlite IR-120 cation exchange resin, for large sample volumes of $^{238}\text{U}$) and by solvent extraction chromatography (EIChrom UTEVA resin, for small sample volumes of $^{233}\text{U}$). In each instance, the chemical species have been identified for each elution stage.

Uranium can be determined by spectrophotometric studies with Arsenazo-III chromophore, or by liquid scintillation counting using either (a) $^{238}\text{U}$, (b) $^{233}\text{U}$ Spiked with 1% $^{233}\text{U}$ and (c) $^{233}\text{U}$. It can be seen in Figures 3.5 and 3.6 that the calibration plots are linear of the range studied and have excellent correlation between points, with $R^2 > 0.999$. 
CHAPTER FOUR

Uranium Solid Phase Characterisation
4. Uranium Solid Phase Characterisation

4.1 Introduction

As discussed in section 1.7, the solubility of uranium depends upon the nature of the precipitate formed. It is therefore important to characterise the uranium precipitates formed at high pH. The information is required to input into speciation codes such as MINTEQA2, in order to model the experimental results. In this work, X-ray powder diffraction has been used and it will be seen that in conjunction with modelling studies, the characterisation of uranium precipitates at high pH has been achieved (see chapter 5).

4.2 X-ray Diffraction Theory

The diffraction of X-rays was discovered and defined by W.L.Bragg in 1912. If pairs of X-ray beams are considered as waves which can interfere, their diffraction properties can be described. Consider an X-ray beam incident on a pair of parallel planes, \( P_1 \) and \( P_2 \), at a distance of \( d \) apart and pair of parallel incident rays, \( R_1 \) and \( R_2 \) at an angle of \( \theta \) degrees to the first pair (Figure 4.1).

![Figure 4.1: Schematic Diagram of Parallel Rays Diffracted at a Plane (1)](image)

In the oscillating field of the incident beam, electrons at points A and B will be forced to vibrate, emitting energy in all directions. Examination of a particular direction, namely that of parallel rays \( R_1' \) and \( R_2' \), at an angle of \( \theta \) to the plane, a
diffracted beam of highest intensity will be observed if the waves in rays \( R_1' \) and \( R_2' \) are in phase.

![Diagram of Parallel Rays Diffracted at a Plane](image)

**Figure 4.2: Schematic Diagram of Parallel Rays Diffracted at a Plane (2)**

On closer inspection (Figure 4.2) it can be seen that angle \( XAB \) is equal to the angle \( YAB \), 0 degrees; and that distance \( XB \) is equal to \( YB \). If this distance is an integer of the wavelength of the beam, ray \( R_1' \) will be in phase with ray \( R_2' \), leading to a maximum intensity. It can therefore be stated that distance \( XB + YB = n\lambda \), where \( \lambda \) is the wavelength of the beam. But as stated earlier, distance \( XB = YB \), and so \( 2XB = n\lambda \). Simple trigonometry shows that distance \( XB = d\sin\theta \) and therefore \( n\lambda = 2d\sin\theta \). This is the relationship known as Bragg’s Law and can be used to describe the diffraction of X-rays and the formation of maximum and minimum intensities.

A hot cathode tube was used to provide primary electrons in the X-ray generator. The filament, normally tungsten, is heated to a temperature where electrons are emitted. These primary electrons are then accelerated towards the anode by means of an electric field. Once at the target anode, the primary electrons have enough energy to knock electrons out of the atomic orbitals in the target metal. If the energy of the primary electrons is typically above 10keV, they have enough energy to remove the innermost ‘K’ electrons from the target, creating an electron deficiency. The electron ‘holes’ are then filled by electrons falling from the adjacent highest electron shells, either ‘L’ or ‘M’. The decrease in the potential energy that results from falling electrons is observed as an emission of almost monochromatic
wavelength electromagnetic radiation. In target materials such as Cu, Mo, Cr and Fe the resultant radiation is an X-ray.

Since ‘K’ electron ‘holes’ can be filled by electrons from either the ‘L’ or ‘M’ shells, there are always two different X-ray lines produced. The energy difference between ‘L’ and ‘K’ shells is smaller than that of the ‘M’ and ‘K’ shells and therefore the wavelength of the radiation emitted from the L-K (α) transition is greater than that of the M-K (β) transition. There are two possible electron configurations within the shell and this manifests in lines being close doublets, Kα₁ and Kα₂, where Kα₁ is twice the intensity of Kα₂. For this reason, unless X-rays are passed through a high grade monochromator, a ‘shoulder’ can be seen on all diffraction peaks. Crystal monochromators are used to remove both the β-line and the shoulder line. A direct X-ray beam is reflected onto a large single crystal where only a very narrow wavelength band is reflected into the aperture collimator.

To provide high powered X-ray generators, a rotating anode is used. Primary electrons impact all over the surface of the anode and are not concentrated on a particular spot. Together with water cooling, this allows a higher influx of primary electrons without overheating the anode target. The more electrons impacting on the target, the more dense the X-ray beam produced. This leads to a much shorter irradiation time.

A schematic diagram of a typical X-ray diffractometer is shown in Figure 4.3. The powdered sample is placed onto petroleum jelly, smeared on a glass microscope slide and positioned on the rotating sample arm, allowing variation of the glancing angle, θ. Diffracted X-rays are detected by means of a scintillation counter. Counts are registered and stored on a personal computer.
Figure 4.3: Schematic Diagram of Key Components in a Diffractometer

Powder diffraction differs slightly from single crystal diffraction in that there are assumed to be many crystals in the powder, some of which will be aligned in the same direction and satisfy the correct orientation.

4.3 Preliminary Solid Phase Characterisation

The uranium solid phases present in experiments at high pH have been characterised. Preliminary characterisation by X-ray powder diffraction (XRPD) will be discussed in this chapter, together with the effects of ageing on the precipitates. Modelling using MINTEQA2 speciation code of the dissolution of the precipitates and the composition of the solid phase is examined later and allows further confirmation of structure. The characterisation of uranium precipitates in chapter 4 is only the first stage of the characterisation and not the final determination.
4.3.1 Experimental Methods

Samples of powdered uranium were prepared for X-ray diffraction. NaOH, KOH, Ca(OH)$_2$, NH$_4$OH and grout leachate were each added to uranyl nitrate solutions in order to form hydrated uranium(VI) precipitates at pH 9 and 11. Sodium-, potassium- and calcium hydroxides were added because these are present in grout leachate. Also, ammonium hydroxide was added to assess whether the additions of complexing ligands (used throughout this work) as ammonium led to the formation of ammonium uranate precipitates.

Precipitates were left for 4 days before being filtered through a 0.45\(\mu\)m membrane filter (Gelman Sciences). The filters and contents were then washed with water to remove any excess nitrate ions and cations. Each precipitate was dried on the filter membrane for 1 week in a desiccator containing dehydrated silica gel. Once dried, the precipitates were scraped from the membranes, ground using a mortar and pestle, and applied to microscope slides smeared with petroleum jelly (BDH).

The XRPD pattern was produced by using Cu K\(\alpha\) (\(\lambda=1.1541\text{\AA}\), 40kV, 20mA) X-rays on a Philips diffractometer (Philips Scientific, Cambridge). The diffracted X-rays were detected using a scintillation counter and the data were interpreted on a PC using Siemens Sietronics XRD Diffractometer Automation SIE122D analysis software (supplied by Hiltonbrooks X-Ray Sales and Services, Grange, Holmes Chapel, Cheshire).

Peaks observed in the diffraction pattern were compared with reference peaks listed in the JCPDS Atlas [110].

A reference schoepite material was produced [111]. Purified uranyl nitrate (50ml, 0.2M) was added to 0.50g lanthanum hydroxide (Aldrich) in a Teflon 100ml bottle and placed in an oven at 55°C. The contents were digested in the oven for 3 days, leading to the formation of a yellow precipitate which was filtered through a
0.45µm membrane (Gelman Sciences) and dried on the filter membrane for 1 week in a desiccator. The sample was then powdered as described above, mounted on a glass slide and examined by XRPD in the usual manner. An excess of lanthanum hydroxide forms an orange precipitate of hydrated lanthanum polyhydroxide, but since the mass of La(OH)$_3$ added was less than the referenced method (0.50g cf. 0.65g) this precipitate was not observed in the above experiment.

4.3.2 Preliminary Characterisation Results

4.3.2.1 Hydroxide Addition and Uranate Formation

The effect of the addition of different hydroxide counter cation solutions, namely NaOH, KOH, Ca(OH)$_2$, NH$_4$OH and grout leachate, on the composition of uranium precipitates at high pH in each system was investigated.

The preliminary assignments of uranium solid phases are detailed below. The diffraction pattern of each precipitate after four days equilibration is shown in Figures 4.4(a - h).

The formation of a standard schoepite, UO$_2$.2H$_2$O, reference precipitate as detailed in section 4.3.1 [111] was performed and the XRPD pattern of the product is shown in Figure 4.4(a). The diffraction peaks for the reference schoepite precipitate were observed at 7.4 Å, 3.6 Å, 3.2 Å, 2.6 Å, 1.9 Å and 1.8 Å. This characterisation forms the basis of all 'schoepite' assignments in the experiments that follow in this chapter.

The addition of sodium hydroxide to uranyl nitrate at pH 9 led to rapid precipitation of a compound whose XRD pattern is shown in Figure 4.4(b). Preliminary assignment yields a uranium hydrate with peaks observed at 7.4 Å, 3.4 Å, 3.1 Å and
1.9 Å. However, no distinction could be made between β-UO₂(OH)₂, UO₃.H₂O and UO₃.2H₂O at this point, further discussion is presented in sections 4.4 and 5.

The addition of sodium hydroxide to uranyl nitrate at pH 11 led to the rapid precipitation of sodium diuranate and the XRPD pattern observed is shown in Figure 4.4(c) in which it can be seen that peaks are observed at 6.0 Å, 3.4 Å, 3.1 Å and 1.9 Å. The diffraction pattern differs from that obtained by precipitates formed at pH 9 in that the ‘schoepite’ peak at 7.4 Å has been replaced by a peak at 6.0 Å and is characteristic of sodium diuranate.

The addition of potassium hydroxide to uranyl nitrate at pH 11 led to the rapid formation of a uranium precipitate and the XRPD pattern obtained is shown in Figure 4.4(d). Again, this pattern is different to that of the ‘schoepite’ reference material in that the peak at 7.4 Å is replaced by a peak at 6.7 Å, assigned to a potassium uranate. Other peaks are observed at 3.4 Å, 3.1 Å, 2.4 Å and 1.7 Å. However, no distinction could be made between K₂UO₄ and K₂U₂O₇ at this point for further discussion, see section 4.4 and 5.

The addition of calcium hydroxide to uranyl nitrate at pH 11 led to rapid precipitation. The XRPD pattern is shown in Figure 4.4(e). In the absence of a defining peak in the pattern, and based on the previous results of the addition of sodium and potassium hydroxides, calcium uranate was predicted, although the compound cannot be distinguished between CaUO₄ and CaU₂O₇. The schoepite peak at 7.4 Å disappeared in the calcium hydroxide system. Valsami-Jones [112] proposes a compound of the formula CaU₁₆O₅₈.2.5H₂O as the solid phase (peaks are quoted at 7.2 Å, 7.0 Å, 4.7 Å and 3.5 Å) and a formation constant, logKf = -23.96 [29]. These peaks do not appear in the XRPD patterns presented in this thesis, although the large amount of background noise may have hidden such peaks if, in fact, they are present. Further examination of this system will be detailed in section 4.4 and 5.

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Figure 4.4 XRPD Patterns Observed for Preliminary Uranium Precipitates Formed at High pH

(a) schoepite reference precipitate produced by digestion with La(OH)₃
(b) Uranium precipitate produced by addition of NaOH at pH 9
(c) Uranium precipitate produced by addition of NaOH at pH 11
Figure 4.4 (cont) XRPD Patterns Observed for Preliminary Uranium Precipitates Formed at High pH

(d) Uranium precipitate produced by addition of KOH at pH 11

(e) Uranium precipitate produced by addition of Ca(OH)$_2$ at pH 11

(f) Uranium precipitate produced by addition of NH$_4$OH at pH 9-12
Figure 4.4 (cont)  XRPD Patterns Observed for Preliminary Uranium Precipitates Formed at High pH

(g) Uranium precipitate produced by addition of grout leachate at pH 9
(h) Uranium precipitate produced by addition of grout leachate at pH 11
During the complexation experiments detailed in chapter 5, ammonium salts were added to uranium in order to alter the concentration of ligand and to avoid common ion effects (e.g. Na\(^+\)) and the formation of further diuranate precipitate. In order to examine the effect of the ammonium ion on the precipitate formed at high pH, ammonium hydroxide was added to a solution of uranyl nitrate and the XRPD pattern is shown in Figure 4.4(f). The pattern shows peaks at 7.4 Å, 3.5 Å, 3.2 Å, 2.6 Å and 2.0 Å and appears to be almost identical to that of the reference schoepite material detailed above. It can therefore be concluded that the addition of ammonium ions to a solution of uranium at high pH does not affect the composition of the precipitate.

The addition of grout leachate to uranyl nitrate at pH 9 and 11 led to the rapid formation of a precipitate. The XRPD patterns of the precipitates are shown in Figure 4.4(g) and (h) respectively. The precipitate at pH 9 appears to be a composite pattern showing similar peaks to that of a calcium uranate (as detailed above) but with a peak at 6.7 Å, suggesting the presence of a potassium uranate. This is not surprising since the grout leachate solution contains both calcium and potassium ions. However, there seems to be no evidence of a peak at 6.0 Å indicating the presence of sodium diuranate. The precipitate at pH 11 appears to be similar to that produced after the addition of calcium hydroxide, having lost the peak at 6.7 Å when compared to the pattern produced at pH 9 in grout leachate.

With the exception of the precipitates formed by addition of lanthanum hydroxide and ammonium hydroxide, all of the above XRPD patterns have a small signal to noise ratio. This can be attributed to the amorphous nature of the precipitates.

It can be seen that, as expected, several different precipitates are produced from the addition of different counter cations at high pH.

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4.4 Ageing Effects on the Nature of Precipitates

The nature of a crystal depends on the conditions during crystallisation. Two such factors are time for precipitation and temperature.

The ageing of a precipitate can lead to a phase transition and sometimes a chemical transition. In order to understand why changes occur, an examination of ageing is described below.

Kolthoff [113] details different types of precipitate ageing as follows:

1. Recrystallisation of a precipitate in the liquid film surrounding the particles to form a more perfect crystal.
2. Agglomeration of primary particles by sharing the liquid film that surrounds them, driven by the requirement to decrease the surface area.
3. Perfection of metal precipitates by the presence of local elements; the electrolytic solution tension at the active surface is more negative than at the normal surface; as the metal ions enter the liquid film, they are redeposited at the normal surface.
4. Transformation of a metastable state. The initial precipitate may not always be the most thermodynamically stable one, but will change over time to the latter.
5. Chemical ageing where particles react with one another, especially true for amorphous precipitates of hydrous oxides and hydroxides.

The latter two reasons are the most likely for the ageing of the uranium precipitates studied in this work. There are a further two theories which must also be considered;

Firstly, Ostwalds law of stages states that if crystallisation is from supersaturated solutions, the system is already in an unstable state and that the stability of the
precipitate formed will tend to resemble that of the saturated solution, i.e. unstable and not the most thermodynamically favoured phase.

Secondly, the Gibbs-Volmer theory states that there is a contradiction in free energy requirements. If the system is at equilibrium, it has a constant energy and any changes of its state (however small they may be) either reduce or have no effect on the entropy. If a small change increases the entropy, a meta-stable state is formed. A transition from unstable to stable states is (a) usually driven by a decrease in free energy, (b) spontaneous and (c) does not require any work. However, the formation of a new phase does require work and this is in contradiction with the previous statement.

The addition of hydroxide to uranyl nitrate leads to the rapid precipitation of uranium. The time over which the precipitate was allowed to stand in solution was extended, mainly as a result of previous XRPD patterns containing a large amount of background ‘noise’, due to the amorphous nature of the precipitate. There was also concern as to the nature of the precipitate over time and whether the precipitate would change from one compound to another over time.

4.4.1 Experimental Method for Investigating Ageing Phenomena

The experimental procedure described above was repeated with the exception of the addition of ammonium hydroxide. Precipitates were produced and allowed to stand in the mother liquor for varying periods of time up to and including ten weeks. The precipitates were then filtered, dried, powdered and analysed as above.

The temperature at which precipitates were formed and equilibrated with the mother-liquor was also varied. Previous precipitates had been formed at room temperature and so precipitates were produced at 40°C and 60°C. Only schoepite
precipitates were studied at elevated temperatures. The experimental method was as described above.

4.4.2 Ageing Results

The effect of contact time between the precipitates (uranium hydrate, sodium / potassium / calcium uranates, uranium / grout leachate mixture) and the mother liquor was studied in an attempt to gain further characterisation information. The results are shown in Figures 4.5 to 4.9.

The XRPD patterns of uranium precipitates formed at pH 9 by the addition of sodium hydroxide is shown in Figure 4.5 and are investigated over a period of 4 days to 10 weeks. It can clearly be seen that the magnitude of the peaks increases over time and that the signal to noise ratio of the overall pattern increases over time and this is evidence of an increase in the crystallinity of the precipitate. However, the peaks did not move in comparison to those presented in Figure 4.4 and did not shift over time. Therefore we can state that the precipitate did not change chemically. A similar effect was observed by Torrero et al [114] in which they observed a growth in XRPD peak height between two samples taken over 3 months.

Uranium-trioxide monohydrate, \( \text{UO}_3\cdot\text{H}_2\text{O} \) is known to be amorphous and is chemically equivalent to uranium hydroxide, \( \beta-\text{UO}_2(\text{OH})_2 \), while uranium-trioxide dihydrate, \( \text{UO}_3\cdot2\text{H}_2\text{O} \) (schoepite) is crystalline. The apparent increase in crystallinity over time as observed in the above experiments is attributed to the transition of uranium-trioxide monohydrate to uranium-trioxide dihydrate, i.e. schoepite.
The effect of contact time on the XRPD patterns of uranium precipitates formed at pH 11 by addition of sodium hydroxide, which produced sodium diuranate, is shown in Figure 4.6. It can be seen again that the d-spacing does not alter, but the intensity of the peaks increases over time, as does the signal to noise ratio. It can be concluded that the sodium uranate precipitate does not change over time, except to become more crystalline. The same can be said for the precipitates formed at pH 11 by the addition of potassium hydroxide, except that the changes are even less significant over the same time scale.
Figure 4.5  XRPD Patterns Observed for Uranium Precipitates Formed at pH 9 by Addition of NaOH and Aged for (a) 4 days; (b) 1 week; (c) 2 weeks;
Figure 4.5 (cont.) XRPD Patterns Observed for Uranium Precipitates Formed at pH 9 by Addition of NaOH and Aged for (d) 3 weeks; (e) 4 weeks; (f) 5 weeks;
Figure 4.5 (cont.)  XRPD Patterns Observed for Uranium Precipitates Formed at pH 9 by Addition of NaOH and Aged for (g) 6 weeks; (h) 8 weeks; (i) 10 weeks.
Figure 4.6 XRPD Patterns Observed for Uranium Precipitates Formed at pH 11 by Addition of NaOH and Aged for (a) 3 weeks; (b) 6 weeks; (c) 9 weeks.
Figure 4.7  XRPD Patterns Observed for Uranium Precipitates Formed at pH 11 by Addition of KOH and Aged for (a) 3 weeks; (b) 6 weeks; (c) 9 weeks.
The addition of calcium hydroxide to a solution of uranyl nitrate at high pH forms a calcium uranate precipitate. The XRPD pattern of this precipitate changes over time, with the peak at 3.4 Å becoming larger in intensity (see Figure 4.8). A peak may be developing over the time studied in the range of 7.0 to 7.6 Å and this could either be described as a schoepite peak (7.4 Å) or a peak due to a transition to calcium diuranate at 7.2 Å or 7.0 Å [112].

The XRPD pattern of the precipitate formed by the addition of grout leachate to uranyl nitrate at high pH shows a change over time also, with increasing peak intensity. The XRPD patterns shown in Figure 4.9 are very noisy, suggesting a low degree of crystallinity. With the extra contaminating ions in the grout leachate solution (see section 2.2.2), the poor quality of the pattern may be attributed to the co-precipitation of other compounds. Diaz-Arocas [115] found that sodium polyuranates were capable of extensive co-precipitation. The presence of a peak at 6.7 Å as detailed in section 4.3 suggests the presence of a potassium uranate precipitate combined with a form of calcium uranate. After 9 weeks, a shoulder peak can be seen at 7.4 Å on the side of the 6.7 Å peak and this indicates that schoepite might also be precipitated.

Several papers have considered the transformation of schoepite into becquerelite, CaU₆O₁₉·1·1H₂O, over time. Sowder et al [116] observed a transformation after one day at 90°C indicated by a loss of a 7.35 Å peak, which was replaced by peaks at 7.45 Å and 3.73 Å. This phenomenon was not observed in this investigation. Sowder also concluded that the addition of silica hindered the transformation while phosphate accelerated the schoepite transformation into becquerelite (instead, leading to the formation of autunite, Ca(UO₂(PO₄)₂·10H₂O), and that neither uranophane, Ca(UO₂)₂(SiO₃OH)₂, nor soddyite, (UO₂)₂SiO₄·2H₂O, were present. Sandino and Grambow [117] also examined the transformation into becquerelite as well as further transformations to compreignacite, K₂U₆O₁₉·11H₂O after a short contact time, with a peak at 7.4 Å. This may be the peak observed as a shoulder to the peak described above.
Figure 4.8  XRPD Patterns Observed for Uranium Precipitates Formed at pH 11 by Addition of Ca(OH)$_2$ and Aged for (a) 3 weeks; (b) 6 weeks; (c) 9 weeks.
Figure 4.9  XRPD Patterns Observed for Uranium Precipitates Formed at pH 11 by Addition of Grout Leachate and Aged for (a) 3 weeks; (b) 6 weeks; (c) 9 weeks.
The effect of contact time at 40°C and 60°C on the XRPD of uranium precipitates formed by the addition of sodium hydroxide to a uranyl nitrate solution at pH 9 was studied and the results are shown in Figures 4.10 and 4.11 respectively.

Firstly, the position of the peaks in the diffraction patterns are unchanged over the temperature range and the time scale studied.

Secondly, when the diffraction patterns at 40°C and 60°C are compared to those at 25°C over a similar time scale, several points can be made:

1. The signal to noise ratio of the XRPD pattern at 25°C increases with time;
2. The signal to noise ratio of the XRPD pattern at 40°C decreases slightly with time;
3. The signal to noise ratio of the XRPD pattern at 60°C decreases with time.

Finch [118] states that pure schoepite is unstable in water above 40°C, leading to the irreversible formation of a dehydrated schoepite-type compound (UO$_3$.xH$_2$O, where 1 > x > 0.8) with XRPD peaks at 5.1 Å and 2.8 Å. These peaks are not observed in the XRPD patterns presented in this work.

Van-Hook [119] states that a unique feature of the polymeric state is that part of the extended monomolecule is capable of distinct ordering while the other part remains amorphous, and quotes Flory [120] stating that “the crystallinity of a polymer will decrease as the temperature increases due to the extension of the amorphous ends of the polymer.”

With this last statement in mind, together with Ostwalds law of stages (quoted earlier in this chapter), this is perhaps evidence of a polymeric uranium hydrate formed from polymeric uranyl hydroxides (such as (UO$_2$)$_3$(OH)$_7$) rather than monomeric hydroxides (such as UO$_2$(OH)$_3$).
Figure 4.10  XRPD Patterns Observed for Uranium Precipitates Formed at pH 9 by Addition of NaOH and Aged at 40°C for (a) 2 days; (b) 4 days; (c) 1 week.
Figure 4.10 (cont.) XRPD Patterns Observed for Uranium Precipitates Formed at pH 9 by Addition of NaOH and Aged at 40°C for (d) 3 weeks;
(e) 6 weeks and (f) 9 weeks
Figure 4.11  XRPD Patterns Observed for Uranium Precipitates Formed at pH 9 by Addition of NaOH and Aged at 60°C for (a) 2 days; (b) 4 days; (c) 1 week.
Figure 4.11 (cont.) XRPD Patterns Observed for Uranium Precipitates Formed at pH 9 by Addition of NaOH and Aged at 60°C for (d) 3 weeks; (e) 6 weeks and (f) 9 weeks.
4.5 Anaerobic Solid Phase Characterisation

4.5.1 Experimental Method

A uranium containing precipitate was produced at high pH and under anaerobic conditions, which was examined by XRPD analysis.

All solutions were degassed by bubbling nitrogen for two hours before being placed in a glove bag (Aldrich, 280L capacity) which was continually purged with oxygen-free nitrogen (BOC Gases). The glove bag was attached to a Dreschel flask containing water to allow a constant flow of fresh nitrogen throughout the experiment, without allowing air to re-enter the system.

A 25ml portion of a purified (ion exchange) uranyl nitrate solution (25mM) was slowly added to 200mls of sodium dithionite solution (1mM) containing a pellet of potassium hydroxide. Potassium hydroxide was then added to the solution, while the pH and $E_h$ were monitored, until a pH of 10 was obtained.

The resulting solution was left under nitrogen for 48 hours before being filtered through a Qualitative-2 filter paper (Whatman International Ltd, Springfield Mill, Maidstone, Kent) placed in a filter funnel. The paper and precipitate were transferred to a silica desiccator housed in the glove bag and allowed to dry again under a nitrogen atmosphere. After a period of one week, the precipitate was removed from the desiccator and scraped from the paper, powdered using a mortar and pestle and fixed onto a glass microscope slide (76mm x 26mm x 1.2mm, Blue Star Slides, Chance Propper Ltd, Spon Lane, Smethwick, Warley) using petroleum jelly (BDH). XRPD analysis was then performed on the sample and the peaks in the diffraction pattern compared to reference patterns [110].
4.5.2 Characterisation Results

The solution resulting from the addition of uranyl nitrate to sodium dithionite was dark brown in colour, indicating that a different species of uranium was present other than U(VI). On addition of potassium hydroxide solution to the uranium/dithionite mixture, a dark brown precipitate was formed above pH 5. This precipitate settled rapidly and did not appear to contain any yellow precipitate which could be assumed to be U(VI).

The precipitate present at the powdering stage was brown in colour and appeared to be a harder compound to crush than the U(VI) powder observed in aerobic precipitation.

However, at the time of XRPD analysis, the precipitate changed slightly in colour. The dark brown colour faded to yield a cream precipitate. This was reflected in the XRPD diffraction pattern recorded which is shown below in Figure 4.12. On comparison to patterns identified for aerobic studies, the XRPD pattern is similar to that of schoepite.

On leaving the sample slide in air for a further two weeks, the brown colour completely gave way to the familiar yellow of U(VI).

It can therefore be concluded that the XRPD methodology used here is unable to maintain uranium in the reduced +IV state. This may be due to the moisture created by the petroleum jelly required to hold the precipitate on the slide. A sample of unused U(IV) precipitate housed in a sealed glass sample tube in air did not turn yellow.

It is also possible that the uranium precipitate formed in the above procedure is not uranium(VI), but some other oxidation state of uranium.
Figure 4.12  XRPD Pattern Observed for Uranium Precipitates Formed at pH 10 by Addition of KOH in Na$_2$S$_2$O$_4$/N$_2$ Atmosphere.
4.6 Summary

The solid phases involved in the precipitation of uranium at high pH have been investigated by conducting a range of XRPD studies at room temperature and higher temperatures (40 and 60°C) over time. Further consideration of the nature of the precipitates will be given in chapter 5, where modelling is used to compare and evaluate experimental complexation / dissolution studies.

Information from the XRPD studies alone are summarised below:

Addition of sodium hydroxide or potassium hydroxide to uranyl nitrate at pH 9 yields a uranium hydrate. The addition of ammonium hydroxide at pH 9 to 12 produces the same precipitate. The precipitate is either $\beta$-UO$_2$(OH)$_2$, UO$_3$.H$_2$O or UO$_3$.2H$_2$O. It will be shown in chapter 5 that the modelling of the dissolution of a uranium precipitate at pH 9 and 10 gives a closer fit when schoepite, UO$_3$.2H$_2$O, is assigned as the solid phase. This conclusion is supported by the XRPD pattern of a standard schoepite precipitate formed from the digestion of uranyl nitrate with lanthanum hydroxide. The pattern is very similar to that observed in the above systems. Ageing studies show that the precipitate becomes more crystalline over time, possibly due to further hydration of remaining UO$_3$.H$_2$O to UO$_3$.2H$_2$O.

The addition of sodium hydroxide or potassium hydroxide to uranyl nitrate solutions at a pH of 11 produces an alkali uranate precipitate. Again, modelling will show in chapter 5 that the precipitates which best fit experimental results are sodium diuranate and potassium diuranate respectively, Na$_2$U$_2$O$_7$ and K$_2$U$_2$O$_7$, rather than mono uranates (namely Na$_2$UO$_4$ and K$_2$UO$_4$). Ageing experiments show that these precipitates become slightly more crystalline over time, but do not change chemically.

The addition of calcium hydroxide to uranyl nitrate solutions at pH 9 produced a precipitate whose XRPD pattern resembled that of schoepite. At higher pH values,
the XRPD pattern lost the peak at 7.4 Å. The precipitate was assumed to be calcium uranate (CaUO₄). It appeared that the precipitate became slightly more crystalline over time, together with the appearance of a small, broad peak between 7.0 and 7.6 Å. This additional peak could be due to the presence of schoepite peak at 7.4 Å or due to the formation of calcium diuranate, CaU₂O₇, with a peak at 7.2 or 7.0 Å. Modelling studies performed in chapter 5 will show how the precipitate that gave the best fit to experimental complexation / dissolution work was in fact calcium uranate.

Grout leachate contains a mixture of cations that can form various uranate precipitates. At pH 9, the precipitate could best be described as a combination of CaUO₄ and K₂U₂O₇, while at pH 11, the precipitate was CaUO₄ alone. As the precipitate aged, a shoulder peak appeared at 7.4 Å. This could either be the formation of a schoepite precipitate, calcium diuranate, compreignacite (K₂U₆O₁₉.11H₂O) or becquerelite (CaU₆O₁₉.11H₂O).

The examination of a uranium(IV) precipitate was unsuccessful. A dark brown precipitate was produced, but during the course of examination, oxidation occurred and the XRPD pattern produced suggested reoxidation to a uranium(VI) hydrate.
CHAPTER FIVE

Aerobic Complexation Of Uranium At High pH
5 Aerobic Complexation of Uranium at High pH

5.1 Introduction

Once low-level waste material is grouted in place at the Drigg site, the first stage of possible mobilisation is initiated. This stage is based on the hydration of the grout material and leaching of the grout components described in chapter 2 of this work, leading to an increase in pH and the availability of alkali metals to complex with uranium housed in the waste matrix. The addition of these alkali hydroxides and grout leachate leads to the formation of uranium precipitates at high pH. The precipitates are characterised in chapter 4 of this work. The effect of pH on the solubility of these precipitates must be examined.

The presence of any complexing ligands either in the waste matrix, in the vault water, leached from the grout material or produced from the action of aerobic microbes, is of key importance with regard to the stability of uranium and its transport from the waste matrix. The ligands themselves may affect the pH of the waste and may compete with uranium for the alkali metals which would normally maintain uranium in the solid phase by formation of uranates.

The work presented in this chapter is a study of the effect of twelve complexing ligands on the solubility of uranium precipitates formed in sodium-, potassium- and calcium hydroxide solutions and in grout leachate (where the combined effect of these hydroxides is encountered), over a pH range of 9 to 12. The ligands studied can be grouped into 5 categories:

- **pH effects**
- **Inorganic ligands**
- **Simple organic ligands**
- **Anthropogenic ligands**
- **Dissolved organic matter**

hydroxide

carbonate, phosphate, sulphate, chloride

acetate, citrate

EDTA, NTA

humic / fulvic acids, iso-saccharinic acid.
The observed experimental behavior of uranium at high pH in the presence of increasing concentrations of each ligand is compared with model predictions derived using literature formation constants and the MINTEQA2 speciation code together with the dataset listed in Appendix 1.

The method used for the study is detailed in section 5.2 below and the overall procedure is shown schematically in Figure 5.1.

![Figure 5.1 Schematic Diagram of the Experimental and Modelling Procedure of the Aerobic Complexation of Uranium](image)

### 5.2 Experimental Methods for Complexation Studies

As detailed in chapter 3, moderate uranium concentrations were determined by liquid scintillation counting of $^{238}\text{U}$ or by spectrophotometry using the chromogenic reagent Arsenazo-III. Low concentrations of uranium were determined by doping $^{238}\text{U}$ solution with 1% $^{233}\text{U}$.

The variation in uranium solubility with pH was studied for sodium-, potassium- and calcium hydroxides and grout leachate for $7 < \text{pH} < 11.8$. The pH of a 5ml
aliquot of 0.01M purified uranyl nitrate (doped with 1% $^{233}$U to lower the limit of detection compared to standard uranyl nitrate, if necessary) was adjusted by addition of the alkali hydroxides or grout leachate in each case. The volume was then corrected to 10mls using deionised / degassed water and the pH checked and adjusted if necessary. The resulting solid solutions were stoppered to avoid ingress of atmospheric gases and left to equilibrate for 1 week. The supernatant was then filtered through a 0.2µm Acrodisc syringe filter (Gelman Sciences) and a sample was taken for liquid scintillation counting and compared to standards of known activity.

For investigating the effect of complexing ligands on the solubility of the uranium precipitates formed at high pH, samples were prepared again by over-saturation of uranium with alkali hydroxide and grout leachate addition. Samples were sealed and allowed to equilibrate for 3 days before addition of the complexing ligand at a variety of concentrations as an ammonium salt. The volume of each sample was taken to 10mls with degassed / deionised water pH of each sample was rechecked and adjusted if necessary, before being resealed and allowed to equilibrate for a further 24 - 48 hours with occasional shaking. The supernatant solution was then filtered through a 0.2µm Acrodisc syringe filter (Gelman Sciences) and the uranium concentration determined by either liquid scintillation counting or spectrophotometry using Arsenazo-III.
5.3 Uranium(VI) - Ligand Systems

5.3.1 Uranium(VI) Hydrolysis by pH Variation

Figure 5.2 Effect of pH on the Solubility of Uranium Precipitates Produced in (a) NaOH, (b) KOH, (c) Ca(OH)\(_2\) and (d) Grout Leachate. Diamonds represent experimental results, curves represent modelling.

The effect of pH on the solubility of uranium precipitates formed by addition of sodium-, potassium-, calcium hydroxides and grout leachate is shown in Figure 5.2, above. Each system initially shows a decrease in the solubility of the precipitate with increasing pH. Both the potassium hydroxide and the grout leachate system show an increase in the solubility of uranium after pH 10.
For the sodium hydroxide system, previous studies by XRPD had identified a uranium hydrate precipitate such as schoepite at pH 9 and a sodium uranate precipitate at pH 11 and above. The exact composition of the uranate was not achieved by XRPD, suggesting either Na$_2$UO$_4$ or Na$_2$U$_2$O$_7$. Modelling of the pH titration experiment above using formation constants for mono- and di- uranate precipitates of 30.3 and 22.6 [29] shows clearly that only the diuranate could reproduce the experimental results.

XRD analysis of the potassium hydroxide system showed a potassium uranate precipitate. Again, no distinction could be made as to whether a mono- or di-uranate was the solid phase. Modelling of the system using a formation constant of 30.46 [19] for the mono-uranate showed that no potassium uranate precipitate was formed. Unfortunately, a literature formation constant was not available for potassium diuranate. Investigation of the carbonate complexation of uranium in each alkali system and grout leachate [26] suggested that experimental dissolution results were best fitted with a formation constant, log$K_f = 26.80$. The solubility of this solid phase increases slightly as the pH is increased from pH 10 to 11.8.

The solubility of uranium precipitates in calcium hydroxide are shown together with the effect of pH, in Figure 5.2(c). The results show that the solubility decreases with increasing pH. The XRPD characterisation of this solid phase suggested a calcium uranate precipitate. Modelling of the above system supports the finding that the precipitate is in fact best described as a mono-uranate rather than di-uranate.

The effect of pH on the solubility of uranium precipitates formed at high pH in grout leachate is shown in Figure 5.2(d). The results are somewhat similar to those of the potassium hydroxide system in that the solubility of the solid phase increases slightly at very high pH. Modelling performed on the carbonate dissolution of precipitates in grout leachate [26] suggested that unless the uranium precipitate was modelled as a mixture of schoepite, calcium uranate, sodium uranate and potassium...
uranate, uranium solubilities would be largely underestimated and controlled by calcium uranate alone. This is supported by the modelling performed in the examination of the pH titration experiments. Below pH 10.5, the precipitate is a mixture of schoepite and calcium uranate. Above pH 10.5, the model predicts the formation of calcium-, sodium- and potassium- uranates, which is not surprising since grout leachate contains all these constituent metal ions. XRPD characterisation of the solid phase suggests a mixture of schoepite, potassium hydroxide and calcium hydroxide. Clearly, with the relative concentration of potassium in grout leachate higher than that of sodium and calcium, it can be assumed that more potassium diuranate might be precipitated rapidly than predicted thermodynamically.

In each system, the experimental uranium solubility is slightly higher than that of the model. This may be in part due to the amorphous nature of the precipitate and the rapid precipitation leading to a solid phase which cannot be described exactly by modelling.

It should also be noted that the modelling of the above pH titration experiments showed that the major uranium species at the higher pH values was the polymeric (UO$_2$)$_3$(OH)$_7$ species which is shown in Figure 5.3. Modelling using the monomeric hydroxides, UO$_2$(OH)$_3$ and UO$_2$(OH)$_4^{2-}$ showed complete dissolution of the uranium precipitate, which was not observed experimentally. It may therefore be assumed that at the concentrations studied in this work (mM), polymeric uranyl hydroxides dominate over monomeric species.
5.3.2 Uranium(VI) - Carbonate System

Carbonate was the first ligand to be investigated and modelled. The work was published [26] and is detailed in this chapter.

Resolubilisation data following the addition of ammonium carbonate to uranium precipitates formed in NaOH, KOH, Ca(OH)₂ and grout leachate are shown in Figures 5.4, 5.5, 5.6 and 5.7 respectively, together with the model predictions for each system. It can be seen that complete redissolution of the uranium precipitates occurs in almost all cases. In other cases, complete dissolution was not achievable at the required high pH because the large concentrations of ammonium carbonate needed buffered the pH to lower values.
Figure 5.4 The Effect of Added Carbonate on the Dissolution of Uranium Precipitates formed in Sodium Hydroxide at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 12. Diamonds represent experimental results, curves represent modelling.
Figure 5.5  The Effect of Added Carbonate on the Dissolution of Uranium Precipitates formed in Potassium Hydroxide at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 12. Diamonds represent experimental results, curves represent modelling.
The sodium hydroxide system shows complete experimental redissolution from pH 9 to 11. Modelling of this system, over the pH range studied, showed good correlation with experimental results using solid phases of schoepite and sodium diuranate. Modelling studies using either $\beta$-UO$_2$(OH)$_2$ or sodium mono-uranate as the solid phase showed poor correlation and so these two precipitates could be disregarded. Closer examination of the modelling of the solid phase showed how its composition changed as the pH increased. The greatest correlation with experimental results was achieved by using the formation constants listed in Appendix 1, and by assuming that the precipitates at pH 9 and 10 were schoepite. At pH 11, almost 50% of the precipitate was best modelled as sodium diuranate and the remaining 50% as schoepite. At pH 12, the precipitate was best modelled as 100% sodium diuranate. These findings agree with the XRPD characterisation shown in chapter 4.

Examination of the modelled speciation of the dissolution of uranium with added carbonate shows that at lower carbonate concentrations, the dominant ion is a mixed hydroxycarbonate species, $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$. At higher concentrations of added carbonate the dominant species is the uranyl tricarbonato ion, $\text{UO}_2(\text{CO}_3)_3^{4+}$.

As expected, the potassium hydroxide system shows very similar characteristics to that of the sodium hydroxide system. Again, complete experimental redissolution is achieved from pH 9 to 11. Modelling of experimental results gave best correlation when potassium diuranate was used rather than mono-uranate. A formation constant, log$K_f$ of 26.8 was derived to fit the experimental results since the formation constant did not previously exist. Using this constant, the composition of the solid phase at each pH could be modelled as 100% schoepite at pH 9 and 10. However, at pH 11, only 22% of the precipitate was schoepite with 78% diuranate. At pH 12, the precipitate was almost completely diuranate with only 2% of the precipitate as schoepite. Again, these findings agree with the experimental characterisation of the uranium solid phase by XRPD in chapter 4.
Figure 5.6  The Effect of Added Carbonate on the Dissolution of Uranium 
Precipitates formed in Calcium Hydroxide at (a) pH 9, (b) pH 10, (c) pH 11 
and (d) pH 12. Diamonds represent experimental results, curves represent 
modelling.
The redissolution profile of uranium precipitates formed in calcium hydroxide are somewhat different to those already described for sodium and potassium hydroxide. Experimental results show a stepped dissolution profile with increasing carbonate. Modelling of these results was achieved by means of a mixed precipitate containing schoepite and calcium uranate. Note that modelling using calcium diuranate as the solid phase did not produce a good correlation with experimental results, supporting XRPD evidence that the solid phase was a mixture of schoepite and calcium uranate. The stepped profile is reflected in the large relative difference in formation constants between schoepite and calcium uranate. The relative difference is not as large in the sodium and potassium hydroxide systems and this is reflected in the continuous dissolution profile rather than a stepped profile.

At low concentrations of added carbonate, the primary increase in uranium solubility in calcium hydroxide solution is due to the carbonate complexation of uranium via the dissolution of a schoepite precipitate. The primary plateau is observed at a point where the added carbonate concentration is not high enough to effect the dissolution of the thermodynamically more stable calcium uranate and the formation of calcite is favoured. Once the added carbonate concentration is high enough to satisfy the thermodynamic dissolution of calcium uranate, the formation of further $\text{UO}_2(\text{CO}_3)_3^{4-}$ is achieved together with the formation of additional calcite. The height of this second step was found to be proportional to the calcium hydroxide concentration added to increase the pH of the initial uranium solid solution.

Modelling the dissolution of the precipitate led to the further characterisation of the solid phases formed by the addition of calcium hydroxide. At pH 9 and 10, the ratio of schoepite to calcium uranate is approximately 1:2, and at pH 11 calcium uranate reached 70% of the total precipitate. The characterisation of the precipitate at pH 12 by modelling suggested a composition entirely of calcium uranate. These findings support the conclusions found by XRPD in chapter 4.
The addition of grout leachate to uranyl nitrate led to the rapid formation of a precipitate which could be completely redissolved at pH 9 and 10. Again, the dissolution of uranium precipitates by the addition of carbonate showed profiles similar to those observed in the calcium hydroxide system. Complete redissolution was not achieved at pH 11 and 12 due to the inability to maintain the high pH at the higher ammonium carbonate concentrations. Modelling of the experimental results suggested that not all the calcium present in the leachate was forming calcium uranate (cf. calcium hydroxide system, above). Modelling also suggested that the precipitate was a mixture of schoepite and calcium uranate, 30% / 70% for pH 9 and 37.5% / 62.5% for pH 10. At pH 11, the model predicts the formation of calcium together with sodium and potassium diuranates in favour of schoepite formation, with a composition of 50%, 12% and 38% for the three uranates respectively. A mixed precipitate was suggested by XRPD analysis described in chapter 4 of this work.

At pH 11.8 in grout leachate, the model failed to predict the experimental results and a fitting method was used by changing the relative composition of the solid phase to produce the greatest correlation with a precipitate containing calcium uranate, sodium uranate and potassium diuranate at 30%, 14% and 56% respectively. This was justified in that the rate of precipitation of uranium by addition of grout leachate was rapid. Thermodynamics favours the formation of calcium uranate, but there is an excess of sodium and potassium in solution and therefore the probability of a uranium ion combining with a potassium ion is greater than complexation with a calcium ion. Over much longer timescales, the composition of the solid phase may change to the thermodynamically favoured composition.
Figure 5.7  The Effect of Added Carbonate on the Dissolution of Uranium Precipitates formed in Grout Leachate at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 11.8. Diamonds represent experimental results, curves represent modelling.
The composition and therefore the chemistry of the grout leachate solution makes the prediction of the behaviour of uranium in such solutions difficult. It can be seen that the modelling of carbonate dissolution of uranium precipitates in the 'pure' hydroxide systems acted as an aid to the characterisation of the uranium precipitates in grout leachate by carbonate complexation.

5.3.3 Uranium(VI) - Phosphate System

The effect of phosphate on the solubility of uranium containing precipitates is shown in Figures 5.8 to 5.11 for NaOH, KOH, Ca(OH)₂ and grout leachate respectively. Experimental points are plotted together with modelling curves produced using the MINTEQA2 speciation code and the dataset listed in Appendix 1. It can clearly be seen that the solubility of uranium precipitates increases with increasing added ammonium phosphate and in some cases, complete redissolution was achieved.

The dissolution of uranium precipitates formed in sodium hydroxide and potassium hydroxide show similarities to each other and to the dissolution using carbonate which has already been detailed in section 5.3.2. Modelling of the dissolution profiles show excellent correlation with experimental results and shows the complexation of uranium by the $\text{UO}_2(\text{HPO}_4)_2^{2-}$ ion.

The dissolution profile of uranium precipitates formed in calcium hydroxide by phosphate addition is similar to that of carbonate addition, showing a stepped profile. Modelling of this profile again shows good correlation with experimental results and provides information on the complexation occurring in the system which leads to such a dissolution profile. As with carbonate, the initial dissolution step is caused by the dissolution of schoepite, followed by the formation of a solid phase, namely hydroxyapatite, $\text{Ca}_3(\text{PO}_4)_2\text{OH}$. 

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Figure 5.8  The Effect of Added Phosphate on the Dissolution of Uranium Precipitates formed in Sodium Hydroxide at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 12. Diamonds represent experimental results, curves represent modelling.
Figure 5.9  The Effect of Added Phosphate on the Dissolution of Uranium Precipitates formed in Potassium Hydroxide at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 12. Diamonds represent experimental results, curves represent modelling.
Figure 5.10   The Effect of Added Phosphate on the Dissolution of Uranium Precipitates formed in Calcium Hydroxide at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 12. Diamonds represent experimental results, curves represent modelling.
The plateau in the profile can also be explained by the increasing difficulty of dissolving CaUO₄. As in the case of carbonate addition, the height of the observed step depends on the initial added calcium concentration, as calcium hydroxide.

The dissolution of uranium containing precipitates in grout leachate at high pH by the addition of phosphate is shown in Figure 5.11. Examination of the dissolution profile at pH 9 shows very similar results to that of the calcium hydroxide system, with a stepped profile. Modelling of these experimental results using the dataset requires adjustment of the calcium concentration in order to fit the plateau.

At higher pH values, complete redissolution could not be achieved experimentally due an inability to maintain the high pH at such high added ammonium phosphate concentrations. This effect is due to the weakly acidic nature of the ammonium ion. However, steps in the dissolution profiles were still observed experimentally at pH 10 and 11, and this effect could be modelled in the same manner as pH 9 by increasing the added calcium concentration to reflect the height of the step. At pH 11.8 in grout leachate, no dissolution was observed experimentally, but modelling predicted dissolution later in the profile (at very high phosphate concentrations).
Figure 5.11  The Effect of Added Phosphate on the Dissolution of Uranium Precipitates formed in Grout Leachate at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 11.8. Diamonds represent experimental results, curves represent modelling.
5.3.4 Uranium(VI) - Sulphate System

The effect of sulphate on the dissolution of uranium containing precipitates formed in sodium, potassium, calcium hydroxides and grout leachate are shown in Figures 5.12 to 5.15 respectively for pH values between 9 and 12. It can be seen that sulphate has no effect on the solubility of these precipitates under the conditions investigated.

Uranyl sulphate complexes of 1:1, 1:2 and 1:3 were included in the modelling of experimental results which showed that sulphate was not able to compete with the formation of polymeric uranyl hydroxide complexes and uranate precipitates at high pH.
Figure 5.12  The Effect of Added Sulphate on the Dissolution of Uranium
Precipitates formed in Sodium Hydroxide at (a) pH 9,
(b) pH 10, (c) pH 11 and (d) pH 12.
Figure 5.13  The Effect of Added Sulphate on the Dissolution of Uranium Precipitates formed in Potassium Hydroxide at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 12.
Figure 5.14  The Effect of Added Sulphate on the Dissolution of Uranium Precipitates formed in Calcium Hydroxide at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 12.
Figure 5.15  The Effect of Added Sulphate on the Dissolution of Uranium
Precipitates formed in Grout Leachate at (a) pH 9, 
(b) pH 10, (c) pH 11 and (d) pH 11.8.
5.3.5 Uranium(VI) - Chloride System

The effect of chloride on the dissolution of uranium containing precipitates formed in sodium, potassium, calcium hydroxides and grout leachate are shown in Figures 5.16 to 5.19 respectively for pH values of between 9 and 12. It can be seen that chloride has no effect on the solubility of these precipitates under the conditions investigated.

Uranyl chloride complexes of 1:1, 1:2 and 1:3 were included in the modelling which showed that chloride was not able to compete with the formation of polymeric uranyl hydroxide complexes and uranate precipitates at high pH and at these uranium concentrations (mM). It may also be noted therefore that predictive modelling correlated with experimental results as with sulphate.
Figure 5.16  The Effect of Added Chloride on the Dissolution of Uranium Precipitates formed in Sodium Hydroxide at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 12.
Figure 5.17  The Effect of Added Chloride on the Dissolution of Uranium Precipitates formed in Potassium Hydroxide at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 12.
Figure 5.18 The Effect of Added Chloride on the Dissolution of Uranium Precipitates formed in Calcium Hydroxide at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 12.
Figure 5.19  The Effect of Added Chloride on the Dissolution of Uranium Precipitates formed in Grout Leachate at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 11.8.
5.3.6 Uranium(VI) - Acetate System

The effect of acetate on the dissolution of uranium containing precipitates formed in sodium, potassium, calcium hydroxides and grout leachate are shown in Figures 5.20 to 5.23 respectively for pH values between 9 and 12. Once again, it can be seen that acetate has no effect on the solubility of these precipitates under the conditions investigated.

Uranyl acetate complexes of 1:1, 1:2, 1:3 and 1:4 were included in the modelling of experimental results. The presence of the 1:4 complex led to the model predicting dissolution of precipitates at pH 9, 10 and 11, in contradiction to the experimental results. Large and unacceptable changes to the formation constant detailed in the HATCHES database were required to make $\text{UO}_2(\text{acetate})_{4}^{2-}$ insignificant, so the species was removed from the model in order to fit experimental work. The fitted model shows that 1:1, 1:2 and 1:3 acetate complexes were not able to compete with the formation of polymeric uranyl hydroxide complexes and uranate precipitates at such high pH values and uranium concentrations (mM). Once the dataset was altered, predictive modelling thus showed good correlation with experimental results. The corrections therefore question the 1:4 species and the literature formation constant.
Figure 5.20  The Effect of Added Acetate on the Dissolution of Uranium

Precipitates formed in Sodium Hydroxide at (a) pH 9,
(b) pH 10, (c) pH 11 and (d) pH 12.

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Figure 5.21  The Effect of Added Acetate on the Dissolution of Uranium Precipitates formed in Potassium Hydroxide at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 12.
Figure 5.22  The Effect of Added Acetate on the Dissolution of Uranium Precipitates formed in Calcium Hydroxide at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 12.
Figure 5.23  The Effect of Added Acetate on the Dissolution of Uranium  
Precipitates formed in Grout Leachate at (a) pH 9, 
(b) pH 10, (c) pH 11 and (d) pH 11.8.
5.3.7 Uranium(VI) - Citrate System

The effect of addition of ammonium citrate on the solubility of uranium precipitates at high pH is shown in Figures 5.24 to 5.27. It can be clearly seen that the presence of citrate increases the solubility of uranium in each system and at all pH values studied. Thermodynamic formation constants for 1:1 and 2:2 U(VI)-citrate complexes are available and quoted as logK_f = 8.7 and 21.18 [29] respectively. Predictive modelling of experimental results using these literature formation constants could not be achieved unless both logK_f values were increased by between 9 or 10 units. Clearly, this is an unacceptable change and therefore a new complex was invoked which contained a mixed hydroxy-citrate ligand. Justification of this addition to the dataset was by virtue of the high solubility of uranium at high pH shown in the experimental results.

Model-fitting of the citrate complexation of uranium in the sodium hydroxide system was performed by addition of a 1:1:1 mixed species (UO_2(OH)Citrate^3-) with a formation constant of logK_f = 5.05 determined by trial and error at pH 9 and 10. The model was then used to predict experimental results for the uranium dissolution in sodium hydroxide system at pH 11 and 12. Modelling of experimental desorption profiles could only be achieved by changing the composition of the solid phase to 100% sodium diuranate.

Modelling of the dissolution of precipitates formed by addition of potassium hydroxide showed similar dissolution profiles to that of sodium hydroxide, again the composition of the solid phase was controlled at pH 11 and 12.
Figure 5.24  The Effect of Added Citrate on the Dissolution of Uranium
Precipitates formed in Sodium Hydroxide at (a) pH 9, (b) pH 10, (c) pH 11 and
(d) pH 12. Diamonds represent experimental results, curves represent
modelling.
Figure 5.25  The Effect of Added Citrate on the Dissolution of Uranium Precipitates formed in Potassium Hydroxide at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 12. Diamonds represent experimental results, curves represent modelling.
For the citrate complexation of uranium in the calcium hydroxide system, predictive modelling suggested a step in the dissolution profile (similar to that seen in the addition of carbonate to uranium precipitates), with the solid phase of CaUO$_4$ being increasing difficult to dissolve by citrate addition due to the relatively high formation constant of the uranate phase.

However, in the case of citrate addition, no step was observed experimentally. This could only be modelled by removal of the CaUO$_4$ precipitate from the dataset, although it is realised that this is an unacceptable change to make to the model.

The addition of citrate to uranium-containing precipitates, which had been formed in grout leachate at high pH, showed similarities to those obtained in the calcium hydroxide system. Thermodynamic modelling of the dissolution profile could be achieved by removing the CaUO$_4$ solid phase.

While experimental results are best ‘fitted’ with the addition of a new mixed hydroxy-citrate species and corresponding formation constant, there is no other experimental evidence for these mixed citrate species and it should be remembered that this species was invoked purely as a ‘fitting’ species. There is however, evidence of mixed hydroxy species for uranyl carbonate, uranyl humate and other metal-ligand complexes. However, fitting experimental results by means of mixed species is just one possibility. Other possible explanations are (a) the nature of the precipitate (although modelling pure schoepite at higher pH values would not account for the experimentally observed results) or, (b) the deprotonation of the citrate$^{3-}$ ion at the hydroxyl functional group attached to the $\beta$-carbon. The latter possibility would lead to an ion of the type (Citrate$_{3H}$)$^+$ as shown in the reaction below, and would only occur at very high pH.

\[
\text{OH}^+ + \text{HCOO}^-(\text{Citrate}_{3H}) + \text{H}_2\text{O} \leftrightarrow \text{Citrate}_{3H}^+ + \text{H}_2\text{O}^+
\]

Fitting of experimental results was achieved by using a formation constant of $\log K_f = 7.1$ for the uranyl-citrate species, UO$_2$(Cit$_{3H}$)$^{3-}$. 

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Figure 5.26  The Effect of Added Citrate on the Dissolution of Uranium Precipitates formed in Calcium Hydroxide at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 12. Diamonds represent experimental results, curves represent modelling.
Figure 5.27  The Effect of Added Citrate on the Dissolution of Uranium Precipitates formed in Grout Leachate at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 11.8. Diamonds represent experimental results, curves represent modelling.
5.3.8 Uranium(VI) - EDTA System

The addition of EDTA to uranium containing precipitates at high pH showed slight dissolution of the precipitates in some cases. The results are shown in Figures 5.28 to 5.31 for sodium-, potassium-, calcium hydroxides and grout leachate respectively.

For uranium precipitates formed by the addition of sodium hydroxide, the presence of EDTA led to an increase in uranium solubility at higher EDTA concentrations at pH 9 and 10, although complete dissolution was not achieved. At higher pH values (11 and 12), dissolution was not observed over the range of EDTA concentrations added. Modelling of experimental results could be achieved by inclusion of a 1:1 uranyl EDTA complex. As detailed in section 1.8.4, the formation of polymeric mixed uranium-EDTA-hydroxide species and dimeric uranium-EDTA species is possible even when steric requirements for EDTA are not fulfilled with $\text{UO}_2^{2+}$ [18]. In this case, the species formed are often polymeric complexes formed by bridging between metal and ligand molecules. The inclusion of such mixed species and dimers into the model proved to be unfavourable and modelling results suggested that a 1:1 complex was the most stable of all the complexes considered. Experimental results and uranium dissolution profiles could be modelled using the 1:1 species alone.

Addition of EDTA to uranium precipitates formed by addition of potassium hydroxide showed similar solubilities and dissolution profiles to that of sodium hydroxide.

In the presence of calcium hydroxide, uranium forms calcium uranate at high pH. The addition of EDTA to the precipitate showed an increase in uranium solubility at pH 9 and 10 with higher EDTA concentrations. At higher pH values, there was no observable change in uranium solubility. EDTA has a known affinity for calcium and therefore calcium complexation was favourable and expected.
Modelling of this system showed how EDTA preferentially complexes with calcium present in calcium uranate until all uranate is left to precipitate as schoepite. As the pH increases, so does the effective stability of the uranate precipitate and therefore more EDTA is required to complex and dissolve this phase. Again, modelling showed good correlation with experimental results.

The addition of EDTA to uranium precipitates formed in grout leachate showed similar solubility results and dissolution profiles to that of precipitates formed in the calcium hydroxide system and potassium hydroxide system. Again, at the higher pH range studied, high EDTA concentrations were not achievable due to the effect of the weakly acidic properties of the ammonium ion added as a counter ion to EDTA.

As in the case of phosphate complexation (section 5.3.3) experimental dissolution was not always achieved at higher pH values, but was predicted by modelling alone using the formation constants in the HATCHES database, as detailed above.
Figure 5.28  The Effect of Added EDTA on the Dissolution of Uranium Precipitates formed in Sodium Hydroxide at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 12. Diamonds represent experimental results, curves represent modelling.
Figure 5.29  The Effect of Added EDTA on the Dissolution of Uranium Precipitates formed in Potassium Hydroxide at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 12. Diamonds represent experimental results, curves represent modelling.
Figure 5.30  The Effect of Added EDTA on the Dissolution of Uranium Precipitates formed in Calcium Hydroxide at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 12. Diamonds represent experimental results, curves represent modelling.
Figure 5.31 The Effect of Added EDTA on the Dissolution of Uranium Precipitates formed in Grout Leachate at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 11.8. Diamonds represent experimental results, curves represent modelling.
5.3.9 Uranium(VI) - NTA System

The effect of added nitritotriacetic acid (NTA) on the solubility of uranium precipitates produced from the addition of sodium-, potassium-, calcium hydroxides and grout leachate at pH values between 9 to 12 is shown graphically in Figures 5.32 to 5.35 below. The concentration of added NTA was limited by the low solubility of the salt at high pH.

It can be seen that in all cases except in the calcium hydroxide system at pH 12, the addition of NTA increases the experimental solubility of the uranium precipitates. Both calcium hydroxide and grout leachate systems show stepped profiles similar to those of carbonate and phosphate.

Initial modelling of the dissolution profile was only possible by fitting since the uranium-NTA formation constants were not available in the literature. The gradient of the pH 9 dissolution profile for the sodium hydroxide system suggests a 1:2 uranyl:NTA stoichiometry and this was supported by the almost complete dissolution of 5mM uranium precipitate with 10mM added NTA. A species UO_2(NTA)_2^{4-} was entered into the speciation model and the formation constant, logK_f, of 19.5 was derived by a trial and error method to fit experimental data. This new species was then used in the model to predict the dissolution profiles at other pH values and other hydroxide systems.

The complexation of uranium precipitates in potassium hydroxide are similar to those observed for sodium hydroxide and modelling was able to predict the dissolution profiles once the above species was invoked.

In the calcium hydroxide system, stepped profiles could be modelled if the calcium hydroxide concentration was known, except at pH 12 where experimental results suggested no change in the solubility of uranium over the added NTA range.
Figure 5.32 The Effect of Added NTA on the Dissolution of Uranium Precipitates formed in Sodium Hydroxide at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 12. Diamonds represent experimental results, curves represent modelling.
Figure 5.33  The Effect of Added NTA on the Dissolution of Uranium Precipitates formed in Potassium Hydroxide at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 12. Diamonds represent experimental results, curves represent modelling.
Figure 5.34  The Effect of Added NTA on the Dissolution of Uranium Precipitates formed in Calcium Hydroxide at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 12. Diamonds represent experimental results, curves represent modelling.
Figure 5.35  The Effect of Added NTA on the Dissolution of Uranium Precipitates formed in Grout Leachate at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 11.8. Diamonds represent experimental results, curves represent modelling.
For the grout leachate system, the stepped profiles could again be modelled, but as with carbonate and phosphate, the concentration of calcium in the grout leachate had to be reduced significantly in order to reproduce steps at the correct uranium concentrations. No adjustments to the solid phase were required.

5.3.10 Uranium(VI) - Humic Acid System

The effect of humic acid on the solubility of uranium precipitates at high pH in sodium, potassium, calcium hydroxides and grout leachate are shown graphically in Figures 5.36 - 5.39. The low concentrations of humic acid used in these experiments reflects the concentration predicted to be available in the groundwater at the Drigg site. It can be seen that in most cases, the addition of humic acid causes a very slight increase in the uranium solubility.

In order to examine the U(VI)-HA-OH system better and to evaluate the modelling, higher concentrations of humic acid were used only in the sodium hydroxide system at pH 9 which is known to form schoepite as the only solid phase. The results are shown in Figure 5.40 and it can clearly be seen that the addition of larger concentrations of humic acid significantly increase the uranium solubility at pH 9. This fact is also reflected in the modelling which shows good agreement with the experimental results. Variation between model and experimental results may be due to the difference in humic acid used. The model predicts the major species responsible for dissolution to be $\text{UO}_2(\text{OH})\text{HA}$, as detailed by Kim et al [74] with a formation constant, $\log K_f$, equal to 14.7. Modelling of dissolution profiles at the higher pH values shows similar results to that at pH 9 in the presence of sodium hydroxide, since the increase in hydroxide concentration with pH favours both the formation of a mixed complex as well as the precipitation of diuranates.
Figure 5.36  The Effect of Added HA on the Dissolution of Uranium Precipitates formed in Sodium Hydroxide at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 12.
Figure 5.37  The Effect of Added HA on the Dissolution of Uranium
Precipitates formed in Potassium Hydroxide at (a) pH 9,
(b) pH 10, (c) pH 11 and (d) pH 12.
Figure 5.38  The Effect of Added HA on the Dissolution of Uranium
Precipitates formed in Calcium Hydroxide at (a) pH 9,
(b) pH 10, (c) pH 11 and (d) pH 12.
Figure 5.39  The Effect of Added HA on the Dissolution of Uranium
Precipitates formed in Grout Leachate at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 11.8.
Predictive modelling of uranium dissolution by HA in potassium- and calcium hydroxide showed that the potassium hydroxide system behaves in the same manner as experiments performed in sodium hydroxide, while calcium uranate is formed in the calcium hydroxide system which, with its comparatively larger formation constant, is more difficult to complex and dissolve. However, even at pH 12 where the precipitate is predicted to be completely CaUO₄, humic acid dissolves 1.7% of the precipitate compared to 8% at pH 9. The grout leachate system behaves in a similar manner to that of calcium hydroxide.

Figure 5.40 The Effect of Additional HA on the Dissolution of Uranium Precipitates formed in Sodium Hydroxide at pH 9. Diamonds represent experimental results, curves represent modelling.
5.3.11 Uranium(VI) - Fulvic Acid System

The effect of fulvic acid on the solubility of uranium precipitates at high pH produced in sodium, potassium, calcium hydroxides and grout leachate systems is shown graphically in Figures 5.41 - 5.44 and can be compared to that of humic acid. Again, the low concentrations of fulvic acid used in these experiments reflect the concentrations of fulvic acid predicted to be available in the groundwater at the Drigg site. It can be seen that in most cases, the addition of fulvic acid causes a very slight increase in the uranium solubility.

In order to examine the U(VI)-FA-OH system better and to evaluate the modelling, higher concentrations of fulvic acid were used only in the sodium hydroxide system at pH 9. At this pH, schoepite is the only solid phase. The results are shown in Figure 5.45 and it can clearly be seen that the addition of larger concentrations of fulvic acid significantly increases the uranium solubility at pH 9. This is also reflected in the modelling of the experimental results which show excellent correlation. Experimental results that could not be modelled based on binary UO₂-FA complexes alone, but could be modelled by introducing a mixed U(VI)-FA-OH species (similar to that used in the uranium complexation by HA) and a formation constant, \( \log K_f \), equal to 3.6 was derived by fitting experimental results. Modelling of higher pH values shows a decrease in the complexation and therefore dissolution of uranium with increasing pH. This differs to that of humic acid in that although mixed species and uranate precipitates are both favoured by high pH, the formation constant of a mixed fulvic complex is much lower than that of a mixed humic complex (cf. 14.7). Predictive modelling of uranium dissolution by HA in potassium- and calcium hydroxides and grout leachate (using the formation constant derived above) showed that the potassium hydroxide system behaves in the same manner as experiments performed in sodium hydroxide. Again, as in the case of humic acid, calcium hydroxide forms calcium uranate which, with its comparatively larger formation constant, is more difficult to complex and dissolve.
Figure 5.41  The Effect of Added FA on the Dissolution of Uraniu
Precipitates formed in Sodium Hydroxide at (a) pH 9,
(b) pH 10, (c) pH 11 and (d) pH 12.
Figure 5.42  The Effect of Added FA on the Dissolution of Uranium Precipitates formed in Potassium Hydroxide at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 12.
Figure 5.43  The Effect of Added FA on the Dissolution of Uranium

Precipitates formed in Calcium Hydroxide at (a) pH 9,
(b) pH 10, (c) pH 11 and (d) pH 12.
Figure 5.44  The Effect of Added FA on the Dissolution of Uranium
Precipitates formed in Grout Leachate at (a) pH 9,
(b) pH 10, (c) pH 11 and (d) pH 11.8.
In the case of fulvic acid at pH 12, where the precipitate is predicted to be completely CaUO₄, dissolution is not predicted compared to a uranium dissolution of 1.7% for that of humic acid. The grout leachate system behaves in a similar manner to that of calcium hydroxide.

![Figure 5.45](image)

**Figure 5.45**  The Effect of Additional FA on the Dissolution of Uranium Precipitates formed in Sodium Hydroxide at pH 9. Diamonds represent experimental results, curve represent fitted modelling using logKᵢ = 3.6 for UO₂(OH)FA species.

5.3.12 Uranium(VI) - Iso-Saccharinic Acid System

As detailed in section 1.8, cellulose degradation in the presence of cement at high pH and ambient temperatures may lead to the formation of iso-saccharinic acid, ISA. The solubility of uranium precipitates in ISA has been examined at high pH in the presence of sodium-, potassium- and calcium hydroxides as well as grout leachate and these results are shown in Figures 5.46 to 5.49. It can be seen that in
all cases, the concentration of uranium in solution is increased with increasing concentrations of ISA.

Examination of the ISA dissolution of uranium containing precipitates in sodium hydroxide show that the effect decreases with increasing pH. Examination of the experimental results taken at pH 9, show that the most likely species is a 1:1 uranium-ISA species. At higher pH values, the effect of this ion is much less significant than that at pH 9 and infact modelling of experimental results greatly under-estimates the uranium solubility. For this reason, a mixed uranyl hydroxy-ISA species was invoked and the formation constant was derived by trial and error to yield the best fit of experimental results at pH 9 and 11. Literature formation constants for uranium-ISA complexes at high pH are not available and modelling of the experimental results was not achievable using similar complexes of uranyl-saccharinate and gluconate (the latter having formation constants more similar to those of ISA [78]). However, modelling could be made to reproduce some of the experimental results provided a new species, UO$_2$(OH)ISA was invoked, with a formation constant, log$K_f = 5.7$. Modelling at pH 10 and 12 showed good correlation with experimental results. At pH 11 and 12, the model predicts a stepped dissolution profile in which the presence of excess sodium diuranate is increasingly difficult to dissolve by the addition of excess ISA. No experimental results of this step could be obtained at this high ISA concentration while maintaining the high pH values required.

Examination of the potassium hydroxide system showed similar results to the experiments performed in sodium hydroxide. Again, modelling depended on the inclusion of the mixed species derived above, but produced good correlation with experimental results. Again, the model predicts steps in the dissolution profile at pH 12 that cannot be detailed by experiment.
Figure 5.46  The Effect of Added ISA on the Dissolution of Uranium Precipitates formed in Sodium Hydroxide at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 12. Diamonds represent experimental results, curves represent modelling.
Figure 5.47  The Effect of Added ISA on the Dissolution of Uranium
Precipitates formed in Potassium Hydroxide at (a) pH 9, (b) pH 10, (c) pH 11
and (d) pH 12. Diamonds represent experimental results, curves represent
modelling.
Figure 5.48  The Effect of Added ISA on the Dissolution of Uranium
Precipitates formed in Calcium Hydroxide at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 12.
Figure 5.49 The Effect of Added ISA on the Dissolution of Uranium
Precipitates formed in Grout Leachate at (a) pH 9, (b) pH 10, (c) pH 11 and (d) pH 11.8.
The experimental dissolution of uranium containing precipitates at high pH by the addition of ISA in the presence of calcium hydroxide shows that the solubility of uranium increases with increasing added ISA, but not to the same extent as in the sodium- and potassium hydroxide systems. Modelling was unable to predict the experimental results shown in Figure 4.48.

Experimental dissolution of uranium by ISA addition to grout leachate showed results that resemble both the calcium hydroxide system and the potassium (or sodium) hydroxide system, with uranium solubilities for respective ISA additions in-between those observed for the calcium and potassium systems. Modelling was not performed due to the problems in modelling uranium solubility in calcium hydroxide with increasing added ISA.

Again, as in the case of citrate, the introduction of mixed species is just one possibility of fitting the experimental results. Other possible explanations are (a) the nature of the precipitate (although even modelling pure schoepite at higher pH values would not account for the experimentally observed results) or, (b) the deprotonation of the ISA' ion at a hydroxyl functional group. The latter explanation would possibly lead to an ion of the type (ISA_{H^+})^2- and would only occur at very high pH. Fitting of experimental results could be achieved by using a formation constant of \( \log K_f = 5.6 \) for the uranyl-ISA species, \( \text{UO}_2(\text{ISA}_{H^+}) \), derived by trial and error, and which compares to \( \log K_f = 2.7 \) and 1.8 for similar uranyl-gluconate and saccharate species respectively, listed in the HATCHES database.

5.4 Summary

The solubility and speciation of uranium at a range of high pH values has been investigated by a combination of experimental and modelling studies in the absence and presence of complexing ligands that might be available to uranium disposed of in LLW containers at the Drigg site.
In the absence of any complexing ligands, the solubility of uranium was determined, between pH values of 6 to 12, by oversaturation and by liquid scintillation counting. The results show a sharp decrease in the uranium concentrations with increasing pH due to the formation of uranyl hydroxide precipitates, hydrates and uranates. Modelling using the HATCHES [29] database and the MINTEQA2 [12] speciation code provided speciation information which suggested that, under the experimental conditions, the major species were polymeric hydroxides, namely 3:5, 4:7 and 3:7 with increasing respective predominance at higher pH values, as shown in Figure 5.3.

<table>
<thead>
<tr>
<th>System and Component</th>
<th>pH 9</th>
<th>pH 10</th>
<th>pH 11</th>
<th>pH 12†</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NaOH</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Schoepite</td>
<td>100</td>
<td>100</td>
<td>53</td>
<td>0</td>
</tr>
<tr>
<td>Na₃U₂O₇</td>
<td>0</td>
<td>0</td>
<td>47</td>
<td>100</td>
</tr>
<tr>
<td><strong>KOH</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Schoepite</td>
<td>100</td>
<td>100</td>
<td>22</td>
<td>2</td>
</tr>
<tr>
<td>K₂U₂O₇</td>
<td>0</td>
<td>0</td>
<td>78</td>
<td>98</td>
</tr>
<tr>
<td><strong>Ca(OH)₂</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Schoepite</td>
<td>38</td>
<td>34</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>CaUO₄</td>
<td>62</td>
<td>66</td>
<td>70</td>
<td>100</td>
</tr>
<tr>
<td><strong>Grout Leachate</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Schoepite</td>
<td>30</td>
<td>37.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>K₂U₂O₇</td>
<td>0</td>
<td>0</td>
<td>38</td>
<td>56</td>
</tr>
<tr>
<td>Na₃U₂O₇</td>
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<td>0</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td>CaUO₄</td>
<td>70</td>
<td>62.5</td>
<td>50</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 5.1 Percentage Modelled Composition of Uranium Precipitates at High pH by Examination of Carbonate Dissolution

† pH = 11.8 for grout leachate system

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The examination of carbonate addition on the dissolution of uranium containing precipitates was detailed by Sutton et al [26] and showed that modelling of experimental results could be used to provide more information on the composition of the solid phase produced in each high pH system. The results are summarised in Table 5.1. This proved very useful especially in the case of the grout leachate system, where XRPD evidence was unsatisfactory.

The effect of carbonate and other complexing ions has been examined and the results show that even at high pH, where uranium forms stable solid phases and where hydrolysis of uranium is very favourable, certain ligands can still complex uranium and redissolve precipitates. In some cases, the dissolution profiles could be predicted using literature formation constants, while in other cases, the nature of the solid phase had to be modified to fit the experimental results. In other cases, a new uranyl complex was needed to fit the experimental dissolution profile, usually in the form of a mixed hydroxide complex. A summary of each ligand and the complex responsible for dissolution in each case is given in Table 5.2. As stated in sections 5.3.3 and 5.3.12, the introduction of such mixed hydroxide species is only one possible method of ‘fitting’ experimental results. Changes to the composition of the uranium solid phase could be made, but the phases determined in [26] allow model prediction for the majority of the ligands studied. The formation of further deprotonated ligands (such as (Citrate$_{\mathrm{H}^-}$)$_4^+$ and (ISA$_{\mathrm{H}^-}$)$_2^-$) are a more likely alternative to mixed species.

Both HA and FA used in this study are site specific to Drigg and therefore the formation constants reported in the literature may not be exactly relevant.
<table>
<thead>
<tr>
<th>Ligand</th>
<th>Best-Fit Species</th>
<th>Speciation Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonate</td>
<td>$\text{UO}_2\text{CO}_3^{4-}$</td>
<td>no changes required</td>
</tr>
<tr>
<td>Phosphate</td>
<td>$\text{UO}_2(\text{HPO}_4)_2^{2-}$</td>
<td>no changes required</td>
</tr>
<tr>
<td>Sulphate</td>
<td>$\text{(UO}_2\text{)}_3\text{(OH)}_7^-$</td>
<td>no changes required, no dissolution observed</td>
</tr>
<tr>
<td>Chloride</td>
<td>$\text{(UO}_2\text{)}_3\text{(OH)}_7^-$</td>
<td>no changes required, no dissolution observed</td>
</tr>
<tr>
<td>Acetate</td>
<td>$\text{(UO}_2\text{)}_3\text{(OH)}_7^-$</td>
<td>1:4 species removed, no dissolution observed</td>
</tr>
<tr>
<td>Citrate</td>
<td>$\text{UO}_2\text{(OH)Citrate}^{2-}$</td>
<td>species invoked to fit data, log$K_r = 5.05$</td>
</tr>
<tr>
<td></td>
<td>or $\text{UO}<em>2\text{(Cit}</em>{4\text{H}})^{2-}$</td>
<td>species invoked to fit data, log$K_r = 7.1$</td>
</tr>
<tr>
<td>EDTA</td>
<td>$\text{UO}_2\text{EDTA}^{2-}$</td>
<td>no changes required</td>
</tr>
<tr>
<td>NTA</td>
<td>$\text{UO}_2\text{(NTA)}_2^{4-}$</td>
<td>species invoked, no log$K_r$ available, log$K_r = 19.5$</td>
</tr>
<tr>
<td>HA</td>
<td>$\text{UO}_2\text{(OH)HA}$</td>
<td>no changes required</td>
</tr>
<tr>
<td>FA</td>
<td>$\text{UO}_2\text{(OH)FA}$</td>
<td>species invoked, no log$K_r$ available, log$K_r = 3.6$</td>
</tr>
<tr>
<td>ISA</td>
<td>$\text{UO}_2\text{(OH)(ISA)}$</td>
<td>species invoked to fit data, log$K_r = 5.7$</td>
</tr>
<tr>
<td></td>
<td>or $\text{UO}<em>2\text{(ISA}</em>{4\text{H}})$</td>
<td>species invoked to fit data, log$K_r = 5.4$</td>
</tr>
</tbody>
</table>

Table 5.2 Summary of Modelled Speciation of Experimental Aerobic Uranium(VI) Dissolution Profiles at High pH

Several attempts were made to examine the stoichiometry of a complex formed between uranium and ISA by means of crystal diffractometry. Sodium hydroxide was added to a uranyl nitrate solution in order to obtain a uranium precipitate at high pH. This precipitate was then redissolved by adding ISA with the resulting solution being crystallised by slow evaporation in an oven at 40°C. Yellow crystals formed and were examined by crystal X-ray diffraction (XRD). The results of XRD showed that sodium nitrate was in fact the crystal phase with uranium trapped inside. This was supported by examination under a microscope in which clear crystals could be seen containing yellow portions. Further samples were produced and examined under a microscope. The selected crystals were entirely yellow in colour. However, XRD examination proved inconclusive since the yellow ‘crystals’ were found to be far too amorphous to provide information on the composition and structure.
In the case of carbonate, phosphate and NTA, the grout leachate solution behaves as though it contains much less calcium than expected. This may be due to the composition of the grout leachate which contains higher concentrations of sodium and potassium. This may mean that rapid precipitation of sodium and/or potassium diuranates occurs preferentially to the expected calcium uranate precipitation alone. The experiments were performed over a relatively short time period compared to the time scale of vault lifetime, or final equilibrium assumed by thermodynamic speciation models. It may well be that the solid phases change very slowly to become the most thermodynamically stable phase.
CHAPTER SIX

Anaerobic Complexation Of Uranium At High pH
6. Anaerobic Complexation of Uranium at High pH

6.1 Introduction

When the vault pore-water comes into contact with the steel ISO-freight containers and the canisters, iron will corrode and dissolve. As more and more iron dissolves, so the system becomes more reducing due in part to the ferric-ferrous redox couple,

\[
Fe^{3+} + e^- = Fe^{2+} \quad E^0 = 0.771 \text{ V} \quad [121]
\]

Once the measured redox potential, \(E_h\), falls sufficiently below 0.267 V (as defined in section 1.8.1 and based on the \(\Delta G^0\) value taken from the NEA review [19]), uranium(VI) will be reduced to uranium(IV)

\[
UO_2^{2+} + 2e^- + 4H^+ = U^{4+} + 2H_2O \quad E^0 = 0.267 \text{ V}
\]

At this point, the vault environment will have reached what can be described as the secondary stage, which will last for as long as there is iron present. Therefore, it is of importance to examine the solubility, complexation and speciation of U(IV) at high pH in the presence of complexing ligands.

6.2 Achievement of Reducing Potentials

Two different methods for producing reducing \(E_h\) potentials were investigated, (a) ferric/ferrous iron and (b) dithionite. Both methods were tested under inert nitrogen atmospheres.
6.2.1 Ferrous Iron in Hydroxide

The first method involved the use of the ferric-ferrous redox couple which not only provided a reducing potential, but also gave the opportunity to examine how the presence of iron would affect uranium solubility, in the 'real' case.

At high pH, the presence of the hydroxide ion influences the redox potential and increases the reduction product,

\[
\frac{1}{2} \text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O} + e^- = \text{Fe(OH)}_2 + \text{OH}^- \quad E^0 = -0.56 \text{V} \quad [121]
\]

Uranyl nitrate solution was degassed and placed into a round-bottom flask which was fitted with a Pt redox electrode (Ag/AgCl reference) and a pH electrode. The flask was then sealed except for nitrogen entrance and exit ports via hypodermic needles. The system was purged with oxygen-free nitrogen gas (BOC Gases) for several hours before injecting different concentrations of degassed ammonium ferrous sulphate solution into the flask followed by degassed sodium hydroxide. As sodium hydroxide was added, the pH of the solution rose. At the same time, the $E_h$ fell and the colourless iron solution changed to a green solution and eventually formed a green precipitate. The $E_h$ and pH could be controlled by careful addition of either ferrous or hydroxide ions.

However, even with continual nitrogen purging, the $E_h$ was not stable. The green ferrous precipitate became orange-brown in colour after 24 hours and the Fe(II) completely oxidised to Fe(III), as described by Cotton and Wilkinson [121]. Furthermore, there was concern as to the sorption of uranium onto the voluminous iron precipitate and therefore vast underestimation of the uranium solubility, hence another method was sought.
6.2.2 Dithionite in Hydroxide

Sodium dithionite, Na$_2$S$_2$O$_4$, is an ideal agent for producing U(IV) since it is most effective under alkaline conditions. The redox couple responsible is that of dithionous acid, as follows,

\[ 2\text{SO}_3^{2-} + 2\text{H}_2\text{O} + 2e^- = 4\text{OH}^- + \text{S}_2\text{O}_4^{2-} \quad E^0 = -1.12\text{V} \[121] \]

The reaction is rapid in alkaline solutions and in oxygen free solutions, there is further transformation yielding the radical ion of SO$_2^\cdot$.

The chemistry of the dithionite ion in solution is complex, with decomposition based on the reaction

\[ 2\text{S}_2\text{O}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{S}_2\text{O}_3^{2-} + 2\text{HSO}_3^- \]

which would have been a problem in acidic solutions [121].

Zinc powder was added to maintain the stability of the reducing potentials. At high pH, a zinc redox couple is produced:

\[ \text{Zn} + 4\text{OH}^- \leftrightarrow \text{ZnO}_2^{2-} + 2\text{H}_2\text{O} + 2e^- \quad E^0 = 1.216\text{V} \]

While this method did not allow for examination of the presence of iron on the solubility of uranium, there was no concern regarding the possible sorption of uranium by any precipitate. Sorption effects by Zn(OH)$_2$ which may be formed are minimised due to the small amount of added zinc (compare with the flocculant precipitate formed in the ferrous-hydroxide method) and due to the formation of Zn(OH)$_4^{2-}$ rather than the less favoured Zn(OH)$_2$ at very high pH due to the reaction shown below [81]
\[ \text{Zn(OH)}_2 + 2\text{OH}^- \rightarrow \text{Zn(OH)}_4^{2-} \]

Experiments were carried out in a glove bag (Aldrich, 280L capacity) continually purged with nitrogen (BOC Gases) and all solutions were degassed in the glove bag before use. Uranyl nitrate was added to glass sample tubes containing 5mg of zinc powder, followed by varying concentrations of sodium dithionite. The pH and Eh of the solutions were studied with addition of sodium hydroxide to the glass vials. As the hydroxide was added, the pH rose and the Eh fell dramatically. A dark brown precipitate formed only when uranium was present and this was assumed to be either UO$_2$·xH$_2$O (chemically equivalent to U(OH)$_4$) or UO$_2$(am). XRPD examination detailed in chapter 4 failed to prove the identity of the solid phase.

The system could be left for approximately 48 hours with continuous nitrogen purging while the Eh and pH remained constant, after which time the Eh rose and the pH fell slightly. This was the procedure chosen for the examination of uranium(IV) solubility.

6.3 Experimental Method for Complexation Studies

Experiments described below all used the dithionite method. Complexation studies were conducted to parallel the aerobic studies detailed in chapter 5. The experimental procedure can be shown by means of a schematic diagram, Figure 6.1.
Figure 6.1  Schematic Diagram of Anaerobic Complexation Experimental Procedure

All solutions were degassed with nitrogen in a glove bag before use and all work was carried out in the glove bag up to and including the filtration stage. Uranyl nitrate (2ml, 10mM, doped with 1% $^{233}$U) was pipetted into glass vials followed by 5ml of 0.01M sodium dithionite containing 0.1mM sodium hydroxide. Zinc powder (5mg) was added to each vial and 10ml grout leachate was then added followed by known, small amounts of sodium hydroxide to the resulting solution until a pH of 9.0 or 11.0 was reached. A dark-brown precipitate was formed over a period of approximately 30 minutes. The samples were then left to equilibrate for 6 hours before known amounts of complexing ligand were added to each vial and the pH readjusted with more sodium hydroxide and the volume taken to 20ml de-ionised water. Sodium was used as the counter-ion to the added ligand instead of ammonium salts (c.f. aerobic complexation) to avoid possible degradation of the dithionite ion (leading to the rapid formation of $S_2O_3^{2-}$) by the addition of the weakly acidic ammonium ion. After a further 24 hours equilibration time, each
sample was filtered through a 0.2μm Acrodisc syringe filter (Gelman Sciences) and aliquots of the filtrate were transferred to scintillation counting vials which could then be removed from the inert atmosphere bag. EcoScintA scintillation fluid (National Diagnostics) was added to each of the vials and samples were then counting by liquid scintillation (LKB-Wallac). The results obtained were compared against a calibration curve produced from known uranium standards, as detailed in chapter 3.4.2.

6.4 Uranium(IV) - Ligand Systems

6.4.1 Uranium(IV) Hydrolysis by pH Variation

The chemistry of uranium(IV) hydroxides is complicated. There is uncertainty as to whether monomeric or polymeric species are formed, depending on the concentration of uranium and there is also uncertainty in the nature of the solid phase. Several authors have suggested the formation of crystalline forms [e.g. 31,122], amorphous forms [e.g. 123,124] and hydrated forms [e.g. 33,81] of UO₂. This subject is discussed in the NEA review [19] where the decision is made not to recommend a specific value for the Gibbs free energy of formation for UO₂(am) and UO₂.xH₂O. The rapidly formed precipitate in this work at high pH could not be characterised by XRPD. This leads to an immediate problem in defining the basic chemistry of the system. However, the information gained from both the solubility of the precipitate, together with the effect of the carbonate ion on the solubility (discussed in section 6.4.2) was used to build a model of the precipitate.

Examination of the solubility of the uranium(IV) precipitate, see Figure 6.2(a), formed by the addition of sodium hydroxide shows a decrease with increasing pH until pH 7, where a plateau is reached. The decrease and plateau observed are due to the formation of a solid phase, typically a uranium(IV) hydrated oxide or hydroxide.
The HATCHES database provides details of possible formation constants proposed by a variety of authors. By comparing experimental results with modelling of the solubility of a given precipitate, several of the literature formation constants could be dismissed. The HATCHESv10 database conforms with the NEA review chaired by Grenthe [19] in which a formation constant for the 1,4 hydroxide as $\log K_f = 4.53$ is proposed. In order to model experimental data performed at AEAT [29], the formation constant for the solid phase, hydrated $\text{UO}_2$ (am), in the HATCHES
database was changed to 1.97. However, modelling of the work presented in this thesis shows much lower solubilities than those observed by experiment, with the formation constant for hydrated UO$_2$$_{(am)}$ requiring change to 0.82. This change was then found to cause further problems since modelling of the addition of carbonate required large and unacceptable changes to the formation constant for the U(CO$_3$)$_5^{6-}$ species in order to fit experimental results.

Modelling of the carbonate addition to uranium(IV) precipitates (chapter 6.4.2, below) could only be performed when the original formation constant for the 1,4 hydroxide listed in HATCHES ($\log K_f = -10.5$) was used together with a corresponding value for the solid phase, hydrated UO$_2$$_{(am)}$ of -5.2. This can be compared to the original value proposed by [33] of -4.0 and can be explained in terms of a difference in solid phase composition.

Returning to the hydrolysis of uranium with increasing pH, modelling of the increase in uranium solubility observed above pH 10 was only possible when an anionic species, U(OH)$_5^{-}$ was introduced. This species is supported by several authors including Ryan and Rai [81] and Allard [24]. The speciation of uranium(IV) hydroxides derived by modelling is shown in figure 6.2(b). In order to fit the experimental results, alteration of the formation constant for the 1,5 hydroxide from $\log K_f = -22.7$ [82] to -21.0 was required.

The effect of adding a variety of counter cations to the uranium(IV) such as calcium, potassium, ammonium did not alter the pH-solubility profile significantly compared to sodium hydroxide addition. This was expected since the solid phase is predicted to be a uranium(IV) oxide (cf. aerobic uranium(VI) precipitation detailed in chapters 4 and 5). The addition of grout leachate did however increase the solubility of the uranium(IV) precipitate and this was assumed to be due to the variety of complexing anions such as carbonate which are present in grout leachate.
6.4.2 Uranium(IV) - Carbonate System

The effect of added carbonate on the solubility of uranium(IV) precipitates formed in grout leachate at high pH is shown in figure 6.3 at pH values of (a) 9 and (b) 11. It can be seen that the addition of carbonate causes dissolution of the uranium precipitate. The effect of the carbonate ion is marginally less at the higher pH, and this evidence supports the formation of a 1:5 hydroxide complex. This also suggests the absence of a mixed hydroxy-carbonate species. Speciation modelling predicts the species, $\text{U(CO}_3\text{)}_5^{6-}$, as the most thermodynamically stable carbonate complex. This, in turn, leads to the dissolution of the precipitate. Modelling successfully predicted the dissolution of the uranium precipitate.

![Graph showing the effect of added carbonate on the dissolution of uranium(IV) precipitate in grout leachate at pH 9 and pH 11.](image)

**Figure 6.3** The Effect of Added Carbonate on the Dissolution of U(IV) Precipitate in Grout Leachate at (a) pH 9 and (b) pH 11

A comparison of solubility modelling in sodium hydroxide and grout leachate highlights how calcite ($\text{CaCO}_3$) is formed preferentially to that of a uranium(IV) carbonate complex in grout leachate. The effect is observed at both pH 9 and pH 11 but, at higher carbonate concentrations, the formation of the $\text{U(CO}_3\text{)}_5^{6-}$ species was observed in grout leachate.
6.4.3 Uranium(IV) - Phosphate System

The effect of the addition of phosphate on the dissolution of a uranium(IV) precipitate is shown graphically in Figure 6.4 at (a) pH 9 and (b) pH 11.

It can be seen that at both pH values investigated, the solubility of U(IV) increased with increasing added phosphate. Modelling of the dissolution profiles was only possible when (as in the case of U(VI) complexation and sorption) a calcium phosphate precipitate (Ca$_5$(PO$_4$)$_3$OH, hydroxyapatite) was included in the database. This finding was supported in the experimental observations, in that a white precipitate was observed in some sample vials. Speciation modelling using the data available in the HATCHES database suggested that the major phosphate species responsible for the dissolution of uranium(IV) precipitates was U(HPO$_4$)$_4^{4-}$.

![Figure 6.4](image)

**Figure 6.4** The Effect of Added Phosphate on the Dissolution of U(IV) Precipitate in Grout Leachate at (a) pH 9 and (b) pH 11

As in the case of carbonate addition, the uranium precipitate dissolved earlier in the NaOH profile than that of grout leachate, i.e with less added phosphate than that shown in the above Figure 6.4.
6.4.4 Uranium(IV) - Sulphate System

The addition of sulphate to the uranium(IV) precipitate formed at high pH in grout leachate showed no increase in the solubility of uranium within experimental errors at both pH 9 and 11. The results of experimental investigations are shown in Figure 6.5, below.

![Graphs showing the effect of added sulphate on the dissolution of U(IV) precipitate in grout leachate at pH 9 and pH 11.](image)

**Figure 6.5** The Effect of Added Sulphate on the Dissolution of U(IV) Precipitate in Grout Leachate at (a) pH 9 and (b) pH 11

Modelling of the dissolution profiles was performed using the MINTEQA2 code and thermodynamic data listed in the HATCHES database, namely U:SO$_4^{2-}$ complexes with stoichiometry 1:1, 1:2 and 1:4. Modelled results agreed with experimental results and showed that none of the sulphate species were able to compete with the stable hydrated UO$_2$(am) precipitate or the hydroxide species, U(OH)$_5^-$ over the concentration range studied.
6.4.5 Uranium(IV) - Chloride System

The addition of chloride to the uranium(IV) precipitate formed at high pH in grout leachate showed no increase in the solubility of uranium within experimental errors at both pH 9 and 11. The results of experimental investigations are shown in Figure 6.6, below.

Modelling of the dissolution profiles was performed using the MINTEQA2 code and thermodynamic data listed in the HATCHES database, namely U:Cl complexes with stoichiometry 1:1, 1:2 and 1:4. Modelled results agreed with experimental results and showed that no chloride species were able to compete with the stable hydrated UO$_2$(am) precipitate or the hydroxide species, U(OH)$_5$\(^{-}\) under the conditions reported.

![Figure 6.6](image)

**Figure 6.6** The Effect of Added Chloride on the Dissolution of U(IV) Precipitate in Grout Leachate at (a) pH 9 and (b) pH 11
6.4.6 Uranium(IV) - Acetate System

The addition of acetate to the uranium(IV) precipitate formed at high pH in grout leachate showed no increase in the solubility of uranium within experimental errors at both pH 9 and 11. The results of experimental investigations are shown in Figure 6.7, below.

![Graph a and b showing the effect of added acetate on the dissolution of U(IV) precipitate in grout leachate at pH 9 and pH 11.](image)

**Figure 6.7** The Effect of Added Acetate on the Dissolution of U(IV) Precipitate in Grout Leachate at (a) pH 9 and (b) pH 11

Modelling of the dissolution profiles was performed using the MINTEQA2 code and thermodynamic data listed in the HATCHES database, namely U:acetate complexes with stoichiometry 1:1, 1:2, 1:3 and 1:4. Modelled results agreed with experimental results and showed that none of the acetate species were able to compete with the stable hydrated UO$_2$(am) precipitate or the hydroxide species, U(OH)$_5^-$ over the concentration range examined.
6.4.7 Uranium(IV) - Citrate System

The addition of citrate to the uranium(IV) precipitate formed at high pH in grout leachate was investigated and results are depicted in Figure 6.8, below. It can clearly be seen that the presence of citrate increases the solubility of uranium(IV) at both pH 9 and 11.

![Figure 6.8](image)

**Figure 6.8** The Effect of Added Citrate on the Dissolution of U(IV) Precipitate in Grout Leachate at (a) pH 9 and (b) pH 11

Modelling attempts using 1:1 and 1:2 U(IV):citrate complexes were unsuccessful. The modelled solubilities suggested much lower uranium solubilities than experimentally observed. The gradient and position of the dissolution profile suggested a 1:2 complex, but experimental results could only be modelled by large, unacceptable changes to the formation constants in the database. Alternatively, a mixed species was invoked, with the formula U(Citrate)$_2$(OH)$^-$ . Experimental results were fitted using a formation constant, log$K_f$ equal to 32.3, derived by trial and error; however, there is no literature evidence for this species. The results were also fitted by invoking a uranium(IV) deprotonated citrate complex (as previously defined in chapter 5), with a log$K_f$ = 24.6 derived by trial and error, and formula U(Cit$_{-H}$)$_2^{4-}$.
6.4.8 Uranium(IV) - EDTA System

The addition of EDTA to the uranium(IV) precipitate formed at high pH in grout leachate was investigated by experiment, shown in Figure 6.9, below. It can clearly be seen that the presence of EDTA increases the solubility of uranium(IV) at pH 9 but not at pH 11 over the concentration range studied.

![Figure 6.9 The Effect of Added EDTA on the Dissolution of U(IV) Precipitate in Grout Leachate at (a) pH 9 and (b) pH 11](image)

Modelling of the dissolution profiles detailed above was possible using the formation constants listed in the HATCHES database. A 1:1 complex was predicted using the MINTEQA2 speciation code, but showed lower uranium solubilities than those observed at each point on the profile, shown in Figure 6.9(a). By changing the formation constant for the 1:1 species from log$K_f = 29.1$ to 31.4, the experimental results could be modelled. This change cannot be attributed to a mixed species, since the experimental solubility of uranium at pH 11 did not increase with higher concentrations of added EDTA. Clearly, a mixed hydroxy-EDTA complex would lead to higher uranium solubilities at higher pH values. The difference in formation constants may be attributed to the steric hindrance of uranium-EDTA complexes as stated [18,52].
6.4.9 Uranium(IV) - NTA System

The addition of NTA to the uranium(IV) precipitate formed at high pH in grout leachate was investigated by experiment and the results are shown in Figure 6.10, below. It can clearly be seen that the presence of NTA increased the solubility of uranium(IV) at pH 9 but not at pH 11 over the concentration range studied.

![Figure 6.10](image)

**Figure 6.10** The Effect of Added NTA on the Dissolution of U(IV) Precipitate in Grout Leachate at (a) pH 9 and (b) pH 11

No literature formation constants for U(IV)-NTA complexes could be found and so in order to fit experimental results, a formation constant was predicted. Examination of the gradient and position of the uranium dissolution profile at pH 9 suggested a 1:2 complex and so the U(NTA)\(_2\)\(^{2-}\) species was invoked. The experimental dissolution profile at pH 11 did not show any increase in uranium solubility with increasing added NTA, therefore suggesting that no mixed hydroxy-NTA species were present. A formation constant of logK\(_f\) = 35.7 was then derived by trial and error fitting of experimental results at pH 9 and 11.
6.4.10 Uranium(IV) - Humic Acid System

The addition of HA to the uranium(IV) precipitate formed at high pH in grout leachate showed no increase in the solubility of uranium within experimental errors at both pH 9 and 11. The results of experimental studies are shown in Figure 6.11, below.

Modelling of the dissolution profiles was performed using the MINTEQA2 speciation code and thermodynamic data listed in the HATCHES database, namely U:HA complexes with stoichiometry 1:1 and 1:2. Modelled results agreed with experimental results and showed that none of the uranium(IV)-HA species were able to compete with the stable hydrated UO$_2$(am) precipitate or the hydroxide species, U(OH)$_5$\textsuperscript{-} over the concentration range studied.

![Diagram showing the effect of added HA on the dissolution of U(IV) precipitate in grout leachate at pH 9 and pH 11](image)

Figure 6.11 The Effect of Added HA on the Dissolution of U(IV) Precipitate in Grout Leachate at (a) pH 9 and (b) pH 11
6.4.11 Uranium(IV) - Fulvic Acid System

The addition of FA to the uranium(IV) precipitate formed at high pH in grout leachate showed no increase in the solubility of uranium within experimental errors at both pH 9 and 11. The results of experimental observations are shown in Figure 6.12, below.

Modelling of the dissolution profiles was performed using the MINTEQA2 speciation code and thermodynamic data listed in the HATCHES database, namely U:FA complexes with stoichiometry 1:1 and 1:2. Modelled results agreed with experimental results and showed that none of the uranium(IV)-FA species were able to compete with the stable hydrated UO$_2$(am) precipitate or the hydroxide species, U(OH)$_5^-$ over the concentration range studied.

![Figure 6.12 The Effect of Added FA on the Dissolution of U(IV) Precipitate in Grout Leachate at (a) pH 9 and (b) pH 11](image)
6.4.12 Uranium(IV) - Iso-Saccharinic Acid System

It can be seen clearly in Figure 6.13 that the presence of ISA increases the solubility of uranium(IV) at both pH 9 and 11 in the presence of grout leachate.

Figure 6.13 The Effect of Added ISA on the Dissolution of U(IV) Precipitate in Grout Leachate at (a) pH 9 and (b) pH 11

U(IV)-ISA species are not detailed in HATCHES and therefore none were entered into the dataset used in the modelling of experimental results. The gradient and position of the dissolution profile at pH 9 suggests the formation of a 1:2 U(IV)-ISA species. However, the results at pH 11 in the dissolution profile are almost identical to those obtained at pH 9, suggesting the formation of a mixed hydroxy-ISA species. At high pH, anionic species are expected to be present. Therefore, hydroxide ligands were added to the theoretical U(IV)-ISA complex to explain the above observation and to create a neutral or anionic complex. A U(OH)$_2$ISA$_2$(aq) species was therefore invoked to fit experimental results. A formation constant was derived to be log$K_f = 13.6$ by trial and error fitting of experimental data-points. There is evidence of actinide mixed OH-ISA species [125]. As an alternative to a mixed species, a deprotonated ISA complex was also used to fit experimental results, U(ISA-H)$_2$(aq), log$K_f = 0.4$ determined by trial and error.
6.5 Summary

Two methods of achieving reducing potentials were investigated. The first method used ammonium ferrous sulphate in sodium hydroxide and utilised the redox couple

\[
\frac{1}{2}Fe_2O_3 \cdot 3H_2O + e^- = Fe(OH)_2 + OH^- \quad E^o = -0.56V \quad [121].
\]

A voluminous precipitate was formed and there was concern as to possible sorption of uranium on the precipitate. Therefore, a second method was examined, in which sodium dithionite was used in conjunction with sodium hydroxide and a small amount of zinc powder. This method utilised the redox couple

\[
2SO_3^{2-} + 2H_2O + 2e^- = 4OH^- + S_2O_4^{2-} \quad E^o = -1.12V \quad [121].
\]

This second method was chosen as the preferred method for examination of uranium(IV) solubility at high pH.

The effect of pH on the solubility of uranium(IV) was investigated and the results are shown graphically in Figure 6.2. There is a clear decrease in the uranium solubility with increasing pH until pH 7. This was predicted to be due to the formation of a uranium precipitate, hydrated UO₂ (am) and a formation constant was derived to be \( \log K_f = -5.2 \) by means of fitting experimental results. At pH values less than 7, uranium(IV) hydroxide complexes were present, namely \( U(OH)^{3+} \), \( U(OH)_2^{2+} \) and \( U(OH)_3^{+} \). At pH 7, the major aqueous species was predicted to be the 1:4 complex and a formation constant of \( \log K_f = -10.5 \) [32] was chosen to fit experimental results. As the experimental pH was increased further to pH 10, an increase was observed in the uranium solubility. This could only be due to the formation of a hydroxide complex of higher stoichiometry than 1:4, and so the formation constant of a 1:5 species was estimated to be \( \log K_f = -21.0 \), based on fitting experimental results, and compares to \( \log K_f = 22.7 \) [81].
The effect of complexing ligands on the solubility of a uranium(IV) precipitate was also investigated at pH 9 and 11 in grout leachate. The results of modelling studies and species responsible for precipitate dissolution are summarised in Table 6.1.

Several complexing ligands increased the solubility of uranium(IV) (namely carbonate, phosphate, citrate, EDTA, NTA and ISA). Of these ligands, only the carbonate and phosphate systems could be accurately modelled by speciation modelling. However, several refinements to the database were necessary, for example, invoking new species such as mixed species. Justification of inclusion of these species was based on enhanced uranium(IV) solubility at high pH. Formation constants have been derived in each case, by a trial and error method of fitting experimental uranium solubility results. Deprotonation of ligands such as citrate and ISA at very high pH could also be used to explain the results observed experimentally. The formation constants which have been derived to fit the experimental results are also shown in Table 6.1. There is a large uncertainty regarding the nature of the uranium(IV) precipitate formed in experiments under anaerobic conditions and this may have influenced the effectiveness of the speciation modelling.

The other complexing ligands (namely sulphate, chloride, acetate, HA and FA) were unable to affect the solubility of uranium(IV) precipitates at high pH.
<table>
<thead>
<tr>
<th>Ligand</th>
<th>Best-Fit Species</th>
<th>Speciation Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonate</td>
<td>U(CO₃)₅⁶⁻</td>
<td>no changes required</td>
</tr>
<tr>
<td>Phosphate</td>
<td>U(HPO₄)₄⁴⁻</td>
<td>hydapatite precipitate required</td>
</tr>
<tr>
<td>Sulphate</td>
<td>U(OH)₅⁻</td>
<td>no changes required, no dissolution observed</td>
</tr>
<tr>
<td>Chloride</td>
<td>U(OH)₅⁻</td>
<td>no changes required, no dissolution observed</td>
</tr>
<tr>
<td>Acetate</td>
<td>U(OH)₅⁻</td>
<td>no changes required, no dissolution observed</td>
</tr>
<tr>
<td>Citrate</td>
<td>U(Citrate)₂(OH)³⁻ or U(Citrate·H)₂⁴⁻</td>
<td>species invoked to fit data, logKᵣ = 32.3  (\text{or}) species invoked to fit data, logKᵣ = 24.6</td>
</tr>
<tr>
<td>EDTA</td>
<td>UEDTA(aq)</td>
<td>better fit using logKᵣ = 31.4 (c.f. 29.1)</td>
</tr>
<tr>
<td>NTA</td>
<td>U(NTA)₂²⁻</td>
<td>species invoked, no logKᵣ available, logKᵣ = 35.7</td>
</tr>
<tr>
<td>HA</td>
<td>U(OH)₅⁻</td>
<td>no changes required, no dissolution observed</td>
</tr>
<tr>
<td>FA</td>
<td>U(OH)₅⁻</td>
<td>no changes required, no dissolution observed</td>
</tr>
<tr>
<td>ISA</td>
<td>U(OH)₂ISA₂(aq) or U(ISA·H)₂(aq)</td>
<td>species invoked to fit data, logKᵣ = 10.3  (\text{or}) species invoked to fit data, logKᵣ = 0.4</td>
</tr>
</tbody>
</table>

Table 6.1 Summary of Modelled Speciation of Experimental Anaerobic Uranium(IV) Dissolution Profiles at High pH
CHAPTER SEVEN

Sorption of Uranium by Drigg Grout Material at High pH
7. Sorption of Uranium by Drigg Grout Material at High pH

7.1 Introduction

When canister corrosion has finished and all the available calcium has been leached from the grout material, anaerobic potentials may subside giving way to the re-emergence of aerobic environments. The timescale for this transition may be of the order of 100,000 years and it may be assumed that at this time, the transport of uranium could be sorption-controlled [126].

With no real evidence of the composition of the grout material after such large timescales, the sorption of uranium has been studied on fresh grout. The information acquired could be of relevance to both the early and potentially later aerobic stages.

The chemistry of the grout material used is described in chapter 2. It may be assumed that there are a large number of sites available for sorption of metal ions. Oxides in the grout material include SiO$_2$, Fe$_2$O$_3$, Al$_2$O$_3$, MgO, CaO and other components such as CaCO$_3$ are all expected to compete for the sorption of radionuclides. However, at high pH values (and even as low as pH 4) uranium(VI) is hydrolysed and forms anionic hydroxide species. For this reason, little sorption, if any, may be expected on electrostatic grounds alone.

7.2 Sorption Theory

Adsorption can be described as a concentration enhancement of one phase at the interface of another. It is not to be confused with absorption which differs in that it specifically denotes the equilibrium of components between gas and liquid phases on an intermolecular level with each other. In absorption the equilibrium is a function of the chemical properties of the components and phases, and the fugacity
of any gaseous phase. Adsorption depends on the chemical and physical properties of the solid phase and the solution, and therefore the energy involved in such a process is much more complex than that of absorption.

There are effectively two types of sorption processes: chemical and physical. One way of differentiating between the two requires heating the system to temperatures where physical sorption is less significant than chemical sorption.

Chemical sorption (often termed 'chemisorption') is, as one would expect, a chemical interaction between the solution (solute) and the surface (sorbent). These interactions are characteristic of true chemical bonds since they have large adsorption energies (~100-400kJ/mol) and considerable activation energies.

Attraction between components can also be described in terms of electrostatic forces and the net Coulombic force, $F_c$

$$F_c = \frac{1}{K_E} \cdot \frac{z_+ z_-}{l_D^2}$$

where $K_E$ is the dielectric constant, $z$ is the respective charge on each ion and $l_D$ is the distance of separation.

Charged surfaces can arise either from a chemical reaction of ionisable groups at the surface or, from lattice imperfections. The grout material under investigation in this work will possess charged surfaces due to both of the above.

### 7.2.1 Double Layer Theory

The variation of charged ions from a surface with opposite charge through the bulk solution is described in three main models.
The first and most basic model assumes a charged surface with a monolayer of ions attached to the surface at a distance defined by the ion hydration sphere. An imaginary plane through the centre of the ions defines the Helmholtz plane. However, this model does not account for thermal motion of the ions in the bulk solution nor the weaker forces experienced further away from the Helmholtz plane.

The Gouy-Chapman model shows a charge distribution throughout the solution which is inversely dependent on the distance from the charged surface, known as the diffuse double layer. But although this model accounts for the thermal motion and the variation of charge with distance, it relies too heavily on these factors; it is not accurate at very small distances from the surface and assumes the ions to be point charges rather than possessing a diameter.

The Helmholtz and Gouy-Chapman models are combined to form the Stern model, which has a fixed Helmholtz plane and a charge distribution through the solution.

![Figure 7.1 Charge Variation with Distance from the Charged Surface](image)
The zeta potential, $\zeta$, is defined as the potential at the 'mobile' interface of the double layer where ions that are adsorbed on a charged particle move freely with the particle from the ions in the bulk solution in an applied electric field. The plane that bisects the two regions is termed the shear plane, which exists at some distance from the surface and the potential is usually lower than that at the surface of the charged particle.

### 7.2.2 Point of Zero Charge, $pH_{pzc}$

A sorption site on the grout material may be represented as a surface, $S$, with hydroxyl groups attached, -OH'. At low pH, the hydroxyl group is protonated and the net surface charge will be positive. At high pH, the hydroxyl group is deprotonated and the net surface charge will be negative.

The pH at which the surface group is uncharged is termed the point of zero charge, $pH_{pzc}$ and is characteristic of the type of surface mineral. A list of typical $pH_{pzc}$ for a selection of mineral phases [127] is shown in Table 7.1. It is important to know where the point of zero charge lies since it will determine whether cationic, neutral or anionic species could sorb.

$$> S - O^- \xrightarrow{H^+} > S - OH \xleftarrow{H^+} > S - OH_2^+$$

high pH     $pH_{pzc}$     low pH

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<table>
<thead>
<tr>
<th>Mineral Phase</th>
<th>pH\textsubscript{PZC}</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-Al\textsubscript{2}O\textsubscript{3}</td>
<td>9.1</td>
</tr>
<tr>
<td>$\alpha$-Al(OH)\textsubscript{3}</td>
<td>5.0</td>
</tr>
<tr>
<td>$\gamma$-AlOOH</td>
<td>8.2</td>
</tr>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{4}</td>
<td>6.5</td>
</tr>
<tr>
<td>$\alpha$-FeOOH</td>
<td>7.8</td>
</tr>
<tr>
<td>$\gamma$-Fe\textsubscript{2}O\textsubscript{3}</td>
<td>6.7</td>
</tr>
<tr>
<td>Fe(OH)\textsubscript{3}</td>
<td>8.5</td>
</tr>
<tr>
<td>MgO</td>
<td>12.4</td>
</tr>
<tr>
<td>SiO\textsubscript{2}</td>
<td>2.0</td>
</tr>
<tr>
<td>Feldspar</td>
<td>2 - 2.4</td>
</tr>
</tbody>
</table>

Table 7.1  Typical pH\textsubscript{PZC} for a Selection of Relevant Mineral Phases [127]

7.2.3  Microelectrophoresis

The charge at the shear plane (zeta-potential) of a particle can be measured by microelectrophoresis, and will yield the point of zero charge if this ‘measurable’ charge is investigated at a variety of pH values. Microelectrophoresis is the study of the velocity of a charged particle in a suspension between an applied electrical potential.

The velocity of a particle, $v$, is proportional to the applied electric potential, $E$ (volts) and the electrophoretic mobility, $\mu_e$,

$$v = \mu_e E$$
The velocity of the particle is opposed by the viscosity of the suspension, \( \eta \), and can be related to the effective charge on the particle, \( Q_e \), and its radius, \( r \), by the equation

\[
\mu_E = \frac{Q_e}{6\pi r \eta}
\]

Measurement of the particle velocity can be performed by using two coherent laser beams whose paths cross and scatter light due to their interference. As the particle moves between the beams at the crossover point, a frequency shift is observed, known as the Doppler effect, which can in turn be related to the velocity of the moving particle and the charge at the shear plane.

### 7.2.4 Sorption Isotherms

The effect of sorption is commonly described by means of a sorption 'isotherm' in which the concentration of species adsorbed onto the solid phase \( (C_s') \) is plotted against the concentration of species remaining in the solution phase \( (C_l) \). \( C_s' \) is related to \( C_l \) and the total concentration of species in the system, \( C_o \) by:

\[
C_s' = C_o - C_l
\]

The form of this plot can take on three different shapes: convex, concave or linear. When plotted, a convex sorption isotherm is characteristic of 'favourable' sorption processes (i.e. sorption is likely to occur) and is termed Type-I, in which the sorbed concentration reaches a maximum and plateau is seen. This plot indicates that with small increases in \( C_o \), the adsorption observed (in terms of \( C_s' \)) increases rapidly. If the plot yields a linear slope and no plateau is observed, sorption is still favourable and is termed Type-II. Sorption is unlikely to occur (unfavourable) when the isotherm plot is concave in shape and is termed Type-III. This is shown graphically in Figure 7.1.
The extent of sorption onto a solid surface can be predicted by means of several mathematical relationships. The simplest form assumes linearity between the concentration sorbed per unit mass and the concentration remaining in solution, and can be described as:

\[ C_s = R_d \cdot C_l \]

where \( R_d \) is the distribution ratio and can be obtained from the gradient of a standard sorption isotherm.

![Diagram of sorption isotherms](image)

**Figure 7.2  Theoretical Sorption Isotherm Plots to Describe Types of Sorption**

More complicated mathematical formulae have been devised to explain the deviations from linearity which are evidence of a contribution to the attractive forces other than basic partitioning between two phases. These deviations can also be described by mathematical formulae. The Freundlich equation allows for all types of profiles,

\[ C_s = K_{adsF} \cdot C_l^n \]
in which \( K_{adsF} \) is the Freundlich sorption constant and \( n_s \) is a constant that describes the type of sorption. When \( n \) is equal to unity the sorption profile is linear. When \( n_s \) is less than unity the profile is convex and if \( n_s \) is greater than unity sorption is unfavourable and the profile is concave. Both \( K_{adsF} \) and \( n_s \) can be determined by plotting \( \log C_s \) against \( \log C_i \) to yield a gradient equal to \( n \) and an intercept equal to \( K_{adsF} \). Freundlich isotherms are applicable to heterogeneous sorption surfaces.

The Langmuir Isotherm equation was developed in 1918 for monolayer sorption onto surfaces and takes into account the plateau seen in Type-I sorption;

\[
C_s = C_{s,max} \frac{K_{adsL} \cdot C_s}{1 + K_{adsL} \cdot C_i}
\]

where \( C_{s,max} \) is the maximum concentration of adsorbed species (sorbate) possible onto the solid phase (sorbent) and \( K_{adsL} \) is the Langmuir adsorption constant. A plot of \( 1/C_s \) against \( 1/C_i \) allows calculation of \( C_{s,max} \) from the intercept and \( 1/(K_{adsL} \cdot C_{s,max}) \) from the gradient. Concentrations \( C_s \) and \( C_{s,max} \) can be replaced by the fractional coverage term, \( \theta_s \)

\[
\theta_s = \frac{C_s}{C_{s,max}}
\]

After determination of \( \theta_s \), mathematical relationships can be used to assess whether lateral interaction occurs between sorbate molecules at the sorbent surface. By use of the Frumkin model, deviation from isotherm linearity can be attributed to attractive or repulsive forces depending upon whether the interaction coefficient, \( a_{ic} \), is greater or less than zero respectively using the relationship

\[
\frac{\theta_s}{(1-\theta_s)} \cdot \exp(-2a_{ic} \theta_s) = K_{ads} \cdot C_i
\]

A plot of \( \theta_s \log(\theta_s/(1-\theta_s)) \) against \( \log C_i \) allows calculation of \( a_{ic} \) from the gradient and \( K_{ads} \) from the intercept.
BET sorption isotherm theory (developed by Brunauer, Emmett and Teller in 1938) is an extension of the Langmuir equation, taking into account the adsorption of multiple layers of sorbate molecules. After this first (mono-) layer has attached to the sorbent surface, further layers attach to the mono-layer by means of condensation reactions:

\[ C_s = \frac{\beta_{ad} \cdot C_1 \cdot C_{sat}}{(S_1 - C_1) \left[ 1 + (\beta_{ad} - 1) \left( \frac{C_1}{S_1} \right) \right]} \]

where \( S_1 \) is the solubility limit, \( \beta_{ad} \) is the energy of adsorption and \( H_a \) is the net enthalpy of sorbate mono-layer adsorption onto the sorbent.

7.3 Experimental Methods

7.3.1 Grout Preparation

Grout material obtained from BNFL was sieved through a 90\( \mu \)m test sieve (Endecotts Ltd, Lombard Road, London, SW19 3BR) before use to ensure a fine particle size.

7.3.2 Determination of \( \text{pH}_{\text{pzc}} \)

The point of zero charge is defined in section 7.2.2 as the pH at which the surface charge on the sorbent is zero.

The complex nature of the grout material (containing many different types of sorption sites) and the fact that the grout dissolves to form grout leachate (which differs as the pH decreases and more of the grout dissolves), meant that a
potentiometric titration with acid did not yield an accurate point of zero charge determination. The $pH_{PZC}$ for grout was therefore determined by direct measurement of the charge using electrophoresis, previously discussed in section 7.2.3.

Samples of grout were prepared in grout leachate and the pH was adjusted between 1 and 11 with addition of hydrochloric acid. The samples were shaken periodically and left for one week. Aliquots of each grout / grout leachate sample were then subject to microelectrophoresis (ZetaMaster, Malvern Instruments).

The zeta potential results obtained by the electrophoresis study were plotted against pH and are shown graphically in Figure 7.3. It can be seen that as the pH is decreased from pH 11, the charge on the grout material becomes less negative. At pH 4 there is a steeper increase in the zeta potential and pH 2.3 is the point of zero charge. Below pH 2.3, the zeta potential becomes more positive.

The $pH_{PZC}$ for the grout material can be compared to those listed in Table 7.1 and it can be seen that the grout is similar to SiO$_2$ (pH 2) or Feldspar (pH 2.0-2.4) [127], although this is an overall average figure since there are many possible sites for sorption on the grout material (e.g. Fe$_2$O$_3$, Al$_2$O$_3$, MgO, CaO and CaCO$_3$), with local $pH_{PZC}$ values.

![Figure 7.3 Determination of $pH_{PZC}$ by Electrophoretic Mobility](image)
7.3.3 Uranium-Grout Sorption Isotherms and \( R_d \) Determination

The sorption of uranium onto grout material was investigated in two slightly different systems. Firstly, the sorption of uranium by grout in water and secondly, the sorption of uranium by grout in pre-formed grout leachate. The concern was that the grout material would react with water and that components of the grout would dissolve to form fresh leachate (characterised in chapter 2.2). Using grout leachate, the solid component remained unchanged.

Aliquots of uranium (1ml of 40µM, \(^{233}\text{U}, \text{AEAT}\)) were added to increasing amounts of sieved grout (from 5mg to 500mg) in 20ml of either water or pre-formed grout leachate in sealed glass vials. The vials were then shaken in a thermostatted water bath at 25°C for one week before sampling the supernatant solution and liquid scintillation counting. The results can be plotted in a variety of ways, each one giving different information about the sorption of uranium onto grout.

The standard ‘linear-type’ sorption isotherm plots of the concentration of uranium sorbed onto grout against the concentration of uranium in solution are shown in Figure 7.4 and show that uranium sorption is favourable and follows the linear equation,
Linear-type relationships are discovered and the gradient yields $R_d$ sorption values of 1510 ml/g and 3640 ml/g for water and pre-equilibrated leachate respectively. The isotherm for grout in leachate shows evidence of a plateau, i.e. saturation after a loading of 3.4μmol uranium per gram of grout material, suggesting that the sorption iostherms cannot be described as linear.

The characterisation of the sorption isotherms in terms of Freundlich sorption theory described in section 7.2.4, have been shown graphically in Figure 7.5.
\[ C_s = K_{adsF} C_1^{n_s} \]

Figure 7.5  Freundlich Sorption Isotherms of Uranium on Grout in (a) H₂O and (b) Pre-Equilibrated Grout Leachate

Both plots are linear and yield both the Freundlich sorption constant, \( K_{adsF} \) (taken from the intercept on the y-axis) and the sorption order constant, \( n_s \), (taken from the gradient). For uranium sorption onto grout in water at high pH, \( \log K_{adsF} = 1.18 \) and \( n_s = 0.77 \), while for the same study in pre-equilibrated grout leachate \( \log K_{adsF} = 2.49 \) and \( n_s = 0.89 \). This shows that, since \( n_s \) is slightly less than unity, sorption is favourable in both cases (convex, Type-I, tending away from linear Type-II) and that sorption of uranium appears to be greater when the grout is in equilibrium with pre-equilibrated leachate compared to water.
The Langmuir sorption isotherms for uranium on grout in water and grout leachate are shown in Figure 7.6. These isotherms allow for the plateau seen in the ‘linear-type’ isotherm of uranium sorption by grout to be taken into account, in terms of a saturation of available sites for sorption. Using the Langmuir equation, plotting $1/[C_s]$ against $1/[C_i]$ allows determination of $K_{ads}$ and $C_{s,max}$ from the intercept and gradient respectively.

\[
C_s = C_{s,max} \frac{K_{ads} C_i}{1 + K_{ads} C_i}
\]

and therefore

\[
\frac{1}{C_s} = \frac{1}{C_{s,max}} + \frac{1}{K_{ads} C_i}
\]

(a)

Figure 7.6  Langmuir Sorption Isotherms of Uranium on Grout in (a) $H_2O$ and (b) Pre-Equilibrated Grout Leachate
Using the Langmuir equation, the maximum uranium loading capacity of the grout is $1.6 \times 10^{-6}$ and $2.7 \times 10^{-6}$ mol/g in water and grout leachate respectively. The Langmuir adsorption constant, $K_{\text{ads}}$, equates to $2.35 \times 10^{6}$ for sorption in water and $1.95 \times 10^{6}$ in grout leachate.

The lateral interaction of uranium ions with each other at the grout surface can be investigated by using the Frumkin isotherm plot, shown in Figure 7.7.

\[
\frac{\theta_s}{(1-\theta_s)} \exp(-2a_i\theta_s) = K_{\text{ads}} C_1
\]

![Figure 7.7 Frumkin Sorption Isotherms of Uranium on Grout in (a) H\textsubscript{2}O and (b) Pre-Equilibrated Grout Leachate](image)

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Calculation of the interaction coefficient, $a_{ic}$, from the gradient of the isotherm for sorption in water and grout leachate yields values greater than zero (1.2 and 1.03 respectively). This shows that there are slight attractive forces acting between uranium ions at the grout surface. This is somewhat unusual since the sorbed uranium species at such a high pH will be $\text{UO}_2(\text{OH})_3^-$ and one would expect the hydroxyl ligands to repel each other because of their negative charge. This is discussed more in section 7.5.

Resubstitution of the numerical value of $a_{ic}$ into the Frumkin equation, together with the intercept of the isotherm leads to calculation of the adsorption constants, $K_{ads}$, which are $1.03 \times 10^6$ for sorption in water and $1.2 \times 10^6$ in grout leachate.

### 7.3.4 Effect of pH on Uranium-Grout Sorption

The effect of pH on uranium sorption onto grout was investigated because the pH can affect the speciation of uranium and, change the surface charge of the sorption sites.

Aliquots of uranium (1ml of 40$\mu$M, $^{233}$U, AEAT) were added to 100mg of sieved grout in 20ml of pre-formed grout leachate adjusted to pH values between 2 and 12 in sealed glass vials. The vials were then shaken in a thermostatted water bath at 25°C for one week before sampling the supernatant solution and liquid scintillation counting. The results are shown in Figure 7.8, where the experimentally measured sorption is plotted against the pH and compared to modelled speciation using the MINTEQA2 code and the uranium hydroxide species listed in appendix 1.

It should be noted that at the uranium concentration used for sorption studies (2$\mu$M), monomeric uranyl hydroxide species are expected to dominate over polymeric uranyl hydroxides [27,28]. Modelling of the speciation supports this statement.
It can be seen that uranium sorbs to the grout material over a variety of pH values studied. At low pH values, the uranium species predicted is the uranyl ion, UO$_2^{2+}$. Sorption of uranium occurs even at low pH values and the sorption increases with pH due to the decrease in proton concentration and therefore a decrease in the competition of sorption sites. Even at low pH, the grout material still carries a negative charge (see Figure 7.3). As the pH increases, the major uranium species becomes the monohydroxide (UO$_2$OH$^+$) and sorption still increases with pH. At pH 5, the neutrally charged uranyl dihydroxide, UO$_2$(OH)$_2$ is formed and the sorption profile appears to plateau. A pH of 5 also sees the formation of UO$_2$CO$_3$ is
predicted by the model; grout leachate contains 0.125mM carbonate. This is followed by the formation of the dicarbonato ion, \( \text{UO}_2(\text{CO}_3)^{2-} \) and the mixed trihydroxy diuranyl carbonato ion, \( (\text{UO}_2)_2\text{CO}_3(\text{OH})_3^- \). At higher pH values, the model predicts the formation of negatively charged uranyl trihydroxide, \( \text{UO}_2(\text{OH})_3^- \) in favour of the above mentioned hydroxides and carbonates. Note that the most stable uranyl carbonate, \( \text{UO}_2(\text{CO}_3)^{4-} \), does not form anywhere, since it requires a higher carbonate concentration, at which (in this case) hydroxide complex formation is much more favourable. Sorption is also favourable at these higher pH values, although there is a slight decrease in the sorption with increasing pH. The model predicts a rise in the formation of uranyl tetrahydroxide, \( \text{UO}_2(\text{OH})_4^{2-} \), at pH 12.

The results of the effect of pH on the sorption of uranium onto grout material show that below pH 5, ion exchange processes can be assumed since uranium is positively charged and the grout surface is negatively charged. Above pH 5, The fact that negatively charged uranyl hydroxide ions appear to sorb to a negatively charged surface is somewhat unexpected and suggests sorption by means of -OH ligand exchange (chemical processes). This subject will be discussed more in section 7.5.

7.3.5 Rate of Uranium-Grout Sorption:

In order to check that equilibrium had been reached in the sorption experiments, it was necessary to determine the rate of sorption of uranium onto grout material. This was achieved by the analysis of replicate samples at set times over the course of 2 weeks. Aliquots of uranium (1ml of 40\( \mu \text{M, } ^{233}\text{U} \)) were added to 100mg of sieved grout in 20ml of grout leachate. Samples were continually shaken in a water bath (Grant, UK) and removed in duplicate after 2, 4, 6, 8, 10, 20, 30, 50, 65 minutes, 2, 3, 5, 8 hours and 1, 2, 3, 5, 10 and 15 days. Each sample was filtered through a 0.2\( \mu \text{m} \) acrodisc filter (Gelman Sciences) and 1ml of each sample was
taken for liquid scintillation counting in 10ml of EcoScintA (National Diagnostics) cocktail on a scintillation counter (LKB Wallac) for 5 minutes each. The count rates were then compared with a blank standard which contained uranium and leachate without grout (representing no sorption). The results are shown graphically in Figure 7.9.

![Figure 7.9 Rate of Uranium Sorption onto Grout](image)

A study of the rate of sorption of uranium onto grout material shows two apparent stages, the first being fast sorption of uranium and the second sorption at a slower rate. This can be investigated further by studying the rate constants for the sorption.

The rate of sorption can be expressed as a function of changing unbound uranium in solution, $C_t$ (mol l$^{-1}$), at time, $t$ compared to the maximum sorption achieved, $C_{t,\text{max}}$ (mol l$^{-1}$) and the rate constant, $k_t$ (s$^{-1}$),

$$\frac{dC}{dt} = k_t \cdot (C_t - C_{t,\text{max}})$$

Integration of the above rate equation allows determination of the rate constant for sorption,
\[
\ln \left( \frac{1}{1 - \frac{C_t}{C_{\text{max}}}} \right) = k_1 t 
\]

and so a plot of the left side of the equation against time should be linear and yield a gradient numerically equal to the rate constant. This has been performed for the sorption of uranium onto grout material at high pH and is shown in Figure 7.10.

![Figure 7.10](image)

**Figure 7.10  Determination of Rate Constants for the Sorption of Uranium onto Grout**

The results of the rate constant determination show that two different rates and types of sorption are occurring. The first step is fast \((k_{11} = 6.82 \times 10^{-3} \text{ s}^{-1})\) while the second step is slow \((k_{22} = 1.07 \times 10^{-4} \text{ s}^{-1})\). The rate of actual physical adsorption is fast when the majority of sites are available to the sorbate ions. Once sites become more and more full (and therefore unavailable), the rate of diffusion of the sorbate through the solution to available sorption sites is slower. The latter step is therefore the one which in turn determines the overall rate.
7.4 Uranium Desorption from Grout by Complexation

To investigate the effect of grout material on complexation of uranium at high pH and to compare with previously reported complexation studies in the absence of grout material, uranium-grout-leachate-complexant studies were performed. Essentially the same method as in chapter 5 was followed, but in the presence of grout and with much less uranium (μM cf. mM for aerobic and anaerobic uranium complexation studies). The experiments were designed to show the effect of complexing agents on the extent of sorption/desorption of uranium onto the grout material.

Aliquots of uranium (1 ml of 40 μM, $^{233}$U) were added to 100 mg of sieved grout in 20 ml of grout leachate in glass vials. Increasing concentrations of complexing agent were added to each vial, covering a range of three orders of magnitude ($10^{-4}$ - $10^{-2}$ M added ligand). Samples were then left to equilibrate for 1 week before being filtered through a 0.2 μm syringe filter (Gelman Science). Aliquots of 1 ml of filtrate were then analysed by liquid scintillation counting and the counts obtained compared with a calibration curve.

The results obtained were used to select appropriate concentration ranges for each complexing agent under investigation within a single order of magnitude so as to effect complete desorption of uranium from the grout material.

Speciation modelling was used to ascertain the probable species responsible for desorption using literature formation constants. In some cases, where modelling was unable to predict desorption, new species were invoked based on fitting experimental results. The stoichiometry of the species could be determined by model-fitting the experimental gradient of the desorption profile, while the actual numerical value of the formation constant is determined from a fit of the point at which desorption is 100% effective. Where the formation constant is not in reasonable agreement with literature values, mixed hydroxide species are proposed.
since the system is at high pH (11.8) and hydroxide complexation is favourable. However, this method does not account for competition reactions between uranium and the added ligand for grout sorption sites.

7.4.1 Desorption Results

![Graphs showing desorption results](image)

Figure 7.11 The Effect of Added Carbonate on the Desorption of U(VI) onto Grout Material in Grout Leachate (a) Experimental Solubility and (b) Modelled Speciation

The experimental desorption of uranium from grout with increasing added carbonate is shown in Figure 7.11(a), together with speciation modelling of the
experiment in Figure 7.11(b) using MINTEQA2 together with the dataset shown in Appendix 1. The model successfully predicts the carbonate complexation of uranium after formation of calcite has been achieved and the free carbonate concentration is large enough to compete with the high hydroxide concentration at pH 11.8. The species responsible for desorption is $\text{UO}_2(\text{CO}_3)_3^{4-}$.

![Figure 7.12 The Effect of Added Phosphate on the Desorption of U(VI) onto Grout Material in Grout Leachate](image)

The effect of added phosphate on the sorption of uranium by grout material is shown in Figure 7.12. The addition of increasing concentrations of phosphate led to the rapid precipitation of a milky-white precipitate and the concentration of free uranium in solution decreased slightly. Modelling of aerobic experimental complexation (chapter 5) suggests that in the pH range of 9 - 11, a complex ion $\text{UO}_2(\text{HPO}_4)_2^{2-}$ is responsible for dissolution of uranium precipitates and that the milky-white precipitate was in fact hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$. However, at pH 11.8, the uranyl phosphate species is unable to compete with hydrolysis of uranium and dissolution was not observed. The results suggest that free $\text{UO}_2(\text{OH})_3^-$ was coprecipitated with the hydroxyapatite precipitate.
Desorption of uranium from grout with increasing added sulphate is shown in Figure 7.13 and clearly shows desorption by means of sulphate addition. Speciation modelling showed that neither the 1:1 nor the 1:2 uranyl sulphate complexes could reproduce experimental desorption. A 1:3 species was required to model experimental desorption. However, the literature formation constant for the 1:3 species of log\(K_f = 3.4\) [128] would require a change to 20.1 in order to fit experimental desorption results. This is a clearly unacceptable alteration.
The desorption of uranium from grout by addition of chloride is shown in Figure 7.14. Formation constants are available for 1:1, 1:2 and 1:3 complexes. The experimental desorption profile gradient would be best fitted with a 1:2 complex. However, $\log K_f$ would need to be increased from 1.9 [19] to 19.5 in order to fit experimental results.

The addition of acetate at pH 11.8 strongly desorbs uranium from grout material, as can be seen in Figure 7.15(a). Speciation modelling of the desorption allowed for the formation of 1:1, 1:2, 1:3 and 1:4 complexes, whose formation constants are available in the literature [19]. The gradient of the experimental desorption profile is large and this is best explained by a 1:4 complex formed between $UO_2^{2+}$ and acetate. The modelling shows good agreement with experimental results. However, this species was removed from the aerobic complexation studies detailed in chapter 5 in order to reproduce experimental results. This suggests that this species is only formed at the lower uranium concentrations encountered in the sorption studies, i.e. 2μM.
Figure 7.15  The Effect of Added Acetate on the Desorption of U(VI) onto Grout Material in Grout Leachate (a) Experimental Solubility and (b) Modelled Speciation

The effect of citrate ions on uranium sorption by grout material at pH 11.8 is shown in Figure 7.16. It can be clearly seen that uranium is desorbed from the grout material with increasing added citrate. Speciation modelling of citrate addition to uranium using the available literature formation constants showed poor agreement with the profile in Figure 7.16. The mixed species detailed in chapter 5 was introduced to the desorption model and produced a fit better than that of literature species, but not to a satisfactory correlation with experimental results. However, considering the results detailed in chapters 5, 6 and 7 for citrate complexation, problems are encountered in modelling experimental uranium solubilities.
The effect of addition of EDTA on the desorption of uranium from grout material is shown above in Figure 7.17(a). Modelling of the experimental results did not provide a sufficient prediction of the desorption profile using the dataset available in the HATCHES database. The major species below pH 11 is $\text{UO}_2\text{EDTA}^{2-}$ but, at higher pH values, this species is unable to compete with the hydrolysis of uranium and therefore the formation of $\text{UO}_2(\text{OH})_3^-$.
The desorption of uranium from grout with added nitrilotriacetic acid (NTA) is shown in Figure 7.18. No uranium-NTA complex formation constants were available in the literature and so the species predicted in chapter 5 were used. Both 1:1 and 1:2 uranium-NTA complexes were considered and formation constants estimated by a trial and error method. The \( \text{UO}_2(\text{NTA})_2^+ \) species showed moderate correlation with experimental desorption results.
The experimental effect of adding humic acid (HA) to uranium which had been sorbed onto grout material is shown in Figure 7.19(a). Modelling of the desorption by HA complexation of uranium was performed using the species $\text{UO}_2\text{HA}^+$, $\text{UO}_2\text{HA}$ and $\text{UO}_2(\text{OH})\text{HA}$ which are available in the literature. The results of the modelling prediction showed that mixed species, $\text{UO}_2(\text{OH})\text{HA}$, is formed and that desorption occurred to a much greater extent than that which was observed experimentally. Alternatively, the discrepancy may be due to either competition for the grout sorption sites between HA and uranium.

The experimental effect of adding fulvic acid (FA) to uranium sorbed onto grout material is shown in Figure 7.20(a), above. The results are very similar to that of desorption by HA and so a similar approach was taken to model the FA system. Modelling considered $\text{UO}_2\text{FA}^+$, $\text{UO}_2\text{FA}_2$ and the $\text{UO}_2(\text{OH})\text{FA}$ species derived in section 5.3.11. The modelling results show a reasonable correlation with the experimental desorption profile and that the complexing species is $\text{UO}_2(\text{OH})\text{FA}$. 

![Figure 7.19 The Effect of Added HA on the Desorption of U(VI) onto Grout Material in Grout Leachate](image)
The effect of added ISA on the sorption of uranium on grout material is shown above in Figure 7.21. No uranium-ISA formation constants were available in the literature, but modelling of aerobic complexation of uranium precipitates (chapter 5 of this thesis) showed that desorption should occur due to the formation of 1:1 uranium-ISA species such as $\text{UO}_2(\text{OH})\text{ISA}$ or $\text{UO}_2(\text{ISA}_n)$. 
No further model-fitting can be performed unless desorption occurs. The range covered by the experimental concentration of added ISA was large enough at pH 9 to 11 to induce complete dissolution of uranium precipitates containing 2500 times more uranium compared to the above sorption experiments (see chapter 5).

7.5 Summary

The sorption of uranium onto Drigg grout material has been investigated at high pH. The grout material has a pH$_{pzc}$ of 2.3 and it may therefore be assumed that the active site for sorption of metal ions is similar to that of SiO$_2$ or feldspar. Since the grout material is 42.3% SiO$_2$ (as determined in chapter 2.1.2), the sorption of uranium onto grout material may be assumed to be analogous to that on SiO$_2$. However, Fe$_2$O$_3$ and Al$_2$O$_3$ make up 3% and 27% of the grout material respectively (determined in chapter 2.2) and the pH$_{pzc}$ of 2.3 (determined in chapter 7.3.2) suggests the active sorption site may be Feldspar rather than simply silica.

The uranium species responsible for its sorption onto the grout material at low uranium concentrations used in this work (2µM) are monomeric hydroxides, as shown by modelling using the MINTEQA2 code [12] and the database constructed in Appendix 1 and supported by recent work by Moulin [27]. Although polymeric hydroxides were included in modelling studies, their existence is negligible compared to the monomeric hydroxides. This is considered to be a different case to that examined in chapter 5, where much higher uranium concentrations are used and monomeric species are removed for reasons of modelling experimental results.

The effect of pH on the sorption of uranium onto grout leachate showed that both ion exchange and complex formation occur at the surface. The sorption of U(VI) is controlled predominantly by co-ordination rather than simple electrostatics [129]. Maximum sorption occurred at pH 5, where the major uranium species is UO$_2$OH$^-$ and sorption occurs by ion exchange with protons at the surface of the grout. At pH
5, $\text{UO}_2\text{CO}_3$ is formed and limits the sorption onto grout, while at pH 6, the mixed hydroxy-carbonate, $(\text{UO}_2)_2\text{CO}_3(\text{OH})_4^-$ is predicted and does not appear to affect the sorption of uranium. [130] states that this species is adsorbed onto hematite as an inner sphere complex.

At the high pH controlled by grout leachate, the species responsible for sorption are identified by modelling as $\text{UO}_2(\text{OH})_3^-$. Although the sorption of uranium decreases slightly as the pH is increased from 8 to 12, it can clearly be seen in Figure 7.8 that a significant proportion of uranium is still bound. This clearly indicates that complex formation is responsible for sorption at high pH.

Suggestions can be made as to the form of sorption of uranium onto the grout material. For ion association to take place the sorbent and sorbate must be of opposite charge. However, this is not the case here since $\text{UO}_2(\text{OH})_3^-$ and grout ($\text{pH}_{pzc} = 2.3$) both have a negative charge under the conditions studied in this work. Therefore, we can eliminate physi-sorption in favour of chemi-sorption.

More likely methods for uranium(VI) sorption at high pH are either outer-sphere ligand exchange or inner-sphere complex formation. A hydroxyl group of the grout material could replace one of the hydroxyl groups of the trihydroxyuranyl ion (Figure 7.22a), i.e. ligand exchange leading to $\text{UO}_2(\text{OH})_2\text{O-Si}^<$. Alternatively, a hydroxyl group of the grout material could be shared between the grout and the trihydroxyuranyl ion, leading to the stabilisation of the tetrahydroxyuranyl ion, $\text{UO}_2(\text{OH})_4^{2-}$, via a transition state leading to the formation of $\text{UO}_2(\text{OH})_3\text{O-Si}^<$, as is shown in Figure 7.22b. The last process could then be repeated to lead to bidentate binding of the uranium to the cement sorption site by -O- bridging. The formation of an inner sphere bidentate bound uranium ion to silica surfaces has recently been supported by EXAFS studies performed by Reich et al [131] and Hudson et al [132]. The latter states that at low pH, ion exchange is favoured and an outer sphere complex is formed, while at higher pH the formation of inner sphere complexes is favoured for surface complex formation in which neighbouring...
uranium atoms attract to form oligomeric complexes at the surface (a statement which supports the findings presented here that Frumkin isotherm analysis suggested attractive interaction between uranium ions at the grout surface).

Figure 7.22 Schematic Diagram of Possible Surface Complexation Sorption Mechanisms for Uranium on Grout by (a) Ligand Exchange or (b) Complex Formation

Sorption isotherms were constructed for uranium in both water and pre-formed grout leachate solution at pH 11.8 at 25°C. The results are summarised below in Table 7.2 which show that there is a slight difference between sorption in the two solutions. This difference may be due to competition for uranium sorption sites from calcium, potassium and sodium.
The rate of sorption onto grout material at high pH was investigated and showed that the overall sorption can be described by two rate constants, \( k_1 = 6.82 \times 10^{-3} \text{ s}^{-1} \) followed by \( k_2 = 1.07 \times 10^{-4} \text{ s}^{-1} \). The rate of physical sorption of the sorbate to the sorbent is very fast with respect to the rate of diffusion of the sorbate through the solvent to reach the sorbent surface, and the latter therefore becomes the rate limiting step. The two rate constants observed can only be attributed to the accessibility of the sorption sites to the uranium ion over time, with ‘open’ sites becoming more difficult to find.

The effect of ligands on the desorption of 2\( \mu \text{M} \) uranium from 100mg of grout at high pH was investigated and is summarised in Table 7.3.

In some cases (carbonate, phosphate, acetate, NTA, humic acid and fulvic acid), modelling was able to satisfactorily explain the desorption profiles obtained by adding increasing concentrations of complexing ligand. In the case of citrate, the gradient of the desorption profile indicated a 1:2 species, for which a formation
constant is not available in the literature. A 1:2 species was therefore introduced into the model and a formation constant was derived by trial and error fitting of experimental results. This species affects the modelling of aerobic complexation studies reported in chapter 5. This was also true for the modelling of desorption by acetate addition, suggesting that the 1:4 U-acetate species available in the literature and later dismissed in chapter 5 was true for cases of low uranium concentration. Similar procedures were required for the modelling of uranium desorption by the addition of EDTA, where formation constants was available for a number of mixed species, but not a 1:1:1 mixed species, U(VI)-EDTA-OH. Again, a formation constant was derived by trial and error, \( \log K_f = 7.0 \) for \( \text{UO}_2(\text{EDTA})(\text{OH})^+ \). Remodelling of aerobic complexation described in chapter 5 shows that this species would lead to excessive uranium solubility at high pH and added EDTA concentration.

The addition of sulphate and chloride to uranium which had been previously sorbed by grout showed significant effects on the free uranium concentration. Experiments detailed in chapter 5 showed no uranium complexation at high pH by these ligands. For means of fitting experimental desorption profiles, mixed species were invoked as \( \text{UO}_2(\text{SO}_4)_3(\text{OH})^+ \) and \( \text{UO}_2\text{Cl}_2(\text{OH})^- \) with formation constants, \( \log K_f \), equal to 7.2 and 7.6 respectively (derived by trial and error). Such ternary mixed species are proposed by Peterson [133] and Dunsmore et al [134], but dismissed by the NEA review of uranium thermodynamics [19]. It should also be noted that if the mixed sulphate species is included in the modelling of aerobic experimental results shown in chapter 5, it does not affect the solubility of the precipitate. As the pH increases, so one would imagine this species to predominate at high sulphate concentrations. However, due to the formation of the more stable and insoluble uranates, the effect of the mixed species is lost. The same cannot be said for the chloride mixed species, and this casts doubt on this species and its formation constant derived above. Perhaps future studies could involve examination of such mixed species by recent methods such as time resolved laser induced fluorescence spectroscopy.
or even radiochemical techniques with the study of uranium, tritium and a labelled ligand, for example $^{36}\text{Cl} (\beta)$, $^{35}\text{S} (\beta)$, $^{14}\text{C} (\beta)$, or $^{32}\text{P} (\beta)$.

Modelling of uranium desorption from grout material by addition of ISA showed that desorption should have occurred. However, the experimental uranium desorption produced no such desorption. This finding was accounted for by evidence that ISA itself sorbs to cement [76]. This does however, disagree with the work performed by AEAT [77] in which the sorption of uranium onto cement was greatly reduced in the presence of ISA.

Other possibilities for the poor correlation between modelling and experimental desorption results are (a) competition between the uranium and the added ligand for the grout sorption sites or (b) physical degradation of the grout material or sorption sites by the addition of the ligand at such high concentrations.

Another possible reason for failure of the model to predict desorption by complexation without including unreasonable mixed species is that at higher concentrations of added ligand, more sodium hydroxide was required in order to maintain the high pH. This may have led to competition for sorption sites and decreased the amount of uranium sorbed to the grout material.

It should also be noted that the concentration of ligand required for desorption of $2 \times 10^{-6}$ M uranium from grout is, in some cases, of the same order of magnitude as that required for dissolution of a uranium precipitate containing $5 \times 10^{-3}$ M uranium. This fact, together with the observation that the desorption profiles for the eleven ligands examined are very similar, suggests that there is some process other than 'pure' complexation taking place.
<table>
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<th>Ligand</th>
<th>Uranium Species</th>
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<td>Tricarbonate species</td>
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<td>Coprecipitation observed</td>
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<td>Sulphate</td>
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<td>Mixed species invoked, dismissed by results in Ch 5</td>
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<td>Mixed species taken from Ch 5, moderate fit with experimental results</td>
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<td>HA</td>
<td>$\text{UO}_2(\text{OH})\text{HA}$</td>
<td>Incomplete desorption</td>
</tr>
<tr>
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<td>Mixed species taken from Ch 5, moderate fit with experimental desorption results, incomplete desorption</td>
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<tr>
<td>ISA</td>
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<td>No desorption observed, possibly due to ISA sorption on grout</td>
</tr>
</tbody>
</table>

Table 7.3 Summary of Uranium Desorption-Complexation Studies

The results of this study into the desorption of uranium from grout material shows that the system is not easy to predict by modelling using the data currently listed in both the HATCHES database [29] or the NEA review [19]. The task is made more difficult since the complicated nature of the grout material could be affected by so many of the complexing ligands of interest. Modelling of the desorption of uranium by complexation alone showed poor predictive capabilities, and in most cases model fitting was required.

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CHAPTER EIGHT

Summary and Conclusions
8. Summary and Conclusions

The work detailed in this thesis has investigated the solubility, speciation, complexation and sorption of uranium at high pH in a variety of situations relevant to low level nuclear waste disposal in Vault 8 at the Drigg site.

Drigg grout material is a composite grout produced by mixing ordinary Portland cement (OPC) and pulverised fuel ash (PFA) in a 1:3 ratio. The chemistry of the grout material used to physically stabilise the compacted waste canisters has been investigated by X-ray fluorescence (XRF) and analysis of several grout leachates has been performed. The results indicate a high silica and alumina content and lower calcium content compared to a theoretical grout material defined in section 1.5.2. Leachates were found to have high concentrations of sodium, potassium and calcium. Although the grout material buffers the pH of the leachate initially at 11.8, the rapid leaching of alkali metal hydroxides together with variations in the grout mixture suggest a short-lived, high pH plume. Hence studies of uranium solubility have been performed at pH 11.8 and below. It should also be remembered that the grout material cannot be critically compared to specially designed 'buffer' backfill materials such as the Nirex Reference Vault Backfill (NRVB), since Drigg grout was chosen for its flow (rheological) properties only and not for its radionuclide sorbing or buffering properties.

Two methods have been used to separate uranium from daughter decay products such as thorium. Ion exchange using Amberlite-IR-120 resin and extraction chromatography using ElChrom-U/TEVA resin. Both provided easy and adequate separation for accurate uranium determination without interference from decay products.

Uranium has been analysed by two different procedures. Spectrophotometrically with the chromogenic reagent Arsenazo-III (AAIII) and by liquid scintillation counting. Both procedures produced linear calibration curves and were used
throughout this work. Lower limits of detection were obtained using liquid scintillation counting by doping natural $^{238}$U with $^{233}$U, or by using $^{233}$U in place of $^{238}$U.

The nature of the solid phases formed by the precipitation of uranium at high pH by a number of hydroxides and by grout leachate has been investigated. Initial characterisation was by X-ray powder diffraction (XRPD) and was later improved by modelling of complexation studies. Schoepite, $\text{UO}_3\cdot 2\text{H}_2\text{O}$, appeared to be the solubility limiting phase in most cases at the lower pH range studied (pH 9 and 10). In the presence of sodium and potassium hydroxides, diuranates ($\text{Na}_2\text{U}_2\text{O}_7$ and $\text{K}_2\text{U}_2\text{O}_7$) were formed at higher pH. The addition of calcium hydroxide to uranium led to the formation of a phase determined to be a mixture of schoepite and calcium uranate, $\text{CaUO}_4$, at all pH values studied. The solid phases produced by the addition of grout leachate reflected the complex chemical composition of the leachate. XRPD showed evidence of a mixture of schoepite, calcium uranate and potassium diuranate. Modelling supported these findings and also predicted the presence of sodium diuranate.

A study of ageing of the precipitates formed by uranium at high pH showed an increase in crystallinity in most cases, especially that of schoepite, where uranium monohydrate is amorphous and ages to form the more crystalline uranium dihydrate (schoepite). Ageing studies were also performed at 40°C and 60°C in the case of schoepite. These results indicated a decrease in the crystallisation of schoepite over time with increasing temperature. This ageing phenomenon is probably due to the instability of schoepite above 40°C [118]. A decrease in crystallinity with increasing temperature is also a characteristic of polymeric amorphous materials and since the thermodynamics of the precipitate mostly reflect that of the mother liquor, it may be evidence of polymeric uranium hydroxide species in favour of monomeric species.
Three stages of vault life have been identified: (a) primary aerobic, (b) anaerobic and (c) secondary aerobic in which radionuclide mobility is dependent on sorption by cementitious material. The solubility, complexation and speciation of uranium has been examined in each of these stages.

The solubility of uranium at high pH under both aerobic and anaerobic conditions has been investigated together with the effect of complexing ligands. Modelling using the MINTEQA2 speciation code [12] and the HATCHESv10 database [29] has been used to compare experimental results. In some cases, predictive modelling was used, while in others, model fitting of experimental results was undertaken. In each case, modelling was used in order to explain the speciation and complexation of uranium and where fitting has been used, new formation constants are proposed.

Modelling of uranium(VI) at high pH could only be reproduced when monomeric uranyl hydroxides, namely $\text{UO}_2(\text{OH})_2$ and $\text{UO}_2(\text{OH})_3^-$ were removed from the database. Inclusion of these species predicted that a precipitate would not be formed, which was in direct disagreement with experimental results. Once these species were removed, the major uranyl species was found to be $(\text{UO}_2)_n(\text{OH})_n^-$ and the solid phases were predicted. The use of such monomeric hydroxide species should be limited only to uranium concentrations less than $10^{-5}$ M. The compositions of these solid phases were better understood by modelling of the carbonate complexation and dissolution of the precipitates. The findings were supported by experimental XRPD evidence.

At high pH, uranium solid phases are present and aqueous species are in the form of very stable polymeric hydroxides (i.e. $(\text{UO}_2)_n(\text{OH})_n^-$). Of the ligands studied, several were found to complex uranium and therefore dissolve uranium precipitates even at high pH, namely carbonate, phosphate, citrate, EDTA, NTA, HA, FA and ISA. In the cases of the addition of citrate, HA, FA and ISA to uranium precipitates, experimental results could only be modelled by means of a mixed hydroxy species. Formation constants for each new species are proposed and these
are detailed in table 8.1. Derivation of a new species is based on fitting the experimental dissolution profiles in which the gradient is used to identify the best-fit stoichiometry. The formation constant is calculated by exact fitting of experimental points in the profile and the point at which complete dissolution is achieved. In the case of unacceptable changes to literature formation constants, a mixed species was assumed. Although there is no experimental evidence for such mixed citrate complexes, there is evidence of U(OH)HA and An(OH)ISA complexes as well as (UO₂)₂(OH)₃CO₃. Alternatively, in the case of citrate and ISA, deprotonation of the ligand at the hydroxyl groups was postulated and formation constants were again determined by trial and error fitting of experimental results.

<table>
<thead>
<tr>
<th>Species Proposed</th>
<th>Formation Constant, logKᵢᵢ, for I=0</th>
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</thead>
<tbody>
<tr>
<td>K₂U₂O₇(s)</td>
<td>26.8</td>
</tr>
<tr>
<td>UO₂(SO₄)₂(OH)⁺</td>
<td>7.2</td>
</tr>
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<td>UO₂(OH)Citrate⁻ or UO₂(Cit⁻)²⁻</td>
<td>5.05</td>
</tr>
<tr>
<td>UO₂(NTA)₂⁻</td>
<td>19.5</td>
</tr>
<tr>
<td>UO₂(OH)FA</td>
<td>3.6¹</td>
</tr>
<tr>
<td>UO₂(OH)ISA or UO₂(ISA₃⁻)</td>
<td>5.7</td>
</tr>
<tr>
<td>Hydrated UO₂ (am)</td>
<td>-5.2</td>
</tr>
<tr>
<td>U(OH)₅⁻</td>
<td>-21.0</td>
</tr>
<tr>
<td>U(Citrate)₂(OH)⁺ or U(Citrate⁺)₂⁺</td>
<td>32.3</td>
</tr>
<tr>
<td>UEDTA(aq)</td>
<td>31.4</td>
</tr>
<tr>
<td>U(NTA)₂⁻</td>
<td>35.7</td>
</tr>
<tr>
<td>U(OH)₂ISA₂(aq) or U(ISA⁻)₂(aq)</td>
<td>10.3</td>
</tr>
<tr>
<td>or U(ISA⁺)₂(aq)</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table 8.1 Additional Uranium Species and Formation Constants Proposed to Fit Experimental Dissolution Profiles of Uranium Precipitates at High pH

¹ FA is Drigg site-specific
In most cases, predictive modelling showed good correlation with experimental results. In the cases of carbonate, phosphate and NTA addition to uranium(VI) precipitates, the calcium concentration in the modelled grout leachate had to be reduced in order to fit experimental data. This behaviour may be due to the composition of the grout leachate with its higher concentrations of sodium and potassium. This may imply that rapid precipitation of sodium- and potassium-diuranates would be because of the excessive sodium and potassium concentrations with respect to calcium. This could reduce the actual amount of calcium uranate precipitation. The experiments are performed over a relatively short time period when compared to the time scale of vault lifetime, or final equilibrium assumed by thermodynamic speciation models. Over longer timescales, it may be that the solid phases change very slowly to become the most thermodynamically stable phase.

Anaerobic conditions were achieved by using sodium dithionite at high pH and this system was used to investigate the solubility and complexation of uranium(IV). The uncharacterised U(IV) solid phase was designated as a hydrated $\text{UO}_2^{2+}$ precipitate and a formation constant $\log K_f$ equal to -5.2 was determined by modelling experimental solubilities. An increase in uranium solubility was observed at higher pH and this was attributed to the formation of a pentahydroxide species, $\text{U(OH)}_5^-$. A formation constant was determined by modelling experimental results, yielding $\log K_f = 21.0$. This value can be compared to that published by Rai et al [82] of $\log K_f = -22.7$.

The effect of complexing ligands was investigated to mirror that of aerobic studies. Again, certain ligands are able to complex U(IV) and redissolve the uranium precipitate (namely carbonate, phosphate, citrate, EDTA, NTA and ISA). Of these ligands, several new species and formation constants were proposed in order to model experimental results, and are detailed in Table 8.1.
The sorption of uranium onto grout material has been investigated at high pH. The grout material was found to have a negative surface charge with a point of zero charge (pH$_{pzc}$) of 2.3 which was determined by microelectrophoresis. This value can be compared with that of silicates (pH$_{pzc} = 2$) and feldspar (pH$_{pzc} = 2.0 - 2.4$), while examination of the chemistry of the grout material shows evidence of silicates and Feldspar. Adsorption isotherms have been investigated and show favourable sorption of uranium onto the grout material and evidence of attractive forces between uranium molecules at the grout surface. This can be explained in terms of oligomeric complexes being formed between uranium ions at the grout surface and this has been supported by extended X-ray absorption fine structure (EXAFS) of uranium adsorbed onto silicate minerals [132]. Sorption has been defined in terms of linear, Freundlich, Langmuir and Frumkin isotherms, with sorption coefficients determined in each case. At the low uranium concentrations used in sorption experiments (μM), uranium is most likely to be present as monomeric hydroxides such as UO$_2$(OH)$_3$ and UO$_2$(OH)$_4$.

The effect of complexing ligands on the desorption of uranium from Drigg grout material at high pH was also investigated and modelled. The results show that some ligands (carbonate, sulphate, chloride, citrate, acetate, EDTA, NTA, humic acid and fulvic acid) are able to desorb uranium from the grout material, while others do not (phosphate and iso-saccharinic acid). There is evidence that ISA sorbs to cement [76] and therefore is unable to desorb uranium. The modelling of the addition of phosphate to uranium which had been sorbed onto grout material predicted uranium desorption by complexation. This was in disagreement with experimental results which indicated a slight increase in sorption and the formation of a milky white precipitate. This was explained in terms of the formation of a precipitate (hydroxyapatite, Ca$_5$(PO$_4$)$_3$OH) and co-precipitation of uranium ions by inclusion in the hydroxyapatite precipitate. Modelling of other desorption experiments in terms of pure complexation alone showed poor correlation with experimental results. In most cases, modelling could only be performed either by unacceptable changes to formation constants or by invoking new species (especially mixed ligand-hydroxide
species) to account for desorption at a given ligand concentration. This inability to predict uranium desorption suggests that mechanisms other than that of uranium complexation are responsible. Such mechanisms are possibly (a) the competition for sorption sites between uranium and the added ligand or, (b) the degradation of the grout material, for example in the case of EDTA which has a known affinity for calcium. The use of speciation modelling in this chapter is only to serve as evidence against simple complexation of uranium for desorption by ligand addition.

Overall, this work has added to the knowledge-base required for the site characterisation of Drigg Vault 8 and the source term for uranium. It has been shown that certain complexing ligands, if available, can complex with uranium aerobically and anaerobically, perhaps leading to the solubilisation of uranium within the waste material. The work also serves to prove that modelling of complex systems such as uranium at high pH in cementitious waters is inherently difficult to predict. Investigative experiments should always be performed where possible to support the inclusion of species and solid phases in a database, and to support model predictions.
CHAPTER NINE

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Appendix One

Thermodynamic Data Used in Modelling Uranium Solubility and Complexation
<table>
<thead>
<tr>
<th>Formula</th>
<th>Reactants (Master Species)</th>
<th>Formation Constant, logKf</th>
<th>Database Reference</th>
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<td>Aqueous Species</td>
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<tr>
<td>UO$_2^{2+}$</td>
<td>U$^{+}$ + 2 H$_2$O - 4 H$^-$ - 2 e$^-$</td>
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<td>UO$_2$OH$^-$</td>
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<td>19, 29</td>
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<td>19, 29</td>
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<td>(UO$_2$)$_2$(OH)$_2^{2+}$</td>
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<td>19, 29</td>
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<td>(UO$_2$)$_2$OH$^{1+}$</td>
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<td>19, 29</td>
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<td>(UO$_2$)$_2$(OH)$_3^{2+}$</td>
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<td>(UO$_2$)$_2$(OH)$_4^{3+}$</td>
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<tr>
<td>(UO$_2$)$_3$(OH)$_2^{3+}$</td>
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**Solid Phases**

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Notes: \(^{1}\) Monomeric hydroxides, UO_{2}(OH)_{i}^{-} and UO_{2}(OH)_{2}^{2-}, only used for low-level uranium speciation (e.g. sorption studies). \(^{1}\) HATCHESv8
Appendix Two

Carbonate Induced Dissolution of Uranium Containing Precipitates Under Cement Leachate Conditions
Carbonate induced dissolution of uranium containing precipitates under cement leachate conditions

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The effects of carbonate on uranium (vi) solubility under aerobic and cementitious conditions have been investigated. The information is of relevance to low level nuclear waste disposal. Aqueous NaOH, KOH, Ca(OH)2 and a cement leachate solution were added to uranyl nitrate solution. Afterwards, increasing amounts of ammonium carbonate were added to re-dissolve the precipitates. The precipitates were characterised by means of X-ray powder diffraction (XRPD) measurements and modelling studies. The model calculations were performed using the MINTEQA2 speciation code, with an expanded database incorporating uranium stability constants taken from the HATCHES database. The measured and predicted amounts of CO32- needed to dissolve the precipitates were compared. The knowledge gained from the 'pure' systems was used to rationalise the precipitation and re-dissolution behaviour observed in the leachate system. The lack of uranium solubility at low carbonate levels brought into question literature formation constants for UO2(OH)3 and UO2(OH)32-. An approximate log K value of 26.8 for K2U2O5 formation was estimated from the KOH results at pH 12. Generally, uranium solubilities are expected to be insignificant at low level nuclear waste sites because anaerobic conditions should persist.

However, this study has demonstrated that solubility in leachate could rise at high pH and high carbonate levels, if aerobic conditions were to develop. Soluble U(vi) species would be formed. The novel part of the study has been to reproduce the effects and to correlate enhanced solubilities with model predictions. Consequently, the study has re-emphasised the need for appropriate environmental monitoring of such sites.

1 Introduction

Conditions such as pH and Eh in low level nuclear waste repositories will evolve. Steel will corrode, organic waste will degrade and cementitious materials, if present, will partially dissolve. The effects of such changes on radionuclide solubilities in ground and surface waters must be predicted.

Microbial degradation of organic waste produces CO2 and CH4. However, cementitious materials, if present, will undergo partial dissolution creating alkaline conditions; CO2 will then dissolve. The resulting carbonate/bicarbonate systems will encourage dissolution of actinides. Complex carbonato species could form.

Accordingly, the first aim of this study was to measure the levels of carbonate needed to re-solubilise uranium(vi) solids, precipitated under conditions relevant to waste disposal in cementitious environments. Aerobic studies were undertaken because such conditions could arguably arise at the outset or later in a repository, after the organic waste has degraded and aerated water has re-infiltrated the site. Under anaerobic conditions, highly insoluble uranium(iv) dioxide would be formed so re-solubilisation would be minimal.

Uranium(vi) precipitates were produced in NaOH, KOH, Ca(OH)2 and cementitious grout leachate solutions, then treated with increasing amounts of ammonium carbonate to effect re-dissolution. The grout leachate was used to approximate real conditions. The eutectitic grout is used as a backfill for low level radioactive waste. The experiments were carried out at selected pH values in the range 9–12.

The second major aim of the study was to identify the precipitates formed in the 'pure' NaOH, KOH and Ca(OH)2 systems. Two approaches were used. In the first, the precipitates were investigated using the X-ray powder diffraction (XRPD) technique and, in the second, the dissolution effects of carbonate were compared with predicted effects. The predictions were made using the MINTEQA2 speciation model, augmented with stability constants taken from the HATCHES database. The complete uranium database used is given in Table 1.

The final aim of the study was to use the knowledge gained from the 'pure' systems to rationalise and model the dissolution behaviour observed in the grout leachate system. Of course, the hydrolytic behaviour of uranium and its complicated reactions with carbonate have received a great deal of attention over the years. However, investigations have generally been confined to low carbonate concentrations, at low CO2 partial pressures (Pco2) and low pH values. For example, Ciavatta et al.14 experimented at pH = 2.95–4.88, whilst Malya15 operated at pH = 4.87–8.41 and a Pco2 value between 10-3 and 10-12 atm. Kramer-Schnabel et al.16 employed pH = 3.63–5.71 and a Pco2 range of 10-5–10-11 atm. Meinrath et al.17 used pH = 4.75 and Pco2 = 10-6 to 10-13. The topic has been reviewed by Grenthe et al.7

Of more direct relevance to this study, the work of Brownsword et al.18 may be cited. These workers conducted a uranium solubility study, using water equilibrated with an ordinary Portland cement (OPC) and pulverised fly ash (PFA) mixture, at pH = 11–12, but they purposely used nitrogen glove boxes to exclude CO2 to avoid uranium carbonate complexation. In the pH range 9–10, the uranium solubility was found to be between ~10-5 M and ~10-6 M when sodium uranate was the solubility limiting phase, and ~10-4 M when calcium uranate was the solid phase. Similarly, Baston et al.19 who studied uranium solubility over the range pH = 4–13 in a cement leachate system, noted uranium solubilities of ~8 x 10-6 M for pH 9 and ~7 x 10-7 M for pH = 10–11, but again the carbonate concentration was only 2.2 x 10-5 M.
Finally, Heath et al., 20 using an OPC/BFS (blast furnace slag) mixture, reported a uranium concentration of ~1 x 10^-6 M at pH = 10, but again under negligible PCO2 conditions. Clearly, further solubility studies at higher carbonate concentrations were warranted.

2 Experimental

2.1 Equipment

pH values were determined using a ROSS combination electrode (Orion Research, Quadramchem, Forest Row, East Sussex, UK) and a digital pH meter (model 720A, Orion Research). The pH meter was calibrated with commercial buffers at pH values of 4.0, 7.0 and 10.0. The accuracy at high pH was confirmed by measuring the pH of a mixture comprising 6 cm³ of 0.2 M NaOH and 25 cm³ of 0.2 M KCl known to possess pH values of 4.0, 7.0 and 10.0. The accuracy at high pH was

2.2 Preparation of radiochemically purified uranium solutions

Uranium was purified radiochemically by removing thorium and protactinium decay products from uranyl nitrate hexahydrate using ion exchange. A column packed with Amberlite IR-120 cation exchange resin (BDH/Merck, Lutterworth, Leics., UK) was prepared (length= 30 cm, internal diameter= 2 cm) and washed with 200 cm³ of 5 M hydrochloric acid followed by 1000 cm³ of deionised water. The purified uranyl nitrate (250 cm³ of a 0.02 M solution) was added and Pa was removed by elution with 100 cm³ of HCl acid (0.5 M). The uranium was then eluted with 100 cm³ of hydrochloric acid (4 M). The thorium remained on the column. The resulting uranium solution was reduced in volume using a rotary evaporator and allowed to crystallise. The resulting crystals were re-dissolved in 4 M nitric acid, and the crystallisation was repeated once in 4 M nitric acid and twice in deionised water. The purified uranyl nitrate was dissolved in deionised water and used as required.

2.3 Determination of uranium(vi) using arsenazo-iii colorimetric reagent

The method of uranium determination was based on the arsenazo-iii (AAIII) method described by Saveni.22 Stock AAIII solution (2.5 mM) was prepared by dissolving the solid (205 mg, Fluka, Gillingham, Dorset, UK) in deionised water (100 cm³), containing a few drops of 0.2 M nitric acid and 0.5 g sodium acetate at pH 2.5. The stock was stored in amber coloured glass bottles. For each determination, the sample solution was filtered through 0.2 µm Acrodisc syringe filters (Gelman Sciences, Northampton, UK). Then AAIII solution (0.35 cm³) was added to the filtrate before adjusting the volume to 10 cm³ using deionised water. After standing for ten minutes, the absorbances of the U-AAIII complexes were measured at 655 nm. Calibration plots were produced using standard uranium solutions and subjecting them to the same

Table 1 Formation constants for aqueous species and minerals used in MINTEQA2 modelling of uranium solubility and speciation

<table>
<thead>
<tr>
<th>ID number</th>
<th>Species</th>
<th>Formula</th>
<th>Reactants</th>
<th>Formation constant, log Kf</th>
<th>Reference</th>
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<tr>
<td>893</td>
<td>Aqueous species</td>
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<td>U^4+ + 2H2O</td>
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<td>8930030</td>
<td>HCO3^-</td>
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<td>+H^+</td>
<td>HCO3^-</td>
<td>10.33</td>
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<tr>
<td>8930030</td>
<td>UO2(CO3)4^-</td>
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<td>+3CO3^-</td>
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<td>8930030</td>
<td>UO2OH^-</td>
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<td>+H2O</td>
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<tr>
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<td>UO2(OH)(aq)</td>
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</tr>
<tr>
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<td>UO2(OH)3(CO3)^^-</td>
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<td>+5H2O</td>
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<td>UO2(CO3)2^-</td>
<td>UO2^-</td>
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<td>16.94</td>
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Minerals

<table>
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<tr>
<th>ID number</th>
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<th>Reactants</th>
<th>Formation constant, log Kf</th>
<th>Reference</th>
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<td>+3H2O</td>
<td>-6H^-</td>
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<tr>
<td>20899302</td>
<td>UO2(OH)2</td>
<td>UO2^-</td>
<td>+H2O</td>
<td>-2H^+</td>
<td>4.94</td>
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<td>20899303</td>
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<tr>
<td>5015004</td>
<td>U2O7</td>
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<td>+4H2O</td>
<td>-4H^-</td>
</tr>
<tr>
<td>9989304</td>
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<td>Na2UO4</td>
<td>+2Na^+</td>
<td>+2H2O</td>
<td>-2H^-</td>
</tr>
<tr>
<td>20899305</td>
<td>K2UO4</td>
<td>K2UO4</td>
<td>+2K^+</td>
<td>+3H2O</td>
<td>-4H^-</td>
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<tr>
<td>20899306</td>
<td>CaU2O7</td>
<td>CaU2O7</td>
<td>+2Ca^2+</td>
<td>+3H2O</td>
<td>-6H^-</td>
</tr>
<tr>
<td>5015000</td>
<td>Ca2(UO2)2</td>
<td>Ca2(UO2)2</td>
<td>+2Ca^2+</td>
<td>+3H2O</td>
<td>-6H^-</td>
</tr>
<tr>
<td>5015000</td>
<td>Ca(UO2)2</td>
<td>Ca(UO2)2</td>
<td>+Ca^2+</td>
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<td>-4H^-</td>
</tr>
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<td>5015000</td>
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<td>+CO3^-</td>
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<td>Ca3(OH)2CO3</td>
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<tr>
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<td>Ca(OH)2</td>
<td>+2Ca^2+</td>
<td>+2H2O</td>
<td>-2H^-</td>
</tr>
</tbody>
</table>

*Removed from model. *Estimated to model KOH pH 12 system.
procedures as the samples. The plots were used to determine the uranium concentrations in the dissolved samples.

2.4 Preparation of the cementitious grout leachate solution

A cementitious grout, kindly supplied by BNFL plc (Seascale, Cumbria, UK), was leached with water. A suitable amount of grout (25 g) was contacted with deionised water (250 cm³) in a sealed glass flask for 4 days until the pH became constant at 11.8. Then, the resulting suspension was filtered (0.45 μm membrane, Gelman Sciences), and analysed for major cations and anions. The concentrations of the major cations were determined by ICP-MS [VG-Elemental (Winsford, Cheshire, UK) PlasmaQuad 2+, 1000 °C] and major anions by ion exchange chromatography ( Dionex, Sunnyvale, CA, USA). The results are given in Table 2.

2.5 X-Ray powder diffraction (XRPD) measurements

Uranium containing precipitates were prepared by adding NaOH and KOH solutions in turn to aliquots of uranyl nitrate solution, at pH values of 9, 10, 11 and 12. After three days aging, the precipitates were filtered off, using 0.2 μm membranes, washed with deionised water, stored in a desiccator for 2 weeks, then powdered and analysed by XRPD.23 Precipitates were formed in Ca(OH)₂ solution at the same pH values but, for reference purposes, because mixed precipitates were always formed, a solid was prepared by mixing the uranyl nitrate solution with calcium nitrate solution at pH 5.5.

2.6 Dissolution tests

The initial series of tests was performed in aqueous NaOH. The alkali was added to uranyl nitrate solution (5 cm³ aliquots of 1 x 10⁻² M UO₂⁺ ions). Precipitates were produced at pH values of 9.0, 10.0, 11.0 and 12.0, in four series of duplicated glass vials. The vials were sealed to prevent ingress of atmospheric carbon dioxide and the precipitates were allowed to age for 3 days. Increasing aliquots of ammonium carbonate solution, in air-free deionised water, were subsequently added to each series of vials to give carbonate concentrations ranging from 1 x 10⁻⁴ to 0.1 M. The pH values were maintained by the addition of fresh aqueous NaOH and the final volumes were brought to 10 cm³ by adding deionised, degassed water. Immediately after treatment, each vial was resealed and the contents left for a further 24 h. The resulting mixtures were filtered using 0.2 μm Acrodisc syringe filters and the filtrates were analysed for uranium using the AAIII method and the leachate solution for the cement system.

Table 2 Analytical data obtained for the cementitious grout leachate solution

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration/mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>41.13</td>
</tr>
<tr>
<td>K⁺</td>
<td>91.28</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>19.25</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.01</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.00</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.31</td>
</tr>
<tr>
<td>CO₃⁻</td>
<td>0.13</td>
</tr>
<tr>
<td>pH</td>
<td>11.77</td>
</tr>
</tbody>
</table>

3 Results and discussion

3.1 Identification of the precipitates formed in the 'pure' NaOH, KOH and Ca(OH)₂ systems using X-ray powder diffraction (XRPD)

The XRPD patterns of the precipitates formed at pH values of 9 and 10 in the NaOH system showed broad peaks at 7.4 Å. However, both uranyl hydroxide (UO₂(OH)) and schoepite (UO₂.2H₂O) give peaks in this region and no distinction between the two solid phases was possible. At pH 11 and 12, a peak at ca. 6.0 Å indicated the presence of sodium diuranate (Na₂U₂O₇). However, the possibility of the precipitate being a mixture of UO₂.2H₂Oβ-U₂O₇(OH)₂ and Na₂U₂O₇ could not be dismissed. All the X-ray diffraction patterns were 'noisy' due to the amorphous nature of the precipitates.

The XRPD patterns of the precipitates formed in KOH at pH values of 9 and 10 were identical to those in NaOH but, at higher pH values of 11 and 12, a peak was observed at 6.6 Å indicating the presence of another species, probably either K₂UO₄ or K₂U₂O₇.

The precipitate formed at pH 9 using Ca(OH)₂ showed the usual peak at 7.4 Å but, at pH values of 10–12, the peak moved to 7.7 Å indicating CaUO₄ or Ca₂U₃O₇ formation. The precipitate produced at pH 5.5 gave a similar pattern. However, Linklater et al.24 state that high temperatures are needed to produce the high crystallinity of calcium uranate and Berner25 states that calcium uranate would not be stable in hyperalkaline cement pore waters.

The XRPD patterns of the precipitates formed in the cement leachate system could not be resolved.

An aging test was carried out on the precipitate produced at pH 9.0 in the NaOH system. Over 8 weeks, the peaks narrowed, but their positions did not alter. The observations indicated that the precipitate was becoming more crystalline, but not changing chemically.

3.2 Measurement of the levels of carbonate needed to re-solubilise uranium (VI) precipitates

The dissolution behaviour of each precipitate, as a function of added CO₃²⁻ concentration, is presented graphically in Fig. 1.
Fig. 2 The effect of added carbonate on the dissolution of uranium precipitates formed at pH values of (a) 9, (b) 10, (c) 11 and (d) 12 in KOH solution. Solid diamonds represent experimental results. The curves at pH 9 and 10 are composite predictions; the curves at pH 11 and 12 are fitted. Important solid phases within the MINTEQA2 model were \(\beta\)-\(\text{UO}_2(\text{OH})_2\), \(\text{UO}_2\cdot2\text{H}_2\text{O}\), \(\text{K}_2\text{UO}_4\) and \(\text{K}_2\text{U}_2\text{O}_7\).

Fig. 3 The effect of added carbonate on the dissolution of uranium precipitates formed at pH values of (a) 9, (b) 10, (c) 11 and (d) 12 in Ca(OH)\(_2\) solution. Solid diamonds represent experimental results. The curves are MINTEQA2 predictions in which model \(\beta\)-\(\text{UO}_2(\text{OH})_2\), \(\text{UO}_2\cdot2\text{H}_2\text{O}\) and \(\text{CaUO}_4\) were simultaneously considered as possible solid phases.

Figs. 1–4. From the plots, the minimum amounts of added \(\text{CO}_3^{2-}\) needed to dissolve the precipitates completely were estimated. These 'experimental' values are presented alongside the predicted values (see below) in Table 3.

It may be noted that complete dissolution was not achieved in any system at pH 12 nor in the Ca(OH)\(_2\) system at pH 11. In these cases, the MINTEQA2 predicted values are presented alone. The higher pH values could not be maintained with increasing amounts of added ammonium carbonate. The weakly basic \(\text{NH}_4^+\) ions affected the hydroxide concentration. The higher pH values could have been reached using NaOH or KOH, but common ion effects would have been introduced, affecting the speciation.

In the NaOH system, the amount of added \(\text{CO}_3^{2-}\) needed to effect complete dissolution increased significantly at pH 11, suggesting a change in the solid phase.

In the KOH system, no significant change was noted up to and including pH 11.

In the Ca(OH)\(_2\) system, steps were observed in the dissolution profiles (Fig. 3), which clearly indicated that the precipitates were mixtures of two components with considerably different solubilities. The amount of \(\text{CO}_3^{2-}\) required for complete dissolution at pH 10 exceeded that required at pH 9.

The grout system showed stepped dissolution profiles, similar to the Ca(OH)\(_2\) system, but the steps were not so well defined.

3.3 Identification of the precipitates formed in the 'pure' NaOH, KOH and Ca(OH)\(_2\) systems from the MINTEQA2 model predictions

Speciation models assume the attainment of equilibrium, whereas rapid precipitation reactions often give amorphous precipitates. Also kinetics may influence solid phase composition with effects which may not be nullified even by aging. However, following a choice regarding the important aqueous species, only one discrepancy between the initially predicted and observed precipitation/re-dissolution patterns was noted (see below).

The correlation between predictions in the NaOH system and experimental observations can be seen in Fig. 1. All relevant solid phases were included as 'possible' solids, but only \(\text{UO}_2\cdot2\text{H}_2\text{O}\) and \(\text{Na}_2\text{U}_2\text{O}_7\) were found to be important. At pH values of 9.0 and 10, the solid modelled as 100\% \(\text{UO}_2\cdot2\text{H}_2\text{O}\) but, at pH 12, as 100\% \(\text{Na}_2\text{U}_2\text{O}_7\). At pH 11, the proportions were 53\% \(\text{UO}_2\cdot2\text{H}_2\text{O}\) and 47\% \(\text{Na}_2\text{U}_2\text{O}_7\). It may be noted that \(\text{Na}_2\text{U}_2\text{O}_7\) modelled as undersaturated even in the absence of carbonate. The predicted changes reflected the XRPD evidence. The solid phase composition is summarised in Table 4.

The KOH system (Fig. 2), at pH values of 9 and 10, also provided experimental results which correlated with predictions. The solid phase was \(\text{UO}_2\cdot2\text{H}_2\text{O}\). However, at pH values of 11 and 12, the XRPD data suggested an additional solid
Table 3 Experimental and modelled concentration of added carbonate required to re-dissolve a 5 mM uranium precipitate at pH 9, 10, 11 and 12 in NaOH, KOH, Ca(OH)₂ and grout leachate (pH 11.8)

<table>
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<tr>
<th>Carbonate concentration (mM)</th>
<th>pH 9.0</th>
<th>pH 10.0</th>
<th>pH 11.0</th>
<th>pH 12.0</th>
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<tr>
<td></td>
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<td>Model</td>
<td>Expt</td>
<td>Model</td>
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<td>14</td>
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<tr>
<td>KOH</td>
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<td>15</td>
<td>14</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
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<td>40</td>
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<td>90</td>
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<tr>
<td>Grout leachate</td>
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<td>45</td>
<td>66</td>
<td>60</td>
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Table 4 Percentage modelled composition of uranium precipitates at pH 9, 10, 11 and 12 in NaOH, KOH, Ca(OH)₂ and grout leachate

<table>
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<td>CaUO₄</td>
<td>70</td>
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*pH = 11.8 for grout leachate.

The dissolution of uranium containing precipitates in the cement leachate system at pH values of 9, 10, 11 and 11.8 is shown graphically in Fig. 4. The dominant aqueous species were UO₂(OH)₂⁻ and UO₂(OH)₄²⁻. It is concluded that either the literature formation constants for these species were too large or kinetic effects were hindering their formation. Certainly Grenthe states that, at high uranium concentrations, polymeric species such as (UO₂)₃(OH)₇⁻ are more likely to form than monomeric species such as UO₂(OH)₃⁻.

3.4 Rationalising the dissolution behaviour of the precipitates formed in the grout leachate system

The dissolution of uranium containing precipitates in the cement leachate system at pH values of 9, 10, 11 and 11.8 is shown graphically in Fig. 4. The dominant aqueous species were UO₂(OH)₂⁻ and UO₂(OH)₄²⁻. It is concluded that either the literature formation constants for these species were too large or kinetic effects were hindering their formation. Certainly Grenthe states that, at high uranium concentrations, polymeric species such as (UO₂)₃(OH)₇⁻ are more likely to form than monomeric species such as UO₂(OH)₃⁻.

4 Conclusions

This study has contributed to the knowledge base needed for nuclear waste risk assessment. The processes involved in the aerobic dissolution of uranium(vi) have been highlighted. With the exception of the KOH system at pH 11, the precipitates in the 'pure' systems and their dissolution patterns were predicted using solubility product principles alone. In the cementitious grout leachate system, kinetics appeared to influence the results. CaUO₄ formation was not quantitative. Problems associated with CaUO₄ formation cited earlier may have been involved in the leachate system. 24, 25 Of course, in
waste repositories fully equilibrated outcomes are likely since the changes will be slow.

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References

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