Iron Oxyhydroxide Formation in the Enhanced Actinide Removal Plant

A thesis submitted to the University of Manchester for the degree of Doctor of Philosophy in the Faculty of Science and Engineering.

2017

Joshua S Weatherill
School of Earth and Environmental Sciences
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<td>Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy</td>
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<td>BET</td>
<td>Brunauer-Emmett-Teller method of specific surface area analysis</td>
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<td>Bq</td>
<td>Becquerel, SI unit of radioactivity defined as one nuclear decay per second</td>
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<td>Scanning Transmission Electron Microscopy</td>
</tr>
<tr>
<td>STP</td>
<td>Solvent Treatment Plant</td>
</tr>
<tr>
<td>TBP</td>
<td>Tri-butyl phosphate</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
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<tr>
<td>THORP</td>
<td>Thermal Oxide Reprocessing Plant</td>
</tr>
<tr>
<td>WPEP</td>
<td>Waste Package Encapsulation Plant</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray Absorption Near Edge Spectroscopy</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray Absorption Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>ZPC</td>
<td>Zero Point of Charge</td>
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<tr>
<td>$\epsilon$</td>
<td>Aggregate weighting factor (in SAXS modelling)</td>
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Thesis Abstract

The Enhanced Actinide Removal Plant (EARP), located on the Sellafield site, is one of the UK’s most crucial radioactive effluent treatment plants. EARP removes actinides and select fission products from routine reprocessing effluents by association with a ferric iron oxyhydroxide floc, which is precipitated from acidic effluent streams by the addition of NaOH. The effluent compositions that EARP receives will change in character as the Sellafield site transitions from its current routine reprocessing operations to post-operational clean-out and accelerated decommissioning activities over the next few years. An enhanced understanding of the iron oxyhydroxide formation processes occurring in EARP would help underpin optimisation of current plant efficiency and allow better prediction of changes in efficiency as effluent composition varies.

In this study, iron oxyhydroxide formation, properties and evolution with time under EARP-relevant conditions were characterized. These processes were investigated in a pure ferric nitrate system and systems with added sulfate, phosphate and boric acid using a range of techniques including SAXS, TEM and FTIR. In all the experimental systems the iron oxyhydroxide floc was composed of nanoparticulate ferrihydrite aggregated into extensive mass fractal structures. In situ SAXS experiments showed that formation proceeded via a precursor cluster pathway whereby Fe(III) clusters ~0.45 nm in radius form rapidly at pH 0.12 – pH 1.5 upon dropwise addition of strong NaOH to the acidic effluent simulants. Further analysis indicates these clusters are Fe$_{13}$ Keggin clusters, which have previously been shown to be an important structural motif in the ferrihydrite structure. With further pH increase, cluster aggregation occurs along with precipitation of low molecular weight Fe(III) species (mostly monomers), leading to formation of ferrihydrite nanoparticles which preserve the Keggin cluster in the core. Phosphate, sulfate and boric acid exhibit varying interactions with the solid phase throughout the formation process, with both inner and outer sphere adsorption observed for different species. Ageing experiments show that the ferrihydrite floc readily undergoes transformation leading to predominantly hematite formation, except in the presence of phosphate (concentrations > 10 ppm) where transformation is entirely inhibited due to phosphate adsorption to the floc. These results progress the fundamental understanding of the iron oxyhydroxide formation and ageing processes occurring in EARP.
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Acknowledgements

A special thank you to my supervisors, Sam Shaw and Kath Morris, for their consistent support and brilliant guidance throughout my PhD; for their invaluable insight; for steering my personal development; and for improving my confidence in my own work. I also thank Sellafield Ltd. and the University of Manchester for providing funding and giving me the opportunity to undertake this research project.

I am in gratitude to the following colleagues: Pieter Bots for sharing his extensive knowledge; John Waters for helping with XRD and BET analysis; Paul Lythgoe for undertaking all the ICP-AES analysis; Arne Janssen for his supreme TEM skills; Liam Abrahamsen for invaluable help with PHREEQC; Richard Blackham and Simon Kellet for guidance on EARP and Sellafield; Heath Bagshaw for training and TEM support; and Oliver Street for answering every random question I ever had.

I would like to thank my friends. Thank you to the Geomicro research group for being a friendly and fun bunch. A special mention to Hannah and Edwin for being my office buddies over these past four years - you made coming into work more enjoyable. In particular, I thank Hannah for your listening ear and willingness to help and Edwin for your extraordinary generosity and banter. Also a special mention to Ellen for being my EARP buddy and sharing ideas. Thank you to Daisy for being a caring, cheerful and irreplaceable flat mate these past three years: a friendship surviving three moves, an evil landlord, and your constant hair shedding has to be a good one. I thank Oz for sharing a significant portion of my Manchester life and making it more fun, supportive and loving. Thank you to Fay, Rachael and Sarah for staying in contact and keeping alive a set of friendships I value so much.

Finally, I thank my family, without whom this would not have been possible. In particular Mum for loving counsel and listening to my regular moaning, Dad for indispensable advice and support, Alice and Caroline for being much better at messaging than I am (I appreciate it), Granny for regular letter updates, and Grandad for all the good times.
About the Author

The author graduated from The University of East Anglia with a first class BSc (Hons) in Environmental Chemistry, which included a year spent studying abroad at The University of British Columbia, Canada. Following this, the author spent three months working as a Geoenvironmental Engineer at Harrison Environmental, a land investigation company, before enrolling at The University of Manchester in The School of Earth and Environmental Sciences, where the work reported in this thesis was undertaken. In addition to the work reported here, the author also undertook a six month research project funded by the Environmental Radioactivity Network.
CHAPTER 1

Introduction

1.1. Project context

The Sellafield nuclear complex is a nuclear decommissioning and nuclear fuel reprocessing site located on the Irish Sea coast in west Cumbria which has operated as the hub of the UK’s nuclear fuel cycle activities for 60+ years. It is the largest nuclear site in Europe and has been described as the most complicated nuclear site in the world (Temperton, 2016). The Sellafield nuclear licensed site incorporates nuclear reactor sites at Windscale and Calder Hall, both of which are now undergoing decommissioning. Reprocessing of spent nuclear fuel from both UK and overseas reactors is also currently undertaken at Sellafield. As a direct result of reprocessing and decommissioning activities, a variety of radioactive wastes, including a range of effluent wastes, are produced at Sellafield which are treated in a range of processing plants on site. After their radioactivity has been suitably reduced, liquid effluents are ultimately discharged via pipelines to the Irish Sea (Gray et al., 1995).

The Sellafield site is soon to undergo a period of significant change in the main activities conducted there: spent fuel reprocessing will end at Sellafield by 2020 and post operational clean-out (POCO) and decommissioning activities will instead become dominant. This will mean that the effluent feeds generated on site will have fundamentally different compositions to those which are currently produced. The total cost to decommission the entire Sellafield site is currently estimated at ~ £100 billion and is expected to take until 2120 for full site clean-up (Nuclear Decommissioning Authority, 2015).

The Enhanced Actinide Removal Plant (EARP) is an effluent treatment plant at the Sellafield site that currently removes actinides and select fission products from routine reprocessing effluents by association with a ferric iron oxyhydroxide floc. The EARP process works by addition of sodium hydroxide to acidic, iron(III)-rich, radioactive effluent, resulting in the precipitation of an iron oxyhydroxide floc. A range of radionuclides including the actinide elements are incorporated and/or adsorbed to the iron floc, which is subsequently dewatered using ultrafiltration and encapsulated in cement as a wasteform. Although EARP is very efficient and
decontamination factors are routinely high, the types of iron oxyhydroxides formed, the mechanism of floc formation and changes in the floc over time are not well characterised and need further consideration. Additionally, as spent fuel reprocessing ends at Sellafield and the site transitions to decommissioning and POCO activities, EARP will play a vital role in processing non-routine effluents which will have a range of compositions which differ from the standard reprocessing derived effluents. Therefore, a fundamental understanding of the EARP process such that the effects of perturbations from the normal operations are predictable as new decommissioning effluents are treated is crucial.

1.2. Aims and objectives

The aim of this project is to gain a detailed understanding of iron oxyhydroxide floc formation, properties and evolution with time under EARP-relevant conditions. In this way, the project aims to provide molecular scale understanding of the EARP treatment processes and underpin optimisation of current plant efficiency and allow better prediction of changes in efficiency as effluent composition varies. Additionally, this work provides valuable insights into iron oxyhydroxide formation, which is not fully understood, despite the ubiquity of iron oxyhydroxides in both industry and the natural environment.

Three main areas of research were formulated, which were investigated using a range of mineralogical, spectroscopic, geochemical and electron microscopy techniques, including the use of numerous synchrotron-based analyses to provide the in-depth information to develop mechanistic models for formation pathways and evolution.

(i) Iron oxyhydroxide floc formation and floc physiochemical properties in a “pure” ferric nitrate system, i.e. where the EARP effluent simulant was composed of only ferric nitrate dissolved in nitric acid. The EARP process was mimicked in the laboratory using an innovative batch reactor system and samples were taken for characterisation by a variety of techniques including X-ray diffraction (XRD), transmission electron microscopy (TEM) and BET surface area analysis. Synchrotron-based time-resolved small angle x-ray scattering (SAXS) was used to follow floc formation in situ with an aim to characterise the particle formation mechanism and growth processes.
(ii) The effects of additional non-radioactive species on iron oxyhydroxide floc formation and properties, including investigation of the interactions of the added species with the floc. Non-radioactive chemical species can be present at significant concentration in EARP effluent, and their concentrations may vary as new decommissioning effluents are treated by EARP. We characterised the effect of three of the most significant non-radioactive species – phosphate, sulphate and boric acid – on floc formation and properties using a variety of techniques including XRD, TEM, in situ SAXS, Fourier transform infrared spectroscopy (FTIR), solution analysis and geochemical modelling.

(iii) Investigation of the ageing of iron oxyhydroxide floc produced under EARP-relevant conditions. On plant, EARP floc spends approximately four weeks in the ultrafiltration process and can sometimes be left for extended periods of time before being put through ultrafiltration. During this time, the floc is liable to undergo changes which may affect its mineralogical and morphological properties and consequently the floc filterability and radionuclide retention. We investigated changes in the floc mineralogy (e.g. crystallinity, dominant mineral phase) and properties (e.g. particle size, settling behaviour, settled solids volume) with time, including any related re-release of associated species. This included an investigation of the effect of added phosphate, sulfate and boric acid on the ageing process.

1.3. Thesis structure

The bulk of this thesis comprises three research papers covering the three main areas of research detailed above. These papers are preceded by a review of the relevant literature, including an overview of effluent management at Sellafield, and a detailed description of the methodologies used. The thesis ends with a summary and a discussion of future work directions.

Chapter 2: Literature review. An introduction to effluent generation and management at Sellafield, an overview of the Enhanced Actinide Removal Plant (EARP), and a review of the current state of knowledge concerning iron(III) hydrolysis, iron oxyhydroxide formation and ageing is detailed.

Chapter 3: Methodology. Covers all the methods used in this project, including theoretical descriptions and practical details.
Chapter 4: Research chapter. Contains the paper “Ferrihydrite Formation: The Role of Fe$_3$ Keggin Clusters” and associated supporting information. This paper characterises iron oxyhydroxide (i.e. ferrihydrite) floc formation during base hydrolysis of acidified ferric nitrate solution under EARP-like conditions. In situ time-resolved small-angle X-ray scattering (SAXS) experiments were undertaken to follow the floc formation, and were supported by ex-situ X-ray diffraction (XRD), transmission electron microscopy (TEM) and solution analysis techniques.

Chapter 5: Research chapter. Contains the paper “Ferrihydrite Formation via Fe$_3$ Keggin Clusters in the Presence of Sulfate, Phosphate and Boric Acid”. This paper extends the experiments of the first paper to investigate the effects of added phosphate, sulphate and boric acid on the ferrihydrite floc formation process. In addition to the use of SAXS, XRD, TEM and solution analysis, other techniques utilised were pair distribution function (PDF), extended X-ray fine structure spectroscopy (EXAFS), and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR).

Chapter 6: Research chapter. Contains the paper “Ferrihydrite Transformation in the Presence of Sulfate, Phosphate and Boric Acid: Relevance to Radioactive Effluent Treatment.” This paper investigates the mineralogical changes that occur during ageing of the iron oxyhydroxide floc and the effect this has on the physical properties of the floc. The effects of added phosphate, sulfate and boric acid on the ageing process is considered, as well as changes in the interactions of these added species with the iron oxyhydroxide phase with time.

Chapter 7: Conclusions and future work directions. Comprises a summary of the work presented in the thesis and a discussion of possible future work directions.

1.4. Paper status and author contributions

Chapter 4: “Ferrihydrite Formation: The Role of Fe$_3$ Keggin Clusters”, submitted to Environmental Science and Technology in May 2016 and published in August 2016.

J.S. Weatherill Principal author; all experimental work including collection of SAXS, XRD, TEM and solution data; all data analysis.
K. Morris Input to experimental concept; review pre- and post-submission; aided with SAXS data collection; aided with data interpretation.

P. Bots Aided with SAXS data collection and interpretation; review pre- and post-submission.

T.M. Stawski Aided with SAXS data analysis and interpretation.

A. Janssen Aided with TEM data collection and interpretation.

L. Abrahamsen Aided with PHREEQC geochemical modelling.

R. Blackham Provided information about EARP and helped ensure relevance of work to EARP.

S. Shaw Principal supervisor; input to experimental concept; aided with data interpretation; review pre- and post-submission.

Chapter 5: “Ferrihydrite Formation via Fe$_{13}$ Keggin Clusters in the Presence of Sulfate, Phosphate and Boric Acid”

J.S. Weatherill Principal author; all experimental work; all data analysis.

K. Morris Input to experimental concept; manuscript review; aided with SAXS data collection; aided with data interpretation.

P. Bots Aided with SAXS data collection and interpretation.

T.M. Stawski Aided with SAXS data analysis and interpretation.

A. Janssen Aided with TEM data collection and interpretation.

L. Abrahamsen Aided with PHREEQC geochemical modelling.

R. Blackham Provided information about EARP and helped ensure relevance of work to EARP.

G. Burke Aided with TEM data collection.
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<td>M. Florianová</td>
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<tr>
<td>S. Shaw</td>
<td>Principal supervisor; input to experimental concept; aided with data interpretation; manuscript review.</td>
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CHAPTER 2

Literature Review

2.1. Sellafield and the EARP process

2.1.1. Brief history and overview of activities at Sellafield

Sellafield is a nuclear site with a rich history. Located on the Irish Sea coast in West Cumbria, Sellafield has acted as the hub of the UK’s nuclear fuel cycle activities over the past 60+ years (Figure 2.1). The Sellafield site incorporates the original Windscale Piles reactor (1950 – 1957), which were used to produce plutonium-239 for the UK’s first nuclear weapons, and the Calder Hall nuclear power station (1956 – 2003), which was the world’s first commercial nuclear reactor. The site also includes The Windscale Advanced Gas-cooled Reactor, which was a prototype and forerunner to the UK’s 14 advanced gas cooled reactors (Sellafield Ltd., 2015). Today these facilities and their associated infrastructure are undergoing decommissioning and clean-up, which will cost an estimated £100 billion and is expected to take 100+ years (Nuclear Decommissioning Authority, 2006).

As well as decommissioning activities, Sellafield handles almost all the nuclear waste produced in the UK’s 15 operational nuclear reactors. Spent nuclear fuel from the UK’s reactors is currently reprocessed at Sellafield, as well as some fuel from overseas reactors in Europe and Japan. Spent fuel reprocessing involves using a series of solvent extraction stages to separate out the reusable uranium (96%) and plutonium (1%) from the high level waste (3%), thereby allowing 97% of the fuel to be recycled (Leafe, 2017). The reprocessing of irradiated fuel at Sellafield commenced in 1952 when the Plutonium Purification Plant was commissioned to extract plutonium from spent fuel from the Windscale Piles to provide fissile material for the UK’s atomic weapons programme. A second facility, designed to reprocess Magnox fuel to extract fissile material for recycling, was brought online in 1964. Later, in 1994, the treatment of high burn up oxide fuel from UK and foreign reactors was enabled with the opening of the THERnal Oxide Reprocessing Plant (THORP). Uranium and plutonium separated in the Magnox Reprocessing Plant and THORP can be used to make new fuel, with fabrication of mixed oxide fuel (MOX) occurring at The Sellafield...
MOX Plant between 2001 and 2011. In addition to managing Magnox and Oxide fuels, Sellafield also receives fuel from the UK’s fleet of Advanced Gas-cooled Reactors. This fuel is dismantled and decay stored in the Fuel Handling Plant, but is not currently reprocessed.

As a direct result of reprocessing and decommissioning activities, a variety of radioactive wastes are produced at Sellafield which are treated in a range of processing plants on site. After the radioactivity has been suitably reduced, liquid effluents are ultimately discharged via pipelines to the Irish Sea (Gray et al., 1999).

**Figure 2.1:** Timeline highlighting some of the significant events in the history of the Sellafield site. Author’s own figure put together using information from Sellafield Ltd. 2015; Nuclear Decommissioning Authority 2016; Gray et al. 1999.

### 2.1.2. Waste management at Sellafield

Fuel reprocessing and decommissioning activities result in the generation of six main radioactive liquid effluent streams (Hutson, 1996; Gray et al., 1999), namely:

- **Pond purges** from the legacy, spent fuel storage ponds.
- **Highly active effluent**, mostly from the first stage of fuel reprocessing which contains the vast majority of fission products and minor actinides.
- **Medium active effluent**, mainly from extraction steps to separate and purify uranium from plutonium.
- **Low active effluents, high risk (alpha).**
- **Low active effluents, low risk.**
- **Waste process solvents** from fuel reprocessing.

Pond purge water, in which caesium (\(^{137}\text{Cs};\ ^{134}\text{Cs}\)) and strontium (\(^{90}\text{Sr}\)) are the main contaminants (Hutson, 1996), is treated through the Site Ion Exchange Plant (SIXEP) which commenced operation in 1985 and removes the radionuclides by passing effluent through an array of sand filters and clinoptilolite ([\(\text{Na,K,Ca}_{2}\cdot \text{Al}\cdot [\text{Al,Si}]_{3}\text{Si}_{3}\text{O}_{12}\text{H}_{12}\text{O}\), a natural zeolite]) ion exchangers. Commissioning of this plant resulted in significantly reduced beta activity discharges to the Irish Sea (Gray et al., 1999). Today, SIXEP also treats liquid effluents from the Magnox Encapsulation Plant and the Waste Encapsulation Plant (Sellafield Ltd., 2015).

The highly active effluents are concentrated up to 100-fold by evaporation in the Highly Active Liquor Evaporation and Storage (HALES) department, followed by storage in high integrity steel tanks. Since the opening of the Waste Vitrification Plant in 1991, the concentrate goes on to be converted to glass cylinders for long term storage of around 50 years, after which they will be safer to dispose of (Hildred, 1996). Conversion to dense solid glass blocks reduces the liquid waste volume to about a third of its original size (Sellafield Ltd., 2015).

The medium active effluents are evaporated to reduce their volumes and decay-stored (typically for at least three years) to permit the decay of short-lived isotopes such as iodine-131 (half-life 8 days), ruthenium-103 (39 days), and zirconium/niobium-95 (64 and 35 days respectively). The resulting concentrates, as well as the high risk (alpha) low active effluents, were previously discharged to the Irish Sea following a period of storage of up to five years. However, it was identified that these effluents contained levels of actinides that, if removed, would reduce the levels of alpha activity discharges greatly. It was subsequently decided to build EARP which opened in 1994, through which these effluents are now treated (Hutson, 1996; Gray et al., 1999).
Commissioning of EARP left only one untreated effluent stream, namely radioactive waste process solvents, leading to the opening of The Solvent Treatment Plant (STP) in 1997. Treatment of waste process solvent in STP generates additional low active effluent which is subsequently also treated in EARP.

Low risk, low active effluents which don't require rigorous treatment are received at the Segregated Effluent Treatment Plant (SETP) where they are buffer stored and sampled prior to discharge to the Irish Sea. A simplified overview of the reprocessing and pond effluents treatment scheme at Sellafield is shown in Figure 2.2.
Figure 2.2: Simplified overview of the reprocessing and effluents treatment scheme at Sellafield. *Magnox Reprocessing Plant and THORP are separate facilities.
2.1.3. The EARP process

Effluent feeds to EARP are highly acidic and contain significant amounts of dissolved ferric iron (Fe(III)). Based on these characteristics, it was determined that precipitation of an iron oxyhydroxide floc by the addition of sodium hydroxide (NaOH) was the most suitable method to adopt for the EARP process (Hildred, 1996). As such, EARP is based on the principal of coagulation-flocculation, which describes the process by which a colloidal phase destabilises and aggregates to form a settleable/ filterable solid (Bratby, 1980). During coagulation-flocculation, contaminants are removed from solution and concentrated in the phase-separated solid phase by various processes which differ depending on the contaminant and flocculent (Duan and Gregory, 2003). Iron oxyhydroxide flocs are widely used in industry for effluent treatment since they have a number of properties which make them particularly effective at removing contaminants from solution, including:

- Large adsorption capacity due to their reactivity and high surface areas (e.g. Waite et al., 1994; Grafe et al., 2002; Filip et al., 2007; Swedlund et al., 2009; Johnston and Chrysochoou, 2016).
- Ability to incorporate contaminants within their structure during co-precipitation (e.g. Erbs et al., 2010; Mitsunobu et al., 2010; Marshall et al., 2014b, 2015).
- Readily aggregate to form an extensive floc structure which can entrap contaminants (Duan and Gregory, 2003).

The EARP process can be thought of as a two stage process comprising a chemical reaction to precipitate the iron oxyhydroxide floc followed by a physical separation of the floc from the aqueous phase (Figure 2.3). In the first stage, the effluent (initial pH 0 – 1) enters a neutralisation tank where the pH is raised to a final value of 8 – 11 by adding NaOH in two steps: first with 7.0 M NaOH until pH 2.5 is reached and secondly with 0.2 M NaOH until the final pH value is achieved. The pH rise induces dissolved Fe(III) to hydrolyse and precipitate out of solution, forming a gelatinous ferric oxyhydroxide floc in which radionuclides are trapped, likely by a combination of processes including adsorption, incorporation and physical entrapment (i.e. capture of small particles within the flocs) (Figure 2.4). In addition, the pH raise may induce particular radionuclides to precipitate out as a distinct solid phase.
The base-induced precipitation of iron can be crudely represented by the following reaction:

\[
\text{Fe}^{3+}_{(aq)} + 3\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3(s) + 3\text{H}^+_{(aq)}
\]  

(2.1)

In EARP, Nickel ferrocyanide (Ni₂Fe(CN)₆)₅ is subsequently added to the slurry to increase decontamination factors for beta emitters, particularly Cs, by acting as an effective adsorbent for these radionuclides (Hutson, 1996). The temperature is maintained at < 40 °C throughout the neutralisation process to minimise decomposition of the ferrocyanide.

In the second stage, the treated liquor, which is now very low activity, is separated from the flocculent until a suitable level of dewatering has been reached. This is achieved using ultrafiltration units which dewater the floc using cross-flow filtration until a target viscosity of 0.7 Pa s is reached (Hildred, 1996); higher viscosities would result in slurry which is difficult to process. In cross-flow filtration the feed flows tangentially across the filter surface rather than directly through the filter, with the benefit that the filter cake, which can block the filter, is continually washed away during filtration. The floc crystallinity, surface charge, particle size and morphology all influence the ultrafiltration efficiency and the final volume reductions achieved (Hildred, 1996).
The floc is subsequently washed with pH conditioned water to dilute the dissolved salt concentration to less than 1 g l⁻¹ sodium nitrate in order to reduce viscosity and enable further dewatering and volume reduction. Lastly, the concentrated floc is transferred to the Waste Packaging and Encapsulation Plant (WPEP) where it is encapsulated within cement drums for temporary storage (at least 100 years) in a surface store prior to eventual disposal.

**Figure 2.4:** Possible radionuclide uptake mechanisms in the EARP process.

### 2.1.4. Feed streams to EARP

The high ferric iron content in EARP effluent arises from the addition of ferrous sulphamate (FeH₄N₂O₆S₂) in the Magnox reprocessing plant as a reductant to separate Pu from U. Oxidation of the ferrous iron to ferric iron occurs upstream of EARP.

Effluent feeds to EARP are classified as “bulks” or “concentrates”. The bulk feed is a blend of various low active streams comprising of ~ 1 M HNO₃ with on average 200 - 400 ppm of dissolved ferric iron, together with a wide range of other chemical species including a significant amount of sulfate and sometimes significant phosphate and boron. Alpha activity is on average 200 Bq ml⁻¹, while total beta activity is ~ 25 Bq ml⁻¹.
The bulks effluent arises at a steady level, with approximately 250 m³/day of effluent treated on a continuous basis.

The concentrates feed was traditionally sub-divided into two categories – medium active concentrate (MAC) and salt evaporate concentrate (SEC). Processing of MAC feed through EARP was discontinued when it was instead diverted to the highly active waste stream in order to prevent discharges of Tc⁹⁹ to the Irish Sea, which EARP is inefficient at removing. The SEC feed comprises evaporated wash liquors from both THORP and Magnox reprocessing and contains ~ 0.4 M HNO₃ and 5 M NaNO₃, and is treated on a batch wise basis (50 m³ maximum). Iron content is usually low and it was initially dosed with ferric nitrate to an iron concentration of 2000 ppm, but more recently 500 ppm has been shown to be adequate. Alpha activity is approximately 10³⁴ Bq ml⁻¹, while ⁶⁰⁰Ru, ¹³⁷Cs and ⁹⁰Sr are the most significant beta nuclides at ~ 10⁴ Bq ml⁻¹ each. SEC feeds have proved difficult to accurately simulate because of the variability in their compositions and have previously caused operational problems (Hildred, 1996).

### 2.1.5. Decontamination factors

Decontamination factors (DFs) describe the ratio of activity prior to and after decontamination of the effluent streams. The EARP process provides excellent DFs for alpha and moderate DFs for beta radionuclides (Table 2.1). For example, the DF for total alpha is 2500 – 4500, while DFs for ¹³⁷Cs and ⁹⁰Sr, two of the most significant beta radionuclides, are 25 – 40 and 3 respectively (Table 2.1).

Effluents are neutralised to a final pH of 8 – 11, with the final pH optimised largely for Cs and Sr while DFs of other radionuclides are largely unaffected over this range. Sr DFs are probably controlled by adsorption to the floc surface and increase exponentially with pH increase. In contrast, Cs DFs are driven by adsorption to the added nickel ferrocyanide and are favoured by lower pH since the ferrocyanide decomposes at elevated pH.

Despite the reliably high DFs obtained in EARP, the detailed mechanisms of activity removal for many radionuclides are not well understood. The removal mechanisms are expected to differ between the radionuclides and likely include adsorption, incorporation, and entrapment within/ to the floc, and base-induced precipitation (Figure 2.4).
Table 2.1: EARP bulk feed activities and decontamination factors for radioactive species. Dashes indicate no value has been provided. Table is adapted from National Nuclear Laboratory (NNL) document which used data from Farrell (2001) and Bell and Eaves (2002).

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<th>Average BULK feed composition (mol l(^{-1}))</th>
<th>BULK feed decontamination factor (DF)</th>
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</tr>
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<td>Pu alpha</td>
<td>-</td>
<td>129</td>
<td>-</td>
<td>2600-8500</td>
<td></td>
</tr>
<tr>
<td>Pu(^{239})</td>
<td>14</td>
<td>4500</td>
<td>4.9E-09</td>
<td>4700-6400</td>
<td></td>
</tr>
<tr>
<td>Am(^{241})</td>
<td>433</td>
<td>20</td>
<td>6.5E-10</td>
<td>2500</td>
<td></td>
</tr>
<tr>
<td>Np(^{237})</td>
<td>2,140,000</td>
<td>5</td>
<td>8.1E-07</td>
<td>70-340</td>
<td></td>
</tr>
<tr>
<td>Cm(^{243})</td>
<td>0.45</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Cm(^{243/244})</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Co(^{58})</td>
<td>5.3</td>
<td>2.7</td>
<td>1.1E-12</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Zr(^{95})</td>
<td>0.18</td>
<td>240</td>
<td>3.2E-12</td>
<td>8000-20000</td>
<td></td>
</tr>
<tr>
<td>Nb(^{95})</td>
<td>0.10</td>
<td>7.5</td>
<td>5.4E-14</td>
<td>170-500</td>
<td></td>
</tr>
<tr>
<td>Sb(^{125})</td>
<td>2.8</td>
<td>1.4</td>
<td>2.9E-13</td>
<td>8-27</td>
<td></td>
</tr>
<tr>
<td>Ag(^{110m})</td>
<td>0.68</td>
<td>0.5</td>
<td>2.6E-14</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Ce(^{144})</td>
<td>0.78</td>
<td>5.5</td>
<td>3.2E-13</td>
<td>22-390</td>
<td></td>
</tr>
<tr>
<td>Eu(^{147})</td>
<td>2.6</td>
<td>9</td>
<td>1.8E-12</td>
<td>1-250</td>
<td></td>
</tr>
<tr>
<td>Eu isotopes</td>
<td>-</td>
<td>&lt; 1</td>
<td>-</td>
<td>6-20</td>
<td></td>
</tr>
<tr>
<td>Cs(^{134})</td>
<td>2.1</td>
<td>3</td>
<td>4.7E-13</td>
<td>20-100</td>
<td></td>
</tr>
<tr>
<td>Cs(^{137})</td>
<td>30</td>
<td>110</td>
<td>2.5E-10</td>
<td>25-40</td>
<td></td>
</tr>
<tr>
<td>Sr(^{89})</td>
<td>29</td>
<td>38</td>
<td>8.3E-11</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Sr(^{90})</td>
<td>0.14</td>
<td>&lt; 0.1</td>
<td>-</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

Actinides are removed to a solubility level in equilibrium with hydroxide precipitates and therefore decontamination factor is proportional to feed concentration. It is thought that Am and Np are probably removed by sorption and Pu by precipitation.

Many of the beta/ gamma emitters are present at too low concentrations for direct precipitation and sorption must be the main mechanism for removal. Evidence for some Fe concentration and pH sensitivity.

Removal by addition of nickel ferrocyanide. DFs controlled by pH: the ability of nickel ferrocyanide to adsorb Cs increases with pH, but since its solubility also increases with pH, the net effect is a decrease in Cs removal.

pH sensitive. At pH 8 DF ~ 1. At pH 12 > 10-100.

Sr DF is also a complex function of Mg, Ca, inactive Sr, Ba, carbonate and phosphate concentrations.
Main concern is volatile aerial releases under acid conditions. Iodine bearing streams have been diverted away from EARP or pretreated in the STP.

Table 2.2: EARP bulk feed concentrations and decontamination factors for non-radioactive species. Dashes indicate no value has been given. Table adapted from National Nuclear Laboratory (NNL) document which used data from Farrell (2001) and Bell and Eaves (2002).

<table>
<thead>
<tr>
<th>Species</th>
<th>Average BULK feed composition (ppm)</th>
<th>BULK feed decontamination factor</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.7-1.2</td>
<td>(a)</td>
<td>Most heavy metals removed down to solubility concentration in equilibrium with the metal hydroxides.</td>
</tr>
<tr>
<td>Ni</td>
<td>1-2</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>5-10</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.2-0.4</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>U</td>
<td>0.2-2</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>-</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>-</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>Cr(III)</td>
<td>0.1-0.5</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>200 - 400</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>Mn(II)</td>
<td>0.3</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>Sn(II)</td>
<td>-</td>
<td>(a)</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>0.7 - 1 Molar</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>Element</td>
<td>Value</td>
<td>Note</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>-------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>0.3</td>
<td>(b)</td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>-</td>
<td>(b)</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>25</td>
<td>(b)</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>0.3</td>
<td>(b)</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>-</td>
<td>(c)</td>
<td></td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>-</td>
<td>(c)</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0-300</td>
<td>(c)</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>-</td>
<td>(c)</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>-</td>
<td>(c)</td>
<td></td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>32</td>
<td>(b)</td>
<td></td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>1800</td>
<td>(b)</td>
<td></td>
</tr>
</tbody>
</table>

Impact on Sr DF

Impact on Cs DF

(a) Typically removed to 0.1 – 1.0 ppm. (b) Some DF is possible depending on interaction of alkaline earth hydroxides and carbonates/ phosphates. Al expected to be partially precipitated as hydroxide. Sulfate removal is unlikely without excess alkaline earths. (c) No DF expected.
2.1.6. The future role of EARP

EARP was designed to treat effluents resulting from site operational activities as they were expected to be from the 1990s. This was primarily effluents resulting from reprocessing activities. However, the Sellafield site is now approaching a period of fundamentally changed operational activity, from primarily reprocessing operations to primarily decommissioning and clean-up activities (Cameron and Eaves, 2013).

Reprocessing in both the Magnox and THORP plants is expected to be finished by ~2020, after which these reprocessing plants and some downstream plants will undergo post-operational clean out (POCO). While the quantity of effluent arising from POCO is expected to be less than that resulting from current activities, the chemical and radiochemical compositions of POCO effluents will be significantly different from current arisings and may, for example, contain decontamination agents such as EDTA or citrate. These changes could affect any of the key processes occurring in EARP, namely: (i) the iron hydrolysis and precipitation process; (ii) interactions with the radionuclides and final DFs; (iii) ultrafiltration and cement encapsulation properties of the floc. Therefore, it is important to further underpin knowledge of the fundamental processes operating in EARP so that the response of EARP to these new effluents can be better understood.

2.2. Introduction to the iron (oxyhydr)oxides

Iron (oxyhydr)oxides are ubiquitous in both natural and industrial environments. Their formation is a key part of the global biogeochemical iron cycle (Jickells, 2005) and they are widespread in the rocks, sediments, soils, rivers and oceans on the Earth’s surface. They have many industrial applications including as catalysts (Hermanek et al., 2007), magnetic materials, (Laurent et al., 2010) and pigments (Cornell and Schwertmann, 2003), as well as acting as effective decontaminates in wastewater treatment processes (Richmond et al., 2004; Shibata et al., 2008), including EARP. Iron (oxyhydr)oxides also have important biological roles: they are used by living organisms in metabolism and are bio-mineralised by some organisms for their mechanical and magnetic properties. In fact, one of the most commonly occurring iron oxyhydroxides, ferrihydrite, is present in almost all living organisms
where it acts as a bioavailable store of iron within the protein ferritin (Hiemstra and Zhao, 2016).

2.2.1. Composition and structure of the iron (oxyhydr)oxides

Iron oxides, hydroxides and oxyhydroxides, collectively known as iron (oxyhydr)oxides, exist in a diverse range of structures. There are currently 16 iron (oxyhydr)oxides recognised (Faivre, 2016) which include ferric Fe(III), ferrous Fe(II), and mixed valence phases (Table 2.3). Most of these can form from and transform in aqueous solutions. They all consist of arrays of iron and oxygen and/or hydroxide, with the Fe predominantly octahedrally coordinated by oxygen but sometimes in tetrahedral coordination.

In EARP, effluents are treated under ambient atmospheric conditions and Fe is only expected to be present in its ferric form. As such, we will discuss only ferric iron (oxyhydr)oxide phases in depth in this review. The three most common ferric phases are ferrihydrite, hematite and goethite (Cornell and Schwertmann, 2003). Ferrihydrite is a poorly structured nanocrystalline iron oxyhydroxide which is typically the first phase to precipitate from ferric solutions, particularly during base-induced ferric hydrolysis in acid media (Section 2.4). Ferrihydrite is therefore expected to be the dominant phase which initially forms in EARP. Ferrihydrite is only thermodynamically metastable in aqueous solution and, with time, will transform to either the iron oxide hematite ($\alpha$-Fe$_2$O$_3$) or iron oxyhydroxide goethite ($\alpha$-FeOOH), both of which are crystalline and thermodynamically stable phases (Section 2.6).
Table 2.3: Summary of the known iron (oxyhydr)oxides. Adapted from Faivre (2016).

<table>
<thead>
<tr>
<th>Fe(III) compounds</th>
<th>Iron Oxides</th>
<th>Oxyhydroxides</th>
<th>Iron Hydroxides</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>• Hematite</td>
<td>• Goethite</td>
<td>• Bernalite</td>
</tr>
<tr>
<td></td>
<td>[α-Fe₂O₃]</td>
<td>[α-FeOOH]</td>
<td>[Fe(OH)₃]</td>
</tr>
<tr>
<td></td>
<td>• Maghemite</td>
<td>• Akaganéite</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[γ-Fe₂O₃]</td>
<td>[β-FeOOH]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• β-Fe₂O₃</td>
<td>• Lepidocrocite</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• δ-Fe₂O₃</td>
<td>• Feroxyhyte</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• ε-Fe₂O₃</td>
<td>• Ferrihydrite</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>[γ-FeOOH]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>[δ-FeOOH]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>[5Fe₂O₃.9H₂O]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>[Fe₈O₈(OH)₆(SO₄).nH₂O]</td>
<td></td>
</tr>
<tr>
<td>Mixed valence</td>
<td>• Magnetite</td>
<td>• “Green rusts” –</td>
<td></td>
</tr>
<tr>
<td>(Fe(II) – Fe(III))</td>
<td>[Fe₃O₄]</td>
<td>Fougère</td>
<td></td>
</tr>
<tr>
<td>compounds</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(II) compounds</td>
<td>• Wüstite</td>
<td>• “White rust”</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[FeO]</td>
<td>[Fe(OH)₃]</td>
<td></td>
</tr>
</tbody>
</table>

2.3. Iron (III) hydrolysis

Iron (oxyhydr)oxide formation from aqueous solution begins with hydrolysis of the Fe cation. In highly acidic solutions (pH < 1), the Fe³⁺ cation is present as the hexaaquo ion [Fe(OH₂)₆]³⁺ (Baes and Mesmer, 1976; Jolivet et al., 2004). The high positive charge density of the Fe³⁺ cation induces the H₂O ligands to act as acids and deprotonation of the bonded H₂O (i.e. hydrolysis) readily occurs to form species with the general formula [Fe(OH)ₓ(H₂O)₆-x]^(3-x)+. Hydrolysis can be induced by the addition of base to increase pH (as in EARP), as well as by heating, dilution, solvent exchange and ion exchange (Baes and Mesmer, 1976).
Hydrolysis leads to the progressive replacement of $H_2O$ ligands with $OH^-$ ions, resulting in a lowering of the positive charge ($H_2O$ ligands are omitted for brevity):

$$\text{Fe}^{3+} \rightleftharpoons \text{Fe(OH)}^{2+} \rightleftharpoons \text{Fe(OH)}_2^+ \rightleftharpoons \text{Fe(OH)}_3^+ \rightleftharpoons \text{Fe(OH)}_4^- \quad (2.2)$$

Condensation of these hydroxylated complexes to form Fe species of higher nuclearity occurs by olation and oxolation processes.

In olation, polymerisation proceeds by the elimination of water and the formation of hydroxo bridges, for example:

$$[\text{Fe}(H_2O)_3OH]^{2+} + [\text{Fe}(H_2O)_6]^{3+} \rightleftharpoons \{\text{Fe}(H_2O)_5(\mu-OH)\text{Fe}(H_2O)_5\}^{5+} + H_2O \quad (2.3)$$

Where $\mu$-OH signifies a bridging hydroxide ligand. This is typically a rapid reaction due to the high lability of coordinated $H_2O$ molecules (Jolivet et al., 2004) and is reversible (Dousma and de Bruyn, 1976; Blesa and Matijevic, 1989).

In contrast, oxolation proceeds via the formation of oxo bridges and typically occurs during the later stages of hydrolysis when there is no water to act as a leaving group in the coordination sphere of the iron. Oxolation requires the initial dehydration of a hydroxo bridge and therefore occurs in two steps. Consequently, it is a slower process than olation and oxo bridges are more stable and less dynamic than hydroxo bridges (Flynn Jr., 1984; Scheck et al., 2016).

It is these hydrolysis and polymerisation processes which lead to formation of polynuclear Fe species, discussed further below, and the eventual precipitation of a solid iron (oxyhydr)oxide phase.

### 2.3.1. Polynuclear Fe(III) ions

A significant amount of research has been undertaken to characterise the polynuclear ions formed by Fe(III) hydrolysis. However, this has proved challenging since the high charge density of Fe(III) renders the hydrolysis reactions very rapid and isolation of the polynuclear species difficult. Nevertheless, the formation of an Fe dimer in partially hydrolysed ferric solutions is well reported in the literature, with studies utilising organic chelating ligands reporting both a dihydroxo dimer $[(H_2O)_2\text{Fe(OH)}_2\text{Fe}(H_2O)_4]^{4+}$ (Schugar et al., 1969; Coggins et al., 2013) and a $\mu$-oxo aquo dimer $[(H_2O)_3\text{FeOFe}(H_2O)_3]^{4+}$ (Schugar et al., 1970; Elam et al., 1982; Brown et
More recent research utilising in situ spectroscopy has reported the µ-o xo aquo dimer to be the most dominant and stable dimer form in ferric solutions which were partially hydrolysed via addition of either the weak base HCO$_3$ (Zhu et al., 2013; Zhu et al., 2016) or 2 M KOH (Collins et al., 2016).

Evidence for the formation of stable Fe trimers is scarcer. In early studies, a trimer Fe$_3$(OH)$_2^{4+}$ was reported as a minority species in partially hydrolysed ferric perchlorate solutions based on calorimeter data (Arnek and Schlyter, 1968). Later studies utilising EXAFS analysis of partially hydrolysed ferric chloride solutions (Bottero et al., 1994) and ferric nitrate solutions (Rose et al., 1997) reported formation of trimers with edge and corner-sharing octahedra: in the ferric chloride study, coalescence of the trimers played an important role in iron oxyhydroxide nucleation, while in the ferric nitrate study the trimers were only detected as a minority species. However, more recent studies utilising a variety of spectroscopic methods, including EXAFS, found no evidence for trimers, bringing into question the stability and relative importance of these species (Zhu et al., 2013a, 2016; Collins et al., 2016).

Evidence also exists for the formation of some larger polynuclear Fe(III) cations with defined structures. An Fe$_{24}$ polycation, 1.5 nm in diameter, was reported to form by condensation of trimer units, and is thought to be important in the formation of the Fe(III) oxyhydroxide/ chloride mineral akaganéite (Tchoubar et al., 1991; Bottero et al., 1994). An Fe$_{13}$ cluster with the Keggin structure (Dias et al., 2014) was long postulated to exist due to comparisons with the analogous Al hydrolysis system where an Al$_{13}$ Keggin cluster is known to form and be important in aluminium hydroxide (Al(OH)$_3$) formation (Bradley and Kydd, 1993; Casey, 2006). Furthermore, the Keggin motif is evident in both the ferrihydrite and magnetite structures (Michel et al., 2007), which bolstered the search for an Fe$_{13}$ Keggin cluster. The Keggin unit is a metal-oxo structural motif consisting of a central, tetrahedrally-coordinated metal ion surrounded by 12 octahedrally-coordinated metal ions which are arranged into three triads (Figure 2.5). There are five isomers of the Keggin structure depending on the linkage between the octahedral units (edge vs. corner sharing). In 2015, Sadeghi et al. (2015) first synthesised and isolated a Fe$_{13}$ cluster via Fe(III) hydrolysis in aqueous solution. They found that Bi$^{3+}$ ions were necessary to stabilise the highly reactive Keggin cluster, while trichloroacetic acid (TCA) ligands could be used to crystallise the clusters in the solid state. The Fe$_{13}$ could only be dissolved in water by
displacement of the Bi$^{3+}$, but this led to rapid conversion to ferrihydrite. In a subsequent paper, Sadeghi and co-workers reported use of trifluoroacetic acid (TFA) instead of TCA yielded an Fe$_3$ cluster much more soluble and stable in water (Sadeghi et al., 2016).

**Figure 2.5:** The Keggin structural motif: central tetrahedral metal ion surrounded by 12 octahedral metal ions which are arranged into four triads. The figure shows the δ-Keggin isomer whereby three of the triads are edge sharing and one corner sharing. This is the same isomer present in the ferrihydrite structure according to the Michel et al. (2007) model (Section 2.5).

### 2.3.2. Thermodynamic modelling of Fe hydrolysis

When undertaking thermodynamic modelling of Fe(III) hydrolysis, only hydrolysed monomers and dimers are typically considered. Other species are neglected because the structural and thermodynamic data is scarce and sometimes contradictory (Baumgartner and Faivre, 2015). The Nuclear Energy Agency (NEA) (Lemire et al., 2013) recently undertook a critical review of iron hydrolysis constants and recommended three reactions to describe Fe(III) hydrolysis (Table 2.4). They did not include the Fe(OH)$_3$(aq) species because it exists only at very small concentrations and there are large uncertainties in the equilibrium constant. They also did not include Fe(OH)$_4$ species, although it is unclear why, since there is strong evidence for the formation of this species at high pH (Baes and Mesmer, 1976; Stefánsson, 2007). The NEA report also reviews the solubility products ($K_{sp}$) of common Fe phases, which should also be included in thermodynamic models.
Table 2.4: NEA recommended thermodynamic data for Fe(III) hydrolysis.

<table>
<thead>
<tr>
<th>Species</th>
<th>Reaction</th>
<th>( \log_{10} K^* )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeOH(^{2+} )(_{aq})</td>
<td>( \text{Fe}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{FeOH}^{2+} + \text{H}^+ )</td>
<td>-2.150</td>
<td></td>
</tr>
<tr>
<td>Fe(OH)(<em>2^{+} )(</em>{aq})</td>
<td>( \text{Fe}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe(OH)}_2^{+} + 2\text{H}^+ )</td>
<td>-4.800</td>
<td>Lemire et al. (2013)</td>
</tr>
<tr>
<td>Fe(_2)(OH)(<em>2^{4+} )(</em>{aq})</td>
<td>( 2\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}_2\text{(OH)}_2^{4+} + 2\text{H}^+ )</td>
<td>-2.820</td>
<td></td>
</tr>
</tbody>
</table>

Although this approach is often effective at modelling experimental data, its weakness is that it makes an assumption of the predominance of certain hydrolysed species; larger Fe clusters and colloids, which may be important under particular conditions, are neglected.

2.4. Iron (oxyhydr)oxide formation from solution

The properties of iron (oxyhydr)oxides (e.g. reactivity, surface area) are sensitive to the aqueous conditions and mechanism of formation (Fu et al., 2011; Liu et al., 2014). Since iron (oxyhydr)oxides are ubiquitous in the environment and are effective decontamination agents, having a full understanding and control over iron (oxyhydr)oxide formation has been a long sought after goal and has been extensively studied using a wide range of techniques. These include both macroscopic methods which consider the bulk properties of the system, such as titration and uv-vis studies, and nanosopic techniques which probe systems at the molecular level, such as EXAFS.

2.4.1. Ferrihydrite formation

In the majority of studies which investigate iron (oxyhydr)oxide formation from ferric solutions, the poorly ordered nanocrystalline phase ferrihydrite forms, which is also known by other names such as hydrous ferric oxide (HFO) and amorphous ferric oxide (AFO) (Jambor and Dutrizac, 1998). Ferrihydrite is known to be the first phase that typically forms from induced ferric hydrolysis due to its high kinetic accessibility (i.e. it has a low free energy barrier to formation). Additionally, the surface energy of ferrihydrite is significantly smaller than the crystalline phases, making ferrihydrite
thermodynamically competitive at small particle sizes (Navrotsky et al., 2008). Upon formation, ferrihydrite readily aggregates and often forms extensive flocs (Section 2.5.1). There is no agreed upon chemical formula for ferrihydrite due to the lack of a definite known structure and variable water content (Section 2.5).

The details of the mechanisms of ferric hydrolysis and polymerisation which lead to solid formation are complex, and the extensive literature does not provide a unified view of ferrihydrite formation. In part, this is due to the rapidity of the hydrolysis reactions and precipitation of ferrihydrite often being instantaneous, rendering identification and characterisation of the intermediate precursor species difficult. To facilitate observation of the precursor species, the majority of experiments have been conducted in quasi-equilibrated solution at constant pH or a given hydrolysis ratio (OH/Fe) (Baumgartner and Faivre, 2015).

Dousma and de Bruyn (1976) used a spectrophotometric method to investigate the titration of acidified ferric nitrate solutions with NaOH. They proposed a model for the formation of ferrihydrite floc which was based on successive polymerisation (olation and oxolation) and aggregation steps (Figure 2.6). With increasing hydrolysis ratio, the ferric cation undergoes olation to form small polycations (a.k.a. clusters), followed by oxolation to form larger clusters and finally aggregation processes to form secondary particles and a settleable floc (Figure 2.6). In this way, formation proceeds by a series of discrete steps, with each step being an equilibrium process involving deprotonation, condensation, aggregation, or a combination of these (Knight and Sylva, 1974). This same sequence of steps occurs when base addition is stopped partway through hydrolysis, although the process takes longer (Dousma and De Bruyn, 1978). It is difficult to identify exactly when a particle of the solid phase nucleates during this process, but presumably occurs after oxolation to form species with zero intrinsic charge (Jolivet et al., 2004). Other earlier studies also interpret their findings in terms of successive polymerisation steps, whilst not identifying any particular polycation or cluster as being critical to the process (Knight and Sylva, 1974; Van Der Woude et al., 1983). This model of ferrihydrite formation, with a clear continuity from the monomers to the floc, is also supported by early X-ray scattering investigations which suggest a structural continuity from the smallest Fe colloids to the precipitate (Atkinson et al., 1968; Magini, 1977). More recently, Rose et al. (2014) investigated iron oxyhydroxide formation at pH 3 using small angle X-ray scattering
(SAXS) and they reported a similar successive process whereby hydrolysis resulted in rapid formation of polycations < 2 nm, followed by condensation to form primary particles and finally secondary aggregation to form a mass fractal floc. The initial small polycations formed within one second by olation and oxolation processes, which was too rapid to resolve, highlighting how quickly the hydrolysis and polymerisation reactions occur at pH 3.

Figure 2.6: Ferricydrite formation via successive polymerisation and aggregation steps, based on the conceptual model proposed by Dousma and De Bruyn (1976).

Extended X-ray absorption fine structure spectroscopy (EXAFS) is a popular technique to elucidate changes in the Fe bonding environment during ferricydrite formation since it is element specific and can be used on both liquid and solid samples (Combes et al., 1990; Masion et al., 1997; Rose et al., 1997b; Pokrovski et al., 2003; Mikutta, 2011; Zhu et al., 2013a, 2016; Collins et al., 2016). EXAFS results indicate that the initial stages of nucleation from ferric nitrate solutions are characterised by formation of edge-sharing linkages between Fe octahedra, whilst the growth of formed nuclei are associated with increasing double corner sharing, which appears to be critical for ferricydrite formation (Rose et al., 1997b; Collins et al., 2016). The resulting nuclei contain a mix of both edge-sharing and various types of corner-sharing octahedra.

It is unclear whether growth of the polycations/ clusters is driven by monomer addition or by condensation/ aggregation of smaller clusters, or whether a particular critical cluster is required for ferricydrite formation. Some recent studies have focused on identification of a critical intermediate cluster, since this is considered a crucial step in understanding formation mechanisms (Michot et al., 2000; Zhu et al., 2016). Zhu et al. (2016) reported that the dominant species in ferric nitrate solutions with hydrolysis ratios 0.7 – 2.5 were Fe(III) monomers, an µ-oxo aquo dimer, and small ferricydrite particles; no larger intermediate Fe(III) clusters were detected.
However, they note that the µ-oxo dimer structure is incompatible with ferrihydrite since the octahedra are bonded by single corner sharing rather than edge sharing, and therefore structural reconfiguration of this dimer may be the rate limiting step to ferrihydrite nucleation. The structurally reconfigured dimer and/or larger clusters may be rapidly consumed in the nucleation process and therefore evade detection. The dominance of an µ-oxo aquo dimer in partially hydrolysed solutions was also reported in other studies (Zhu et al., 2013a; Collins et al., 2016), with Collins et al. reporting that transformation of the dimer during solid formation was rapid. While these studies did not identify a critical cluster larger than a dimer, Sadeghi et al. (2015 & 2016) reported isolation of a Fe₁₃ Keggin cluster during Fe(III) hydrolysis via use of Bi³⁺ to stabilise the cluster, with rapid conversion to ferrihydrite upon removal of the Bi³⁺. This provides evidence for a critical cluster-based pathway to ferrihydrite formation whereby the Fe₁₃ cluster acts as a critical building block. The mechanism by which Fe₁₃ Keggin clusters convert to ferrihydrite is unclear, but is likely more complex than a simple aggregation process since the tetrahedral Fe to octahedral Fe ratio is smaller in the Fe₁₃ cluster (1:12) than ferrihydrite (1:4) (Sadeghi et al., 2016). A molecular dynamics simulation study by Zhang et al. (2015) also provided evidence for a cluster-based pathway whereby ferrihydrite-like nanoparticles formed via aggregation of molecular clusters, although Fe₁₃ Keggin clusters were not directly identified in this pathway.

Considering the diversity of evidence, there may be a variety of pathways to ferrihydrite formation depending on the solution conditions, rather than one single pathway. Indeed, variation in the structure of ferrihydrite, and much of the controversy over its structure (Section 2.5) may arise because it can form from different precursors (Navrotsky et al., 2008). Rose et al. (1997) even suggested that hydrolysis of ferric nitrate salts, and subsequent iron oxyhydroxide formation, does not follow a defined pathway: samples left to age at different hydrolysis ratios each evolved differently with time, although edge sharing linkages between Fe octahedra was associated with initial nucleation in every system.

2.4.2. Effect of additional species on iron (oxyhydr)oxide formation

Ferrihydrite formation in natural and industrial environments is usually accompanied by the presence of additional chemical species. These species can influence the formation processes discussed above, and therefore affect the properties of the final
ferrihydrite phase, or lead to formation of alternative iron (oxyhydr)oxide phases. For example, complexing anions such as sulfate and phosphate, abundant in the environment and wastewaters, can compete with O and OH ligands during Fe(III) hydrolysis and perturb regular pathways. Sulfate complexation has been shown to inhibit double corner sharing but promote edge sharing between Fe(III) octahedra (Collins et al., 2016), leading to formation of the poorly crystalline ferric oxyhydroxy-sulfate phase schwertmannite (Fe₆O₆(OH)₁₂(SO₄)₃); either directly from solution (Collins et al., 2016) or by transformation from ferrihydrite (Zhu et al., 2012), with which schwertmannite shares some structural features (Bigham et al., 1994; Fernandez-Martinez et al., 2010). The schwertmannite structure includes two outer sphere sulfate ions H-bonded to the structure (S₂ and S₄ in Figure 2.7) and two inner sphere sulfate ions directly bonded to the Fe (S₁ and S₃ in Figure 2.7). Schwertmannite formation is favoured by sulfate levels of 1000 – 3000 ppm in the pH range 2 – 4 (Bigham et al., 1994).

**Figure 2.7:** Structure of schwertmannite viewed along the y and z axes, based on refinements by Fernandez-Martinez et al. (2010). Oxygen anions are shown in red, ferric cations in orange and sulfate ions in yellow and grey (labelled S₁ – S₄). Figure adapted from (Bishop et al., 2015).
Phosphate has been shown to inhibit both corner sharing and edge sharing of Fe(III) octahedra, resulting in limitation of Fe hydrolysis to the dimer stage (Manceau et al., 1996; Rose et al., 1997a). Phosphate can subsequently bridge between the Fe octahedra, with solid formation driven primarily by continuous growth of the Fe-PO₄ network rather than individual nucleation events (Manceau et al., 1996; Rose et al., 1997a; Neil et al., 2014; Hiemstra and Zhao, 2016), resulting in formation of a ferrihydrite-like amorphous ferric phosphate phase (Thibault et al., 2009). Inhibition of Fe polymerisation has similarly been reported for silica (Pokrovski et al., 2003) and arsenate (Wang et al., 2016).

In the presence of chloride, akaganeite (β-FeOOH) can be formed directly from Fe(III) hydrolysis, with the chloride ions thought necessary to stabilise the structure (Bottero et al., 1994). However this is typically only observed for precipitation from a solution with a pH less than 5, since Cl⁻ is displaced by OH⁻ above this pH (Schwertmann and Cornell, 2000). Other anions with smaller charge/size ratios, such as nitrate, are typically weak binding (Lay and Wu, 1995), so their use as background electrolytes makes it easier to resolve effects of other added species.

2.4.3. Classical nucleation theory and classical growth

Nucleation is a fundamental part of any precipitation process and describes the moment the smallest manifestation of the solid phase (i.e. a nucleus) first forms in solution. The prevailing theoretical framework describing nucleation is classical nucleation theory (CNT) (Thanh et al., 2014). In CNT, nucleation is conceptualised as occurring by a clustering of single atoms or molecules which form a stable nucleus in supersaturated solution if the clusters are larger than a critical size, whose value is largely determined by the balance between bulk and surface energies of the new phase (Thanh et al., 2014). The bulk energy, ΔG_{bulk}, results from the chemical bonding within the nucleus and is the driving force for formation of the new phase, while the surface energy, γ, is a consequence of the development of an interface between the nucleus and solution and is the energetic cost of emergence of the new phase. The total Gibbs free energy, ΔG of nucleation is the sum of the bulk and surface energies:

\[ \Delta G = 4\pi r^2 \gamma + \frac{4}{3} \pi r^3 \Delta G_{\text{bulk}} \]  

(2.4)

Where r is the spherical nucleus radius. As seen from equation 2.4, the favourable bulk energy term scales with the volume of the nucleus (\(\frac{4}{3} \pi r^3\)) while the unfavourable
surface energy term scales with the surface area ($4\pi r^2$). The central tenant of CNT is to describe nucleation as a competition between these two forces as a function of nucleus size (Figure 2.8). The critical nucleus size $r_{\text{crit}}$ is defined as the radius at which the bulk energy contribution compensates for the energetic cost of the surface contribution (i.e. where $d\Delta G/dr = 0$, Figure 2.8). $\Delta G$ at $r_{\text{crit}}$ is a local maximum which represents the energy barrier to nucleation, $\Delta G_{\text{crit}}$ (Figure 2.8). $r_{\text{crit}}$ can be calculated with the following equation:

$$r_{\text{crit}} = \frac{-2\gamma}{\Delta G_{\text{bulk}}} = \frac{2\gamma v}{k_B T \ln(S)}$$ (2.5)

Where $k_B$ is the Boltzmann constant, $T$ is temperature, $v$ is the crystal molar volume, and $S$ the solution supersaturation. The critical size is a thermodynamically metastable state since any infinitesimal change towards a smaller or larger radii will destabilise the cluster and lead to dissolution or unlimited growth, respectively (Figure 2.8) (Gebauer et al., 2014).

**Figure 2.8:** Free energy versus radius of nucleus, as per classical nucleation theory. The point at which the bulk energy contribution compensates for the energetic cost of the surface contribution is the critical nucleus size, $r_{\text{crit}}$.

$\Delta G_{\text{bulk}}$ is itself dependent on the solution supersaturation, $S$: 

53
\[ \Delta G_{\text{bulk}} = \frac{-k_B T \ln(S)}{v} \] (2.6)

The negative sign in equation 2.6 means that \( \Delta G_{\text{bulk}} \) will only be favourable, and nucleation will only occur, in supersaturated solution.

The rate of nucleation is thought to be thermally driven and is dependent on \( \Delta G_{\text{crit}} \):

\[ \text{Nucleation rate} \approx e^{-\frac{\Delta G_{\text{crit}}}{k_B T}} \] (2.7)

Therefore phases with lower energy barrier nucleate more rapidly. An important implication of this is that amorphous, highly hydrated phases (e.g. ferrihydrite) typically form more rapidly than crystalline, less hydrated phases because the former tend to have lower surface energies and therefore a lower energy barrier to nucleation (Navrotsky, 2004; Navrotsky et al., 2008). When the amorphous phase is metastable with respect to more crystalline counterpart(s) then a transformation to the more stable phase occurs. This is known as the Ostwald step rule, which states that crystallisation from solution can occur in steps via the initial formation of less thermodynamically stable polymorphs, instead of a single nucleation-growth event (Van Santen, 1984). This phenomena is observed for iron (oxyhydr)oxides whereby crystalline goethite and hematite typically form via the transformation of ferrihydrite, which is a poorly ordered and more highly hydrated phase (Section 2.6.).

Following nucleation of the solid phase, growth can occur. Classical growth theories, such as the terrace-ledge-kink model of crystal growth, typically consider crystal growth as occurring by monomer-by-monomer addition of molecular-scale species (Markov, 2003; De Yoreo et al., 2015). These species may be dissolved ions in solution or they may diffuse from smaller particles to larger ones in the process known as Ostwald ripening (Ostwald, 1897).

Marchand and Rancourt (2009) utilised the principles of CNT to model ferrihydrite precipitation and found they could reproduce experimentally observed ferrihydrite precipitation kinetics and resulting size distributions, including the dependence on pH, temperature and level of supersaturation. However, some studies point to iron (oxyhydr)oxide formation occurring via the accretion of primary clusters or particles (e.g. ferrihydrite formation via \( \text{Fe}_{13} \) Keggin clusters (Sadeghi et al., 2015); magnetite formation via amorphous 1 nm particles (Baumgartner et al., 2013)), apparently...
contradicting CNT which considers nucleation as occurring from atoms or small molecules. However, Baumgartner et al. (2013) argue that nanometric sized particles/clusters (1 – 2 nm) have molecule-like behaviour and, therefore, nucleation via accretion of these primary species is comparable to nucleation via accretion of atoms and molecules and both processes can be described by the well-known predictions of CNT theory. This approach requires accounting for the consumption of the primary species free energy, $f$, during the nucleation process:

$$\Delta G_{\text{from cluster}} = \Delta G + Vf$$  \hspace{1cm}(2.8)$$

Where $V$ is the volume of the primary cluster/particle consumed (Baumgartner et al., 2013; Baumgartner and Faivre, 2015).

### 2.4.4. Non-classical nucleation and growth

There have been a number of observations that challenge CNT and classical monomer-by-monomer growth. For example, the formation of stable species called prenucleation clusters prior to nucleation of the solid phase have increasingly been reported (Gebauer et al., 2014), which contradicts the CNT concept that subcritical species are unstable. Figure 2.9 shows the difference in the free energy landscape for a simple nucleation process occurring via a classical pathway and a non-classical prenucleation pathway. The so-called prenucleation clusters (PNCs) are described as small, thermodynamically stable solutes which are highly dynamic and have encoded structural motifs which relate to the final nucleation phase (Gebauer et al., 2014; Zahn, 2015). With changing solution conditions, the PNCs can become metastable with respect to the solid phase and nucleation proceeds typically by aggregation of the PNCs. PNCs have been reported for numerous mineral systems including calcium carbonates (Gebauer et al., 2008), calcium phosphates (Dey et al., 2010), silica (Gebauer et al., 2014), as well as iron (oxyhydr)oxides (Scheck et al., 2016). The Fe$_{13}$ Keggin cluster characterised by Sadeghi et al. (2015) (Section 2.3.1) has been proposed to qualify as a PNC for ferrihydrite formation.
Related to this, a key aspect of CNT is that the formation of a stable nucleus is governed by a critical size. However, in contradiction to this, Scheck et al. (2016) demonstrated that the nucleation of iron oxyhydroxide was not controlled by growth to a critical size but instead by the dynamics of clusters forming in the prenucleation regime. Specifically, a change in the chemistry of the linkages within Fe(III) polymers from dynamic hydroxo bridges (olation) to more stable oxo bridges (oxolation) led to nucleation and phase separation. Their study employed a careful titration procedure where the Fe(III) concentration was slowly raised while pH was kept constant. This acted to minimise mixing artifacts, which can otherwise make the distinct stages of phase separation unresolvable due to rapid nucleation at the mixing interface.

Non-classical growth processes have also been gaining attention, particular those occurring via particle attachment processes (De Yoreo et al., 2015), which contradicts the classical notion that growth occurs by addition of single atoms or molecules. In particular, orientated attachment (OA) growth mechanisms have been reported in iron (oxyhydr)oxide systems (Banfield et al., 2000; Penn et al., 2001; Frandsen et al.,

**Figure 2.9:** Free energy profile of nucleation following a classical pathway and a non-classical, pre-nucleation cluster based pathway.
OA proceeds by repeated attachment events of primary crystallites, which fuse together if they are orientated in such a way that they are lattice matched. For example, Li et al. (2012) observed the growth of 6-line ferrihydrite nanoparticles via OA in real time by using in situ TEM, whereby nucleated ferrihydrite nanoparticles underwent continuous rotation until they reached a perfect lattice match and coalesced.

2.5. Ferrihydrite structure

Ferrihydrite was originally thought to be entirely amorphous until Towe and Bradley (1967) showed it did in fact possess an X-ray diffraction pattern with two broad peaks, and was therefore better described as nanocrystalline with individual particles < 7 nm (Pinney et al., 2009). By nature, a nanocrystalline phase lacks long range order. This has rendered the development of a definitive crystal structure by the traditional means of single crystal and powder X-ray crystallographic techniques difficult, and the structure of ferrihydrite remains controversial (Hiemstra, 2013). What is known is that ferrihydrite is a hydrated iron oxyhydroxide phase. Hydroxyl groups (OH) are present both within the ferrihydrite structure and adsorbed to the surface, as indicated by infrared spectroscopy (Russell, 1979) and thermal analysis (Stanjek and Weidler, 1992).

Many structural models for ferrihydrite have been proposed, with Jambor and Dutrizac (1998) providing a detailed review of the earlier models. Today, two models have emerged at the forefront and dominate discussion: the three component model proposed by Drits et al. (1993) and the single phase model proposed by Michel et al. (2007) (hereafter called the Drits model and the Michel model, respectively).

In their study, Drits et al. (1993) evaluated the earlier ferrihydrite models by comparing simulated and experimental XRD and EXAFS data, finding that none corresponded to the actual ferrihydrite structure. They instead proposed a three component model consisting of defect-free ferrihydrite, defective ferrihydrite and an ultradispersed hematite phase. Subsequent studies utilising X-ray absorption near edge spectroscopy (XANES) and EXAFS studies reported that defect-free ferrihydrite was built from Fe(O, OH)$_6$ octahedra sharing corners and edges in a hexagonal cell, and dismissed the existence of tetrahedral Fe (Manceau and Drits, 1993; Manceau and Gates, 1997). Some Fe may be absent and the ligands substituted for OH$_2$, resulting in
poor crystallinity and the broad XRD peaks observed for ferrihydrite. Manceau (2009) later stated that the ultradispersed hematite phase may also contain some magnetite (Fe$_3$O$_4$) and maghemite (γ-Fe$_2$O$_3$).

The three component model was disputed by Michel et al. (2007) who, by comparing pair distribution functions (PDFs) generated from experimental scattering data and those calculated from structural models, argued that ferrihydrite with domain sizes ranging from 2 – 6 nm can be adequately described by a single phase model with an ideal formula Fe$_{10}$O$_{14}$OH$_2$ and a structural similarity to akadalaite [Al$_{10}$O$_{14}$OH$_2$], a natural alumina hydrate. In comparison to the Drits model, the Michel model contains 20% of Fe in tetrahedral sites and has a molar ratio of structural OH/Fe of 0.20, as compared to a ratio of 1.0 in the Drits model. The basic structural motif of the Michel model closely resembles the Baker-Figgis δ-Keggin cluster (Casey, 2006), which consists of a central tetrahedral Fe surrounded by 12 octahedrally coordinated Fe atoms arranged in edge-sharing groups of three (Figure 2.10). However, the model came under significant criticism for not fully satisfying the observed diffraction features, calculated bond valence sums, or the measured density of ferrihydrite (Rancourt and Meunier, 2008; Hiemstra and Van Riemsdijk, 2009; Manceau, 2009; Liu et al., 2010). In addition, Manceau (2009) criticised the model for being fully periodic and defect-free, arguing that this was the reason the new model failed to reproduce XRD data. Michel et al. responded to these criticisms in their subsequent study on PDF analysis of ferrihydrite during ageing to hematite (Michel et al., 2010): based on their new data, they revised the original Michel model with the insertion of extra vacancies to the Fe sites and suggested the formula of ferrihydrite to be Fe$_{8.2}$O$_{8.5}$(OH)$_{7.4}$·3H$_2$O (Michel et al., 2010). Moreover, Harrington et al. (2011) argued that criticisms of the Michel model were based on misconceptions about scattering from nanocrystals and the use of periodic models; they reported that neutron PDF analysis of deuterated ferrihydrite was consistent with the Michel model while the Drits model lead to poorer fits (Harrington et al., 2011). Xu et al. (2011) also investigated the ferrihydrite structure by studying the transformation of ferrihydrite to hematite. By utilising PDF in conjunction with thermogravimetric (TG) and differential scanning calorimetric (DSC) analysis, they found that the ratio of structural OH to Fe in ferrihydrite was 0.18: consistent with the Michel model (OH/Fe = 0.2) but not the Drits model (OH/Fe = 1.0). XAS results (Maillot et al., 2011; Peak and Regier, 2012) and PDF (Gilbert et al., 2013) have provided evidence for
tetrahedral Fe, which is again supportive of the Michel model over the Drits model, and have indicated that Fe-Fe distances are consistent with a δ-Keggin cluster, which is the recurring motif the Michel model is based on.

![Figure 2.10: A) Hexagonal unit cell for ferrihydrite as per the Michel et al. (2007) model. B) Another view of the ferrihydrite structure with the δ-Keggin Fe₁₃ building block emphasised in red (adapted from Sadeghi et al., 2015).](image)

**Figure 2.10:** A) Hexagonal unit cell for ferrihydrite as per the Michel *et al.* (2007) model. B) Another view of the ferrihydrite structure with the δ-Keggin Fe₁₃ building block emphasised in red (adapted from Sadeghi *et al.*, 2015).

However, the debate remains unsettled. Manceau *et al.* (2014) conducted a PDF analysis of ferrihydrite and tested the ability of both the Michel model and a modified akdalaite-based model to fit the data. The modified model had all Fe in octahedral configuration and was analogous to the defect free phase of the Drits model. It was reported that both models provided near identical fits to the ferrihydrite PDF but that the modified model did not suffer from bias and provided a more robust description of the PDF data.

Hiemstra (2013) proposed an update of the Michel model: his surface-depleted model consists of a defect-free, well-ordered core and a water-rich surface layer which is depleted in the Fe₂ octahedra and Fe₃ tetrahedra of the Michel model (Figure 2.10A). This model could account for the particle size dependency observed in PDF data (*Michel et al.*, 2010), thermogravimetric-determined water content and mass densities, as well as the exceptionally low surface enthalpy of ferrihydrite. The surface-depleted model was subsequently supported by Wang *et al.* (2016), whose Mössbauer results indicate that 1.6 nm ferrihydrite particles have an amorphous
surface layer which accounts for 38.4% of their total volume, corresponding to a core size of 1.36 nm and surface layer thickness of 0.12 nm.

Regardless of the structural details, two types of ferrihydrite are generally distinguished – two-line ferrihydrite and 6-line ferrihydrite, so called because of the number of peaks seen in their XRD patterns (Cornell and Schwertmann, 2003). Schwertmann et al. (1999) showed that a complete series of ferrihydrites between the two-line and the six-line varieties could actually be synthesised by varying the rate of hydrolysis at pH 7 of a 0.1 M Fe(NO₃)₃ solution. This indicates that six-line ferrihydrite does not form by gradual ordering of the less crystalline two-line variety, but is rather the outcome of a specific set of reaction conditions. They report that fast rates of crystallisation produce the poorly ordered 2-line ferrihydrite, while slower rates form the more crystalline 6-line ferrihydrite. Average particle sizes of the end members of the ferrihydrite series differ, with 2-line ferrihydrite generally having particle sizes 2 – 4 nm and 6-line ferrihydrite 5 – 6 nm (Janney et al., 2000). Indeed, Michel et al. (2007) concluded from their PDF study that the differences between 2-line and 6-line ferrihydrite are mainly due to their different particle and domain sizes, rather than fundamental differences in their crystal structure.

2.5.1. Ferrihydrite aggregate structure

Once formed, ferrihydrite nanoparticles readily aggregate, even several pH units away from the zero point of charge (ZPC) and at low ionic strengths (Yuwono et al., 2012). Aggregation processes are important because the aggregate structure impacts colloidal stability (Gilbert et al., 2007; Legg et al., 2014a), reactivity (Gilbert et al., 2009; Dale et al., 2015; Stegemeier et al., 2015), and transport behaviour (Legg et al., 2014b). Additionally, the tendency of ferrihydrite to form large aggregates (flocs) is vital for its effective use in wastewater treatment because it provides a settleable or filterable solid (Loan et al., 2002). Ferrihydrite aggregate structures are typically mass fractal, meaning that they are scale invariant and appear the same over a range of scales (Sorensen, 2001). The mass of these aggregates scales with their size via a power law relation where the exponent has a value from 1 – 3:

\[ M \propto Rg^{d_f} \]  

(2.9)

Where M is the mass, Rg is the radius of gyration (the size) and \( d_f \) is the fractal dimension. In practice, the fractal dimension \( d_f \) can be considered a measure of the
packing efficiency whereby a lower d_f indicates less compact, more open structures (Figure 2.11).

The form of the mass fractal arrangements and their extent depends largely on the surface charge of the precipitated particles, which in turn is controlled predominantly by the solution pH and background electrolytes (Lo and Waite, 2000; Legg et al., 2014b). Ferrihydrite aggregates can possess low mass fractal dimensions (< 1.1), enabling formation of large (µm scale), low-density structures that exist as stable colloidal suspensions (Legg et al., 2014a, 2014b). These structures may however collapse to form denser, settleable aggregates (fractal dimensions > 2) upon a change in solution conditions, such as increased pH or ionic strength (Legg et al., 2014b). According to DVLO theory, increasing pH will promote aggregate collapse via progressive neutralization of the aggregate surface charges, thereby enabling attractive van der Waal forces to dominate over long-range repulsive electrostatic charges (Elimelech et al., 1995). Increased ionic strength can have a similar effect via neutralization of the long-range repulsive surface charges by the background electrolytes. Cryo-TEM techniques, which involve flash freezing the sample solution before imaging, have proven particular useful for elucidating ferrihydrite aggregate structures since this technique avoids the drying artefacts associated with standard TEM techniques (Yuwono et al., 2012; Legg et al., 2014a, 2014b).

Figure 2.11: Two-dimensional projections of mass fractal aggregates and their approximate mass fractal dimension. Author’s own figure.

2.6. Hematite and goethite structure

In comparison to ferrihydrite, hematite (α-Fe_2O_3) and goethite (α-FeOOH) are crystalline, thermodynamically stable phases with well-known structures. They often form via ferrihydrite transformation (Section 2.8.).
Hematite is isostructural with corundum ($\alpha$-Al$_2$O$_3$) and is composed of hexagonally close-packed oxygen ions arranged parallel to the (001) plane. Ferric ions fill two thirds of the interstitial sites and are arranged regularly with two filled sites followed by one vacant site. The ferric ions are all in octahedral coordination with oxygen (Fe(O)$_6$), with each octahedron sharing edges with three neighbouring octahedra in the same plane and face sharing with one octahedron in an adjacent plane. The hematite unit cell is hexagonal with unit cell dimensions $a = 5.034$ Å and $c = 13.75$ Å (Blake et al., 1966; Cornell and Schwertmann, 2003).

Goethite is isostructural with diaspore ($\alpha$-AlOOH) and is composed of hexagonally close-packed O$^-$ and OH$^-$ arranged parallel to the (010) plane with ferric ions filling half the ocatahedral interstices within each layer. The ferric ions are arranged in alternating double rows of occupied and unoccupied sites. The ferric ions are all in octahedral coordination, surrounded by three O$^-$ and three OH$^-$ ions, with double chains of these octahedra formed by edge sharing, and adjacent double chains linked by single corner sharing octahedra. The goethite unit cell is orthorhombic with unit cell dimensions $a = 9.956$ Å, $b = 3.0215$ Å and $c = 4.608$ Å (Szytula et al., 1968; Cornell and Schwertmann, 2003). The goethite (100) plane matches structurally with the hematite (003) plane, and therefore epitaxial growth of goethite on hematite can occur (Cornell and Schwertmann, 2003).

2.7. Ion adsorption at the iron (oxyhydr)oxide surface

Adsorption can be defined as the accumulation of matter at the solid-water interface (Drever, 1988; Stumm, 1992). Adsorption reactions are significant in the natural environment where they are a major influence on the geochemical fate of species, and are also important in industrial processes such as EARP where they act as an important mechanism for contaminant removal.

Fe octahedra at the iron (oxyhydr)oxide surface are not fully coordinated and will therefore adsorb a water molecule from solution. The protons attached to the water molecules tend to redistribute so that the (oxyhydr)oxide surface is covered with hydroxyl groups, which can act like ligands and promote surface complex formation with ions in the surrounding solution (Krauskopf and Bird, 1995). A number of surface complex formation equilibria can be established, with Table 2.5 listing some of the most important.
Table 2.5: Some important surface complex formation equilibria (not a comprehensive list). Adapted from Stumm (1992).

**Surface Complex Formation Equilibria**

**Acid base equilibria (S-OH is a surface group)**

\[
\begin{align*}
S-OH + H^+ & \rightleftharpoons S-OH_2^+ \\
S-OH + OH^- & \rightleftharpoons S-O^- + H_2O
\end{align*}
\]

**Metal (cation) binding**

\[
S-OH + M^{z+} \rightleftharpoons S-OM^{(z-1)+} + H^+
\]

**Ligand (anion) exchange (L^- = ligand)**

\[
S-OH + L^- \rightleftharpoons SL + OH^- 
\]

**Ternary surface complex formation**

\[
S-OH + L^- + M^{z+} \rightleftharpoons S-L-M^{z+} + OH^- 
\]

Due to protonation and deprotonation of the surface hydroxyl groups, the (oxyhydr)oxide surface has a variable charge. For each particular solid-solution composition, there exists a pH called the zero point of charge (ZPC) at which the net surface charge of the solid surface is zero (Parks & Bruyn, 1962). At pHs below the ZPC the solid surface will have a net positive charge and anion adsorption (ligand exchange) will be favoured, whilst at pHs above the ZPC the solid surface will have a net negative charge and cation adsorption (metal binding) will be favoured. Iron (oxyhydr)oxides have high ZPCs (~ pH 7 – 9.5) (Cornell and Schwertmann, 2003; Adegoke et al., 2013), making them positively charged over most pH ranges found in the natural environment.

Ions can form surface complexes in either outer sphere or inner sphere coordination (Figure 2.12). Additionally, ions can be in very weak electrostatic association with a solid surface some distance away from it as part of the ‘diffuse-ion swarm’ (Krauskopf and Bird, 1995). The equilibria in Table 2.5 are examples of inner sphere adsorption whereby a direct chemical bond is formed between the ion and solid surface. Inner sphere adsorption is typically either monodentate, where one chemical bond is
formed with the solid surface, or bidentate, where two bonds are formed (Figure 2.12). In contrast, no direct chemical bond is formed in an outer sphere complex; the attraction is purely electrostatic and the ion maintains its hydration shell (Figure 2.12). Outer sphere adsorbed ions are more weakly attached to the mineral surface than inner sphere adsorbed ions, but are not as weakly attached as ions in the diffuse-ion swarm.

Figure 2.12: Schematic of inner and outer sphere adsorption at the iron oxyhydroxide surface. Adapted from (Goldberg et al., 2007).

2.7.1. Ion adsorption in EARP

Non-radioactive ionic species are present in EARP effluent at significant concentrations (Table 2.2). The interaction of these species with the iron oxyhydroxide phase will be of significant importance, since they may compete for surface adsorption sites and modify surface electrostatics, affecting surface retention of trace radioactive species and the tendency of suspended colloids to aggregate (Krauskopf and Bird, 1995). As detailed above, the pH-dependent charging of mineral
surfaces in aqueous solutions largely governs ion sorption. Therefore, the extent of ion adsorption to EARP floc will vary as the neutralisation proceeds and will be dependent on the final floc pH. Since the ions are present throughout the iron (oxyhydr)oxide formation process in EARP, there is also the possibility of coprecipitation whereby the accompanying ions may be incorporated within the iron (oxyhydr)oxide structure (Curti, 1997).

2.7.2. Sulfate, phosphate and boron adsorption to iron (oxyhydr)oxides

Sulfate, phosphate and boron are discussed in greater detail since they are the non-radioactive ions generally of highest concentration in EARP effluent. The adsorption behaviour of sulfate and phosphate on iron (oxyhydr)oxides has been extensively studied, while studies of boron adsorption are more limited. Measured adsorption edges for sulfate, phosphate and boron on ferrihydrite are shown in Figure 2.13. For the anions sulfate ($\text{SO}_4^{2-}$) and phosphate ($\text{PO}_4^{3-}$), the percentage adsorbed to ferrihydrite decreases with increasing pH. This is expected since the ferrihydrite surface charge becomes progressively less positive with increasing pH, and therefore less electrostatically attractive to anions. Phosphate exhibits a higher affinity for ferrihydrite than sulfate, with significant amounts of phosphate still adsorbed above pH 9.

In contrast, boron exhibits a bell shaped adsorption edge with a maximum at ~ pH 8, which can be explained as follows. The pKa of boric acid $\text{B(OH)}_3$ is at pH 9 and so boron is predominantly speciated as boric acid below pH 9 and as borate $\text{B(OH)}_4^{-}$ above pH 9; while boric acid adsorption is favoured at higher pH because the adsorption reaction releases $\text{H}^+$, borate adsorption is favoured at lower pH because of competition with $\text{OH}^-$ (Su and Suarez, 1995). Boron adsorption is therefore a balance between these two influences.
Figure 2.13: Sulfate, phosphate and boron adsorption edges on ferrihydrite at ionic strength of 0.1 M. Sulfate data is redrawn from Fukushi et al. (2013) and is for a sulfate concentration of 0.2 mM. Phosphate data is redrawn from Antelo et al. (2010) and is for a phosphate concentration of 0.6 mM. Boron data is redrawn from (Su and Suarez, 1995) and is for a boron concentration of 0.46 mM. Also shown are approximate pKa values for phosphoric acid (H₃PO₄), sulfuric acid (H₂SO₄) and boric acid (B(OH)₃) (National Institute of Standards and Technology, 2017).

The structures of the sulfate and phosphate adsorption complexes have been extensively studied, particularly using attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy which is an effective in situ means of probing oxyanion adsorption at the water-solid interface (Hind et al., 2001). Sulphate adsorbs to goethite in a mix of outer and monodentate inner sphere coordinations, with inner sphere sorption becoming progressively more important with decreasing pH (Peak et al., 1999; Wijnja and Schulthess, 2000; Elzinga et al., 2001; Zhang and Peak, 2007; Beattie et al., 2008). Studies investigating sulphate interaction with hematite have found monodentate inner sphere surface complexes to be most important (Hug,
1997), with perhaps a small contribution from bidentate complexes (Lefevre & Fedoroff, 2006; Paul et al., 2005). More recent studies investigating sulfate interactions on ferrihydrite have reported both monodentate (Fukushi et al., 2013) and bidentate (Zhu et al., 2013b; Gu et al., 2016; Johnston and Chrysochoou, 2016) inner sphere sorption, as well as outer sphere complexes above pH 6 (Johnston and Chrysochoou, 2016).

The structure of phosphate adsorption complexes on iron (oxyhydr)oxides is an area of debate and it is likely that a variety of structures are possible (Krumina et al., 2016). Regardless of the details, it is clear that phosphate forms strong inner sphere complexes with iron (oxyhydr)oxides and that these complexes can persist at pH values above the ZPC (Antelo et al., 2010). On ferrihydrite, both bidentate (Arai and Sparks, 2001; Antelo et al., 2010; Wang et al., 2013, 2015a) and monodentate (Persson et al., 1996; Krumina et al., 2016) phosphate complexes have been suggested. A combination of both may be present at high pH (Antelo et al., 2010), with non-protonated complexes becoming increasingly important with higher pH (Arai and Sparks, 2001; Wang et al., 2015b). As well as surface adsorption, phosphate is also known to exhibit solid solution behavior with ferrihydrite whereby the phosphate incorporates within the ferrihydrite structure during co-precipitation. The resulting ferric phosphate can have a PO₄/Fe ratio of up to ~ 0.5 (Thibault et al., 2009).

Mechanisms of boron adsorption on iron (oxyhydr)oxides have been less extensively studied. However, there is evidence from FTIR that inner sphere complexes of both boric acid and borate are possible, as well as outer sphere complexes of boric acid (Su and Suarez, 1995; Peak et al., 2003). Notably, borate does not need to be present in solution for tetrahedral adsorption complexes to occur, indicating that adsorbed boric acid can convert from trigonal to tetrahedral geometry on the surface (Peak et al., 2003). Distinguishing between monodentate and bidentate complexes has not so far been possible, although Peak et al. (2003) argue based on their FTIR results that inner sphere boric acid adsorption is most likely via a bidentate mechanism.
2.8. Ferrihydrite transformation to goethite and hematite in aqueous solution

Although ferrihydrite readily forms because of its high kinetic accessibility, it is only thermodynamically metastable with respect to other more crystalline iron (oxyhydr)oxide phases. Ferrihydrite will therefore transform with time in aqueous solution, with hematite ($\alpha$-$\text{Fe}_2\text{O}_3$) and goethite ($\alpha$-$\text{FeOOH}$) by far the most common transformation products (Cornell and Schwertmann, 2003).

It is generally accepted that goethite and hematite form from ferrihydrite in aqueous solution by two different and competitive mechanisms (Cornell and Schwertmann, 2003) (Figure 2.14). Hematite formation involves an *in-situ* dehydration and local rearrangement pathway which does not require dissolution of the ferrihydrite; in contrast, goethite formation commonly occurs via a dissolution-recrystallisation process (Schwertmann and Murad, 1983). Therefore, transformation to hematite is favoured by factors which induce aggregation (pH near ZPC 6 – 9) and promote dehydration (increased temperature), while transformation to goethite is favoured by factors which promote ferrihydrite dissolution (low and high pH) (Figure 2.15).

![Figure 2.14: Overview of ferrihydrite transformation pathways to hematite and goethite.](image)
Figure 2.15: Hematite / (hematite + goethite) ratios vs. pH after 441 days of ageing (after Schwertmann and Murad, 1983), showing how goethite formation is favoured at pH values where ferrihydrite dissolution is high. The increase in hematite proportion below pH 4, despite ferrihydrite dissolution being favoured here, can be attributed to an increasing concentration of the divalent Fe(OH)\(^{2+}\) ion at low pH, which appears to be less favourable for goethite growth than the monovalent Fe(OH)\(^+_2\) (Knight and Sylva, 1974).

However, disregarding these general trends, the detailed pathways of ferrihydrite transformation are not fully resolved and are still subject to research. Hematite formation from ferrihydrite is considered to occur by a combination of aggregation-dehydration-rearrangement processes without the need for dissolution, which is perhaps because a structural continuity from ferrihydrite to hematite exists (Cudennec and Lecerf, 2006). TEM images of ferrihydrite aggregates aged for different time periods appear to show regions within the aggregates undergoing densification with subsequent nucleation of hematite crystallites (Fischer and Schwertmann, 1975; Pariona et al., 2016). An EXAFS study of ferrihydrite transformation to hematite at 92 °C reported a two-step process within the aggregates: (i) conversion of ferrihydrite to an intermediate phase via the elimination of water and development of face-sharing between Fe octahedra, and (ii) redistribution of vacancies in the intermediate phase to form hematite (Combes et al., 1990). Other studies utilising pair distribution function analysis (Michel et al., 2010) and magnetic measurements (Gutiérrez et al., 2016) have similarly found evidence for an intermediate phase, which forms within the ferrihydrite aggregates via
dehydration before rapid transformation and growth to hematite. Recent evidence
(Soltis et al., 2016) suggests hematite growth is not a monomer-by-monomer process
but is a particle-mediated process whereby small hematite particles first nucleate
within the ferrihydrite aggregates followed by crystallisation into larger hematite
particles, likely by orientated attachment. In support of this, Shaw et al. (2005)
reported a large difference in the apparent activation energies for nucleation and
crystallisation of hematite, suggesting two different mechanisms for these processes.

Ferrihydrite transformation to goethite is generally considered a more
straightforward dissolution-crystallisation process, with goethite nucleation and
growth occurring from small, soluble units, likely Fe(OH)$^+$ in acidic solution and
Fe(OH)$_4$ in alkaline solution (Knight and Sylna, 1974; Schwertmann and Murad, 1983;
Cornell and Schwertmann, 2003). However, at low pH, a multistep nucleation
pathway to goethite has also been demonstrated whereby ferrihydrite particles first
phase transform and then undergo orientated attachment (Banfield et al., 2000;
Burleson and Penn, 2006; Yuwono et al., 2010). This pathway has not been
demonstrated at high pH, probably because high negative surface charge on
ferrihydrite at high pH (pH > 13) disfavours aggregation.

Both hematite and goethite particles of various morphologies and sizes can be
prepared by varying the transformation conditions, indicating that different
conversion mechanisms may prevail under different conditions (Faivre, 2016). For
example, Wang et al. (2008) were able to prepare a range of hematite morphologies,
including cubic, spherical, sheetlike and hexagonal structures, by only varying the
nucleation rate, Fe$^{3+}$ concentration, and ageing time. Although goethite particles
exhibit less versatility in morphology and typically assume an acicular shape, goethite
particles with high and low acicular character (Montes-Hernandez et al., 2011) and of
different sizes (Lee Penn et al., 2006) can be produced by altering the transformation
conditions.

2.8.1. Effect of additional species on ferrihydrite transformation

As well as pH and temperature, ferrihydrite conversion is also sensitive to the
presence of additional chemical species. The effects of species, including complexing
anions, metal cations and organic acids, are varied (Cornell, 1987a) and include
inhibition of ferrihydrite crystallisation and/or a change in the crystallisation products.

Baltpurvins et al. (1996) investigated the influence of nitrate, chloride and sulfate on ferrihydrite ageing and found that the rate of transformation decreased with increasing affinity of the anions for the ferrihydrite surface (rate of transformation: nitrate > chloride > sulfate). In agreement with this, high charge density anions such as silicate (Cornell, 1987b; Francisco et al., 2016) and phosphate (Galvez et al., 1999; Shaw et al., 2005), which strongly interact with ferrihydrite at pH values determined by the acid-base properties of the anion, have been shown to particularly retard ferrihydrite transformation. For example, Galvez et al. (1999) investigated the effect of phosphate on ferrihydrite crystallisation at P/Fe solution ratios of 0 – 3% and over a range of pH and temperature conditions, finding that crystallisation was inhibited or only poorly crystallised lepidocrocite (γ-FeOOH) was formed at P/Fe > 2.5%. This was attributed to a twofold effect of the strongly adsorbed phosphate whereby the close contact of ferrihydrite particles, required for transformation to hematite, and the dissolution of ferrihydrite, required for goethite nucleation, were both inhibited (Cornell, 1987a).

In addition to a general inhibition effect, strongly adsorbing anions typically retard crystallisation to goethite more strongly than to hematite, resulting in an increased proportion of hematite in any crystallisation products. This effect may be due to binuclear surface complexes of phosphate or silicate having the ability to act as a template for hematite formation (Cornell and Schwertmann, 2003). Other ligands, such as oxalate and l-tartrate, can promote hematite formation without any accompanying inhibition effect due to this template effect (Fischer and Schwertmann, 1975).

In contrast to the strongly adsorbing anions, cations such as Al and Mn have a very weak crystallisation inhibition effect and appear to influence the transformation mainly via solution effects by complexing with dissolved ferric species (Fe$^{3+}$) (Cornell, 1987a).
2.9. Summary

Sellafield is undergoing a period of fundamental change in its operational focus: spent fuel reprocessing is due to end by 2020 and instead clean-up of the Sellafield site and treatment of legacy waste will become the primary objective. EARP will play a vital role in enabling clean-up operations and helping towards achieving the final end state of a fully cleaned and decommissioned Sellafield, which has a total estimated cost of £100 billion. As such, it is imperative that the EARP process has robust scientific underpinning and can operate as efficiently as possible, both to minimise radionuclide discharges to the environment and to provide the best possible value to the British taxpayer.

Iron oxyhydroxide flocculation processes such as that used in EARP are widely used in waste water treatment, with the nanocrystalline phase ferrihydrite typically the first product formed in these processes. Iron oxyhydroxide formation begins with hydrolysis of ferric iron, with successive polymerization and aggregation processes leading to eventual phase separation. However, the pathway from ferric iron monomers to flocculated ferrihydrite nanoparticles, and the effect of background ions on this process, is still not fully understood. In particular, intermediate hydrolysis species along this pathway and the role they play in ferrihydrite nucleation are not well characterized. Given the diversity of evidence, which is sometimes conflicting, different iron hydrolysis and ferrihydrite formation pathways may prevail under different conditions. For this reason it is important to investigate iron oxyhydroxide flocculation processes under a range of conditions; in this case, by directly mimicking the EARP process.

From experience on plant at EARP, it is known that the initially produced floc undergoes changes with time, with this having potential impacts on the radionuclide retention and processing characteristics of the floc. These changes are most likely due to transformation of ferrihydrite floc to more crystalline and thermodynamically stable iron (oxyhydr)oxides such as hematite and goethite. The crystalline products formed by ferrihydrite transformation and their morphologies are highly sensitive to the solution conditions, so it is also important to investigate this process under EARP conditions.
CHAPTER 3

Methodology

3.1. Introduction

Multiple experimental techniques have been utilised during this research programme to investigate iron oxyhydroxide formation and properties under EARP-like conditions (Figure 3.1). The following chapter describes the experimental approach, including how the EARP process was mimicked in the lab, and theoretical descriptions of individual techniques and details of their application.

Figure 3.1: Summary of experimental techniques used in this project.
3.2. Mimicking EARP

3.2.1. Chemostat reactor

An automated computer-controlled chemostat reactor (Applikon MiniBio) with temperature control was used to mimic the neutralisation process utilized in The Enhanced Actinide Removal Plant (EARP). Figure 3.2 and Figure 3.3 show the main components of the chemostat reactor. The 500 mL reaction vessel which holds the experimental solution (EARP effluent simulant) is comprised of inert borosilicate glass and is strapped to a Peltier heater/cooler to enable temperature control. A bespoke designed head plate (Figure 3.3) is fixed to the top of the reaction vessel, through which two silicone tubes for NaOH addition, a pH probe, and temperature probe are fitted. The head space can additionally be fitted with an Eh meter if required. A motor stirrer sits on top of the head plate to enable mixing of the system, whilst peristaltic pumps are used to pump NaOH into the reaction vessel via the silicone tubes. BioXpert software on the laptop is used to control the reaction and measure variables in situ. This chemostat reactor was also taken to Diamond Light Source to conduct in situ SAXS experiments (Section 3.5.2.).

![Chemostat reactor components](image)

**Figure 3.2:** Overview of experimental setup used to mimic the EARP neutralisation process in the lab.
3.2.2. EARP effluent simulant

The basic EARP effluent simulant was comprised of Fe(NO$_3$)$_3$.9H$_2$O dissolved in 1 M HNO$_3$ (7.16 mM / 400 ppm Fe(III)), consistent with the average acidity and Fe concentration in EARP bulk effluent (Table 2.2). Additionally, this Fe concentration was chosen so that floc was produced in quantities sufficient to conduct a range of analyses on.

In addition to this baseline pure ferric nitrate simulant, other simulants with added Na$_2$SO$_4$, NaH$_2$PO$_4$ or B(OH)$_3$ were used to investigate the effects of sulfate, phosphate and boron respectively on floc formation and ageing. The standard concentrations of sulfate, phosphate and boron used in these experiments were 1000, 100 and 150 ppm respectively, which were chosen to be in line with expected concentrations in EARP effluents (Table 2.2). Although Table 2.1 gives an average phosphate concentration of 32 ppm in bulk effluent, the higher standard concentration of 100 ppm phosphate was used in the present experiments for the following reasons: (i) phosphate
concentrations are variable and can be significantly higher than the average value, (ii) phosphate concentrations are higher in SEC effluents (30 – 120 ppm), (iii) effluent feeds also contain significant concentrations of organic phosphate, derived from the tri-butyl phosphate (TBP) used in fuel reprocessing and its degradation products, which might break down to inorganic phosphate. However, lower concentrations of phosphate (1 and 10 ppm) were also used in some experiments investigating floc ageing, as detailed in Chapter 6.

### 3.2.3. NaOH preparation

Two concentrations of NaOH – 7 M and 0.2 M – were used to neutralise the effluent simulant. Preparation of both these solutions was conducted under standard atmospheric conditions. In a cold water bath, 150 g of NaOH was dissolved in 500 mL of deionised water (DIW) to form a 7 ± 0.1 M NaOH solution. The concentration of this solution was determined by titration with 1 M HCl, and then an appropriate dilution with DIW was made to form an additional 0.2 M NaOH solution. These solutions were stored in sealed high-density polyethylene (HDPE) bottles where the head space had been purged with nitrogen gas, with silicone tubing fed through a seal at the top. Ingress of CO$_2$ to the NaOH during preparation is highly likely. Carbonate-free NaOH was not prepared in order to maintain relevance to EARP, in which NaOH is stored under standard atmospheric conditions. Concentrations of carbonate in the NaOH were not measured but the preparation method was kept highly consistent in order to minimise differences in carbonate concentrations between NaOH batches.

### 3.2.4. Standard synthesis procedure

400 mL of the EARP effluent simulant was used for each experimental run. The stirrer speed was set to 300 rpm and the temperature was controlled at 35 °C. Unless otherwise stated, the initial pH of the experimental solution was 0.1 ± 0.03. For the neutralisation procedure, 7 M NaOH was added at a rate of 1.5 mL min$^{-1}$ until the solution pH reached 2.3, after which the addition of the 7 M NaOH slowed down to 0.3 mL min$^{-1}$ until the pH reached 3. Above pH 3, the 7 M NaOH addition switched off and 0.2 M NaOH was added at 1.5 mL min$^{-1}$ until pH 9 was reached, after which the pH was allowed to stabilise at pH 9 for 10 min with further 0.2 M NaOH addition if pH fell below this set point.
For experiments which required separation of the precipitated solid, the slurry was subsequently centrifuged at ~ 7000 g for 5 min. A sample of the supernatant was passed through a 0.22 μm polyethersulfone (PES) filter for solution analysis by ferrozine analysis (section 3.4.2.) and ICP-AES (Section 3.4.3). Additionally, for some experiments, a sample of the supernatant (filtered) and wet precipitate paste at the bottom of the tube was sampled for infrared spectroscopy analysis (Section 3.3.2.). The remaining supernatant was decanted off and the precipitate washed three times with DIW followed by centrifuging, after which the precipitate was transferred to a watchglass and dried overnight in the oven at 40 °C. The dried product was used for powder XRD (Section 3.3.1.), TEM analysis (Section 3.3.3.), and BET surface area analysis (Section 3.3.4.).

3.3. Solid analysis

3.3.1. Powder X-ray diffraction (XRD)

An ideal crystal consists of a three dimensional array of repeating identical units arranged at regular distances from each other. This regular crystal structure, along with the chemical composition, defines a mineral and forms the basis for its identification. The ordered structure of a crystal means that the atoms lie in parallel planes, with the distance between identical sets of planes called the lattice spacing, or d-spacing. X-rays have wavelengths comparable in size to the d-spacings and therefore any particular set of planes have the potential to reflect an incident X-ray beam, similar to a mirror. This is the phenomena exploited in X-ray diffraction (XRD) analysis to identify mineral phases or determine a crystal structure.

X-rays reflected from crystal planes interfere with each other either constructively or destructively depending on whether they are in phase with one another when they meet. This results in formation of a diffraction pattern which consists of a series of X-ray reflections at angles of incidence where constructive interference occurs. The requirement for constructive interference is that the interfering X-rays have a path length distance which is either the same or an integer multiple of the X-ray wavelength. Since the difference in path length distances of the X-rays is determined by the d-spacing and the angle of incidence, the angles at which constructive interference occurs and a reflection is seen is given by the Bragg equation:
where $n$ is an integer, $\lambda$ the X-ray wavelength, $d$ the d-spacing, and $\theta$ the angle of incidence. Each lattice plane produces a series of $n$ reflections at which constructive interference occurs, and the angles ($\theta$) are which these reflections are seen can be used in the Bragg equation to calculate the d-spacings.

In powder XRD, powdered samples which consist of many small crystals (crystallites) in different orientations are analysed. The sample is rotated during analysis to ensure a large number of different crystal orientations are exposed to the X-ray beam, resulting in smearing of individual diffraction spots to form a series of rings (Figure 3.4). The resulting diffraction intensities are converted to a 2D plot of diffraction intensity vs. incidence angle, which can be used as a fingerprint to identify which solid phases are present in the sample and their relative quantities. Additionally, the width of the diffraction peaks contains information about the degree of crystallinity and the crystal size and shape.

Figure 3.4: Pattern formation in powder XRD. A) Diffraction spots from a single crystal. B) Diffraction spots from three crystals, slightly misaligned with respect to each other. The spots start to form annular rings around the beam centre. C)
Diffraction pattern from a powdered sample consisting of many small crystallites in different orientations. D) Trace through the diffraction pattern in C) showing a series of diffraction (Bragg) peaks as a function of angle 2θ. Adapted from (Glazer, 2016).

Powder XRD was used in this project to identify the solid phase formed when mimicking the EARP process, and for investigating how the solid phase changes with ageing. To prepare samples for powder XRD analysis, a small amount of the dried solid product was ground to a fine powder in a pestle and mortar with a few drops of amyl acetate and spread evenly onto a glass slide and allowed to air dry. This sample slide was loaded into a Bruker D8 Advance Diffractometer equipped with a LynxEye detector and analysed using Cu K-alpha radiation. Scans of the solid were collected from 5 to 80° with a 0.02° step size at a scan speed of 1° min⁻¹. A side effect of using Cu K-alpha radiation to analyse iron samples is that its energy is close to an iron absorption edge. This has a double negative effect on the data quality: (i) the iron absorbs a significant proportion of the incoming X-rays, reducing the diffracted signal, and (ii) the iron fluoresces as the excited state relaxes, increasing the noise level. To minimise this effect during analysis of the iron (oxyhydr)oxide samples in this project, alternative settings for the LynxEye detector were used whereby the low level was increased from 0.11 to 0.19 (to cut out lower energy noise) and the detector window width was reduced from 0.14 to 0.08 (again, to restrict noise reaching the detector).

XRD patterns were collated and background subtracted in EVA (Bruker AXS, 2013) and peak matched using the International Centre for Diffraction Data (ICDD) Powder Diffraction File database. Additionally, Rietveld refinement was performed on samples which contained a mixture of phases to quantify the proportions of each phase. This was performed in Topas (Bruker AXS, 2009) and involved using a least squares method to vary the relative proportions of each component phase until the XRD pattern was best fit. Preferred orientation of hematite had to be considered in the Rietveld refinement in order to accurately fit XRD patterns with hematite.
3.3.2. Attenuated total reflectance Fourier Transform infrared spectroscopy (ATR-FTIR)

The positions of atoms in a molecule are not fixed: their chemical bonds to neighbouring atoms are subject to a number of different vibrations. Each vibration of any particular chemical bond operates at a characteristic energy and can absorb radiation of that particular energy and become excited. The energies corresponding to vibrational modes fall within the infrared (IR) region of the electromagnetic spectrum. Therefore, by scanning a sample with wavelengths (energies) of light within the IR range and measuring at which wavelengths the sample absorbs, we can obtain information about the identity of chemical bonds present (Peak, 2013).

As well as allowing identification of the presence of particular bonds within a sample, IR spectroscopy can also provide information on a molecule’s bonding environment. Based on symmetry rules, only certain vibrational modes of a bond will be IR active and thus absorb radiation. As the bonding environment of a molecule changes, its symmetry, and therefore the number of IR active vibrational modes, also change. A change in molecular symmetry may also result in the splitting of vibrational modes that were previously degenerate in energy. In this way, clues about the molecular bonding environment can be obtained by looking at the number and position of absorption peaks in an IR spectrum (Peak, 2013).

Today, Fourier transform spectrometers are most widely used to perform infrared spectroscopy. In Fourier transform infrared spectroscopy (FTIR), data is collected in the time-domain (beam intensity as a function of time) using an interferometer and subsequently converted to the frequency domain (beam intensity as a function of IR frequency (wavelength)) via a Fourier transform (Skoog et al., 2007). In contrast, conventional dispersive spectrometers directly collect data in the frequency domain by using a grating monochromator to split the IR beam into different wavelengths. Fourier transform spectrometers have few optical elements and no slits to attenuate radiation, and therefore offer better signal-to-noise ratio and higher throughput than dispersive instruments.

Attenuated total reflectance (ATR) FTIR operates by measuring the absorption of an internally reflected IR beam after contact with the sample. The IR beam is directed into an optically dense crystal with high refractive index (e.g. a diamond) and undergoes total internal reflectance, resulting in an evanescent wave that extends...
beyond the crystal surface and into the sample (Figure 3.5). ATR-FTIR is advantageous over transmission FTIR as minimal sample preparation is required and less signal is lost by attenuation of the beam, allowing highly absorbing samples to be readily analysed.

![Figure 3.5: Schematic of an ATR-FTIR experimental setup.](image)

An infrared spectrum is normally presented as a plot of percent radiation transmitted versus the frequency of the incident radiation (given as wavenumbers (cm⁻¹)). The spectrum is useful as a means of identifying iron (oxyhydr)oxides, as well as potentially providing information on crystal morphology, degree of crystallinity, ion adsorption and extent of metal substitution (Cornell and Schwertmann, 2003; Lefèvre, 2004).

ATR-FTIR was used in this project to investigate the interactions of background chemical species (i.e. nitrate, carbonate, sulfate, phosphate, boric acid) with the iron (oxyhydr)oxide phase during its formation (Chapter 5) and subsequent ageing (Chapter 6). IR spectra of the experimental solid/solution slurries were taken on a Perkin Elmer Frontier ATR-FTIR Spectrometer. After centrifuging, spectra of the unwashed wet solid and the supernatant were taken at a scan speed of 0.1 cm⁻¹ s⁻¹ with a resolution of 4 cm⁻¹ and as an accumulation of 64 scans. Final spectra were obtained by subtracting the supernatant spectrum from the wet precipitate spectrum, followed by baseline correction and normalisation of the absorbance intensities to a maximum of one absorption unit. Gaussian peak fitting of the spectra was done in Origin (OriginLab, Northampton, MA).
3.3.3. Transmission Electron Microscopy

Transmission electron microscopy (TEM) produces an image by directing an electron beam at an ultrathin sample and measuring the electrons that are transmitted through the sample. These transmitted electrons contain structural information about the sample due to their interactions with the sample as they pass through (Figure 3.6).

Because the wavelength of the electron beam is much smaller than that of visible light, TEM produces images with resolution many orders of magnitude higher than optical microscopy. In fact, resolution can be high enough to observe individual lattice planes in high resolution (HR) TEM images which can be used to index crystal faces (Goodhew et al., 2001)

In an optical microscope, image contrast arises primarily from attenuation of the light wave amplitude by the sample. In TEM, attenuation of the electron wave amplitude by the sample only plays a secondary role in contrast formation; instead electron scattering is the dominant contrast formation mechanism. There are three main mechanisms which act to produce image contrast in a TEM:

- **Mass-thickness contrast.** Results from the off-axis incoherent elastic scattering of electrons. Thicker areas of the sample and areas with high atomic number (Z) scatter electrons more and therefore transmit fewer electrons to the image plane. These areas appear darker compared to thinner and less mass dense areas. Being incoherent, this contrast mechanism applies to both crystalline and amorphous materials.

- **Diffraction contrast.** Caused by Bragg scattering of electrons from crystalline samples onto discrete locations on the image plane. By using apertures, particular Bragg reflections can be selected, resulting in only the parts of the sample causing scattering of electrons at the selected Bragg reflection to show up.

- **Phase contrast.** Arises from the interference in the image plane of the electron wave with itself due to differences in phase. Phase contrast forms the basis of high resolution (HR) TEM since it allows imaging of the atomic structure of the sample.
Some TEMs can also be operated in scanning TEM (STEM) mode where the electron beam is focused to a narrow spot and is scanned over the sample in a raster. This allows elemental mapping of the sample using analysis techniques such as energy dispersive spectroscopy (EDX) and electron energy loss spectroscopy (EELS). Additionally, operating in STEM mode in combination with a high angle detector enables formation of images where the contrast is directly related to the atomic number (Z). This is known as high angle annular dark field (HAADF) imaging.

TEM also enables the analysis of the crystal structure via selected area electron diffraction (SAED) whereby diffracted electrons are collected at the image plate, forming a diffraction pattern. Electron beams in a TEM have wavelengths significantly smaller than the atomic spacings in a solid phase, and therefore the sample can act as a diffraction grating to the electron beam. Single diffraction spots will be observed if the electron beam is directed at a single crystal, whilst diffraction
rings will be seen if a polycrystalline sample is analysed. In this way, SAED is very similar to XRD, but with the advantage that specific sample areas measuring a few hundred nanometres can be analysed.

One drawback of TEM is that the standard technique requires the sample to be dried and placed in a vacuum. This can introduce drying artifacts which distort how particles were in situ within solution (Bailey and Mecartney, 1992; Michen et al., 2015). For example, sample drying may cause particle aggregation or collapse of pre-existing aggregate structures to denser structures. Cryo-TEM and in situ liquid TEM techniques in principle overcome these problems by analysing flash frozen and liquid samples respectively.

Both standard TEM and in situ liquid TEM techniques were utilised in this project. Standard TEM, which can achieve higher resolutions than in situ TEM, is most appropriate for imaging the primary nanoparticles, whilst in situ liquid TEM is better suited for imaging aggregate structures which are otherwise significantly altered by drying. However, in situ liquid TEM is a considerably more challenging and expensive technique than standard TEM, so only limited data was obtained using this method.

**Standard (in vacuo) TEM**

Two different types of sample were prepared for standard TEM analysis: pre-dried samples and wet colloidal samples. The pre-dried samples were ground to a fine powder and re-suspended in isopropanol with vigorous shaking, followed by slow addition of 1–3 drops of the suspension to a holey carbon coated, 200 mesh copper TEM grid and leaving to air dry. For the wet colloidal samples, 1–3 drops of the solution was directly pipetted onto the TEM grid followed by 3 drops of isopropanol to wash away excess salt and then allowing to air dry. Holey carbon copper grids were used for solutions with pH > 3 while holey carbon gold grids were used for solutions with pH < 3.

Samples were analysed using either a Philips CM200 field emission gun (FEG)-TEM with an Oxford Instruments 80 mm 2 X-Max silicon drift detector (SDD) detector, or an FEI Talos F200X analytical transmission electron microscope (operated at 200 kV) equipped with an integrated Super-X energy dispersive spectroscopy (EDX) system.
with 4 windowless silicon drift detectors. The FEI Talos had the option to operate in STEM mode, allowing collection of elemental maps using EDX and Z-contrast images using HAADF imaging.

**In situ TEM**

Samples of flocculated slurry at pH 9 were directly pipetted onto a Protochips Poseidon P210 analytical liquid cell holder and analysed on a FEI Tecnai F30 300 kV Field Emission Gun Analytical Electron Microscope equipped with an Oxford Instruments Xmax80 SDD.

### 3.3.4. BET surface area analysis

The specific surface area of an iron (oxyhydr)oxide phase has significant influence on its reactivity, including its thermodynamic stability, interaction with sorbents, and dissolution and dehydroxylation behaviour (Cornell and Schwertmann, 2003). Surface area is a property whose value depends on the technique used to measure it, and so measured values are usually interpreted as only indicative (Dzombak and Morel, 1990). The most common method for measuring the surface area of iron (oxyhydr)oxides is the BET method (Brunauer et al., 1938). This method involves the physical adsorption of a gas (typically N₂) onto the sample surface and application of BET-theory - an extension of Langmuir theory (a theory of monolayer adsorption) to multilayer adsorption.

The BET equation expresses a linear relationship between the amount of gas adsorbed, \( v \), (cm³ g⁻¹) and the relative vapour pressure, \( p/p₀ \):

\[
\frac{1}{v(p/p₀-1)} = \frac{1}{v_m c} + \frac{c-1}{v_m c} \cdot \frac{p}{p₀}
\]  

(3.2)

Where \( v_m \) is the monolayer adsorbed gas quantity and \( c \) is the BET constant which is related to the energy of adsorption. Plotting \( 1/v(p/p₀-1) \) against \( p/p₀ \) at constant temperature gives an adsorption isotherm whose slope and intercept can be used to calculate and \( v_m \) and \( c \). From knowing \( v_m \) and the surface area occupied by one gas molecule, the specific surface area of the sample can be calculated.

The BET-method requires that the sample is first outgassed to remove any physically adsorbed water which would otherwise interfere with the surface determination.
is typically done at elevated temperatures (100 – 150 °C), and for most samples this
treatment doesn’t lead to any phase changes or transformation. However, specific
surface areas of iron (oxyhydr)oxides are strongly dependent on the outgassing
conditions, with surface area increasing by as much as 170% with heating, and phase
changes occurring in poorly crystalline samples at temperatures below 100 °C
(Clausen and Fabricius, 2000). To avoid this, an alternative outgassing procedure
recommended by Clausen and Fabricius (2000) was used in the present study
whereby the dried, powdered precipitate samples were outgassed with He at room
temperature for 19 hours. This was followed by measurement of the BET multipoint
surface area using a Micromeritics Gemini with N₂ as the sorbent gas.

3.4. Solution analysis

3.4.1. pH

Solution pH was measured using an Applisens pH sensor designed for use with the
chemostat (recommended pH range 0 – 13). The pH probe was calibrated using two
buffers (pH 1 and 10). The initial pH of the experimental solutions (before NaOH
addition) showed good reproducibility, giving a value of pH 0.1 ± 0.03.

3.4.2. Ferrozine assay

The ferrozine assay is a spectrophotometric method used to measure concentrations
of dissolved Fe in solution (Stookey, 1970; Viollier et al., 2000). The method is based
on the use of the ferrozine reagent (monosodium salt hydrate of 3-(2-pyridyl)-5,6-
diphenyl-1,2,4-triazine-p,p'-disulphonic acid) which forms stable magenta-coloured
complexes with Fe²⁺ with a maximum absorbance at 562 nm. Total Fe (Fe(II) and
Fe(III)) can be measured by introducing an initial reduction step whereby
hydroxylamine hydrochloride (H₂NOH.HCl) solution is used to reduce Fe(III) to
Fe(II) before introduction of the ferrozine reagent. The Beer-Lambert law is followed
up to approximately 5 ppm Fe (Stookey, 1970) and therefore a linear calibration curve
can be produced by measurement of samples with Fe concentrations between 0 – 5
ppm.

Samples for ferrozine analysis were filtered (0.22 µm PES filter) and preserved by
acidification with HNO₃. The ferrozine method of Viollier et al. (2000) was used to
measure total Fe concentration. Briefly, 0.1 mL of sample (diluted to Fe concentration
< 5 ppm) was added to a cuvette followed by 0.9 mL deionised water and 0.2 mL of 1.4 M H$_2$NO.HCl solution. The sample was allowed to reduce for 10 mins before addition of 0.1 mL buffer solution (10 M ammonium acetate) and 0.1 mL of 1 mM ferrozine solution. The colour was allowed to develop for 10 mins before measurement of the absorbance at 562 nm on a Jenway 6850 UV/Vis Spectrophotometer. Background measurements were performed using the same procedure but without Fe present in the sample. Uncertainties were measured by calculating the standard deviation of triplicate measurements.

To enable conversion of absorbance measurements to an Fe concentration, a linear standards curve was produced by measurement of samples with known concentrations of ferric nitrate acidified with HNO$_3$ (Fe(III) concentrations 0 – 5 ppm).

### 3.4.3. Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) was used to measure the solution concentrations of sulphate (measured as sulphur), phosphate (measured as phosphorus) and boron. Sample solutions were filtered through a 0.22 µm polyethersulfone (PES) filter and were preserved by acidification with HNO$_3$.

The samples were analysed using a Perkin-Elmer Optima 5300 dual view ICP-AES. Sample batches were run with standards every 10 samples and the limit of detection was 50 ppb for each analyte.

### 3.5. Synchrotron techniques

#### 3.5.1. Synchrotron radiation

Synchrotron radiation is the name given to electromagnetic radiation produced when charged particles are accelerated in a curved path at relativistic speeds, i.e. very close to the speed of light. The radiation given off under these conditions is confined to a narrow cone in the same direction as the particle motion, much like a searchlight (Willmott, 2011). Because the power radiated by such particles is inversely proportional to the fourth power of its rest mass, the emitted radiation is highly significant for very small particles, such as electrons (Glazer, 2016). The emitted wavelengths range from the hard X-ray to the infrared region, with those from the X-ray region most commonly used in synchrotron experiments.
Synchrotron radiation exhibits a number of special properties which make it highly beneficial for use in experiments. The radiation has exceptionally high brilliance (intensity), many orders of magnitude greater than that produced in conventional X-ray tubes, and possesses high collimation (i.e. very low beam divergence), enabling collection of data with low signal to noise and a high time resolution. As such, element specific techniques, such as X-ray absorption spectroscopy (XAS), can be performed at very low elements concentrations and often in complicated environmental matrices (Burke et al., 2015).

Figure 3.7: Schematic of the most important parts of a modern synchrotron facility (adapted from Willcott, 2011).

Synchrotron facilities have been built to take advantage of synchrotron radiation for experimental purposes, with the most important components of a modern synchrotron shown in Figure 3.7. Low energy electrons are produced in an electron gun, usually by thermionic emission from a hot filament, and are accelerated to about 100 MeV in a linear accelerator (linac) into a booster ring. In the booster ring, the electrons are further accelerated to near light speeds before injection into the storage ring, which circulates the electrons in a closed path using an array of bending magnets whilst also maintaining the electron energy using a radio frequency supply. Synchrotron light is produced when the electrons pass through the bending magnets and also through insertion devices in the straight sections of the storage ring, which ‘wiggle’ the electrons laterally and produce the most intense synchrotron radiation.
The synchrotron radiation is isolated and focused in various beamlines which run tangentially off the storage ring, with each beamline typically optimised for using a specific technique(s) within the fields of spectroscopy, scattering and imaging.

In this project, synchrotron based experiments were performed at the Diamond Light Source, which is a medium energy synchrotron (3 GeV) with ~ 22 currently operational beamlines.

3.5.2. Small angle X-ray scattering (SAXS)

When X-rays interact with matter, the incident photons may be transmitted, absorbed or scattered. Scattering can occur with or without loss of energy, known as elastic and inelastic scattering respectively. Small angle X-ray scattering (SAXS) concerns the measurement and analysis of X-rays scattered elastically at the smallest angles (2θ < 10°). Elastic scattering (also known as Thomson scattering) arises from interaction of the incoming X-ray beam with the electrons, causing them to oscillate at the same frequency as the X-rays. In turn, these oscillating charges give rise to secondary electromagnetic radiation of the same wavelength, which forms the scattered X-rays. Constructive and destructive interference can occur between these scattered X-rays, changing the X-ray intensity, and it is these variations in intensity which forms an interference pattern which contains structural information about the sample (Guinier and Fournier, 1955; Glatter and Kratky, 1982; Willmott, 2011).

SAXS patterns are typically plotted as a function of the scattering vector q, which represents the momentum transfer and is the difference in wave vectors between the scattered and incident radiation (Figure 3.8). q is related to the scattering angle (θ) and wavelength of the incident beam (λ):

\[
q = \frac{4\pi \sin \theta}{\lambda} \quad (3.3)
\]
Figure 3.8: Schematic representation of the scattering vector \( q \). Light incident from the left with wave vector \( k_i \) is scattered by a particle towards the SAXS detector with wave vector \( k_s \) at scattering angle \( \theta \). The scattering vector, \( q \), is the difference \( k_i - k_s \).

Since \( q \) has units of reciprocal length (e.g. nm\(^{-1}\)), scattering at smaller \( q \) values (i.e. smaller scattering angles) contains information about larger scale features (Figure 3.9). Therefore, scattering at low \( q \) contains information about large scale features such as interparticle interactions; scattering at intermediate \( q \) about medium scale features such as particle size and shape; and scattering at high \( q \) about small scale features such as the particle surface (Figure 3.9) (Guinier and Fourner, 1955; Glatter and Kratky, 1982; Willmott, 2011).

Figure 3.9: Size domains in a SAXS experiment. A) SAXS pattern with labelled \( q \) regions. B) Size domains probed at each \( q \) region.
Particles must have an electron density (\( \rho \)) different from the surrounding matrix to be visible by SAXS, otherwise scattering from the particles will be the same as scattering from the matrix and the SAXS signal will be indistinguishable from the background. Therefore SAXS is a contrast method where it is spatial variations in the electronic density (i.e. electron density difference, \( \Delta \rho \)) which SAXS “sees” as objects.

The scattering intensity, \( I \), is dependent on the number of electrons illuminated by the beam. Hence, \( I \) is proportional to the individual particle volume \( (V_p) \) and the number of particles \( (n) \), as well as the electron density difference \( \Delta \rho \):

\[
I \propto \Delta \rho^2 \cdot V_p^2 \cdot n
\]  

(3.4)

Clearly, equation 3.4 alone does not fully describe a scattering pattern since there is no dependence on the scattering vector \( q \). Further terms have to be added which describe the \( q \) dependence of the scattering intensity and contain the structural information about the scatterer.

**Form Factor**

The scattering pattern obtained on an isolated scatterer, such as a single particle, is described by the square of the Fourier transform of the scatterer’s electron-density distribution. As such, the scattering pattern is dependent on the shape (i.e. form) and size of the particle. The form factor, \( P(q) \), is the Fourier transform of a function which describes the particle shape and is utilised to account for the effect of particle shape and size on the scattering pattern. A number of form factors are readily available for different particle shapes (e.g. sphere, cylinder, disc, Figure 3.10) (Li et al., 2016).

The form factor can fully describe the scattering pattern when all the particles are identical in size and shape (i.e. monodisperse) and the sample is dilute (i.e. the particles are far away from each other):

\[
I(q) = \Delta \rho^2 \cdot V_p^2 \cdot n \cdot P(q)
\]  

(3.5)

If the particles are a range of different sizes (i.e. polydisperse) then the average of the form factors for each particle size give the scattering pattern of the whole sample.
Figure 3.10: Simulated SAXS patterns using different form factors, $P(q)$, to represent monodisperse populations of different shaped particles: a sphere (20 nm radius), a cylinder (40 nm long, 4 nm radius), and a disc (4 nm thick, 4 nm radius). Simulated SAXS patterns were generated in Irena macro for Igor Pro (Ilavsky and Jemian, 2009).

**Structure Factor**

In non-dilute samples where the particles are densely packed, then the distances between particles can be on the same order of magnitude as distances within particles. In this case, the scattering pattern also contains contributions from neighbouring particles. This contribution is accounted for by the structure factor, $S(q)$:

$$I(q) = \Delta \rho^2 \cdot V_p^2 \cdot n \cdot P(q) \cdot S(q)$$

(3.6)

Whilst the form factor contains information on the single particle level (high and intermediate $q$, Figure 3.9), the structure factor contains information about how the particles are organised (low $q$, Figure 3.9). Many different structure factors are available which describe a range of different particle organisations, from disordered fractal networks to crystalline structures. A detailed description of the mathematical functions used to express different form and structure factors can be found in Pedersen (1997).
**Guinier approximation**

The Guinier approximation (Guinier and Fourner, 1955) states that any form factor can be approximated in the low angle limit (low q) by a Gaussian function:

$$I(q) = \Delta \rho^2 \cdot V \cdot n \cdot e^{-\frac{q^2 R_g^2}{3}}$$  \hspace{1cm} (3.7)

The constant terms are typically grouped together and termed $I(0)$, which is the extrapolated zero-angle intensity:

$$I(q) = I(0) \cdot e^{-\frac{q^2 R_g^2}{3}}$$  \hspace{1cm} (3.8)

$R_g$ is the radius of gyration, a shape independent measure of size. It is defined as the root mean square distance of all the electrons in the particle from the particle’s centre of gravity. If the particle shape is known and assumed to be of homogeneous density, then the particle dimensions can be calculated from $R_g$ using the appropriate shape-specific equation. For example, the radius of a spherical particle, $R$, is:

$$R = \frac{5}{\sqrt{3R_g}}$$  \hspace{1cm} (3.9)

The high q limit for which the Guinier approximation is valid if defined as $\leq 1.3/R_g$. A Guinier plot is a graph of the natural logarithm of $I(q)$ as a function of $q^2$ and should be linear (Figure 3.11). Values for $I(0)$ and $R_g$ can be obtained by calculating the intercept and slope of the linear plot respectively. If the sample is not monodisperse the Guinier plot will not be linear and Guinier analysis should not be conducted. Additionally, the Guinier approximation requires scattering data with no structure factor.
Figure 3.11: Example of a Guinier plot. The low q data (black) is fitted by a linear line (red), with the linearity of the fitted region assessed by the flatness of the residuals (green). Values for I(0) and R_g are derived from the vertical intercept and slope respectively. Adapted from (Skou et al., 2014).

Porod approximation

At the other end of the q range, the Porod approximation describes asymptotic behaviour at high q (Porod, 1951; Sinha et al., 1988). The scattering signal at high q values (i.e. q >> π/R_g) comes from electron density contrast over distances significantly smaller than the particle size (Figure 3.9, high q). Assuming electron density differences within the particle are much smaller than between the particle and external matrix, scattering will occur primarily from the interface of the particle and matrix. Porod (1951) showed that scattering in this region follows a power law decay of q^(-4) when the interface is sharp and perfectly smooth:

\[
\lim_{q \to \infty} q^4 \cdot I(q) = P
\]  

(3.10)

Where P is the Porod constant, defined as:

\[
P = \Delta \rho^2 \cdot 2\pi S/V
\]  

(3.11)

Where S is the surface area and V the sampling volume.
In a monodisperse sample, an interference pattern is readily seen in the sharp oscillations of the Porod region, while in a polydisperse sample these oscillations become increasingly averaged out (Figure 3.12). The Porod approximation also applies to non-dilute, densely packed systems since scattering from structure factor(s) is insignificant at high $q$. However, a power law exponent of $-4$ is only obtained for systems with a sharp, non-rough interface, with deviation from the Porod approximation occurring in fractal systems (see below).

**Figure 3.12:** Simulated SAXS patterns of a population of 50 Å radius spherical particles with smooth surfaces at various levels of polydispersity. The Guinier and Porod regions of the SAXS curves are highlighted. Simulated SAXS patterns were generated in Irena macro for Igor Pro (Ilavsky and Jemian, 2009).

**Fractal analysis**

Aggregates of particles often form highly irregular structures which are better described by fractal geometry rather than conventional Euclidean geometry (Mandelbrot, 1977). Two types of fractal can be distinguished: mass fractals, where the entire structure is fractal, and surface fractals, where only the surface has fractal properties (Figure 3.13). SAXS is a convenient method for assessing the fractal dimension of a sample (Teixeira, 1988), with the fractal dimension often interpreted as a measure of the compactness of aggregates: this can be seen in Figure 3.13 whereby aggregates with smaller fractal dimensions have less compact, more open structures,
while aggregates with higher fractal dimension are denser. For fractal systems, the power-law decay at high \( q \) is less than the Porod exponent of -4 and is directly related to the fractal dimension (Sorensen, 2001). A Porod law exponent between -3 and -4 represents a surface fractal, while a value between -1 and -3 represents a mass fractal structure (Figure 3.13), with the \( q \) region over which the Porod region is observed indicating the dimensional range over which the system is fractal. Structure factors exist for both mass fractals (Teixeira, 1988) and surface fractals (Wong and Bray, 1988) and can be used in the modelling of SAXS data.

**Figure 3.13:** Fractal structures and their approximate Porod exponent.
**SAXS experiments**

**Figure 3.14:** Simplified schematic of set-up for *in situ*, time-resolved SAXS experiments. The chemostat reactor detailed in Section 3.2.1 was used for these experiments.

All SAXS data was collected on beamline I22 at the Diamond Light Source using a monochromatic X-ray beam at 12.4 keV, with a pixel-array PILATUS 2 M detector to collect the SAXS patterns. As well as measurement of static solution samples, *in situ* time-resolved experiments were undertaken where the neutralisation reaction mimicking EARP was performed on the beamline using the chemostat reactor (Section 3.2.1.) with continual SAXS measurement (Figure 3.14) (Chapters 4 & 5). For these *in situ* time-resolved experiments, a peristaltic pump in closed loop configuration continuously circulated the reacting suspension from the continuously stirred reaction vessel through a quartz capillary in-line with the X-ray beam (Figure 3.14). Flow time between the reaction vessel and the quartz capillary was kept short (<2 s). SAXS patterns were collected throughout the reaction and for 30 min after base addition had finished, with a time resolution of 15 s/frame. For the static solution samples, solutions were directly injected into the quartz capillary and data collected for 20 scans at 15 s/scan.

A camera length of 3.8 m was used in the *in situ* time-resolved experiments, giving a measured q-range of $0.03 - 4.3 \text{ nm}^{-1}$, while a camera length of 1.9 m was used in the static experiments, giving a measured q-range of $0.3 - 8.1 \text{ nm}^{-1}$. 
**SAXS analysis**

2D SAXS patterns were reduced to 1D scattering curves of intensity $I$ vs $q$ by sector integration. The resulting intensity data, $I(q)$, was normalised to the sample transmission and, in the static samples, calibrated using glassy carbon as a standard to yield $I(q)$ on an absolute scale. Background subtraction of the ferric nitrate solution prior to NaOH addition was performed, resulting in SAXS profiles consisting of only scattering from any particles that form during the experiment.

The scattering curves were fit in Origin Pro (OriginLab, Northampton, MA) with the Levenberg-Marquardt Algorithm, using a model that describes the scattering as arising from a population of spherical primary particles (spherical form factor) which may cluster to form aggregates with both mass fractal-like structure (mass fractal structure factor) and non-fractal aggregates (hard sphere structure factor) (Stawski et al., 2011). The full equation describing the scattering model was as follows:

$$I(q) = \Delta \rho^2 \cdot V_p^2 \cdot n \cdot P(q) \cdot [\varepsilon S_F(q) + (1 - \varepsilon) S_{HS}(q)]$$

(3.12)

Where $P(q)$ is the spherical particle form factor, $S_F(q)$ is the mass fractal structure factor, $S_{HS}(q)$ is the hard sphere structure factor, and $\varepsilon$ is a weight factor between (0 – 1) which accounts for changes in the relative scattering contribution from the structure factors over time. A more detailed description of this model is found in Chapters 4 and 5 and in Stawski et al. 2011.

Values for parameters determined by the models had standard errors of < 1%, which were calculated by the fitting routine in Origin Pro using the Levenberg-Marquardt Algorithm. However, this likely underestimates the true uncertainties in these parameters because certain errors inherent in the SAXS data (e.g. uncertainties in background subtraction) are often not well represented in the raw data, and there is currently no widely accepted and tested model for calculating errors in SAXS data (Sedlak et al., 2017). However, further confidence in the parameters was achieved by checking their consistency upon slight variations in background subtractions, finding that they were robust unless otherwise stated.

**3.5.3. Pair distribution function (PDF) analysis**

The pair distribution function (PDF) gives the distribution of distances between pairs of atoms in a sample and is used for structure determination. In contrast to XRD,
which probes long-range structural order and is best suited to analysis of crystalline materials, the PDF technique is particularly useful for investigating the structure of materials which are disordered, nanocrystalline, or in any way lacking long-range order. This is because the PDF reveals the short and intermediate range order via simultaneous analysis of both the Bragg and diffuse scattering (Billinge and Kanatzidis, 2004). Therefore, the PDF technique is particularly suited to structural analysis of ferrihydrite which, owing to its nanocrystallinity, only exhibits short range order.

A PDF, also known as \( G(r) \), is obtained by Fourier transform of a high energy X-ray scattering (HEXS) pattern, which is collected by exposing a sample to a high energy (short wavelength) X-ray beam and measuring the resulting sample scattering. The high energy of the X-rays acts to compress the scattering angle range, allowing collection of scattering data over a very large \( q \)-range which contains both Bragg and diffuse scattering. Figure 3.15 shows a HEXS pattern and its corresponding PDF. The PDF can be interpreted as a distribution of distances whereby individual peaks derive directly from pairs of atoms.

![Figure 3.15](image)

**Figure 3.15:** A) High energy X-ray scattering (HEXS) data collected on a slurry of hematite and goethite (author’s own data). B) The corresponding pair distribution function (PDF) after Fourier transform of the HEXS data.
The PDF technique was used in this project to investigate the structure of the final iron oxyhydroxide phase formed in our experiments. HEXS data was collected on beamline I15 at the Diamond Light Source using an X-ray energy of 76 KeV ($\lambda = 0.16 \text{ Å}$), giving a measured q range of $0 - 50 \text{ Å}^{-1}$. Samples were prepared by injecting freshly prepared ferrihydrite slurry into a 1 mm diameter quartz capillary, followed by centrifuging to concentrate the solid at the capillary end. A single HEXS pattern was collected on this concentrated wet solid every 1 s, with 1440 patterns averaged to give the final data. The 2D raw data was converted to a 1D pattern of intensity versus wave vector (q), followed by conversion to a PDF ($G(r)$) in Gudrun (McLain et al., 2012) via Fourier transform of the reduced structure function ($S(q)$) in the q-range $0.5 - 17 \text{ Å}^{-1}$.

### 3.5.4. Extended X-ray absorption fine structure spectroscopy (EXAFS)

Extended X-ray absorption fine structure spectroscopy (EXAFS) provides element-specific structural information about a sample via analysis of its X-ray absorption spectrum. More specifically, EXAFS involves analysis of the gradual oscillations observed in the X-ray absorption spectrum at energies just above the absorption edge (Figure 3.16).

X-ray absorption spectroscopy (XAS) data is collected by measuring the X-ray absorption coefficient of a sample as a function of energy ($\mu(E)$). The energy range over which $\mu(E)$ is measured is chosen to correspond with the energy required to eject a core electron, i.e. the binding energy, from a chosen element. When X-rays with energy greater than the binding energy are supplied, the core electron is excited and ejected from the atom as a photoelectron, leaving behind an electron hole. A relaxation process subsequently takes place involving decay of a higher energy electron into the electron hole. The corresponding increase in $\mu(E)$ that occurs due to excitation of the core electron is called the absorption edge (Figure 3.16).

At energies ~50 eV above the absorption edge, and extending out to up to 1000 eV, oscillations in $\mu(E)$ are observed which comprises the EXAFS region (Figure 3.16). The origins of these oscillations are wave interactions between the ejected photoelectron and the electrons of other surrounding atoms, with maxima and minima in the oscillations arising from constructive and destructive interference between the waves respectively. Because these oscillations are dependent on the location and identity of
the surrounding atoms, analysis of the EXAFS gives information about the local bonding environment of the element being analysed.

**Figure 3.16:** X-ray absorption spectrum (XAS) of partially hydrolysed ferric nitrate solution, collected at the Fe K-edge with EXAFS region highlighted (author's own data).

EXAFS is an element specific technique since the energy range over which an X-ray absorption spectrum is measured corresponds to the electron binding energy of a specific element. EXAFS is also an average technique because it detects the local bonding environment of all atoms of the chosen element equally, and therefore the resulting EXAFS is an average of all the different bonding environments present in the sample.

EXAFS was used in this project to investigate the local bonding environment of iron in partially hydrolysed solution samples before mass precipitation. The sample solutions were injected into an acrylic plastic cell with each side sealed with Kapton film to form X-ray transparent windows. Fe K-edge spectra were collected in fluorescence mode at beamline B18 at The Diamond Light Source at a rate of one scan per 5 min, with a total of 30 scans collected for each sample. Spectra were averaged and normalized in Athena, followed by fitting in Artemis (Ravel and Newville, 2005).
3.6. Ageing of iron oxyhydroxide slurries

Experiments were undertaken to characterise ageing-induced transformation of the iron oxyhydroxide slurries (Chapter 6). The precipitated slurries were aged in 500 mL HDPE plastic bottles at 40 °C in an oven for periods of 8 weeks. pH change was measured throughout the ageing period and subsamples were taken at periods of 1, 4 and 8 weeks for characterisation by XRD, TEM and ATR-FTIR. Additionally, the transformation kinetics were measured using an ammonium oxalate extraction method Section 3.6.1.), and changes in the settleable solids volume (Section 3.6.2.) and sedimentation kinetics (Section 3.6.3.) were measured.

3.6.1. Ammonium oxalate extraction

For the ageing experiments, the kinetics of ferrihydrite transformation to more crystalline phases was determined by measuring the proportion of ferrihydrite remaining in solution as a function of ageing time. To achieve this, an ammonium oxalate extraction method (Schwertmann and Cornell, 2000) was used whereby only the non-crystalline Fe phases (i.e. ferrihydrite) are selectively dissolved whilst leaving the crystalline phases essentially intact (< 2% dissolved depending on crystallinity (Schwertmann, 1973)). Briefly, 5 mL of 0.2 M ammonium oxalate was added to 5 mL of the sample slurry and pH was adjusted to pH 3 with oxalic acid. The sample was left to digest in the dark with mild agitation for two hours, before filtering (0.22 µm polyethersulfone) and measuring for dissolved Fe(III) using the ferrozine method (Viollier et al., 2000). The ratio of oxalate soluble Fe (Fe_{ox}) to total Fe (Fe_{t}) gives the proportion of ferrihydrite in the sample.

3.6.2. Settleable solids volume

The change in the volume of settleable solids with time was measured by transferring 50 mL of the sample slurry to an Imhoff settling cone and reading the volume of settled solids after periods of 1 and 24 hours. It is expected that the solids volume will decrease with increased ferrihydrite crystallisation since ferrihydrite is highly hydrated with an open porous structure whilst crystalline phases such as hematite and goethite are denser and more compact.

3.6.3. Sedimentation kinetics
Measurement of the sedimentation kinetics provides information about colloidal stability and aggregate structure (Phenrat et al., 2007; Vikesland et al., 2016). A UV-Vis spectroscopy method was used whereby 3 mL of freshly dispersed sample slurry was transferred to a cuvette and the absorption at 508 nm was measured every 10 s for 30 min on a Jenway 6850 UV/Vis Spectrophotometer. Absorption of deionised water was simultaneously measured and subtracted as a background. Measurement at 508 nm was chosen for consistency with the literature (Phenrat et al., 2007; Vikesland et al., 2016). Results are plotted as normalised absorption (absorption at time t (A) divided by absorption at time 0 (A₀)) vs time.

3.6. PHREEQC modelling

To complement the analytical data, a model of the iron oxyhydroxide floc synthesis procedure was created in PHREEQC (Parkhurst and Appelo, 2013) by mimicking the NaOH-induced hydrolysis of Fe(NO₃)₃ undertaken in the experimental method. PHREEQC calculations were preformed using an edited SIT (specific ion interaction theory) database whereby equilibrium constants for FeOH²⁺(aq), Fe(OH)₂⁺(aq) and Fe₂(OH)₄⁴⁺(aq) were replaced with those recommended in a review conducted by the NEA (Nuclear Energy Agency) (Lemire et al., 2013) (Table 3.1). Equilibrium constants for other relevant Fe species were as defined in the SIT database. A single phase – ferrihydrite (Fe(OH)₃) – was allowed to precipitate, with the solubility product defined by Stefánsson (2007) used. Separate models with sulfate, phosphate and boric acid included were run to mimic the experiments including these species.

Table 3.1: Reactions and equilibrium constants recommended by the NEA. The corresponding species already present in the SIT database were replaced with the ones listed here.

<table>
<thead>
<tr>
<th>Species</th>
<th>Reaction</th>
<th>Log₁₀K°</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeOH²⁺(aq)</td>
<td>Fe³⁺ + H₂O ⇌ FeOH²⁺ + H⁺</td>
<td>-2.150</td>
<td>(Lemire et al., 2013)</td>
</tr>
<tr>
<td>Fe(OH)₂⁺(aq)</td>
<td>Fe³⁺ + 2H₂O ⇌ Fe(OH)₂⁺ + 2H⁺</td>
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</tr>
<tr>
<td>Fe₂(OH)₄⁴⁺(aq)</td>
<td>2Fe²⁺ + 2H₂O ⇌ Fe₂(OH)₂⁴⁺ + 2H⁺</td>
<td>-2.820</td>
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CHAPTER 4

Ferrihydrite Formation: The Role of Fe\textsubscript{13} Keggin Clusters

This chapter is a manuscript published in the journal Environmental Science & Technology in August 2016.

The full citation for the published manuscript is as follows:

INTRODUCTION

Ferrihydrite is a nanoparticulate iron oxyhydroxide which is ubiquitous in the natural near-surface environment. It is also present in the core of the protein ferritin and has numerous industrial applications. Due to its high absorptive capacity and ability to coprecipitate aqueous ions, ferrihydrite is a crucial sequester of contaminants in both natural and industrial effluents. Here we characterize ferrihydrite formation during the titration of an acidic ferric nitrate solution with NaOH. In situ SAXS measurements supported by ex situ TEM indicate that initially Fe$_{13}$ Keggin clusters (radius $\sim$ 0.45 nm) form in solution at pH 0.12–1.5 and are persistent for at least 18 days. The Fe$_{13}$ clusters begin to aggregate above $\sim$ pH 1, initially forming highly linear structures. Above pH $\sim$ 2 densification of the aggregates occurs in conjunction with precipitation of low molecular weight Fe(III) species (e.g., monomers, dimers) to form mass fractal aggregates of ferrihydrite nanoparticles ($\sim$ 3 nm) in which the Fe$_{13}$ Keggin motif is preserved. SAXS analysis indicates the ferrihydrite particles have a core–shell structure consisting of a Keggin center surrounded by a Fe-depleted shell, supporting the surface depleted model of ferrihydrite. Overall, we present the first direct evidence for the role of Fe$_{13}$ clusters in the pathway of ferrihydrite formation during base hydrolysis, showing clear structural continuity from isolated Fe$_{13}$ Keggins to the ferrihydrite particle structure. The results have direct relevance to the fundamental understanding of ferrihydrite formation in environmental, engineered, and industrial processes.
the Fe(III) dimer is detectable, while some have reported formation of an Fe(III) trimer, tetramer, and larger polycations. However, there is little consistency on the composition of the larger Fe(III) polymers, and some of them may already be considered a ferrhydrite phase.

Larger metal polycations have been identified in other hydrolysable trivalent element systems such as Cr(III), Ga(III), and Al(III). The most studied of these polycations is the Al₁₃(Keggin) unit, consisting of a central tetrahedral Al unit surrounded by octahedral Al units. Al₁₃(Keggin) is an important intermediate in the pathway from Al monomers to solid Al hydroxides. Due to similar aqueous chemistries of Fe(III) and Al(III), it has been postulated that an analogous Fe₁₃(Keggin) cluster may exist. Indeed, recently Sadeghi et al. successfully synthesized and characterized a Fe₁₃(Keggin) cluster using stabilization with Bi³⁺ ions. Although the details of the ferrhydrite structure remain unclear, the single phase model proposed by Michel et al. and subsequently adopted in the wider literature is based on linked Keggin units. This raises the question of whether Fe₁₃(Keggin) is a precursor (i.e., prenucleation cluster) to ferrhydrite formation, but as yet, a pathway from monomers to Fe₁₃(Keggin) and then ferrhydrite during base hydrolysis has yet to be demonstrated.

After the nucleation and growth of individual ferrhydrite nanoparticles aggregation may occur, even several pH units away from the point of zero charge (PZC). Aggregates of ferrhydrite nanoparticles can possess low mass fractal dimensions (<1.1), enabling formation of large (µm scale), low-density structures that exist as stable colloidal suspensions. These structures may undergo collapse to form denser, settleable aggregates upon a change in solution conditions, such as increased ionic strength. These nanoparticle aggregation processes are important because the resulting ferrhydrite aggregate structure impacts colloidal stability, reactivity, transport behavior, and also filterability in wastewater treatment processes.

In order to observe intermediate species during rapid Fe(III) hydrolysis, the majority of experiments to date has been conducted in quasi-equilibrated solution at constant pH or a given OH/Fe ratio. The conclusions from these studies with Fe₃(II) have limited relevance to ferrhydrite formation in dynamic systems. The Enhanced Actinide Removal Plant (EARP) (Sellafield, UK) is an example of an efficient treatment process where this is relevant. Here, a ferricyanoferrohydroxide floc formed via base hydrolysis is used to treat highly radioactive effluents generated from the reprocessing of spent nuclear fuel. During the EARP process, radionuclides become associated with the floc which is subsequently separated by ultrafiltration and encapsulated in a cement wasteform. The EARP floc compositions are expected to significantly change when the site transitions from reprocessing to postoperational clean-up and decommissioning activities over the next few years. Therefore, to enable better control of the EARP process and similar industrial treatments, an enhanced understanding of the ferrhydrite formation mechanisms under process relevant conditions is essential and provides fundamental knowledge relating to ferrhydrite formation.

In this study we determine the mechanisms by which ferrhydrite nanoparticles form, and the role of Fe₁₃ clusters, during the controlled hydrolysis of an acidic ferric nitrate solution in an experimental protocol designed to mimic ferric oxyhydroxide effluent treatment systems (e.g., EARP). To achieve this, in situ time-resolved small-angle X-ray scattering (SAXS) experiments followed ferrhydrite formation. These were augmented with ex situ X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques. Results show that during base hydrolysis, ferrhydrite nanoparticles form via Fe₁₃(Keggin) clusters. This is key to understanding the pathway of ferrhydrite formation in environmental, engineered, and industrial processes.

**EXPERIMENTAL SECTION**

Ferrhydrite was synthesized in an automated computer-controlled reactor (Applikon MiniBio) with temperature control (Peltier heater/cooler) via NaOH-induced hydrolysis of ferric nitrate solutions. Stirred batch experiments were conducted at 35 °C (representative of EARP conditions), with the pH and temperature monitored throughout. Starting solutions consisted of 400 mL of Fe(NO₃)₃·9H₂O in 1 M HNO₃ (17.6 mM Fe(III)). In the standard base addition experiments 7 M NaOH was initially added at a rate of 1.5 mL min⁻¹ until pH 2.3, then 0.3 mL min⁻¹ until pH 3, and finally, after pH 3, 0.2 M NaOH was added at 1.5 mL min⁻¹ to pH 9 (Video S1). To test the effect of the NaOH addition rate, further slow NaOH addition experiments were performed with 7 M NaOH additions at 0.3 mL min⁻¹ up to pH 1.2. To provide an indication of the reaction progress, Figure S10 shows a change in pH with time in both standard and slow addition experiments. Solid products were isolated by centrifuging and washing three times with deionized water before drying at 40 °C overnight. Powder XRD (Bruker D8 Advance), BET surface area analysis (Micromeritics Gemini), and TEM images of the dried products were obtained (SI).

During the standard NaOH addition experiment (1.5 mL min⁻¹), dissolved iron concentrations were determined following filtration (0.22 µm polyethersulfone) and then analysis for Fe using the ferrozine method. A separate experiment using ultrafilters (10 and 3 kDa) was also undertaken on selected samples (SI).

To enable comparison with iron behavior at thermodynamic equilibrium, the ferrhydrite synthesis procedure was modeled in PHREEQC by mimicking the NaOH-induced hydrolysis of Fe(NO₃)₃ undertaken in the experimental method (SI).

**Time-Resolved In Situ SAXS Experiments.** Ferrhydrite synthesis experiments were performed in situ on beamline I22 at the Diamond Light Source with time-resolved SAXS data collected throughout base addition. A peristaltic pump in closed loop configuration continuously circulated the reacting suspension from the continuously stirred reaction vessel through a quartz capillary in-line with the X-ray beam. Flow time between the reaction vessel and the quartz capillary was kept short (<2 s). A monochromatic X-ray beam at 12.4 keV and a camera length of 3.8 m was used in the time-resolved experiments, and the SAXS patterns were collected using a pixel-array PILATUS 2 M detector. SAXS patterns were collected throughout the reaction and for 30 min after base addition had finished, with a time resolution of 15 s/frame.

SAXS experiments were also undertaken on aged, static samples. For these samples, the ferrhydrite synthesis reaction was stopped at pH 0.5 or pH 1.5, and the resulting solutions aged at 35 °C for 6 and 18 days prior to SAXS analysis. Here, samples were directly injected into a quartz capillary, and SAXS data were collected using a camera length of 1.9 m.

**SAXS Data Analysis.** The scattering curves were fit using a model that describes the scattering as arising from a population...
RESULTS AND DISCUSSION

Solid Phase Characterization and Solution Analysis.

XRD characterization (Figure S1) of solid product isolated at pH 9 indicates that two-line ferrihydrite was the reaction product formed with a BET surface area of 290 ± 15 m² g⁻¹. TEM on samples collected at pH 1, 3, and 9 (Figures 4 and S13) show that the pH, structure, stucture, and morphology of the particles were consistent with 2-line ferrihydrite, with no other phases detected.

In the standard base addition experiment, the "dissolved Fe" (<0.22 μm, Fe(III)ₐq) concentration decreased slightly (~5%) between pH 0.1 and 1, followed by a more significant decrease after pH 1 (Figures 1 and S3). The experimental pH at which Fe(III)ₐq removal occurred (pH 0.1) was lower than that predicted by thermodynamic calculation, which indicated Fe(III)ₐq would be constant until pH 2.5 (Figure 1). The thermodynamic calculations are based on the principles of classical nucleation theory (CNT), and as such Fe(III)ₐq is predicted to remain constant until the solution becomes saturated with respect to ferrihydrite (Fe(OH)₃)ₐq at which point instantaneous precipitation is predicted to occur. However, it should be noted that filtration analysis and thermodynamic modeling can not determine the presence of large Fe(III) polycations (e.g., Keggin) which may be present within the partially hydrolyzed solution. The experimental data instead showed an ~35% decrease in Fe(III)ₐq below pH 2.5. Above pH 2.5, experimental data showed a rapid decrease in Fe(III)ₐq consistent with the thermodynamic predictions for ferrihydrite formation. Above pH 4 there was no detectable Fe(III)ₐq in solution (<0.01 ppm), indicating ferrihydrite formation was complete. A separate experiment, performed under identical experimental conditions but with the additional use of ultrafilters, showed a similar result and is detailed in the SI (Figure S3).

The discrepancy between the experimental and theoretical results reflects the dynamic nature of our experiments. PHREEQC calculations allow thermodynamic equilibrium to be achieved upon each small addition of base, while experimentally, constant base addition means equilibrium is not achieved. Locally high pH at the point of base addition, indicated by bursts of yellow/orange color in the experimental system (Video S1), likely drives Fe(III) cluster/particle formation at lower pH and therefore may explain the discrepancy with the theoretical results. Interestingly, analysis of aged solutions (Figure S2) indicates that the Fe(III)ₐq concentration in pH 1.5 solution remained suppressed after 7 days aging, suggesting the Fe(III)ₐq clusters/particles present are thermodynamically (meta)stable. This was noteworthy considering that ferrihydrite is significantly undersaturated (saturation index ~ −2.7) at pH 1.5 (Figure 1) and suggests irreversible formation of Fe(III)ₐq clusters/particles is occurring during base addition in this system.

Overview of SAXS Data. Figures 2A and S4 show the evolution in the SAXS patterns during the standard NaOH addition experiment as the pH increases. Below pH 0.12 the scattering patterns had no intensity above background confirming that there were no scattering species present, and therefore Fe(III)ₐq was present only as monomers (Figure S5). Above pH 0.12, increased scattering intensity occurred indicating the formation of clusters/particles and allowing fitting of the scattering patterns. Between pH 0.12 and 1, fits were obtained using a single population of clusters/particles, while above pH 1 fits required the addition of the mass fractal/hard sphere structure factor in order to accommodate the increased scattering intensity seen in the low-q region (eqs S2, S3). From this, and in conjunction with other data discussed below, two characteristic stages of ferrihydrite formation were identified.

Stage (i): pH 0.12 to ~1: formation of primary Fe₁₅ Keggin clusters.

Stage (ii): pH ~1 to 9: formation and aggregation of 2-line ferrihydride nanoparticles.

Stage (i): Formation of Primary Fe₁₅ Keggin Clusters. Log−log plots of the SAXS patterns (Figures 2A and S4) showed a visible Guinier region in the high-q area (q > 1 nm⁻¹) at pH 0.15 indicating the presence of a single population of unaggregated clusters. These initiated at pH 0.12 and within 2 min of starting the NaOH addition (Figure S5). From pH 0.12−1, the clusters grew in number density (n, eq S2) while being relatively stable in size, as evidenced by an increasing scattering intensity (I(q)) throughout the q-range without any change in the overall SAXS pattern shape (Figure 2A). The growing number of clusters can also be seen by the increasing value of the prefactor term nVₐr²₂ₐ₂ up to pH 1 (Figure 2B). Fits to the scattering patterns below pH 1 were obtained for q > 0.5 nm⁻¹ using a single cluster population with a spherical form factor (eq S2). The fitted cluster radius (rₙ) was initially 0.44 nm at pH 0.15 and decreased slightly to 0.41 nm by pH ~ 1 (Figure 2B), a decrease of 0.03 nm which is within the inherent uncertainty of SAXS and may be due to slight changes in the background scattering. Similarly, Guinier analysis of the scattering patterns up to pH 1 gives a radius of gyration Rₕ (a shape independent measure of size) of 0.36–0.37 nm (Figure S6), corresponding to a spherical radius of 0.46–0.48 nm. Above pH ~ 1 Guinier analyses was not possible due to development of upward curvature in the low-q Guinier region of the SAXS pattern, indicating cluster aggregation. Overall, these results show strong agreement in the cluster radius and, within the expected limitations imposed by background
In contrast, Figure 3 indicates that they are best described as clusters of ions rather than a phase with extended structure such as a ferrihydrite particle. Additionally, their size is significantly smaller than a phase with extended structure such as a ferrihydrite particle. For these reasons it appears that the primary clusters are most likely precursors to ferrihydrite formation rather than already formed ferrihydrite particles. Sadeghi et al. (2015) recently synthesized and isolated a Fe\(_{13}\) oxo-iron cluster with the α-Keggin structure. Because the ferrihydrite structure in the Michel et al. model\(^{61}\) is considered to be linked Fe\(_{13}\) Keggin units, this Fe\(_{13}\) cluster has been identified as a potential prernucleation cluster to ferrihydrite formation. This is analogous to the Al\(_{13}\) cluster being a precursor to aluminum hydroxide formation.\(^{62}\) The Fe\(_{13}\) cluster has an \(R_g\) of 0.36–0.38 nm (ref 31 and Figure 3), corresponding to a spherical radius of 0.46–0.49 nm. This closely matches the cluster size measured in the current study with a Guinier radius of gyration of 0.36 nm and a corresponding spherical cluster radius of 0.46 nm. In addition, an excellent match is observed between simulated scattering from Fe\(_{13}\) Keggin clusters\(^{61}\) (using Crysol (SI)) and the measured scattering patterns (Figure 3). In contrast, simulated scattering patterns of the Fe oxo-dimer described by Zhu et al.\(^{14,15}\) and an Fe trimer do not match to the experimental data and their \(R_g\)'s are significantly smaller (0.24–0.26 nm, Figure S11). Taken as a whole, this indicates that Fe\(_{13}\) clusters form at low pH as a precursor/prernucleation cluster to ferrihydrite formation. However, it is likely that not all the Fe is present as Fe\(_{13}\) kaggins, with a significant proportion likely to be monomers and smaller hydrolysis products (e.g. dimer) which produce a minimal scattering contribution.

Figure 2. A) A selection of time-resolved in situ SAXS patterns collected during ferrihydrite formation (standard NaOH addition rate) with model fits overlain. B) Evolution of particle radius \(\langle r_p \rangle\), prefactor term \((nV^2\Delta p)^{\lambda}\), aggregate weighting factor \((\epsilon)\), aggregate fractal dimension \((d_f)\) and aggregate radius of gyration \((R_g)\) during ferrihydrite formation (standard NaOH addition rate). The start of stages i and ii of the reaction are marked (see main text).

Figure 3. Simulated scattering curve for a Fe\(_{13}\) Keggin cluster compared to the experimental scattering curve collected at pH 0.3. Inset is an atomic structure model of a Fe\(_{13}\) cluster\(^{61}\) with radii of gyration \((R_g)\) calculated by Crysol based on both the atomic structure model and the Guinier fit of the simulated curve.
SAXS patterns collected on aged pH 0.5 samples (6 and 18 days at 35 °C) also show scattering indicative of a single population of clusters (Figure S8). Due to the use of a shorter camera length in these experiments, the q-range is shifted to higher values than in the main time-resolved experiments. Using Guinier analysis, the $R_g$ of clusters in the pH 0.5 solutions (for 6 and 18 days) was 0.38 nm, identical to the Fe₁₁₃ Keggin cluster.³¹ Again, strong agreement is seen between simulated Fe₁₁₃ scattering patterns and the pH 0.5 aged samples (Figure S9). Therefore, the Fe₁₁₃ clusters we observe forming in the dynamic experiments persist in solution for at least 18 days, consistent with the analogous Al₁₃₃ cluster which is also persistent in solution.⁶³–⁶⁵ Interestingly, the aged pH 1.5 samples also showed scattering indicative of a single population of clusters (Figure S8). Since Fe₁₁₃ clusters begin aggregating above ~ pH 1 in the main dynamic experiment (see below), there may also be aggregates present at pH 1.5 which were unseen in the experimental q-range. Alternatively, disaggregation over time may have occurred. The $R_g$ of clusters in the pH 1.5 solutions is 0.35 nm. This modest change in size from pH 0.5 may be an artifact of small variation in the background solvent scattering as pH increases or may reflect slight changes to the shape/polydispersity of the primary clusters; Keggin clusters are not perfect spheres and can assume different isometric forms, as has been observed for Al₁₃₃ clusters.²⁶ Additionally, lacunary Keggin structures with missing fragment(s) are known.³⁶ Nevertheless, good agreement is seen between simulated Fe₁₁₃ scattering patterns and the pH 1.5 aged samples (Figure S9). Only a slight difference in the scattering intensity ($nV_s^2\Delta \rho/\pi$) was observed between 6 and 18 day samples at pH 0.5 and pH 1.5, suggesting there is no significant difference in the number density of scattering particles ($n$, eq S2) and thus no net formation or dissolution of clusters between these time periods. Additionally, the pH of the solutions were essentially stable during the aging period (Table S2), indicating no further hydrolysis/condensation which would release $H^+$.²⁶

TEM images obtained for the pH 1 sample (Figures 4A and S13A) showed loosely aggregated nanoparticles that vary in size from ~2–5 nm diameter (Figure 4A). This aggregated phase could be identified as 2-line ferrihydrite based on the lattice images and diffraction patterns observed (Figure S13A). Solution data showed a small decrease (~5%) in Fe(III)$_{aq}$ by pH 1 (Figure 1), consistent with particle formation. The high angle annular dark field (HAADF) images provide additional evidence for smaller ~1–2 nm diameter aggregating units, putative evidence for Keggin clusters forming the particles (Figure 4A). Given the SAXS patterns at pH 1 are dominated by scattering from the Fe₁₁₃ clusters, these data suggest that at this pH a small proportion of Fe₁₁₃ clusters, and potentially other hydrolysis products, coalesce to form filterable ferrihydrite nanoparticles. However, TEM images likely over-represent the amount of ferrihydrite nanoparticles present in solution at pH 1, as the individual clusters themselves (as solution polycations) will not be observed via TEM.

Overall, these data confirm Fe₁₁₃ Keggin clusters form rapidly upon NaOH addition and are stable in solution for weeks at low pH. With increasing pH ferrihydrite nanoparticles form and aggregation occurred.

**Stage (ii): Formation and Aggregation of 2-Line Ferrihydrite Nanoparticles.** Increasing scattering intensity in the low-q region of the SAXS patterns was observed above pH 1, indicating that aggregation of primary Fe₁₁₃ clusters occurred. Atom-by-atom growth of the clusters can be ruled out as no increase in the slope of Guinier region was observed (Figure S12). The low-q scattering intensity increase was fitted by introducing a mass fractal structure factor, permitting determination of the aggregate weighting factor ($\epsilon$, smaller value = more aggregation), aggregate size parameter ($\xi$), and aggregate fractal dimension ($d_f$) (eq S2). $\epsilon$ initially decreased slowly above pH 1 before decreasing rapidly from pH 2–3 and reaching a minimum at pH 4.1, indicating that aggregation is complete. This occurred concurrently with continual growth in the scattering intensity of the low-q region and confirms aggregation increases with increasing pH. This is consistent with solution data whereby the rapid decrease in Fe(III)$_{aq}$ between pH 2–3 was concurrent with most rapid aggregate formation. Above pH 4.1, $\epsilon$ shows a small increase until pH 5.

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Figure 4. A) TEM images of particles from pH 1 experimental solution showing aggregates of 2–5 nm sized ferrihydrite particles. Inset high angle angular dark field (HAADF) image of an aggregate. B) TEM images of particles from pH 9 experimental solution showing ferrihydrite aggregates with mass fractal structure. Top left inset showing individual particle sizes of 3–4 nm. Bottom right inset electron diffraction pattern inset showing characteristic 2-line ferrihydrite diffraction.
and then stabilizes, presumably an artifact of the aggregate size increasing to beyond the experimentally measured q-range. This can be seen in Kratky plots ($I(q)/q^2$ vs $q$, Figure S14B) where the low-q scattering intensity peak, indicative of average aggregate size, moves to values outside the measured q-range above pH 4.1 and results in reduced scattering intensity within the low-q area of the measured range.

Aggregation from as low as pH 1 is notable given that ferrihydrite has a PZC of $\sim$ pH 8 and may be due to a number of factors. First, the high ionic strength $^{45,42,44}$ of our experiments, as coagulation of hematite particles has also been reported at low (<1.5) and high (>12) pH due to the elevated ionic strengths. $^{46}$ Second, our experiments were performed at elevated temperature (35 °C) relevant to EARP processes, which gives particles additional thermal energy (kT) to overcome the electrostatic barrier to aggregation. Finally, aggregate formation may be induced by an increase in the concentration of Fe$_{13}$ clusters beyond a certain critical level.

The aggregate fractal dimension, $d_f$, increases from $\sim$1.1 at pH 1 to $\sim$2.3 at pH 3.1 and then stabilizes. A $d_f$ of 1.1 is indicative of highly linear structures $^{47}$ and indicates the Fe$_{13}$ clusters are linking into linear aggregates, potentially with some polymerization. This interpretation is supported by the shape of the SAXS patterns between $\sim$ pH 1 and 2, which show an increase in the low-q slope gradient without significant changes to the high-q region (Figure S12). At pH 3.1, a $d_f$ of 2.3 indicates more densely packed aggregates with mass fractal structure $^{48}$ and therefore shows the aggregates undergo densification with increasing pH, consistent with previous studies which showed densification of iron oxyhydroxide nanoparticles with changing chemical conditions. $^{66,70}$ This is concurrent with the rapid decrease in Fe(III)$_{aq}$ and TEM observation of mass fractal aggregates of $\sim$3 nm ferrihydrite nanoparticles at pH 3 (Figure S13). This highlights that during this stage of the reaction (pH up to 3.1) all dissolved Fe(III)$_{aq}$ i.e. Fe$_{13}$ Keggin and smaller hydrolysis products (e.g., monomers and dimers) precipitate to form aggregates of ferrihydrite nanoparticles. We propose that Fe$_{13}$ clusters are preserved within the structure of the ferrihydrite nanoparticles composing these mass fractal aggregates, further details of which are discussed below. Observations show that solutions with pH < 2.0 remain colloidal homogeneous suspensions after $>$1 month storage, while solutions with pH > 2.0 loc within weeks (Figure S17), consistent with formation of a more densely structured aggregate at increasing pH. $^{40}$

The initial fractal dimension of 1.1 is significantly lower than that predicted by traditional models of colloidal aggregation. Diffusion limited aggregation (DCA) would be expected to give fractal dimensions of 1.6–1.9, $^{41}$ while reaction limited aggregation (RCA) is expected to give fractal dimensions >2.0. $^{72}$ Significantly lower fractal dimensions have previously been reported for iron oxyhydroxide suspensions $^{39,42}$ and may possibly be the result of an orientated attachment process whereby aggregation proceeds by preferential attachment at opposite sides of the cluster. $^{39}$

Below pH 2, a Guinier region is not observed in the low-q range of the data (Figures 2A and S12), indicating that the aggregates are significantly larger than the maximum size that can be resolved by the experimental q-range ($52$ nm radius based on the relation, radius = $r_0$/q$^2$). Correspondingly, the value for $\xi$ (aggregate size parameter) obtained from fitting the scattering patterns between pH 1 and 2 tends to infinity. Above pH 2, the development of curvature in the low-q region (Figure 2A) results in fitting giving considerably smaller values for $\xi$. This decrease is concurrent with continually increasing fractal dimension, supports that aggregates undergo collapse to form more compact structures. Following DVLO theory, $^{72}$ collapse due to pH increase may be initiated by the decrease in repulsive surface charge, enabling attractive van der Waal forces to dominate. Aggregate densification may further be promoted by condensation of remaining smaller hydrolysis products (e.g., monomers, dimers) with/onto Fe$_{13}$ clusters to form ferrihydrite nanoparticle aggregates. Using eq S1 to convert $\xi$ to a radius of gyration ($R_g$), aggregate $R_g$ subsequently increases from $\sim$35 nm at pH 2.3 to $\sim$52 nm at pH 4.8. This increase in size is consistent with observation of the low-q Kratky plot peak moving to lower q values (Figure S14A). Above pH 4.8, the aggregates have grown to a size larger than the measured q-range, and the $R_g$ value obtained from the model stabilizes. Formation of large aggregates is confirmed by the experiments visibly floccing above pH 4.5 and by TEM images obtained at pH 9 (Figure 4B). Finally, no significant changes occur in the scattering patterns during the 30 min period data continued to be collected at pH 9.

It is noteworthy that the scattering signature from Fe$_{13}$ is seen throughout the experiment ($r_0$, Figure 2B). This shows structural continuity between isolated Fe$_{13}$ (pH < 1), Fe$_{13}$ aggregates with low fractal dimension (pH 1 $\sim$ 2), and the ferrihydrite nanoparticle aggregates in which the Fe$_{13}$ motif is preserved (pH $\geq$ 2). This has also been shown for the Keggin-Al$_x$ and Al(OH)$_3$, gel $^{31,73}$ system with Al$_x$ Keggin units similarly aggregating to form linear clusters with some polymerization, followed by rapid formation of dense, less open clusters. $^{25}$

TEM images of the ferrihydrite aggregates at pH 9 (Figure 4B) clearly confirm the expected mass fractal structure from the SAXS analysis. However, higher magnification images show the aggregates are composed of 3–4 nm ferrihydrite particles, rather than aggregates Fe$_{13}$ clusters. This may present an apparent inconsistency with the SAXS data which does not account for the $\sim$3–4 nm ferrihydrite nanoparticles: neither fixing $r_0$ to 1.5–2 nm nor a two particle model with both Fe$_{13}$ clusters and larger ferrihydrite particles gave acceptable fits. Interestingly, a surface-depleted model recently proposed by Hiemstra $^{25,55}$ indicates that ferrihydrite has a nonhomogenous, core–shell structure. We therefore applied fits using the addition of a second structure factor, the hard sphere structure factor, to account for this heterogeneity (eq S3) (Figure S16). These fits indicate agglomerates with volume fraction $\nu = 0.09$ composed of particles with hard sphere radius ($r_{HS}$) 1.47 nm at pH 9, where $r_{HS}$ is calculated based on the mutual spacing between the scatterers (S). This is consistent with the $\sim$3 nm diameter ferrihydrite nanoparticles observed by TEM within aggregates at pH 9 (Figure 4B). Since these hard sphere scatterers are assumed to have the same origin as the $\sim$0.45 nm radii clusters seen in the fractal aggregates, this means that the primary scatterers would have an outer, electron-leash shell (depleted in iron and therefore not directly detected by SAXS measurements) of thickness $r_{HS} - r_0 \sim$ 1 nm. Hiemstra’s surface-depleted ferrihydrite model consists of a defect-free core and a water-rich surface layer which is depleted in the Fe2 and Fe3 polyhedra of the Michel model. $^{52}$ This model is also supported by Wang et al. $^{45}$ whose results indicate that 1.6 nm ferrihydrite particles have an amorphous surface layer which accounts for $\sim$38% of their total volume, corresponding to a core size of 1.36 nm and surface layer thickness of 0.12 nm.
Interestingly, this surface layer thickness is smaller than those calculated for our systems but we note the published work was based on a dried sample, while our work is based on in situ analysis of particle suspended in aqueous solution. Fits obtained with the addition of the hard sphere structure factor are improved compared to regular model fits at pH > 3 (Figure S16 and Table S3), while at pH 2.25 fits give a value of 0 for v, indicating no contribution from this structure factor (Table S3). This is also the critical pH range (pH 2–3) where ferrihydrite nanoparticle formation/aggregation occurs (Figures 1 and 2B). Further, pH 2–3 is when Fe(III)₃ decreases rapidly (Figure 1) which may be related to the condensation of smaller hydrolysis products (e.g., monomers and dimers) onto the Fe₁₃ cluster leading to the development of the core–shell structure whereby surface bound OH and OH⁻ are retained, resulting in a water-rich/Fe-depleted surface layer on a Keggin cluster core in line with the Hiemstra model.34 We propose this is the dominant pathway of ferrihydrite formation in our system. An alternative pathway via direct nucleation of ferrihydrite particles from small hydrolysis products (monomers, dimers), without the involvement of Fe₁₃, can be ruled out because the SAXS data shows no evidence for direct formation of >2 nm particles. Overall, inclusion of the hard spheres structure factor suggests the formation of ∼3 nm ferrihydrite particles with a core–shell structure composed of a Fe₁₃ core (which is what the SAXS directly “sees”) and a Fe depleted shell.

Implications for Ferrihydrite Formation. We provide the first direct in situ observations of Fe₁₃ Keggin prenucleation cluster formation during hydrolysis of a ferric iron solution followed by the formation of aggregated ferrhydrite nanoparticles. The ferrihydrite formation process mimicked the EARP industrial process and involved continual addition of a strong base (7 M) to a highly acidic ferric nitrate solution (1 M HNO₃). Such extremes in pH have rarely been examined with most studies conducted on quasi-equilibrated solutions between pH 1 and 4. In our systems, Fe₁₃ clusters may form rapidly within localized areas of high pH via the well described successive polymerization Fe hydrolysis steps, and, interestingly, their formation seems to be essentially irreversible with the Keggin apparently stabilized against aggregation at pH < ∼1, probably due to the high charge on the clusters. This localized formation model is supported by the absence of Fe₁₃ clusters in pH 1 ferric nitrate solution which was prepared by directly dissolving Fe(NO₃)₃ in 0.1 M HNO₃ (Figure S15). This sensitivity to the preparation method has been found for Al salts, with formation of the Al₁₃ cluster coinciding with strong base neutralization of Al salt solutions.26,27 It is thought that the tetrahedral Al(OH)₄⁻ ion, formed in the locally high pH region at the point of base injection, is required for Al₁₃ synthesis.75,76 An analogous Fe(OH)₄⁻ ion exists25,77 and may similarly promote Fe₁₃ cluster formation. Dependence on solution conditions and experimental protocol may explain why Fe₁₃ was not detected in recent XAS studies.14–16 These used nonacidified ferric solutions that were neutralized with weak bases, concluding that an µ-oxo Fe(III) dimer was the dominant species present. Additionally, EXAFS analysis gives the average local environment of all Fe within a system; therefore, if Fe₁₃ clusters were present at low proportions (<10–20%) this may not be detected by XAS. In contrast, SAXS analysis preferentially detects larger clusters/particles but not smaller molecules (e.g., monomers). However, recent SAXS studies performed at constant pH 3.73 and pH 3.26 reported rapid formation of 3 nm iron oxyhydroxide nano-particles which subsequently grew to 7–10 nm. No smaller clusters were reported, highlighting that Fe₁₃ is either highly transitory or not formed under these higher pH conditions.

In the systems studied, Fe₁₃ clusters were stable in pH 0.5 and 1.5 solution for at least 18 days (Figure S8). Al₁₃ is also stable in aqueous solutions for long periods (>12 years) over a wide pH range.29,64,65 Sadeghi et al.13 used Bi⁵⁺ ions to stabilize Fe₁₃ in solution, whereby the Bi⁵⁺ acts to neutralize high negative cluster charge. Stability in the present study may be promoted by the elevated ionic strength of the solution, with H⁺ and Na⁺ ions acting as inherent stabilizing ions. Indeed, Sadeghi et al.13 found Cs⁺ could partially displace Bi⁵⁺ and maintain the discrete Fe₁₃ units (albeit with a small amount of aggregation), consistent with monovalent ions being able to stabilize these clusters.

Environmental Significance. Given the apparent dependence of Fe₁₃ formation on solution conditions, it is unclear whether the ferrihydrite formation pathway observed in the present study also occurs in the natural environment. A similar debate has taken place about the Al system.64,75,76 Furrer et al.10 reported that Al flocs, which were generated by the mixing of acidic mine streams with higher pH water, comprised of aggregated Al₁₃ clusters. Our study indicates that Fe₁₃ is only stable at pH < 1–1.5, above which it rapidly aggregates. In the natural environment ferrihydrite often forms by oxidation of Fe(II)₃ at near neutral pH,1 and under these conditions Fe₁₃, if formed, would be expected to be highly transitory. In acidic conditions, such as in acid mine runoff, Fe₁₃ may be more persistent. Indeed, Zhu et al.67 reported formation of “ferrihydrite-like” molecular clusters during neutralization of simulated acid mine drainage solutions, speculating that these clusters may resemble the Fe₁₃ motif. Additionally, Sadeghi et al.13 noted that complexing ligands similar to the TCA ligand utilized to stabilize the cluster in their work have parallel models in nature (e.g., carboxylic groups) which may act to stabilize the clusters. Ultimately, further work is required to investigate the importance of an Fe₁₃ pathway to ferrihydrite formation in the natural environment.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b02481.

Further experimental details of SAXS analysis, TEM image collection, ultrafiltration experiments and PHREEQC modeling, XRD pattern, aged sample SAXS patterns, and further solution data, SAXS figures and TEM images (PDF)

Time lapse video (Video S1) of reaction progress (MPG)

AUTHOR INFORMATION

Corresponding Author

*Phone: 0161 275-3826. E-mail: sam.shaw@manchester.ac.uk. Corresponding author address: Williamson Building, School of Earth and Environmental Sciences, The University of Manchester, Manchester M13 9PL, U.K.

Present Address

*Department of Civil and Environmental Engineering, University of Strathclyde, Glasgow G1 1XJ, U.K.
Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

REFERENCES
Sellafeld Ltd. and The University of Manchester cofunded this work via the Eflufs and Decontamination Centre of Excellence. This work was also supported by Environmental Radioactivity Research Network (grant number ST/K001787/1). Diamond Light Source provided beamtime awards (SM12704 and SM11075), and we thank Andy Smith and Nick Terrill for beamline assistance. We also thank Ellen Winstanley, Andy Brown, and Graham Kenyon for assistance during analyses.

Environmental Science & Technology


Supporting Information for Chapter 4:
Ferrihydrite Formation: The Role of Fe_{13} Keggin Clusters

Experimental

BET surface area measurement

The BET-method requires that the sample is first outgassed to remove any physically adsorbed water which would otherwise interfere with the surface determination. This is typically done at elevated temperatures (100 – 150 °C). However, specific surface areas of iron (oxyhydr)oxides are strongly dependent on the outgassing conditions, with surface area increasing by as much as 170% with heating, and phase changes occurring in poorly crystalline samples at temperatures below 100 °C (Clausen and Fabricius, 2000). To avoid this, an alternative outgassing procedure recommended by Clausen and Fabricius (2000) was used in the present study whereby the dried, powdered precipitate samples were outgassed with He at room temperature for 19 hours. This was followed by measurement of the BET multipoint surface area using a Micromeritics Gemini with N\textsubscript{2} as the sorbent gas.

Transmission electron microscopy (TEM) sample preparation

TEM images were obtained using either a Philips CM200 FEG-TEM with an Oxford Instruments 80 mm 2 X-Max SDD detector or an FEI Talos F200X analytical transmission electron microscope (operated at 200 kV) equipped with an integrated Super-X EDS system with 4 windowless silicon drift detectors.

TEM samples were prepared by directly pipetting fresh sample onto the TEM grid followed by a few drops of isopropanol to wash off excess salt. Holey-carbon Au mesh grids were used for samples with pH < 3, whilst holey-carbon Cu mesh grids were used for those with pH ≥ 3.

Ultrafiltration experiment

An ultrafiltration experiment was undertaken whereby a standard NaOH addition experiment was run and small aliquots (~ 500 µl) of sample were withdrawn throughout the reaction and filtered through one of three different filter sizes: 220
nm PES (polyethersulfone) filter, or a 10 kDa or 3 kDa Nanosep Centrifugal Devices (Omega™ membrane filter). 10 kDa and 3 kDa filters correspond to spherical diameters of ~ 3 and ~ 1 nm respectively (Dreissig et al., 2011). Filtration using the Nanosep Centrifugal Devices required centrifuging the sample at 8000 g for 10 min. Filtered sample was acidified with 6.25 M HNO₃ before subsequent measurement of dissolved Fe using a modified ferrozine method (Viollier et al., 2000).

Figure S3 shows the results from this experiment. The change in 220 nm filterable Fe(III)ₐq with pH is very similar to the results seen in Figure 1 which were obtained on a separate experiment performed under identical conditions. This shows the repeatability of the experiment. Use of the ultrafilters shows some Fe(III)ₐq fractionation into different size classes at pH 1, with more significant fractionation occurring above pH 2. This indicates the co-existence of solution species and primary particles/clusters < 3 nm in size, aggregates 3 – 220 nm in size, and larger aggregates > 220 nm. This is in line with SAXS data which showed cluster aggregation commenced from pH 1, followed by more rapid aggregation between pH 2 and 3.

**PHREEQC modelling**

A model of the ferrihydrite synthesis procedure, including Fe concentration and speciation, was created in PHREEQC by mimicking the NaOH-induced hydrolysis of Fe(NO₃)₃ undertaken in the experimental method. PHREEQC calculations were performed using an edited SIT (specific ion interaction theory) database whereby equilibrium constants for the three aqueous species listed in Table S1 were replaced with those recommended in a review conducted by the NEA (Nuclear Energy Agency) (Lemire et al., 2013). Equilibrium constants for other relevant Fe species were as defined in the SIT database. A single phase – ferrihydrite (Fe(OH)₃) – was allowed to precipitate, with the solubility product defined by Stefánsson (2007) used.
Table S1: Reactions and equilibrium constants recommended by the NEA. The corresponding species already present in the SIT database were replaced with the ones listed here.

<table>
<thead>
<tr>
<th>Species</th>
<th>Reaction</th>
<th>Log_{10}K°</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeOH^{2+} (aq)</td>
<td>Fe^{3+} + H$_2$O ⇌ FeOH^{2+} + H$^+$</td>
<td>-2.150</td>
<td>(Lemire et al., 2013)</td>
</tr>
<tr>
<td>Fe(OH)$_2$^{+} (aq)</td>
<td>Fe$^{3+}$ + 2H$_2$O ⇌ Fe(OH)$_2$^{+} + 2H$^+$</td>
<td>-4.800</td>
<td></td>
</tr>
<tr>
<td>Fe$_2$(OH)$_4$^{4+} (aq)</td>
<td>2Fe$^{3+}$ + 2H$_2$O ⇌ Fe$_2$(OH)$_4$^{4+} + 2H$^+$</td>
<td>-2.820</td>
<td></td>
</tr>
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</table>

SAXS data analysis

2D SAXS patterns were reduced to 1D scattering curves of intensity I vs q (scattering vector) by sector integration. The resulting intensity data, I(q), was normalised to the sample transmission and calibrated using glassy carbon as a standard to yield I(q) on an absolute scale. Background subtraction of the ferric nitrate solution prior to NaOH addition was performed, resulting in SAXS profiles consisting of only scattering from any particles that form during the experiment.

To test for the presence of clusters/particles in the starting solution (pH 0.1 ferric nitrate before base addition), a scattering pattern of deionised water was subtracted from the starting solution scattering pattern. The resulting scattering pattern showed no evidence of clusters or particles.

The scattering curves are fit using a model that describes the scattering as arising from a population of primary particles which may cluster to form aggregates with both mass fractal-like structure (mass fractal structure factor) and non-fractal aggregates (hard sphere structure factor) (Stawski et al., 2011).

It was found that the best fits were obtained when the primary particles were modelled with a spherical form factor (P(q, r$_o$)) (Guinier and Fourner, 1955) with radius r$_o$. The polydispersity of the primary particles was not modelled since the measured q-range does not extend to high enough values to observe the Porod region, which would provide information on this. Guinier analysis (Guinier and Fourner, 1955) was further used as an additional measurement of the size of unaggregated primary particles. To account for aggregation, a structure factor for a
mass fractal aggregate $S_f(q, r_o, \xi, d_i)$ (Berry and Percival, 1986; Freltoft et al., 1986; Teixeira, 1988) was used. Here $d_i$ is the fractal dimension and $\xi$ is the aggregate size parameter. The radius of gyration ($R_g$) of the aggregates can be calculated from $d_i$ and $\xi$ (Sorensen and Wang, 1999; Stawski et al., 2011)

$$R_g = \xi * \sqrt{\frac{d_i^{d_i+1}}{2}}$$  \hspace{1cm} (Eq S1)

To account for changes in the relative scattering contribution from the mass fractal aggregates with time, the approach of Stawski et al. (2011) was used whereby a weight factor $0 < \varepsilon < 1$ is introduced. The full scattering equation was then:

$$I(q) = n V_p^2 \Delta \rho^2 * P(q, r_o) * [\varepsilon + (1 - \varepsilon) * S_f(q, r_o, \xi, d_i)]$$  \hspace{1cm} (Eq S2)

Here a smaller value of $\varepsilon$ indicates a bigger contribution from the fractal aggregates to the scattering intensity, with a value of 1 indicating no contribution. $n V_p^2 \Delta \rho^2$ is the pre-factor term where $n$ is the number density of scattering particles (number of particles per volume of solution), $V_p$ is particle volume, and $\Delta \rho$ is the electron density contrast term. The pre-factor term is proportional to the total scattering volume.

An additional “hard sphere” structure factor accounting for non-fractal aggregates was further applied to assess its ability to fit the scattering patterns. Using the hard sphere structure factor $S_{HS}(q, r_{HS}, v)$ (Kinning and Thomas, 1984), these aggregates are described as being composed of a volume fraction $v$ of interacting particles which have hard sphere radius $r_{HS}$. The volume fraction $v$ is defined as the ratio of total particle volume in the local area divided by the total available volume (Besselink et al., 2013). A maximum value of 0.74 represents the most efficient particle packing of close-packed hexagonal or cubic lattices. The addition of the hard sphere structure factor gives a “double structure factor model” (Stawski et al., 2011) described by the following equation:

$$I(q) = n V_p^2 \Delta \rho^2 * P(q, r_o) * [\varepsilon * S_f(q, r_o, \xi, d_i) + (1 - \varepsilon) * S_{HS}(q, r_{HS}, v)]$$  \hspace{1cm} (Eq S3)

Values for parameters obtained by the models had standard errors of < 1%, which were calculated by the fitting routine in Origin Pro using the Levenberg-Marquardt Algorithm. An improvement of fit was judged as occurring when a lower reduced chi square value and when physically realistic values for the fitting parameters were obtained. We note that uncertainties in the calculated parameters are expected to be
greater than the < 1% indicated by the fitting model. This is because certain errors inherent in the SAXS data (e.g. uncertainties in background subtraction) are often not well represented in the raw data and there currently there is no widely accepted and tested model for calculating errors in SAXS data (Sedlak et al., 2017).

**Fe$_{13}$ simulated SAXS curves**

Crysol (Barberato et al., 1995) was used to generate simulated scattering curves of Fe$_{13}$ clusters in pure water, and also fit these simulated curves to experimental scattering curves obtained in the present study (Figure 3, main paper). Crysol fits the simulated scattering pattern to the experimental scattering pattern by varying the following parameters within physically realistic set limits: (i) average displaced solvent volume per atomic group (ii) contrast of the hydration shell. The Fe$_{13}$ Keggin cluster was isolated from Bi$_6$Fe$_{13}$L$_{12}$, synthesised by Sadeghi et al. (2015), using Crystal Maker. It was found that alternatively using a Fe$_{13}$ Keggin cluster isolated from the Michel et al. (2007) model of ferrihydrite made no significant difference to the simulated scattering pattern. Simulated SAXS patterns of a Fe dimer, trimer and Fe$_{13}$ Keggin clusters were also generated without any fitting to experimental data (Figure S1).

**Additional Figures**

![Figure S1: X-ray diffraction spectra of the dried solid product formed after bringing the system to pH 9. The spectra were obtained using Cu K-alpha X-ray energy.](image)
**Figure S2:** Dissolved Fe concentration (filterable through a 220 nm filter) of fresh and 1 and 7 day aged sample. Error bars show ± 1 standard deviation based on three repeated ferrozine measurements. Inset table shows pH of solutions during aging.

**Figure S3:** Ultrafiltration results, collected during a standard NaOH addition experiment, showing the concentration of Fe that was filterable by different filter sizes. Error bars show ± 1 standard deviation based on three repeated ferrozine measurements. The results suggest some Fe(III)$_{aq}$ fractionation into different size classes at pH 1, with more significant fractionation occurring beyond pH 2. This indicates the co-existence of solution species and primary particles/clusters < 3 nm in size, aggregates 3 – 220 nm in size, and larger aggregates > 220 nm.
**Figure S4:** Time-resolved in situ SAXS patterns during ferrihydrite formation (standard NaOH addition rate). For clarity the low-q data of the lower pH scans are omitted due to the presence of noise in the data. The start of stages i and ii of the reaction are marked (see main paper).

**Figure S5:** Scattering patterns from the first 6 min of the reaction, showing the development of a Guinier region within 2 mins.
Figure S6: Radii of gyration (Rg) of primary clusters determined by Guinier analysis of SAXS curves.
Figure S7: A) Time-resolved in situ scattering patterns from the slow NaOH addition experiment, including model fits. The scattering patterns show a Guinier region in the high q region consistent with the standard NaOH addition rate experiment (Fig. 2A) (B) Comparison of primary cluster radius $r_0$, the pre-factor $nVp^2\Delta\rho^2$, the aggregate weighting factor $\varepsilon$, and aggregate fractal dimension $d_f$ between the standard NaOH addition (1.5 ml min$^{-1}$) experiment and the slow NaOH addition (0.3 ml min$^{-1}$) experiment. Remarkable similarity is seen in the values and pH trends of the parameters between the two experiments. Standard errors calculated in the Origin Pro fitting routine were $<1\%$ and are not shown.
Figure S8: SAXS patterns collected on samples aged for either 6 or 18 days at 35°C. The pH of the samples was essentially stable over the ageing period (Table S2).

Table S2: pH of the aged samples during the ageing period.

<table>
<thead>
<tr>
<th>pH during ageing period</th>
<th>Sample</th>
<th>Fresh</th>
<th>1 day</th>
<th>6 days</th>
<th>18 days</th>
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<tbody>
<tr>
<td>pH 0.5 6 days</td>
<td>0.49</td>
<td>0.48</td>
<td>0.47</td>
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<tr>
<td>pH 0.5 18 days</td>
<td>0.52</td>
<td>0.42</td>
<td>0.53</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td>pH 1.5 6 days</td>
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<td>1.48</td>
<td>1.53</td>
<td>n/a</td>
<td></td>
</tr>
<tr>
<td>pH 1.5 18 days</td>
<td>1.55</td>
<td>1.46</td>
<td>1.56</td>
<td>1.5</td>
<td></td>
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**Figure S9:** Simulated scattering curve for a Fe$_{13}$ Keggin cluster compared to aged sample experimental scattering curves.

**Figure S10:** Change in pH with time during both the standard and slow NaOH addition experiments.
Figure S11: Experimental scattering patterns (pH 0.3 from the in situ standard NaOH addition experiment and pH 0.5 aged for 6 days) compared to Crysol-simulated scattering patterns of various Fe clusters. The simulated scattering patterns were not fit to the experimental scattering patterns and were obtained with no scattering contrast in the hydration sphere. Radii of gyration (Rg) were calculated from Guinier analysis of the scattering patterns. The simulated dimer was the oxo-dimer described by Zhu et al. (2013). The trimer was isolated from the Keggin structure and is composed of two edge sharing Fe polyhedra joined to a third Fe polyhedra by double-corner sharing. We note that different trimer structures showed similar scattering patterns.

Figure S12. SAXS curves between pH 0.78 and 1.90 showing increase in the gradient of the low-q slope with increasing pH.
Figure S13: Further TEM images. A) TEM image obtained on dried sample at pH 1 showing lattice images of aggregated ferrihydrite particles with fast Fourier transform inset. B) and C) TEM images obtained on dried sample at pH 3. Inset in image C is a
selected area electron diffraction pattern highlighting the d-spacing indicative of 2-line ferrihydrite. D) Energy dispersive X-ray spectrum collected on aggregates seen in images B and C. The copper (Cu) and carbon (C) signals originate from the holey carbon coated copper mesh TEM grid the sample was prepared on.

Figure S14: Kratky plots. A) The low-q intensity peak moves to lower q values as pH increases, indicating an increase in the average aggregate size. The labelled sizes are best on the relation $R_g = \pi/q$ and were determined by the peak finding routine in OriginPro. B) The average aggregate size increases to values outside the observable q-range at pHs higher than 4.5.
Figure S15: Scattering pattern of ferric nitrate pH 1 solution, prepared by dissolving ferric nitrate in 0.1 M HNO₃. pH 0.1 ferric nitrate solution was used as the background. No scattering from particles is observed, confirming that particle formation is a result of the experimental method of using NaOH to increase the pH.
Figure S16: SAXS curves at selected pHs, including fits obtained with and without the addition of a hard spheres structure factor. For clarity, the SAXS curves are offset on the y-axis. Table S3 below gives detailed comparison of the models.
**Table S3**: Fitting parameters for the fits shown in Fig. S13 comparing the fitting model with and without the inclusion of the hard sphere structure factor (HS-SF). Standard errors calculated in the fitting routine are in parentheses. At pH 2.25, the HS-SF contribution goes to zero and there was no improvement in fit. At pH 2.64, which was during mass precipitation of ferrihydrite (Figure 1, main paper), there was a contribution from the HS-SF but neither model was significantly better than the other, as determined by both a Akaike's Information Criteria Test (AIC) and Bayesian Information Criterion Test (BIC) run in Origin Pro. Fits at pH 3.02 and 9.08, which was after mass precipitation of ferrihydrite, were significantly better with the addition of the HS-SF as represented by the lower reduced chi-squared values and confirmed by both AIC and BIC tests.

### No hard spheres structure factor

<table>
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<th>pH</th>
<th>Reduced chi-square</th>
<th>nV_p Δρ^2</th>
<th>r_0 (nm)</th>
<th>d_f</th>
<th>R_g (aggregates)</th>
<th>ε</th>
<th>ν</th>
<th>r_HS (nm)</th>
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<tr>
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<td>1.21 (0.02)</td>
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<td>1.81 (0.002)</td>
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<tr>
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<td>1.20 (0.06)</td>
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<td>40</td>
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<tr>
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### With hard sphere structure factor

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<th>ε</th>
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<th>r_HS (nm)</th>
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<td>0.010 (0.001)</td>
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<td>0.08 (0.001)</td>
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<td>0.41 (0.006)</td>
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Figure S17: Images of experimental solutions at various pH allowed to age for ~ 1 month, showing that solutions < pH 2.0 remain homogenous colloidal suspensions whilst solutions > pH 2.0 partially sediment out.
CHAPTER 5

Ferrihydrite Formation via Fe13 Keggin Clusters in the Presence of Sulfate, Phosphate and Boric Acid

Joshua S. Weatherill\textsuperscript{a}, Katherine Morris\textsuperscript{a}, Pieter Bots\textsuperscript{a+f}, Tomasz M. Stawski\textsuperscript{b,c}, Arne Janssen\textsuperscript{d}, Liam Abrahamsen-Mills\textsuperscript{e}, Richard Blackham\textsuperscript{f}, Grace Burke\textsuperscript{d} and Samuel Shaw\textsuperscript{a*}

\textsuperscript{a}Research Centre for Radwaste Disposal and Williamson Research Centre, School of Earth and Environmental Sciences, University of Manchester, Oxford Road, Manchester, M13 9PL, UK. \textsuperscript{b}School of Earth and Environment, University of Leeds, Leeds, LS2 9JT, UK. \textsuperscript{c}German Research Centre for Geosciences, GFZ, 14473, Potsdam, Germany. \textsuperscript{d}School of Materials, University of Manchester, Oxford Road, Manchester, M13 9PL, UK. \textsuperscript{e}National Nuclear Laboratory, Chadwick House, Warrington Road, Birchwood Park, Warrington, WA3 6AE, UK. \textsuperscript{f}Sellafield Ltd, Hinton House, Birchwood Park Avenue, Risley, Warrington, Cheshire, WA3 6GR, UK.

5.1. Abstract

Ferrihydrite formation is a key part of the global biogeochemical iron cycle in oceans and rivers, and it is widely used in effluent treatment as a floc to effectively remove contaminants. Its formation often occurs in the presence of additional chemical species which can influence formation pathways and properties of the final solid phase. Here we characterise ferrihydrite floc formation during NaOH titration of an acidic ferric nitrate solution in the presence of sulfate, phosphate and boric acid, commonly occurring species in effluents and the natural environment. \textit{In situ} SAXS data shows that Fe\textsubscript{13} Keggin clusters (~ 0.45 nm radius) form rapidly at pH 0.12 – 1.5 upon addition of strong NaOH, with formation occurring at the same rate in all experimental systems. The Fe\textsubscript{13} clusters aggregate above ~ pH 0.5 in the phosphate system, compared to ~ pH 1.5 in the sulfate and boric acid systems, indicating different interactions of the added species with the clusters. Aggregation initially leads to formation of highly linear, low fractal dimension ($d_f$) structures, but with
further pH increase, aggregate densification occurs concurrently with precipitation of low molecular weight Fe(III) species to form mass fractal aggregates of ferrihydrite nanoparticles (\(~1 - 2\) nm radius). SAXS and PDF analysis indicates that in all systems, the Fe\(_3\) motif is preserved within the nanoparticle core and is surrounded by a disordered and Fe-depleted shell. Infrared spectroscopy analysis provided insight into the mechanisms of phosphate, sulfate and boric acid interactions with the solid phase throughout the formation process, with both inner and outer sphere adsorption observed for different species. Overall, these results confirm the ability of Fe\(_3\) Keggin clusters to act as a pre-nucleation intermediate to ferrihydrite formation, even in the presence of strong Fe complexing species such as phosphate and sulfate.

5.2. Introduction

Ferrihydrite is a nanocrystalline iron oxyhydroxide phase which is typically the first product of rapid Fe(III) hydrolysis (Cornell and Schwertmann, 2003; Jolivet et al., 2004). Due to its high surface area and reactivity, it is a key sequester of contaminants in natural ground and surface waters (Kinniburgh et al., 1976; Violante et al., 2009; Ping et al., 2014) and is widely utilised in industrial effluent treatment (Xu et al., 2012). Given its ubiquity, it is crucial to have a detailed understanding of ferrihydrite formation under a range of conditions, including in the presence of commonly occurring accompanying species which may perturb regular formation pathways (Rose et al., 1997a). Recently it has been shown that Fe\(_3\) Keggin clusters can form as a precursor to ferrihydrite formation in ferric nitrate solutions (Sadeghi et al., 2015, 2016; Weatherill et al., 2016). However, it is unknown whether this formation pathway occurs in compositionally varied systems and whether the pathway from Fe\(_3\) clusters to ferrihydrite aggregates is affected by the presence of additional species in the system.

Ferrihydrite formation is initiated by Fe(III) hydrolysis, which can be induced by different mechanisms such as pH dosing of acidic solutions or oxidation of Fe(II) at near neutral pH, potentially resulting in different pathways to ferrihydrite formation. The formation processes have proven to be complex and aspects remain unresolved, despite extensive investigation (e.g. Spiro et al., 1966; Knight and Sylva, 1974; Flynn Jr., 1984; Schwertmann et al., 1999; Jolivet et al., 2004; Rose et al., 2014; Collins et al., 2016; Zhu et al., 2016). Several studies have proposed a model based on successive
polymerisation and aggregation steps whereby, with increasing hydrolysis ratio, the ferric cation (Fe$^{3+}$) undergoes olation to form small polycations (intermediate clusters), followed by oxolation to form larger clusters and finally aggregation processes to form secondary particles and a floc which settles (Spiro et al., 1966; Knight and Sylva, 1974; Dousma and de Bruyn, 1976; Dousma and De Bruyn, 1978; Van Der Woude et al., 1983; Rose et al., 2014). However, the structure and relative importance of the intermediate cluster species are unclear: EXAFS-based studies have reported an Fe-oxo dimer as the dominant polynuclear species with no larger species detected (Zhu et al., 2013a, 2016; Collins et al., 2016), while other studies using a range of techniques including SAXS, EXAFS and molecular dynamics simulations have reported formation of trimers (Bottero et al., 1994; Rose et al., 1997b), six-member ring-like structures (Zhang et al., 2015), or Fe$_{13}$ Keggin clusters as precursor species to the solid phase (Sadeghi et al., 2015, 2016; Weatherill et al., 2016).

The formation of Fe$_{13}$ Keggin clusters, comprised of a central tetrahedral FeO$_4$ moiety surrounded by twelve octahedral FeO$_6$ units, is particularly pertinent to the evolving ferrihydrite formation pathway since the structural model of ferrihydrite proposed by Michel et al. (2007) and subsequently adopted in the wider literature (Maillot et al., 2011; Peak and Regier, 2012; Hiemstra, 2013, 2015) is based on linked Keggin units. However, given the challenges associated with identifying Fe$_{13}$ Keggin clusters in solution and the likelihood of alternative pathways for ferrihydrite formation, there are few studies which directly identify Fe$_{13}$ clusters during ferrihydrite formation (Sadeghi et al., 2015, 2016; Weatherill et al., 2016). Therefore, the relative importance of an Fe$_{13}$ pathway to ferrihydrite, particularly under different chemical conditions and in the presence of different background ions, is yet to be fully explored.

In past work from our group (Weatherill et al., 2016), we investigated ferrihydrite formation under industrially relevant conditions in a pure ferric nitrate system. Here, ferrihydrite formation proceeded by initial rapid nucleation of Fe$_{13}$ Keggin clusters at low (undersaturated) pH conditions (< pH 1.5), followed by aggregation of the Fe$_{13}$ clusters and precipitation of smaller Fe(III) hydrolysis products to form core-shell ferrihydrite nanoparticles. These nanoparticles consisted of a Fe$_{13}$ core (0.9 - 1 nm) and a more hydrous Fe-depleted shell (~ 1 nm), consistent with the Hiemstra surface-depleted model of ferrihydrite (Hiemstra, 2013, 2015). Interestingly, favorable Fe$_{13}$ formation in this past work may have been promoted by the formation method of
adding a strong base to a highly acidified solution, with Fe$_3$$^+$ forming within the locally high pH “hotspots” at the point of base addition (Weatherill et al., 2016).

Following formation of ferrihydrite nanoparticles, particle growth and/or aggregation may occur depending on the solution composition (e.g. pH and ionic strength), typically leading to development of large mass fractal aggregates (Legg et al., 2014a, 2014b; Neil et al., 2016). Further understanding these aggregation processes is also important since the aggregate structure influences colloidal stability (Gilbert et al., 2007; Legg et al., 2014a), reactivity (Gilbert et al., 2009; Dale et al., 2015; Stegemeier et al., 2015), transport behavior (Legg et al., 2014b) and filterability in wastewater treatment processes (Loan et al., 2002).

Ferrihydrite formation in both natural and industrial settings is usually accompanied by the presence of additional aqueous species. Although the adsorption behaviour of key species on pre-formed iron (oxyhydr)oxide nanoparticles has been extensively studied (e.g. for sulfate: Hug, 1997; Peak et al., 1999; Fukushi et al., 2013; Johnston and Chrysochoou, 2016 and phosphate: Persson et al., 1996; Arai and Sparks, 2001; Elzinga and Sparks, 2007; Wang, Zhu, Q.-L. Fu, et al., 2015), only limited studies have considered the effect of these species during co-precipitation with Fe. These additional species may perturb regular formation pathways during co-precipitation, affecting the properties of the final ferrihydrite phase or lead to the formation of alternative iron (oxyhydr)oxide phases (Cornell and Schwertmann, 2003). For example, complexing anions such as sulfate and phosphate, abundant in many wastewaters and ground/surface water systems, can compete with O$^-$ and OH$^-$ ligands during Fe(III) hydrolysis and alter regular mineral formation pathways (Dousma et al., 1978, 1979; Rose et al., 1997a; Hu et al., 2012). Sulfate complexation has been shown to inhibit double corner sharing and promote edge sharing of Fe(III) octahedra (Collins et al., 2016), leading to the formation of schwertmanite (Fe$_8$O$_6$(OH)$_8$SO$_4$); either directly from solution (Collins et al., 2016) or by transformation from ferrihydrite (Zhu et al., 2012). In contrast, phosphate has been shown to inhibit both corner sharing and edge sharing of Fe(III) octahedra, resulting in limitation of Fe hydrolysis to the dimer stage (Manceau et al., 1996; Rose et al., 1997a). Phosphate can then subsequently bridge between the Fe octahedra, with solid formation driven primarily by continuous growth of the Fe-PO$_4$ network rather than individual nucleation events (Manceau et al., 1996; Rose et al., 1997a; Neil et al., 2014;
Hiemstra and Zhao, 2016), resulting in formation of a ferrihydrite-like amorphous ferric phosphate phase (Thibault et al., 2009). Other anions with smaller charge/size ratios, such as nitrate, are typically weakly binding (Lay and Wu, 1995), so their use as background electrolytes makes it easier to resolve the effects of other added species. The effects on ferrihydrite formation of some relevant species, such as boric acid, which can be present in significant concentrations in industrial wastewater (Itakura et al., 2005; Parks and Edwards, 2005) and groundwater (Gemici et al., 2008), are poorly described.

The Enhanced Actinide Removal Plant (EARP) (Sellafield, UK) is an essential industrial treatment facility which uses a ferrihydrite floc formation process to decontaminate radioactive effluents generated from the reprocessing of spent nuclear fuel (Hutson, 1996; Hildred et al., 2000; Weatherill et al., 2016). In the EARP process, radionuclides react with the ferrihydrite floc (e.g. by adsorption or incorporation), which is formed by base-induced hydrolysis of the acidic radioactive effluent. The floc is subsequently separated by ultrafiltration and then encapsulated in a cement wasteform prior to storage for ultimate disposal as intermediate level waste. The EARP effluent compositions will change when the Sellafield site transitions from reprocessing to post-operational clean-out (POCO) and decommissioning activities over the next several years, including variations in the effluent concentrations of non-radioactive species (e.g. sulfate, phosphate and boric acid). Elevated concentrations of these species may perturb the ferrihydrite formation process and final decontamination factors. In order to underpin plant operations and enable optimization of the EARP process and similar industrial treatments, an enhanced understanding of the effect of accompanying ions on ferrihydrite formation under process relevant conditions is essential, and provides fundamental knowledge relating to ferrihydrite formation.

In the present study, we investigate the effect of phosphate, sulfate and boric acid on ferrihydrite formation during the controlled hydrolysis of an acidic ferric nitrate solution in an experimental protocol designed to mimic the EARP iron oxyhydroxide effluent treatment system. To achieve this, in situ time-resolved small angle X-ray scattering (SAXS) experiments were used to track ferrihydrite particle formation and aggregation, and were augmented with in situ and ex situ transmission electron microscopy (TEM), solution analysis, X-ray diffraction (XRD), extended X-ray fine
structure spectroscopy (EXAFS), and pair distribution function (PDF). Additionally, interactions of the added species with the ferrihydrite floc were characterised using Fourier transform infrared spectroscopy (FTIR). We show that the presence of phosphate, sulfate or boric acid does not inhibit ferrihydrite formation via Fe$_{13}$ clusters, although the different species cause initial aggregation of Fe$_{13}$ clusters to be shifted to different pH values. Our results provide key information on understanding and controlling ferrihydrite formation via Fe$_{13}$ keggin clusters in the presence of phosphate, sulphate and boric acid, key additional species in effluent treatment and natural systems where ferrihydrite forms.

5.3. Experimental

Ferrihydrite was synthesized in an automated computer-controlled reactor (Applikon MiniBio) with temperature control (Peltier heater/ cooler) via NaOH-induced hydrolysis of ferric nitrate solutions according to the method of Weatherill et al. (2016). Briefly, stirred batch experiments were conducted at 35 °C (representative of EARP), with the pH and temperature monitored throughout. Starting solutions consisted of 400 ml of Fe(NO$_3$)$_3$.9H$_2$O in 1 M HNO$_3$ (400 ppm Fe(III)) with the addition of Na$_2$SO$_4$ (1000 ppm / 10.4 mM sulfate) or NaH$_2$PO$_4$ (100 ppm / 1.05 mM phosphate) or B(OH)$_3$ (150 ppm / 13.9 mM boron). Concentrations of sulfate, phosphate and boric acid were selected so as to be representative of potential future effluent conditions on plant. For some analyses, experiments without the additional species were also run (pure Fe nitrate system). Base addition was initiated with 7 M NaOH at 1.5 ml min$^{-1}$ until pH 2.3, then 0.3 ml min$^{-1}$ until pH 3 and finally, above pH 3, 0.2 M NaOH was added at 1.5 ml min$^{-1}$ to a final pH of 9. Additional experiments measuring the change in solution concentration of phosphate and sulfate were run until pH 12. This multi-stage dosing procedure aims to mimic the process employed on the plant. At selected points samples were taken and filtered (0.22 µm polyethersulfone) for solution analysis. The solid products were isolated at the experimental end points by centrifuging and washing three times with deionized water before drying at 40°C overnight. Powder XRD (Bruker D8 Advance), BET surface area analysis (Micromeritics Gemini) and TEM images of the dried products were obtained on a Philips CM200 FEG-TEM with an Oxford Instruments 80 mm 2 X-Max SDD detector (SI).
Aqueous concentrations of total Fe in solution, \([\text{Fe}_{(aq)}]\), and of phosphorus, \([\text{P}_{(aq)}]\), sulfur, \([\text{S}_{(aq)}]\), and boron, \([\text{B}_{(aq)}]\), in their respective systems were determined using the ferrozine method for \([\text{Fe}_{(aq)}]\) (Viollier et al., 2000) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) for \([\text{P}_{(aq)}]\), \([\text{S}_{(aq)}]\) and \([\text{B}_{(aq)}]\).

To enable comparison between experimental Fe, P, S and B behavior and predicted behaviour at thermodynamic equilibrium, the ferrihydrite synthesis procedure in each system was modelled in PHREEQC (Parkhurst and Appelo, 2013). Here, the PHREEQC model was based on the NaOH-induced hydrolysis of \(\text{Fe(NO}_3\text{)}_3\) undertaken in the experiments (supporting information (SI)).

**5.3.1. Time-resolved in situ SAXS experiments**

Ferrihydrite synthesis experiments were performed *in situ* on beamline I22 at the Diamond Light Source with time-resolved SAXS data collected throughout the NaOH addition. A peristaltic pump in closed loop configuration continuously pumped the reacting suspension from the continuously stirred reaction vessel through a quartz capillary in-line with the X-ray beam (Ahmed et al., 2010). A monochromatic X-ray beam at 12.4 KeV and a camera length of 3.8 m were used in the time-resolved experiments, and the SAXS patterns were collected using a pixel array PILATUS 2M detector. SAXS patterns were collected throughout the reaction and for 30 min after base addition had finished, with a time resolution of 15 seconds/frame.

A SAXS pattern was also obtained on a static sample from the phosphate system at pH 0.5 and aged for six days at 35 °C. The aged sample was directly injected into a quartz capillary and SAXS data were collected using a camera length of 1.9 m.

**5.3.2. SAXS data analysis**

The scattering curves were fit using a model that describes the scattering as arising from a population of spherical primary particles which may cluster to form aggregates with both mass fractal-like structure (mass fractal structure factor) and non-fractal aggregates (hard sphere structure factor) (SI) (Stawski et al., 2011).

The starting solution before any NaOH addition (~ pH 0.1) HNO3 with phosphate, sulfate or boric acid) was tested for the presence of clusters/particles by subtracting a background scattering pattern of DI water. No clusters/particles were detected indicating Fe(III) was present only as monomers.
5.3.3. Attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR)

Infrared spectra (IR) of the solid iron oxyhydroxide phase isolated at selected pH values throughout the reaction were taken on a Perkin Elmer Frontier ATR-FTIR spectrometer. A wet moist solid sample was prepared by centrifugation and analysed at a resolution of 1 cm\(^{-1}\) for 64 scans. The lowest pH solid which was analysed was determined by when enough solid had formed in solution to be isolated by centrifugation (pH 2.5 – 3). Processed spectra were obtained by subtracting the supernatant spectrum from the moist solid spectrum, followed by baseline correction and normalisation of the absorbance intensities to a maximum of one absorption unit. Gaussian peak fitting of the spectra was done in Origin (OriginLab, Northampton, MA) (SI).

5.3.4. In-situ transmission electron microscopy (TEM)

The final pH 9 sample from the sulfate system was directly pipetted onto a Protochips Poseidon P210 analytical liquid cell holder and analysed on a FEI Tecnai F30 300 kV Field Emission Gun Analytical Electron Microscope equipped with an Oxford Instruments Xmax80 SDD.

5.3.5. Extended X-ray absorption fine structure spectroscopy (EXAFS)

EXAFS measurements were performed on solution samples from a pure Fe nitrate system at pH 0.1, 0.85 and 1.5. The pH 0.1 solution was taken before any base addition, while the pH 0.85 and 1.5 samples were obtained by pausing the ferrihydrite synthesis reaction at the appropriate pH and withdrawing solutions via a syringe. These solutions were transferred to an acrylic plastic cell where each side was sealed with Kapton film to form a window. Fe K-edge spectra were collected at beamline B18 at The Diamond Light Source (Dent et al., 2009) at one scan per 5 min in fluorescence mode, with a total of 30 scans collected for each sample. Spectra were averaged and processed in Athena and fitted in Artemis (Ravel and Newville, 2005).

5.3.6. Pair distribution function (PDF)

Synchrotron-based high-energy X-ray total scattering (HEXS) data was collected on the final ferrihydrite phase at pH 9 from a pure ferric nitrate system. Samples were prepared by injecting freshly prepared ferrihydrite slurry into a 1 mm diameter quartz
capillary, followed by centrifuging to concentrate the solid at the capillary end. The prepared sample was stored at 3 °C to minimize ageing before analysis on beam (< 3 days storage). Data was collected on beamline I15 at the Diamond Light Source using X-ray energy 76 keV and a Perkin Elmer flat panel 1621 EN detector. A single HEXS pattern was taken every 1 s, with 1440 patterns averaged to give the final data. The 2D raw data was converted to a 1D pattern of intensity versus wave vector (q), followed by conversion to a PDF (G(r)) in Gudrun (McLain et al., 2012) via Fourier transform of the reduced structure function (S(q)) in the q-range 0.5 – 17 Å⁻¹.

5.4. Results and discussion

5.4.1. Solid characterisation

XRD patterns (Figure 1) collected on solid samples isolated at pH 9 in each system (phosphate, sulfate, and boric acid) showed two broad peaks indicative of 2-line ferrihydrite (Cornell and Schwertmann, 2003). In the sulfate and boric acid systems, the peaks were centred at d-spacings of 2.60 and 1.50 Å, while in the phosphate system they were slightly shifted to ~ 2.63 and 1.53 Å, but still consistent with 2-line ferrihydrite (Cornell and Schwertmann, 2003). TEM images obtained on dried samples at pH 9 showed aggregated nanoparticles of ferrihydrite in all three systems, with individual 2 – 4 nm nanoparticles observed at the aggregate edges (Figure S1). BET surface areas were > 230 m² g⁻¹ for all three systems (Table S1) and consistent with those expected for 2-line ferrihydrite (Cornell and Schwertmann, 2003). These XRD, TEM and BET surface area results are also consistent with past work on a pure Fe nitrate system (Weatherill et al., 2016) without additional species.
5.4.2. Iron – added species interactions

Figure 2 shows the experimental data for changes in \([\text{Fe}^{\text{aq}}]\), \([\text{P}^{\text{aq}}]\), \([\text{S}^{\text{aq}}]\) and \([\text{B}^{\text{aq}}]\) (0.22 µm filterable) as well as PHREEQC thermodynamic calculations for changes in \([\text{Fe}^{\text{aq}}]\). The experimental results show \([\text{Fe}^{\text{aq}}]\) decreased slightly (< 10%) between pH 0.1 and 2 in the sulfate and boric acid systems, followed by a more rapid decrease above pH 2 in line with thermodynamic calculations and similar to behavior in a pure Fe nitrate system (Weatherill et al., 2016). In contrast, \([\text{Fe}^{\text{aq}}]\) in the phosphate system decreased rapidly from a lower pH value, with 46 % removal between pH 0.1 and 2 (Figure 2). Despite this, thermodynamic calculations showed no significant differences in \([\text{Fe}^{\text{aq}}]\) removal between the different systems (Figure 2). This suggests a limitation in these calculations to predict dynamic processes and capture full chemical complexities. Above pH 4, \([\text{Fe}^{\text{aq}}]\) decreased to below the detection limit (< 0.01 ppm) in all systems, similar to past observations in pure Fe nitrate experiments (Weatherill et al., 2016) and in line with thermodynamic calculations.

**Figure 1:** X-ray diffraction spectra of the dried solid product formed after raising the pH of each experimental system to pH 9.
Figure 2: Change in concentration of [Fe(aq)], [P(aq)], [S(aq)] and [B(aq)] (0.22 µm filterable), in their respective systems. Dashed grey line is the thermodynamically predicted change in [Fe(aq)] as calculated in PHREEQC. A) Phosphate system. B) Sulfate system. C) Boric acid system.

In the phosphate system, [P(aq)] decreased rapidly above pH 1 concurrent with the decrease in [Fe(aq)], falling to below the detection limit by pH 2.5. Above pH 9 (the typical final pH obtained on the EARP plant), [P(aq)] subsequently increased again and was at ~ 95% of its original concentration by pH 12. [S(aq)] decreased slightly by ~ 5%
between pH 0.1 and 2, before a more rapid decrease of ~ 15% between pH 2 and 3 concurrent with the rapid decrease in \([\text{Fe}^{\text{aq}}]\). Above pH 3, \([\text{S}^{\text{aq}}]\) increased again and reached its original concentration by pH 9. In contrast to \([\text{P}^{\text{aq}}]\) and \([\text{S}^{\text{aq}}]\), \([\text{B}^{\text{aq}}]\) did not exhibit any decrease simultaneous with the decrease in \([\text{Fe}^{\text{aq}}]\) and was at constant concentration until ~ pH 7, after which it decreased by 20% between pH 7 and 9.

In all experimental systems, \([\text{Fe}^{\text{aq}}]\) concentrations decreased at a lower pH than those predicted by the thermodynamic equilibrium calculations (Figure 2). Presumably, this reflects the dynamic nature of the experiments where continual NaOH addition occurs so that equilibrium is not reached (Weatherill et al., 2016). Locally high pH within the solution at the point of NaOH addition is evidenced throughout the reaction by bursts of yellow/orange colour, which are subsequently rapidly dispersed by the stirring action. This suggests Fe(III) hydrolysis and cluster/particle formation is occurring within areas of locally higher pH, which could lead to iron oxyhydroxide formation at pH lower than that predicted by thermodynamic calculations. Additionally, thermodynamic equilibrium calculations do not fully capture the full complexity of Fe hydrolysis chemistry since Fe clusters larger than dimers are not included in the thermodynamic database. Indeed, the SAXS data discussed below indicates that cluster formation and aggregation in the phosphate system can explain the particularly early decrease in \([\text{Fe}^{\text{aq}}]\) in this system which is not captured in the thermodynamic calculations.

Figure S3 and S4 show the predicted thermodynamic speciation of Fe and the additional species in the experiments. Before precipitation, aqueous complexes of Fe with phosphate and sulfate are predicted to be significant contributors to the speciation of Fe(III) in their respective systems while Fe-B complexes are less significant, with boron present overwhelmingly as the neutral boric acid molecule (B(OH)\(_3\)) below pH 8 (Figure S4C).

In each system, including a pure Fe nitrate system, infrared spectra were collected on the solid iron oxyhydroxide phases isolated at select pH values (Figure 3). A peak centered at 1640 – 1610 cm\(^{-1}\) was present in all systems which is attributable to sorbed water (Russell, 1979). Additional peaks centered at 1400 - 1390 and 1340 cm\(^{-1}\) were present at low pH (< ~ pH 5) in all the experimental systems except with sulfate present, and were attributed to adsorbed nitrate (Harrison and Berkheiser, 1982).
These peaks disappear > pH 5 in the phosphate and pure Fe nitrate systems, indicating desorption of nitrate which is expected for this weakly adsorbing anion (Lay and Wu, 1995). In the boric acid system, although the peaks persisted up to pH 9, nitrate desorption was also expected and the peaks remaining in this region were attributed to both boric acid and carbonate adsorption (see below) (Su and Suarez, 1997; Peak et al., 2003).

Figure 3: ATR-FTIR spectra collected on the solid phase isolated at different pHs in the A) phosphate system, B) sulfate system, C) boric acid system and D) pure Fe nitrate system.
Association of phosphate with the iron oxyhydroxide phase is clearly evidenced in IR spectra obtained between pH 2.8 and 9.0 by the absorbance peak centered at 1010 - 1040 cm⁻¹ (Figure 3A) (Arai and Sparks, 2001; Wang et al., 2015b). Additionally, solid phase Fe-P association is evidenced at pH 1 by energy dispersive X-ray (EDX) spectra obtained on Fe(III) particles isolated at pH 1 (Figure S2). These data are in agreement with solution data which showed [P(aq)] removal was occurring between pH 1 – 3. Peak fitting of the IR spectra between 800 – 1200 cm⁻¹ (the phosphate region) at pH 2.8, 4.3 and 5.5 indicated an assemblage of three ν₃ vibrations (1094, 1037, 954 cm⁻¹) and one ν₁ vibration (840 cm⁻¹) (Figure S6), in good agreement with previous studies and consistent with a protonated inner sphere phosphate adsorption complex (Arai and Sparks, 2001; Wang et al., 2015b). As pH increased, splitting of the broad phosphate absorption band became more apparent, resulting in spectra too complex to peak fit reliably. At pH 9 and above, at least four absorption peaks appear to be present in the triply degenerate ν₃ region, therefore suggesting presence of multiple phosphate sorption complexes with varying geometries.

Sulfate association with precipitated iron oxyhydroxide was also clearly evidenced in IR spectra for samples between pH 2.5 and 6.3 due to the presence of absorption peaks centred at 1105 - 1120 cm⁻¹ (Figure 3) (Harrison and Berkheiser, 1982; Hug, 1997; Fukushi et al., 2013). Again, this is in agreement with the solution data which showed suppressed [S(aq)] over this pH region (Figure 2). The low pH spectra (< pH 3.8) were accurately fit between 1250 and 950 cm⁻¹ by an assemblage of three peaks at ~ 1175, 1120 and 1064 cm⁻¹, assigned to the triply degenerate ν₃ vibrations, and one peak at ~ 980 cm⁻¹, assigned to the ν₁ vibration (Figure S7). Splitting of the ν₃ vibration into three absorption peaks is a clear indication of symmetry reduction occurring in the sulfate, consistent with inner sphere surface-adsorbed sulphate (Hug, 1997; Peak et al., 1999; Wijnja and Schulthess, 2000; Fukushi et al., 2013; Johnston and Chrysochoou, 2016). However, splitting of the ν₃ band became less prominent as pH increased (Figure 3), suggesting a change from inner sphere to outer sphere adsorption was occurring (Peak et al., 1999; Wijnja and Schulthess, 2000). Accordingly, ν₃ peaks associated with both inner sphere (1170, 1120, 1064 cm⁻¹) and outer sphere (1110 cm⁻¹) (Peak et al., 1999) adsorbed sulfate were required to fit the pH 5.6 and 6.3 spectra, with the outer sphere contribution strongly dominant over the inner sphere contribution at pH 6.3 (Figure S7). Overall this suggests inner sphere sulfate adsorption below ~ pH 6 with progressive change to outer sphere adsorption above ~
pH 5. Above pH 7.5 the sulfate IR peak quickly decreased confirming desorption of sulfate and again consistent with both solution data (Figure 2) and published adsorption data (Fukushi et al., 2013). Above pH 6.5, further absorption peaks began to develop: sharp peaks centred at 1475 and 1350 cm\(^{-1}\), a small shoulder peak at 1076 cm\(^{-1}\), and a broad peak centred at ~ 915 cm\(^{-1}\). These features are consistent with adsorbed carbonate (CO\(_3^{2-}\)) and/or bicarbonate (HCO\(_3^-\)) (Su and Suarez, 1995), presumably present due to ingress from air into the alkaline solution. In contrast, carbonate adsorption at elevated pH was suppressed in the phosphate system, in agreement with previous work (Rahnemaie et al., 2007; Voegelin et al., 2013), and likely due to adsorbed phosphate altering the electrostatics of the ferrihydrite surface and outcompeting carbonate for adsorption sites (Rahnemaie et al., 2007).

The IR spectra collected on the boric acid system were more challenging to interpret due to overlap of the expected boric acid adsorption wavenumber region with both the nitrate and carbonate regions (Su and Suarez, 1995; Peak et al., 2003). Nevertheless, a shoulder peak at 1250 cm\(^{-1}\) at pH 7 – 9, not present in any of the other systems, is clear evidence for boric acid adsorption (Figure 3) (Su and Suarez, 1995; Peak et al., 2003). Emergence of this peak at pH 7 is consistent with the solution data which showed a decrease in [B\(_{\text{aq}}\)] above pH 7. At pH 8 and 9, coincidence of absorption peaks at ~ 1390, 1335 and 1250 cm\(^{-1}\) (B-O \(_3^\text{v, vibrations}\) ) and a weak peak at ~ 990 cm\(^{-1}\) (B-O \(_1^\text{v, vibration}\) ) is indicative of a mix of inner and outer sphere boric acid adsorption (Peak et al., 2003). A shoulder peak at 1480 cm\(^{-1}\) also indicates adsorbed carbonate, and therefore carbonate will additionally be contributing to these absorption bands (carbonate should also absorb at ~ 1350 cm\(^{-1}\)). At pH 9, an increase in intensity of the broad adsorption feature centered at ~ 915 cm\(^{-1}\) may be interpreted as borate (B(OH)\(_4^-\)) adsorption (Peak et al., 2003), although this feature is also seen in the other experimental systems and overlaps with carbonate adsorption peaks, making this interpretation inconclusive. However, borate adsorption at higher pH would be consistent with thermodynamic speciation calculations which show borate concentrations becoming significant in solution above pH 8 (Figure S4C).

### 5.4.3. Ferrihydrite formation pathway

Figure 4 shows the evolution of the in situ SAXS patterns with increasing pH in the phosphate, sulfate and boric acid systems. Below pH 0.12, no scattering intensity significantly above background was observed confirming that Fe was present only as
monomers (Figure S8). Above pH 0.12, increased scattering intensity indicated formation of clusters/particles and allowed fitting of the SAXS patterns. Between pH 0.12 and 0.5 – 1.5 (depending on experimental system), a single Guinier region (Guinier and Fournier, 1955) was observed which was best fit using a single population of clusters. Above pH 0.5 – 1.5, an additional scattering feature developed at low-q which was fit with the addition of mass fractal and hard sphere structure factors, and was indicative of cluster aggregation and precipitation. Overall, the appearance of the SAXS patterns and their pH evolution are comparable to those collected on an equivalent pure Fe nitrate system (Weatherill et al., 2016), suggesting a similar two-stage process of: (i) Fe$_{13}$ Keggin cluster formation at low pH (< pH 0.5 - 1.5), followed by (ii) cluster aggregation and precipitation to form ferrihydrite particles is occurring in these more complex experimental systems.
Figure 4: A selection of time-resolved in situ SAXS patterns collected in each system between pH 0.12 and 9 with model fits overlain. A) Phosphate system; B) Sulfate system; C) Boric acid system.
Figure 5: Change in fitting SAXS parameters with pH in each system. A) Primary cluster radius ($r_0$); B) Pre-factor term ($nV_p^2\Delta\rho^2$); C) Aggregate weighting factor ($\varepsilon$); D) Aggregate fractal dimension ($d_f$); E) Aggregate radius of gyration ($R_{ag}$); F) Hard sphere radius ($R_{HS}$). The pure Fe nitrate results are taken from our previous publication (Weatherill et al., 2016).
Stage (i) Fe$_{13}$ Keggin cluster formation

Above pH 0.12, log-log SAXS plots show the development of a Guinier region in the high-q region ($q > 1 \text{ nm}^{-1}$) (Figure 4 and S8), indicating the formation of a population of nano-sized clusters (Guinier and Fourner, 1955). In all systems, this Guinier region developed within two minutes of starting the base addition (Figure S8). Guinier analysis was performed on these low pH (< pH 1) scattering patterns, and gives a similar cluster radii of gyration (Rg) of 0.34 – 0.37 nm in each system (Figure S9), corresponding to a radius of 0.44 – 0.48 nm if a spherical shape is assumed. These scattering patterns were also fit to a SAXS model using a spherical particle/cluster form factor (Guinier and Fourner, 1955) (SI), which was found to be the best model for obtaining a fit to the data. Here the resulting spherical cluster radius, r, was 0.4 – 0.45 nm (Figure 5) which is in good agreement with the Guinier analysis. In all systems, these clusters grew in number while being stable in size between pH 0.12 and 1, as evidenced by the increase in the fitted prefactor term $nV_p^2\Delta \rho^2$ with no significant change in $r_0$ (Figure 5) and also by the lack of visual change in the Guinier region. The rate of increase in $nV_p^2\Delta \rho^2$ between pH 0.12 and 1 was very similar in all of the systems (Figure 5) and to the pure Fe nitrate system (Weatherill et al., 2016), showing that the additional species did not inhibit or promote cluster formation kinetics during this early stage of rapid cluster formation.

The size and shape of the clusters defined in these experiments are very similar to those which formed above pH 0.12 in a parallel pure ferric nitrate system (Weatherill et al., 2016). These were identified as Fe$_{13}$ Keggin clusters (herein termed Fe$_{13}$) because of their size, excellent agreement with a simulated Fe$_{13}$ scattering curve and previous observation that Fe$_{13}$ could act as a prenucleation cluster to ferrihydrite (Sadeghi et al., 2015). Excellent similarity was also seen between the experimental scattering patterns collected < pH 1 in the current study and simulated scattering patterns of Fe$_{13}$ clusters (Figure 6), indicating that Fe$_{13}$ also forms at < pH 1 in these experimental systems in the presence of sulfate, phosphate and boric acid. In contrast, the experimental scattering patterns were significantly poorer matches to simulated scattering patterns of Fe dimers and trimers (Figure S10), indicating minimal scattering contribution to the data from these smaller species. The maximum value of the prefactor, $nV_p^2\Delta \rho^2$ was slightly smaller in the phosphate system (~0.0094 cm$^{-1}$) than the other systems (~0.011 cm$^{-1}$) (Figure 5), but this was insignificant within the
limitations imposed by uncertainties in background subtraction. Since the scattering intensity was calibrated to an absolute intensity, we can use the prefactor to calculate an approximate percentage of the total Fe present as Fe\textsubscript{13} clusters (SI). This estimates a maximum of 16 - 17 % of the total Fe was present as Fe\textsubscript{13} in each system. This calculation makes two assumptions: (i) that each system has the same electron density contrast term, which is justified by the solution data indicating no significant incorporation of the added species into the Fe-phase; and (ii) that the scattering signal is predominantly from the Fe\textsubscript{13} clusters, which is justified by the SAXS analysis (Figure S10) and the fact that the scattering intensity has a squared dependence on particle/cluster volume and therefore would be expected to be dominated by the largest species present (the Fe\textsubscript{13}).

Figure 6: Simulated scattering curves of Fe\textsubscript{13} Keggin clusters compared to experimental scattering curves collected at pH 0.3 in the A) phosphate system and pH 0.5 in the B) sulfate and C) boric acid systems. Inset is an atomic structure model of
an Fe$_{13}$ Keggin cluster. Radii of gyration (Rg) were calculated from the experimental and simulated scattering patterns via Guinier analysis (Guinier and Fourner, 1955).

EXAFS data collected on pure Fe nitrate solutions at pH 0.1 (before NaOH addition), 0.85, and 1.5 exhibit no significant systematic changes and were all best fit to an Fe monomer with Fe-O bond length \( \sim 2.00 \) Å. (Figure S14 and S15 and Table S2). Therefore, in contrast to the SAXS, the EXAFS data do not evidence Fe cluster formation. This can be explained by considering the differences between these techniques: SAXS is particularly sensitive to larger species such as Fe$_{13}$ and does not detect monomers, whilst EXAFS detects the average of all Fe species present equally (including monomers) and, as Fe$_{13}$ is only present as a minority species (max 17 % total Fe), would be dominated by other smaller species. Interestingly, our EXAFS data do not indicate substantial formation of Fe oxo-dimers which have been identified in past work utilising EXAFS in which non-acidified ferric solutions were titrated with either NaHCO$_3$ (< 1 M) (Zhu et al., 2013a, 2016) or 2 M KOH (Collins et al., 2016). This suggests that Fe(III) hydrolysis proceeds by a different pathway in the current work. The acidified ferric solution and drop-wise addition of stronger base (7 M NaOH) utilised here may promote Fe$_{13}$ cluster formation (Weatherill et al., 2016), with similar conditions in analogous aluminium systems shown to favour Al$_{13}$ Keggin formation (Akitt et al., 1971; Bertsch, 1986; Kloprogge et al., 1992a). Overall, combination of SAXS and EXAFS data show that, upon NaOH addition, Fe$_{13}$ clusters form rapidly and at similar rates in all experimental systems and are present alongside a dominant population of Fe monomers.

Notably, Fe$_{13}$ formation was most significant below pH 1 while the solution was highly undersaturated with respect to ferrihydrite (Figure S5). Under these conditions, Fe$_{13}$ clusters likely form in the high pH “hot spots” where NaOH is added via rapid olation and oxolation processes, with oxolation processes necessary to form the Fe-O-Fe linkages within the Fe$_{13}$ clusters. This localized formation mechanism is supported by the fact that pH 1 ferric nitrate solution prepared by directly dissolving ferric nitrate in 0.1 M HNO$_3$ does not contain any Fe$_{13}$ (Weatherill et al., 2016). Once formed, oxo-bridges react only slowly with acid (Dousma and de Bruyn, 1976; Dousma and De Bruyn, 1978) and will therefore be relatively stable in our system. Indeed, Fe$_{13}$ clusters have been shown to be present in pH 0.5 and 1.5 pure Fe nitrate solutions aged for 18...
days (Weatherill et al., 2016). In accordance with this, a scattering pattern obtained on six day aged pH 0.5 solution from the phosphate system (Figure S11) shows the presence of clusters with an Rg of 0.38 nm, consistent with an Fe$_{13}$ cluster. The presence of a strong complexing anion, such as phosphate, does not appear to destabilize these clusters under acidic conditions.

(ii) Aggregation and ferrihydrite nanoparticle formation

The scattering intensity in the low q region (q < 1 nm$^{-1}$) began to increase significantly above ~ pH 0.5 in the phosphate and ~ pH 1.5 in the sulfate and boric acid systems (Figure 4), compared to ~ pH 1 in a pure Fe nitrate system (Weatherill et al., 2016). The development of increased low-q scattering without significant change in the high-q Guinier region is strongly indicative of cluster aggregation (Li et al., 2016). The differences in pH between the systems at which aggregation commences points to interactions of the added species with the clusters and is discussed further below. In accordance with cluster aggregation, the fitting parameter $\epsilon$ (smaller value = more aggregation, SI) decreased with increasing pH and reached a minimum at ~ pH 3.2 in all systems, indicating complete aggregation (Figure 5C). This is in line with solution data whereby almost all Fe was a filterable size above pH 3. Differences in the minimal value of $\epsilon$ between the systems can be explained by the measured q-range not fully capturing the aggregate scattering region. Similarly, the subsequent increase in $\epsilon$ above pH 3 in the boric acid system was likely an artefact of the aggregates increasing to a size larger than the measured q-range (52 nm radius based on the relation, radius = $\pi$/q) (Weatherill et al., 2016), as reflected in Kratky plots of the SAXS data (Figure S12).

The addition of structure factors to the SAXS model was necessary to fit the increased scattering at low q, and it was found that a double structure factor model (Stawski et al., 2011) consisting of both a mass fractal and hard sphere structure factor (Eq S1) was best able to fit the data (SI, SAXS data analysis). However, the SAXS data above pH 3 in the sulfate system could not be accurately fit, likely due to polydispersity in the aggregates. Nevertheless, the general appearance of the SAXS patterns and the fits obtained by the model indicate that the nanoscale structure evolution of the aggregates followed the same general pathway in all experimental systems, and was similar to that observed in a parallel pure Fe nitrate system previously described.
This general pathway is discussed first, followed by more in depth discussion of the different experimental systems.

When fitting the scattering patterns during the early stages of aggregation (< pH 2.4 in sulfate and boric acid system and < pH 1 in phosphate system), the hard sphere structure factor parameters tended to zero, indicating that the aggregating clusters initially formed only mass fractal structures. The fractal dimension, \(d_f\), of these aggregates was initially low (\(d_f < 2\), Figure 5D), showing that the mass fractal aggregates had an open, branched structure with high linearity. This presumably represents association of Fe\(_{13}\) clusters into branched chains (Legg et al., 2014a). These aggregate structures undergo progressive densification with increasing pH, as indicated by the increase in \(d_f\) up to pH 3 in all three systems (Figure 5D) (Bottero et al., 1991; Tchoubar et al., 1991; Legg et al., 2014b). Simultaneous to aggregate densification, both \(\varepsilon\) (Figure 5C) and [Fe\(_{\text{aq}}\)] (Figure 2) decreased rapidly, reflecting rapid Fe\(_{13}\) cluster aggregation and precipitation of remaining Fe(III) monomers. The aggregate densification was therefore likely promoted by: (i) an increasing number of Fe\(_{13}\) clusters joining the aggregates, and (ii) condensation of Fe(III) monomers onto the Fe\(_{13}\) aggregate structures. Additionally, according to DVLO theory, increasing pH will promote aggregate collapse via progressive neutralization of the aggregate surface charges, thereby enabling attractive van der Waal forces to dominate over long-range repulsive electrostatic charges (Zhang, 2014). Aggregate densification was also observed in in situ TEM images obtained on the sulfate system (Figure 7) (see below). Interestingly, in the same pH range that this densification and precipitation occurred (~ pH 1 – 2.5 in phosphate system and pH 1.5 – 3 in sulfate, boric acid and pure Fe nitrate systems (Weatherill et al., 2016)), a contribution from the hard sphere structure factor became necessary to obtain a good fit to the SAXS data. This indicates the development of structures with internal correlations which have a hard sphere radius (\(R_{HS}\)) of ~ 0.75 – 1.65 nm. This size range matches well both with the expected size of a ferrihydrite primary particle (Janney et al., 2000; Wang et al., 2016b) and also with the 1 – 1.5 nm radius ferrihydrite nanoparticles observed in the TEM images from each system (Figure S1), indicating that it is during this densification and precipitation step that ferrihydrite nanoparticles principally form. However, throughout this process the radius obtained from the SAXS-derived spherical form factor (\(r_0\)) remained relatively constant (0.4 – 0.45 nm), only increasing a small amount (~ 0.03 nm) in the boric acid system. This suggests that the additional
particle volume which condenses onto the Fe$_{13}$ clusters to form the larger ferrihydrite nanoparticles does not have sufficient electron density contrast to be directly detected by the SAXS data. The inference here is that the ferrihydrite nanoparticles have a core-shell structure with an Fe(III)-depleted and hydrous (adsorbed and trapped H$_2$O) shell compared to the Fe$_{13}$ Keggin core. This model is in good agreement with the Hiemstra surface-depleted model of ferrihydrite (Hiemstra, 2013, 2015), in which ferrihydrite particles have an Fe-depleted and poorly ordered surface layer. Furthermore, pair distribution function (PDF) data from the pure ferric nitrate system at pH 9 (Figure S16) indicate that the ordered range of the particles is limited to ~1 nm (see below), in agreement with an ordered core – disordered shell model. Overall these observations suggest that in all systems ferrihydrite aggregates form by initial association of Fe$_{13}$ clusters into open branched structures, followed by an aggregate densification and precipitation process whereby ferrihydrite nanoparticles form with hard sphere interactions with neighboring nanoparticles. In this way, it is the aggregation behavior of preformed clusters which initiates ferrihydrite particle formation, not the growth of clusters to a critical size as is described by classical nucleation theory (Thanh et al., 2014; Scheck et al., 2016). Scheck et al. (2016) similarly reported that Fe(III) oxide nucleation was initiated by a transition from non-aggregative to aggregative behavior of Fe(III) clusters. Additionally, formation of aluminum hydroxide (Al(OH)$_3$) via Al$_{13}$ Keggin clusters has been similarly shown to proceed via formation of low fractal-dimension aggregates followed by densification to form aluminum hydroxide (Al(OH)$_3$) (Bottero et al., 1987).

The pH at which inclusion of the hard sphere structure factor was necessary to fit the SAXS patterns was lower in the phosphate system (~pH 1.1) compared to the other systems (~pH 2.2–2.5), consistent with aggregation and precipitation at lower pH in this system and thus formation of ferrihydrite nanoparticles at an earlier point in the neutralization reaction. Figure 5f shows the change in the hard sphere radius ($R_{HS}$) in each system with pH. At pH 9, $R_{HS}$ in the phosphate and boric acid systems is 1.3 and 1.65 nm respectively: a good match with the 1–1.5 nm radius nanoparticles observed in TEM images in each of these system respectively (Figure S1). The sulfate data could not accurately be fitted above ~pH 3, perhaps due to high polydispersity of the aggregates in this system, and therefore the $R_{HS}$ at pH 9 was not determined. However, TEM images at pH 9 show the same 1–1.5 nm radius nanoparticles observed in the other systems (Figure S1). Interestingly, $R_{HS}$ decreased slightly with
increasing pH in the phosphate and sulfate systems, whilst the opposite trend was observed for the boric acid and pure Fe nitrate systems, suggesting the complexing ions have some influence on the core-shell formation process. In all systems, the volume fraction (v), a measure of the particle packing density (SI), increased with increasing pH, reaching a maximum of 0.1 in the phosphate system and 0.12 in all other systems (Figure S13), consistent with aggregate densification.

In order to convert the model-derived size parameter (ξ) to an average aggregate radius of gyration (Rg(ag)) we applied equation S2 (SI). Due to the limitation imposed by the measured q-range (maximum resolvable size = 52 nm based on the relation, radius = π/q) and the potential effects of changes in polydispersity, the calculated Rg(ag) value is only considered indicative of size. Rg(ag) was resolved above pH ~ 0.8 in the phosphate system and was initially ~ 50 nm, before subsequently decreasing to ~ 44 nm by pH 1. This approximate aggregate size was consistent with those observed in the ex-situ TEM images of pH 1 sample from the phosphate system, which showed aggregates of ~ 30 – 60 nm in diameter with EDX indicating associated P (Figure S2 A-C). In contrast, ex-situ TEM images obtained on a sample taken at pH 1 from the pure Fe nitrate system showed individual particles without extensive aggregation (Figure S2 D&E), which is in agreement with aggregation occurring from a lower pH in the phosphate system. The decrease in Rg(ag) below pH 1 in the phosphate system is likely related to densification and compaction of the aggregate structures, as evidenced by the large increase in df between pH 0.5 and 1 (Figure 5). Rg(ag) decreased less significantly above pH 1, despite further increases in df, which may be due to a balancing effect from the mass precipitation of Fe above pH 1 ([Feaq], Figure 2). In the sulfate system, aggregate size was resolved from ~ pH 2.3 and also showed an initial decrease from ~ 56 nm at pH 2.3 to ~ 30 nm at pH 3. Below pH 2.3, the aggregate size parameter tended to infinity, indicating the aggregate size was larger than could be resolved by the q-range. In the boric acid system, the initial aggregates at ~ pH 1.5 had a very small Rg(ag) of ~ 5 nm, indicating the association of only a few Fe13 clusters into small, low fractal dimension structures. Such small aggregates cannot be regarded as truly fractal, but they have a structure which can be well approximated by a mass fractal structure factor. Rg(ag) subsequently increased rapidly with pH, reaching a maximum of ~ 70 nm by pH 4.5. This is a larger aggregate size than observed in the other systems, which is also evidenced by Kratky plots whereby the scattering
intensity at smallest q does not reach a plateau within the measured q-range in the boric acid system, unlike in the phosphate and sulfate systems (Figure S12).

*In situ* TEM images obtained on the sulfate system at pH 2.3 and 9 (Figure 7) confirm the presence of the aggregates and support that the aggregates undergo densification with increasing pH. At pH 2.3 the aggregate structure is characterised by its high linearity and branching; by contrast at pH 9 the aggregates are denser with clear rounded structures, while still retaining a diffuse appearance indicative of mass fractal structure. The pH 9 aggregates also appear to be reasonably polydisperse, consistent with problematic SAXS fitting in the sulphate system above pH 3. We note that the observed aggregate size at pH 2.3 in the TEM image is approximately consistent with the $R_g(\text{ag})$ of 56 nm obtained from SAXS, if we consider that the $R_g$ of a low fractal dimension structure ($d_f \sim 2.1$ in this case) is significantly smaller than its space filling size.

The PDF of HEXS data collected on the final ferrihydrite phase at pH 9 in a pure Fe nitrate system is shown in Figure S16. Interestingly, the sample did not exhibit strong scattering peaks above $\sim 1$ nm ($r_{\text{max}}$), indicating the absence of order above this distance. This is in excellent agreement with a ferrihydrite particle that has an ordered Fe$_{13}$ core ($\sim 1$ nm) that is surrounded by a disordered shell. The peak at $\sim 0.2$ nm correlates well with the expected first shell Fe-O distance, and the peak at $\sim 0.34$ nm with Fe-Fe distances between two corner sharing octahedra and/or tetrahedra. Comparing our PDF data to those obtained on a dried ferrihydrite sample collected by Wang *et al.* (2016b), we observe that the major peaks match up (Figure S17), confirming that our PDF signal originates from ferrihydrite. Notably, our PDF data were obtained on a wet concentrated slurry of the ferrihydrite, in contrast to previous studies which have only collected data on dried ferrihydrite samples. Analysis of the slurry eliminates artefacts associated with the drying process, but does introduce some uncertainty in the background subtraction, which affects the scattering peak positions and relative intensities in the PDF. For this reason, the PDF was not fit to a structural model as has been done in previous studies for dried ferrihydrite samples (Michel *et al.*, 2007; Wang *et al.*, 2016b). Despite this, the $r_{\text{max}}$ value was robust and very consistent across a range of background subtractions, giving high confidence in the ordered range of the particles of $\sim 1$ nm.
Figure 7: In situ transmission electron microscopy (TEM) images from the sulfate system at A) pH 2.3 and B & C) pH 9. Some of the aggregates at pH 9 are not in focus because they are positioned at different vocal planes within the solution.

5.4.4. Discussion of the effects of added species

Phosphate

Phosphate is known to strongly complex with Fe, even at pH < 1 (Rose et al., 1997a). In the present study, strong association between phosphate and Fe at low pH is evidenced by the concomitant decrease in both \([\text{P}_{\text{aq}}]\) and \([\text{Fe}_{\text{aq}}]\) at ~ pH 1 (Figure 2). Additionally, EDX spectra obtained on Fe(III) particles isolated at pH 1 confirmed the presence of P (Figure S1C). Co-precipitation studies at P/Fe ratios ranging from 0.12 to 1.2, have previously shown complexation of phosphate with aqueous Fe at low pH can block Fe polymerization sites, thus limiting Fe(III) hydrolysis to the dimer stage (Rose et al., 1996, 1997a; Voegelin et al., 2010). In our study (P/Fe ratio 0.15), the primary
cluster radius in the phosphate system is 0.4 – 0.46 nm (Figure 5 and S9): larger than a dimer or trimer (Figure S10), probably reflecting formation of Fe$_{13}$ and indicating phosphate does not limit Fe(III) hydrolysis. There are various possible reasons for this difference between our study and the cited literature. Firstly, the solutions used in past work contained chloride and/or silicate, both of which are stronger complexation ions than nitrate (Bottero et al., 1991), which was present as the dominant background ion in our study. Indeed, Rose et al. (1996, 1997a) attributed the limited hydrolysis in their system to complexation by both phosphate and chloride. Secondly, the starting pH in the present study (pH 0.1) was significantly lower than in the previous studies which were conducted at ~ pH 1 (Rose et al., 1996, 1997a) or near neutral pH (Voegelin et al., 2010). At pH 0.1, a significant amount of phosphate is speciated as H$_3$PO$_4$ (PHREEQC calculations, Figure S4); it is less favourable for Fe to release H$^+$ from H$_3$PO$_4$ than from H$_2$O (Hsu, 1973, 1976), therefore reducing interactions between Fe and phosphate at this low pH. Lastly, we propose that cluster formation is dominant in high pH zones where the strong base (7 M NaOH) was added (Weatherill et al., 2016): in these high pH transient zones, hydroxide (OH$^-$) will compete strongly with phosphate to complex with Fe. Subsequently, phosphate may complex with the formed clusters after the high pH zone has been dispersed by the mixing action.

The decrease in [Fe$_{aq}$] occurs from a lower pH in the phosphate system than any other system (Figure 2), reflecting earlier aggregation of Fe$_{13}$ clusters in this system (SAXS patterns, Figure 2). We propose two possible causes for this earlier aggregation. Firstly, phosphate can form corner sharing complexes with two Fe octahedra and act as a bridge between them (Neil et al., 2014), with this effect previously shown to induce precipitation of iron oxyhydroxide via bridging between Fe dimers (Rose et al., 1996, 1997a). In our study, phosphate may similarly bridge between the Fe$_{13}$ clusters and induce earlier aggregation and precipitation. Interestingly, the structure of hydrous ferric arsenate, which is analogous to hydrous ferric phosphate (Mikutta et al., 2014), has been shown to be composed of chains of AsO$_4$ tetrahedra and FeO$_6$ octahedra connecting alternately (Wang et al., 2016a), indication of the ability of these tetrahedra to link two Fe octahedra. Secondly, phosphate association with Fe$_{aq}$, expected to be positively charged at low pH, could reduce electrostatic repulsion between the clusters and thus destabilize them. Indeed, previous work has shown that phosphate presence during Fe precipitation results in
particles with a more neutral zeta potential (Neil et al., 2014). P-EXAFS spectroscopy could be used to further investigate interactions between phosphate and the Fe$_3$ clusters, but was not within the remit of this study.

The solution data showed that removed phosphate was almost entirely released back into solution between pH 9 and 12 without any corresponding Fe dissolution (Figure 2), indicating that phosphate was predominantly surface adsorbed to the ferrihydrite (Willett et al., 1988). In contrast, previous research has shown that co-precipitated phosphate-Fe can exhibit solid solution behavior, with the P/Fe ratio of the formed solid having an upper limit of ~ 0.5 (Thibault et al., 2009; Voegelin et al., 2010, 2013). With increasing phosphate incorporation, the XRD pattern of ferrihydrite exhibits systematic changes: the strong ~ 35.5° 2θ CuKα line moves towards 30°, while the weaker ~ 62° 2θ CuKα broadens and eventually vanishes (Thibault et al., 2009). In the present study, the XRD pattern from the phosphate system exhibits a modest downward shift of ~ 0.5° of the strong line and a slight broadening of the weak 62° line (Figure 1). Although this may indicate a small amount of incorporated phosphate, the changes are very modest (Thibault et al., 2009) and overall support that phosphate incorporation is minimal. Therefore, our study shows that under different conditions co-precipitation of phosphate with Fe can occur with minimal phosphate incorporation. This is likely related to the ferrihydrite formation mechanism in our study whereby the precursor Fe$_3$ clusters form rapidly within the high pH hotspots where phosphate competes less effectively with OH$^-$ to complex Fe.

Surface adsorption of phosphate on ferrihydrite exhibits a high degree of complexity and it is likely that a large number of structures are possible (Krumina et al., 2016). In our study, the low pH spectra (< pH 5.5) are consistent with a single inner sphere, protonated phosphate adsorption complex (Arai and Sparks, 2001; Wang et al., 2013, 2015a). However, there is no consensus on the exact structure of these phosphate adsorption complexes, with some studies suggesting a bidentate complex (Arai and Sparks, 2001; Antelo et al., 2010; Wang et al., 2013, 2015a) and others a monodentate one (Persson et al., 1996; Krumina et al., 2016). With increasing pH, further splitting in the broad phosphate absorption band of the IR spectra observed in the current work indicates the presence of multiple phosphate sorption complexes, in accordance with previous studies which reported bidentate and monodentate surface complexes may be present simultaneously at high pH (Antelo et al., 2010) and that non-
protonated complexes also become important (Arai and Sparks, 2001; Wang et al., 2015b).

**Sulfate**

Changes in \([S_{(aq)}]\) below pH 3 exhibited similar behaviour to changes in \([Fe_{(aq)}]\) (Figure 2), suggesting association of sulfate with Fe within this pH range, which is further supported by thermodynamic calculations which show 16 - 55 % of sulphate complexed with aqueous Fe between pH 0.1 and 2 (Figure S3B). \([S_{(aq)}]\) reached a minimum at pH 3, above which it increased back to almost its original concentration by ~ pH 9, indicating that the removed sulfate was primarily surface adsorbed to the ferrihydrite and not incorporated.

Notably, the presence of sulfate shifted the onset of Fe\(_{13}\) aggregation to slightly higher pH (~ pH 1.5) compared to a pure Fe nitrate system (~ pH 1) (Weatherill et al., 2016) and phosphate system (~ pH 0.5). However, this did not result in a significant difference in the pH of mass precipitation of Fe between the sulfate and pure Fe nitrate experiments (Figure 2). Delayed Fe\(_{13}\) aggregation was surprising since sulfate, as a negatively charged ion, may be anticipated to have a charge neutralisation effect on the clusters at low pH, thereby promoting aggregation in a similar way to what was observed in the phosphate system. Indeed, previous studies investigating Fe(III) precipitation with starting pH of 3.7 (Hu et al., 2012), ~ pH 2 (Lay and Wu, 1995) and ~ pH 1 (Dousma et al., 1979) found that added sulfate resulted in more rapid precipitation and aggregation, which was attributed to the reduction in electrostatic repulsions. The lack of a similar effect in the present study suggests this effect of sulfate is dependent on the conditions of formation, and is perhaps due to sulfate stabilization of the Fe\(_{13}\) clusters in our system. Indeed, Zhu et al. (2012) previously reported that sulfate complexed molecular clusters were the largest species present at pH 2.1 – 2.2 in their ferric sulfate solutions, speculating that these clusters may be sulfate-stabilised Fe\(_{13}\) clusters. Additionally, sulfate is commonly used to crystallise aluminium Keggin clusters (Al\(_{13}\)) via hydrogen bonding to the oxygen atoms of sulfate (Kloprogge et al., 1992b; Armstrong et al., 2011), further suggesting this anion can stabilise and preserve the Keggin moiety. In line with this, Majzlan and Myneni (2005) showed that the principle interaction between sulfate and Fe(III) at pH 1 was via hydrogen bonds, albeit also with some inner sphere complexation.
IR results indicate solely inner sphere adsorption of sulfate at low pH (< pH 3.8), with a progressive change to outer sphere adsorption as pH increases before eventual full desorption by pH 9, consistent with previous studies (Peak et al., 1999; Wijnja and Schulthess, 2000; Fukushi et al., 2013; Johnston and Chrysochoou, 2016). Nitrate adsorption peaks are less apparent at low pH in the sulfate system compared to the other systems (Figure 3), probably due to competition with sulfate anions which are in greater mole concentration than phosphate in our systems (10.4 mM sulfate Vs. 1.05 mM phosphate) whilst known to similarly interact strongly with ferrihydrite at low pH.

The specific structure of the inner sphere sulfate structure is a topic of debate with both mondentate and bidentate complexes proposed (Hug, 1997; Peak et al., 1999; Fukushi et al., 2013; Zhu et al., 2013b; Collins et al., 2016; Gu et al., 2016; Johnston and Chrysochoou, 2016). However, our IR spectra are most similar to those reported by Johnston and Chrysochoou (2016) who favoured a bidentate configuration based on FTIR peak positions. Additionally, Gu et al. (2016) recently concluded bidentate-binuclear complexation was the dominant mechanism of sulfate adsorption to ferrihydrite based on XAS results, quantum chemical calculations and surface complexation modelling.

Boric acid

In contrast to phosphate and sulfate, boric acid is removed from solution only above ~ pH 7 (Figure 2), indicating adsorption to ferrihydrite does not occur at low pH. This is consistent with the expected adsorption edge of boric acid on ferrihydrite, which shows a maximum near the pKa of boric acid (pH 9.2) (Su and Suarez, 1995; Demetriou and Pashalidis, 2012). In line with this, IR results indicate a mix of inner and outer sphere boric acid adsorption above ~ pH 7, possibly with some borate adsorption at pH 9. The adsorption mechanism(s) of inner sphere boron complexes have not been resolved and requires further investigation (Peak et al., 2003). Compared to the pure Fe and sulfate systems, carbonate adsorption in the boric acid system appears to be suppressed at pH 9, indicating competitive adsorption between these two species in line with previous observation (Peak et al., 2003).

Similar to the sulfate system, the presence of boric acid shifted the onset of Fe$_{3+}$ aggregation to higher pH values (pH 1.5) compared to a pure Fe nitrate system (pH 1)
(Weatherill et al., 2016). Although the neutral boric acid molecule would not be expected to alter electrostatic forces on the clusters significantly, boric acid contains hydroxyl groups which can form hydrogen bonds with charged surfaces and may therefore stabilize Fe$_{13}$ clusters in a similar way to sulfate. Additionally, hydrogen bonded boric acid may disrupt the network of hydrogen bonded water around the cluster and cause steric repulsion: Sharifalhoseini et al. (2016) proposed that boric acid stabilized their ZnO-SiO core-shell nanoparticles against aggregation by forming hydrogen bonds with the particle surfaces, leading to steric repulsion between the nanoparticles. This steric hindrance effect may also explain why the initial aggregates were smaller in the boric acid system (R$_{agg}$, Figure 5).

**Mixed effluent systems**

In real EARP effluent, phosphate, sulfate and boric acid are present simultaneously, which may modify their behaviour. At low pH, sulfate and phosphate are expected to dominate interactions with the Fe oxyhydroxide clusters/particles over boric acid, since the former are present as charged anionic species at significantly lower pH than boric acid (sulfuric acid and phosphoric acid have lower pKa values than boric acid (National Institute of Standards and Technology, 2017)). Indeed, FTIR results show sulfate and phosphate adsorption to the floc occurs at significantly lower pH than boric acid (Figure 3). Overlap in the pH range at which sulfate and phosphate absorb (pH < 2.5 – 7) and boric acid and phosphate adsorb (pH 7 – > 9) (Figure 3) means that competitive adsorption processes may occur between these species.

Interestingly, compared to a pure ferric nitrate system, phosphate promoted Fe$_{13}$ cluster aggregation to occur at lower pH (~ pH 0.5) while sulfate and boric acid delayed aggregation to higher pH (~ pH 1.5). Whether these effects cancel each other out or one dominates over the other in mixed systems requires further experimentation. However, the higher concentration of ionic species in mixed systems could be expected to promote aggregation due to an increased capacity of the system to shield electrostatic charges.

**5.5. Conclusions**

In situ time-resolved SAXS, in combination with TEM, XRD, IR, PDF, EXAFS and solution analysis, has revealed the ferrihydrite formation mechanisms during a base-
induced ferric hydrolysis process and in the presence of phosphate, sulfate or boric acid. In all systems, formation of 0.9 - 1 nm Fe$_{13}$ Keggin clusters occurred rapidly between pH 0.12 – 1.5 upon the drop-wise addition of strong 7 M NaOH to acidified ferric solution, even when the bulk pH was significantly undersaturated with respect to ferrihydrite. With continued base addition, the Fe$_{13}$ clusters aggregated to form structures with low dimensionality, followed by simultaneous aggregate densification and precipitation of small hydrolysis products to form ferrihydrite nanoparticles, which SAXS data suggest have a hydrous, Fe-depleted shell and Fe$_{13}$ core.

The pH at which initial aggregation of the Fe$_{13}$ clusters occurred varied between the phosphate (pH 0.5), sulfate (pH 1.5), boric acid (pH 1.5) and a previously investigated pure Fe nitrate systems (pH 1) (Weatherill et al., 2016), indicating different interactions of the added species with the clusters. Aggregation was promoted in the phosphate system, likely due to bridging between clusters and/or a charge compensation effect. In contrast, aggregation was delayed in the sulfate and boric acid systems, indicating their ability to stabilise Fe$_{13}$ clusters, possibly due to their ability to form hydrogen bonds with Fe(III) at low pH. Infrared spectroscopy analysis provided further insight into the mechanisms of phosphate, sulfate and boric acid interactions during the hydrolysis process, with both inner and outer sphere adsorption observed for different anions. However, the overall impact of the added species on the ferrihydrite formation pathway was minimal: each system exhibited the same ferrihydrite formation process via Fe$_{13}$ clusters, leading to formation of ~ 3 nm core-shell ferrihydrite nanoparticles. We propose this is a result of our experimental procedure whereby Fe$_{13}$ clusters form rapidly in the locally high pH at the point of base addition, where the added species cannot compete effectively with OH$^-$ to complex Fe and prevent Fe$_{13}$ cluster formation. Since the Sellafield EARP plant utilizes a similar dosing process, it is likely that the behaviour will be consistent.

Overall, these results confirm the ability of Fe$_{13}$ Keggin clusters to act as a pre-nucleation intermediate to ferrihydrite formation, even in the presence of strong Fe complexing species. This has clear implications for the fundamental understanding of ferrihydrite formation in industrial and natural systems.
Supporting Information for Chapter 5:
Ferrihydrite Formation via Fe13 Keggin Clusters in the
Presence of Sulfate, Phosphate and Boric Acid

Experimental details

BET surface area measurement

The dried, powdered precipitate samples were outgassed with He at room temperature for 19 hours (Clausen and Fabricius, 2000), followed by measurement of the BET multipoint surface area using a Micromeritics Gemini with N₂ as the sorbent gas.

Table S1: BET surface areas of dried precipitate isolated at pH 9 in each system.

<table>
<thead>
<tr>
<th>System</th>
<th>BET surface area (m² g⁻¹)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>PO₄</td>
<td>232</td>
<td>4</td>
</tr>
<tr>
<td>SO₄</td>
<td>274</td>
<td>15</td>
</tr>
<tr>
<td>B</td>
<td>288</td>
<td>3</td>
</tr>
</tbody>
</table>

Transmission electron microscopy (TEM) sample preparation

Ex-situ TEM images were obtained using a Philips CM200 FEG-TEM with an Oxford Instruments 80 mm 2 X-Max SDD detector. These TEM samples were prepared by directly pipetting fresh sample onto the TEM grid followed by a few drops of isopropanol to wash off excess salt. Holey-carbon Au mesh grids were used for samples with pH < 3, whilst holey-carbon Cu mesh grids were used for those with pH ≥ 3.

SAXS data analysis

2D SAXS patterns were reduced to 1D scattering curves of intensity I vs q (scattering vector) by sector integration. The resulting intensity data, I(q), was normalised to the
sample transmission and calibrated using glassy carbon as a standard to yield I(q) on an absolute scale. Background subtraction of the ferric nitrate solution prior to NaOH addition was performed, resulting in SAXS profiles consisting of only scattering from any particles that form during the experiment.

The scattering curves are fit using a model that describes the scattering as arising from a population of primary particles which may cluster to form aggregates.

It was found that the best fits were obtained when the primary particles were modelled with a spherical form factor \( P(q, r_0) \) (Guinier and Fourner, 1955) with radius \( r_0 \). The polydispersity of the primary particles was not modelled since the measured q-range does not extend to high enough values to observe the Porod region, which would provide information on this. Guinier analysis (Guinier and Fourner, 1955) was further used as an additional measurement of the size of unaggregated primary particles.

To account for aggregation, a “double structure factor model” (Stawski et al., 2011) was used which accounts for both mass fractal-like structure (mass fractal structure factor) and non-fractal aggregates (hard sphere structure factor) (Stawski et al., 2011).

The mass fractal structure factor can be expressed as \( S_F(q, r_0, \xi, d_f) \) (Berry and Percival, 1986; Freltoft et al., 1986; Teixeira, 1988), where \( d_f \) is the fractal dimension and \( \xi \) is the aggregate size parameter. The hard sphere structure factor can be expressed as \( S_{HS}(q, r_{HS}, v) \) (Kinning and Thomas, 1984) and describes aggregates as being composed of a volume fraction \( v \) of interacting particles which have hard sphere radius \( r_{HS} \). The volume fraction \( v \) is defined as the ratio of total particle volume in the local area divided by the total available volume (Besselink et al., 2013). A maximum value of 0.74 represents the most efficient particle packing of close-packed hexagonal or cubic lattices.

To account for changes in the relative scattering contribution from the mass fractal aggregates with time, the approach of Stawski et al. (2011) was used whereby a weight factor \( 0 < \varepsilon < 1 \) is introduced. The full scattering equation was then:

\[
I(q) = nV_p^2\Delta \rho^2 \times P(q, r_0) \times [\varepsilon S_F(q, r_0, \xi, d_f) + (1-\varepsilon)S_{HS}(q, r_{HS}, v)]
\]

(Eq S1)

Here a smaller value of \( \varepsilon \) indicates a bigger contribution from the fractal aggregates to the scattering intensity, with a value of 1 indicating no contribution. \( nV_p^2\Delta \rho^2 \) is the pre-factor term where \( n \) is the number density of scattering particles (number of
particles per volume of solution), \( V_p \) is particle volume, and \( \Delta \rho \) is the electron density contrast term. The pre-factor term is proportional to the total scattering volume.

The radius of gyration (\( R_g \)) of the fractal aggregates can be calculated from \( d_f \) and \( \xi \) (Sorensen and Wang, 1999; Stawski et al., 2011):

\[
R_g = \xi \sqrt{\frac{d_f^2(d_f+1)}{2}}
\]  
(Eq S2)

Values for parameters obtained by the models had standard errors of < 1%, which were calculated by the fitting routine in Origin Pro using the Levenberg-Marquardt Algorithm. An improvement of fit was judged as occurring when a lower reduced chi square value and when physically realistic values for the fitting parameters were obtained.

**Calculating proportion of Fe present as Fe\(_{13}\) Keggin clusters**

The proportion of Fe present as Fe\(_{13}\) clusters after complete cluster formation (taken as pH 1.5 in each system) was calculated from the pre-factor \( (nV_p^2\Delta \rho^2) \), whose value was obtained from fitting. The maximum value of the pre-factor in each system was used: 0.011 cm\(^{-1}\) in the sulfate, boron and pure Fe nitrate (Weatherill et al., 2016) systems, and 0.0094 cm\(^{-1}\) in the phosphate system. The volume of a single Fe\(_{13}\) cluster \( (V_p) \) was calculated assuming a spherical cluster shape with a radius of 0.48 nm (this is the maximum size obtained from Guinier analysis in our experiments, and is also the Fe\(_{13}\) cluster size reported by Sadeghi et al. (2015)). The electron density contrast \( (\Delta \rho) \) was calculated using the Irena macro (Ilavsky and Jemian, 2009) for Igor Pro using pure water as the background solvent, giving a value of \( 3.1 \times 10^{11} \) cm\(^{-2}\). Plugging these values into the equation for the pre-factor gives a number density \( (n) \) of \( 5.33 \times 10^{17} \) Fe\(_{13}\) clusters ml\(^{-1}\) in the sulfate, boric acid and pure Fe nitrate systems, and \( 4.56 \times 10^{17} \) Fe\(_{13}\) clusters ml\(^{-1}\) in the phosphate system. Knowing the total volume of solution in each system, we can then calculate the total number of Fe\(_{13}\) clusters in each system. If we then multiply this value by 13 to get the total number of Fe atoms present within Fe\(_{13}\) clusters and compare this to the total number of Fe atoms present in the whole system, we can calculate that the percentage of total Fe present as Fe\(_{13}\) is \(~17\%\) in the sulfate, boron and pure Fe nitrate systems and \(~16\%\) in the phosphate system.

**Fe\(_{13}\) simulated SAXS curves**
Crysol (Barberato et al., 1995) was used to generate simulated scattering curves of Fe$_{13}$ clusters in pure water, and also fit these simulated curves to experimental scattering curves obtained in the present study (Figure 6, main paper). Crysol fits the simulated scattering pattern to the experimental scattering pattern by varying the following parameters within physically realistic set limits: (i) average displaced solvent volume per atomic group (ii) contrast of the hydration shell. The Fe$_{13}$ Keggin cluster was isolated from Bi$_6$Fe$_3$L$_{12}$, synthesised by Sadeghi et al. (2015), using Crystal Maker. It was found that alternatively using a Fe$_{13}$ Keggin cluster isolated from the Michel et al. (2007) model of ferrihydrite made no significant difference to the simulated scattering pattern. Simulated SAXS patterns of a Fe dimer, trimer and Fe$_{13}$ Keggin clusters were also generated without any fitting to experimental data (Figure S10).

**PHREEQC modelling**

A model of the ferrihydrite synthesis procedure was created in PHREEQC by mimicking the NaOH-induced hydrolysis of Fe(NO$_3$)$_3$ undertaken in the experimental method. PHREEQC calculations were performed using an edited SIT (specific ion interaction theory) database whereby equilibrium constants for the aqueous species FeOH$^{2+}$(aq), Fe(OH)$_2$$^+$(aq) and Fe$_2$(OH)$_2$$^{4+}$(aq) were replaced with those recommended in a review conducted by the NEA (Nuclear Energy Agency) (Lemire et al., 2013). Equilibrium constants for other relevant Fe species were as defined in the SIT database. A single phase – ferrihydrite (Fe(OH)$_3$) – was allowed to precipitate, with the solubility product defined by Stefánsson (2007) used. Separate models with sulfate, phosphate and boric acid included were run to mimic the experiments including these species.

**Infrared spectral peak fitting**

Peak fitting of the sulfate and phosphate IR spectra was done using Origin (OriginLab, Northampton, MA). Sulfate spectra were fit between 950 and 1250 cm$^{-1}$ and phosphate spectra between 800 and 1200 cm$^{-1}$. A linear baseline was first subtracted within the fitting area and spectra were normalised to the highest peak intensity. The resulting normalised, baseline subtracted spectra were fitted with Gaussian peaks.
Additional figures

Figure S1: TEM images and energy dispersive X-ray (EDX) spectra of dried sample at pH 9. A & B) Phosphate system. C & D) Sulfate system. E & F) Boric acid system
Figure S2: TEM images and energy dispersive X-ray (EDX) spectra of dried sample at pH 1. A, B & C) Phosphate system. D & E) Pure Fe nitrate system. In the EDX spectra, the signals from gold (Au) and carbon (C) originate from the holey carbon gold mesh TEM grid the sample was prepared on.
Figure S3: Change in speciation with pH of Fe in the A) phosphate system, B) sulfate system, and C) boric acid system as determined by thermodynamic modelling in PHREEQC.
Figure S4: Change in speciation with pH of A) phosphate, B) sulfate, and C) boric acid in their respective systems, as determined by thermodynamic modelling in PHREEQC.
Figure S5: Change in saturation index of ferrihydrite (Fe(OH)$_3$) with pH in each system, as calculated in PHREEQC using the solubility product defined by Stefánsson, (2007).

Figure S6: Fits of FTIR spectra from the phosphate system at A) pH 2.6, B) pH 5.5, and C) pH 4.3. The green lines denote the individual peaks composing the fit whilst the red line denotes the resulting cumulative fit.
**Figure S7:** Fits of FTIR spectra from the sulfate system at A) pH 2.5, B) pH 2.9, C) pH 3.8, D) pH 5.6, E) pH 6.3 (5 peaks fit), and F) pH 6.3 (2 peaks fit). The green lines denote the individual peaks composing the fit whilst the red line denotes the resulting cumulative fit.
**Figure S8:** Scattering patterns collected in the first 6 mins after starting NaOH addition in the A) phosphate system, B) sulfate system, and C) boric acid system. Development of Guinier region is seen within 2 mins in each system.

**Figure S9:** Radii of gyration (Rg) of primary clusters determined by Guinier analysis of SAXS curves. The data from the pure Fe nitrate system is taken from our previous publication (Weatherill et al., 2016).
**Figure S10:** Experimental scattering patterns (pH 0.3 from the phosphate system and pH 0.5 from the sulfate and boron systems) compared to Crysol-simulated scattering patterns of various Fe clusters. The simulated scattering patterns were not fit to the experimental scattering patterns and were obtained with no scattering contrast in the hydration sphere. Radii of gyration (Rg) were calculated from Guinier analysis of the scattering patterns. The simulated dimer was the oxo-dimer described by Zhu et al. (2013). The trimer was isolated from the Keggin structure and is composed of two edge sharing Fe polyhedra joined to a third Fe polyhedra by double-corner sharing. We note that different trimer structures showed similar scattering patterns.

**Figure S11:** SAXS pattern collected on pH 0.5 solution from the phosphate system aged for 6 days at 35 °C. Radius of gyration (Rg) was determined from Guinier analysis.
Figure S12: Kratky plots of SAXS data from the A) phosphate system, B) sulfate system, and C) boric acid system.

Figure S13: Change in the hard sphere packing volume, $v$ (eq. S1), with pH, as determined by fitting. The pure Fe nitrate data is taken from our previous study (Weatherill et al., 2016).
Figure S14: $k^3$-weighted Fe K-edge EXAFS spectra (top) and their Fourier transforms (bottom) collected on solutions isolated at different pH from a pure Fe nitrate system.

Figure S15: EXAFS data (solid black) and fits (dotted red): $k^3$-weighted EXAFS (left) and their Fourier transform (right).
Table S2: Details of EXAFS fit parameters from Fe nitrate solutions isolated at different pHs. Fitting errors are given in parentheses. CN denotes coordination number; R denotes atomic distance; $\sigma^2$ denotes Debye-Waller factor; $\Delta E_0$ denotes the energy shift from the calculated Fermi level; $S_0^2$ denotes the amplitude factor.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Path</th>
<th>CN</th>
<th>R (Å)</th>
<th>$\sigma^2$ (Å$^2$)</th>
<th>$\Delta E_0$ (eV)</th>
<th>$S_0^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 1.5</td>
<td>Fe-O</td>
<td>6</td>
<td>2.00 (0.004)</td>
<td>0.004 (0.001)</td>
<td>-2.2 (0.5)</td>
<td>0.90 (0.04)</td>
</tr>
<tr>
<td>pH 0.85</td>
<td>Fe-O</td>
<td>6</td>
<td>2.00 (0.005)</td>
<td>0.004 (0.001)</td>
<td>-2.4 (0.6)</td>
<td>0.93 (0.04)</td>
</tr>
<tr>
<td>pH 0.1</td>
<td>Fe-O</td>
<td>6</td>
<td>2.00 (0.004)</td>
<td>0.004 (0.001)</td>
<td>-2.3 (0.5)</td>
<td>0.92 (0.03)</td>
</tr>
</tbody>
</table>

Figure S16: Pair distribution function (G(r)) of the final ferrihydrite sample at pH 9 from a pure ferric nitrate system. The dashed line marks the approximate size of the Fe$_{15}$ core.
Figure S17: Comparison between pair distribution function ($G(r)$) collected in the present study (same as seen in Figure S16) and that collected by Wang et al. (2016) on a dried 2-line ferrihydrite sample.
CHAPTER 6

Ferrihydrite Transformation in the Presence of Sulfate, Phosphate and Boric acid: Relevance to Radioactive Effluent Treatment

Joshua S. Weatherill, a Katherine Morris, a Markéta Florianová, a Richard Blackham, b and Samuel Shaw a *

a Research Centre for Radwaste Disposal and Williamson Research Centre, School of Earth and Environmental Sciences, University of Manchester, Oxford Road, Manchester, M13 9PL, UK. b Sellafield Ltd, Hinton House, Birchwood Park Avenue, Risley, Warrington, Cheshire, WA3 6GR, UK

6.1. Abstract

Ferrihydrite is a poorly-ordered, nanoparticulate iron oxyhydroxide phase which readily aggregates to form extensive flocs. Due to their large surface area and reactivity, ferrihydrite flocs are widely utilised in effluent treatment processes to effectively uptake contaminants from solution. However, ferrihydrite is thermodynamically metastable relative to more crystalline iron (oxyhydr)oxide phases and transformation readily occurs over time, with potential impacts on floc processing and final waste form properties. Here we characterise time-induced transformation of ferrihydrite floc, which was produced in a process mimicking the Enhanced Actinide Removal Plant (EARP), a radioactive effluent treatment plant at Sellafield. In a pure ferric nitrate system and systems with added sulfate and boric acid, flocs aged at 40 °C and pH 9 began to transform within one week, with full transformation occurring within eight weeks. The dominant transformation product was high sphericity hematite particles of ~ 120 nm diameter, along with small amounts of acicular goethite (< 5%) in the pure ferric nitrate and added sulfate systems. The transformation was accompanied by an order of magnitude decrease in the settleable solids volume and slower solid settling kinetics. In contrast, in systems with added phosphate (100 and 10 ppm phosphate) ferrihydrite transformation was completely inhibited within the 8 weeks ageing period, with phosphate strongly
adsorbed to the ferrihydrite floc throughout the ageing period and no decrease in the volume of settleable solids observed. However, decreasing the phosphate concentration to 1 ppm was sufficient to allow full transformation to hematite to occur within 8 weeks. Ageing the floc at the slightly higher pH of 9.5 induced significant formation of acicular goethite in the pure Fe nitrate and sulfate systems (28% and 39% goethite respectively), while goethite formation was suppressed in the boric acid system with only hematite once again formed. Overall, this data is useful for helping predict the transformation behaviour of ferrihydrite floc relevant to effluent treatment processes and the subsequent effect this will have on waste volumes and floc processing.

6.2. Introduction

Iron oxyhydroxide co-precipitation and flocculation methods are commonly utilised in effluent and water treatment practices as an effective means to remove contaminants including radionuclides (Matsuzuru et al., 1972; Hobbs, 1999; Hildred et al., 2000; Baeza et al., 2004; Collier et al., 2006), organic compounds (Vadasarukkai and Gagnon, 2017), and heavy metals (Hohn et al., 2006; Karapınar, 2016). These processes typically involve formation of an iron oxyhydroxide floc which uptakes contaminants by a combination of adsorption, incorporation and entrapment processes, followed by a physical separation of the floc with its associated contaminants from the solid phase. The initially formed iron oxyhydroxide floc in these rapid treatment processes is often thermodynamically unstable and will transform with time, having potential impacts on the floc filterability, final waste volumes, and contaminant retention. Further understanding these floc transformation processes and the effect on the floc properties is highly important for optimising water treatment processes.

In iron oxyhydroxide floc treatment processes, ferric cations are added to effluents (or are already present) and are induced to undergo hydrolysis, typically by rapid base addition, leading to precipitation of a solid iron oxyhydroxide phase. Ferrihydrite, a poorly-ordered nanoparticulate phase which readily aggregates to form extensive flocs and has a large capacity for contaminant uptake, is typically the initial phase formed due to its high kinetic accessibility (i.e. it has a low free energy barrier to formation) (Navrotsky et al., 2008). Ferrihydrite is also ubiquitous in the natural
environment where it can act as an important sink for contaminants (Faivre, 2016). However, due to its low structural order, ferrihydrite is metastable with respect to more crystalline iron (oxyhydr)oxide phases and transformation readily occurs. Under ambient conditions, hematite (α-Fe₂O₃) and goethite (α-FeOOH) are the most stable Fe₂O₃ and FeOOH polymorphs respectively (Navrotsky et al., 2008), and are by far the most common transformation products (Cornell and Schwertmann, 2003). Transformation of ferrihydrite floc to more crystalline phases has profound impacts on downstream separation of the floc (e.g. filtration, sedimentation). This is highly significant since the success of treatment processes is dependent on efficient separation of the iron oxyhydroxide from the aqueous phase (Karapinar, 2003). Additionally, ferrihydrite transformation may influence subsequent encapsulation processes (e.g. cementation), speciation of the associated contaminants, and final disposal of the floc as a waste form (Collier et al., 2006).

Ferrihydrite is highly hydrated and voluminous due to its open, porous structure, and has poor dewatering properties (Benjamin et al., 1996; Loan et al., 2002; Karapinar, 2003). In contrast, goethite and, particularly, hematite are more dense and are often considered to have better processing characteristics (Schwertmann and Cornell, 2000). Indeed, in some treatment processes the ferrihydrite slurry is heated to actively induce hematite formation (Schwertmann and Cornell, 2000). Additionally, the increased thermodynamic stability of the crystalline phases suggests that they are typically less likely to dissolve and leach their associated contaminants. Finally, adsorbed contaminants can become incorporated in the crystalline phase during ferrihydrite transformation, decreasing contaminant mobility (Marshall et al., 2014a, 2014b, 2015; Bots et al., 2016). Overall, it is often desirable to optimise transformation conditions in order to ensure generation of crystalline iron (oxyhydr)oxide phases with better processing and waste disposal characteristics, since this will manifest in economic and environmental gains.

Ferrihydrite transformation has been extensively studied (Cornell and Schwertmann, 2003). It is generally accepted that goethite and hematite form from ferrihydrite by two mutually exclusive and competitive mechanisms (Schwertmann and Murad, 1983; Cornell and Schwertmann, 2003). The formation of goethite occurs via a dissolution and re-precipitation process and is therefore favoured at pH values where ferrihydrite is most soluble (< pH 5 and > pH 10) (Schwertmann and Murad, 1983). In contrast,
conversion to hematite occurs by a solid state dehydration and recrystallization mechanism and is favoured between pH 5 – 10 and at higher temperatures (Schwertmann and Murad, 1983). Recently, studies utilising detailed magnetic measurements have found conversion of ferrihydrite to hematite occurs via nucleation of an intermediate phase within the ferrihydrite aggregates followed by rapid conversion to hematite (Michel et al., 2010; Gutiérrez et al., 2016; Pariona et al., 2016; Soltis et al., 2016).

As well as pH and temperature, ferrihydrite transformation is also impacted by the presence of additional chemical species (Cornell, 1987a). Outside of the laboratory, ferrihydrite formation and ageing rarely occurs in a chemically pure environment so it is highly important to characterise the effect of commonly occurring species on the ageing process. The effects of accompanying species, such as complexing anions, metal cations and organic acids, are extremely varied (Cornell, 1987a). High charge density anions such as silicate ($\text{SiO}_4^{4-}$) (Cornell, 1987b; Francisco et al., 2016) and phosphate ($\text{PO}_4^{3-}$) (Galvez et al., 1999; Shaw et al., 2005) which exhibit strong inner sphere adsorption to ferrihydrite have been shown to significantly retard ferrihydrite transformation, even at concentrations as low as 1 mole % relative to iron. Sulfate ($\text{SO}_4^{2-}$), which also forms inner sphere adsorption complexes with ferrihydrite, has also been shown to retard transformation, although to a lesser extent than silicate and phosphate (Baltpurvins et al., 1996). The cause of the inhibition effect for silicate, phosphate and sulfate is thought to be anion adsorption to ferrihydrite stabilising it against both aggregation and dissolution which are required for hematite and goethite formation respectively. In contrast, some species such as oxalate have been shown to promote formation of hematite over goethite without any inhibition of the transformation rate (Fischer and Schwertmann, 1975). Furthermore, the effects of some relevant species, such as boric acid, which can be present in significant concentrations in industrial wastewater (Itakura et al., 2005; Parks and Edwards, 2005), have scarcely been investigated. Overall, changes in effluent composition have the potential to significantly impact upon the transformation products of ferrihydrite.

The Enhanced Actinide Removal Plant (EARP) (Hutson, 1996; Hildred et al., 2000) located at Sellafield, UK is an example of a critical wastewater treatment process which uses an iron oxyhydroxide co-precipitation and flocculation process to decontaminate radioactive effluents generated from the reprocessing of spent nuclear
fuel (Hutson, 1996; Hildred et al., 2000). The iron oxyhydroxide floc formed within EARP is subsequently dewatered by ultrafiltration over several weeks, encapsulated in a cement waste form and stored on site as an intermediate level waste, awaiting final disposal in a future geological disposal facility (Hutson, 1996). Generation of small solid waste volumes during this process by efficient dewatering and formation of a compact floc provide great economic advantage. Ageing of the floc during storage both before and after ultrafiltration may induce transformations which can positively affect this (Collier et al., 2006). EARP has successfully treated routine fuel reprocessing feeds for over 20 years. However, the effluent compositions that EARP receives will change in character as the Sellafield site transitions from its current routine reprocessing operations to post-operational clean-out and accelerated decommissioning activities over the next few years. This will include a change in concentrations of non-radioactive species, whose presence may affect the ageing of the iron oxyhydroxide floc to more crystalline and compact forms.

In this study we investigate ageing-induced transformation of ferrihydrite floc which was prepared using an EARP-relevant base-hydrolysis mechanism (Weatherill et al., 2016). We consider the effect of relevant accompanying species (phosphate, sulfate and boric acid) on the ageing process, including investigation of how their interactions with the floc impact on ageing processes. Additionally we consider the effect of small pH changes to the effluent treatment end point on the transformation products. The results have direct application to EARP but are also of general importance to understanding evolution of iron oxyhydroxide waste which is generated in a range of industries, as well as ferrihydrite ageing in the natural environment.

6.3. Experimental

6.3.1. Synthesis and ageing of ferrihydrite

Ferrihydrite was synthesized in an automated computer-controlled reactor (Applikon MiniBio) with temperature control (Peltier heater/ cooler) via NaOH-induced hydrolysis of ferric nitrate solutions (Weatherill et al., 2016). Stirred batch experiments were conducted at 35 ± 1 °C (representative of EARP), with the pH and temperature monitored throughout. Starting solutions consisted of 400 ml of Fe(NO$_3$)$_3$.9H$_2$O in 1 M HNO$_3$ (400 ppm Fe(III)) with the addition of one of the
following: Na$_2$SO$_4$ (1000 ppm / 10.4 mM sulfate), NaH$_2$PO$_4$ (100 ppm / 1.05 mM phosphate) or B(OH)$_3$ (150 ppm / 13.9 mM boron). These separate experimental systems are herein called the sulfate, phosphate and boric acid systems respectively. Experiments with no additional species were also run, called the pure Fe nitrate system. Additional experiments with lower phosphate concentrations (10 and 1 ppm) were also conducted. The concentrations of the added species were relevant to EARP feeds. Using peristaltic pumps, 7 M NaOH was initially added at a rate of 1.5 ml min$^{-1}$ until pH 2.3, then 0.3 ml min$^{-1}$ until pH 3 and finally, after pH 3, 0.2 M NaOH was added at 1.5 ml min$^{-1}$ until either pH 9 or 9.5 was reached. The precipitated slurries were left stirring with pH control for 10 min before transferring to polypropylene bottles and aged for up to 8 weeks in a 40°C oven. Throughout the ageing period aliquots of the precipitated slurries were taken for analysis.

6.3.2. X-ray diffraction (XRD) and Transmission electron microscopy (TEM)

At selected time points, solid products were isolated by centrifuging and excess salt removed by washing three times with deionized water before drying at 40°C overnight. Powder XRD patterns were obtained on a Bruker D8 Advance diffractometer. Samples for TEM analysis were prepared by re-suspending the dried solid in isopropanol and directly pipetting onto a holey carbon Cu TEM grid. TEM images were obtained on an FEI Tecnai TF30 FEG TEM operated at 300kV with images collected via Gatan Digital Micrograph software. Rietveld analysis of select XRD patterns was performed using Topas (Bruker AXS, 2009).

6.3.3. Solution analysis

Dissolved concentrations of phosphorus, [P$_{aq}$], sulfur, [S$_{aq}$], and boron, [B$_{aq}$] (< 0.22 µm polyethersulfone (PES) filter) in the added phosphate, sulfate and boric acid systems respectively were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

6.3.4. Attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR)

Infrared spectra (IR) of the solid phase isolated at different ageing times were obtained on a Perkin Elmer Frontier ATR-FTIR spectrometer. The slurry was centrifuged and spectra of the separated wet solid and the supernatant were taken at a resolution of 4 cm$^{-1}$ and as an accumulation of 64 scans. Final spectra were obtained
by subtracting the supernatant spectrum from the wet solid spectrum, followed by baseline correction and normalisation of the absorbance intensities to a maximum of one absorption unit.

6.3.5. Ammonium oxalate extraction

Ferrihydrite transformation kinetics were determined by measuring the proportion of ferrihydrite remaining in the experimental suspensions as a function of ageing time. An ammonium oxalate extraction method was used which selectively dissolves only the poorly crystalline Fe phases present (i.e. ferrihydrite) by exploiting the difference in dissolution rate between poorly crystalline and well-crystalline Fe phases (Schwertmann and Cornell, 2000). Briefly, 5 ml of 0.2 M ammonium oxalate was added to 5 ml of the sample slurry and pH was adjusted to pH 3 with 0.2 M oxalic acid. The sample was left to digest in the dark with mild agitation for two hours, before filtering (< 0.22 µm PES filter) and measuring for dissolved Fe(III) using the ferrozine method (Viollier et al., 2000). Results were expressed as a decimal fraction of ferrihydrite remaining, calculated using the following equation:

\[ \frac{\text{Oxalate extractable Fe at time } t}{\text{Oxalate extractable Fe at time } 0} = \text{Fraction of ferrihydrite} \]

Where time 0 refers to the freshly prepared ferrihydrite floc before any ageing. The extraction method was successful at dissolving all the Fe at time 0, confirming that only poorly crystalline phases were present initially (i.e. ferrihydrite).

6.3.6. Settleable solids

The volume of settleable solids was measured by transferring 50 ml of the sample slurry to an Imhof cone (i.e. a clear, cone-shaped graduated measuring vessel) and reading the volume of settled solids after 24 hours. From preliminary experiments, it was determined 24 hours was sufficient time for full settling to occur.

6.3.7. Sedimentation kinetics

3 ml of freshly dispersed sample slurry was transferred to a disposable UV-Vis cuvette and the absorption at 508 nm was measured every 10 s for 30 minutes on a Perkin Elmer UV-VIS spectrometer (Phenrat et al., 2007; Vikesland et al., 2016). Absorption of a blank sample was simultaneously measured and subtracted as the background.
6.4. Results

6.4.1. Solid phase analysis

XRD patterns collected on floc samples aged at 40 °C at a pH of 9 show that ferrihydrite transforms predominantly to hematite in the pure Fe nitrate, sulfate and boric acid systems, with strong hematite diffraction peaks seen after aging for 1 week (Figure 1A). In these systems, the background scatter in the XRD patterns became less noisy with increasing ageing time, and additional hematite peaks at ~ 70, 72 and 75 2θ were observed after four weeks ageing, indicating increased hematite formation with ageing time. This is confirmed by oxalate extraction results which show a decreasing fraction of ferrihydrite with ageing time and essentially no ferrihydrite after 8 weeks ageing (Figure 2, discussed below). Less intense Bragg peaks at ~ 22 and 36 2θ in aged samples from the sulfate system and, more weakly, the pure Fe nitrate system also indicate a small amount of goethite in the samples. Rietveld analysis of the XRD patterns suggests a small (~ 5 %) contribution of goethite in the pure Fe and sulfate systems, but there was no discernible goethite contribution in the boric acid time series.

In contrast, XRD and oxalate extraction results from the 100 ppm phosphate system indicate no ferrihydrite transformation, even after 8 weeks ageing (Figure 1B and 2), suggesting that phosphate acts to stabilise ferrihydrite and inhibit its transformation. The phosphate concentration dependence of this inhibition effect was investigated by additional ageing experiments using lower phosphate concentrations of 10 and 1 ppm. XRD results again show ferrihydrite was dominant throughout the 10 ppm phosphate time series, while transformation to hematite was observed within 1 week in the 1 ppm phosphate system (Figure 1B). However, the 8 week aged 10 ppm XRD pattern does show the start of peak formation (most prominently at ~ 21 2θ), suggesting the initial onset of crystallisation. This is further confirmed by selected area electron diffraction (SAED) patterns obtained on 8 week aged, 10 ppm phosphate TEM samples showing weak diffraction spots (Figure 4I).
Figure 1: XRD patterns collected on the solid phase as a function of ageing time in the A) pure Fe nitrate, sulfate and boric acid systems, and B) in the phosphate systems (100, 10 and 1 ppm). The initial pH of ageing in all systems was pH 9.

Oxalate extraction results show a decreasing fraction of ferrihydrite with ageing time in the pure Fe nitrate, sulfate, boric acid, and 1 ppm phosphate systems, which is consistent with XRD results confirming formation of crystalline phases in these systems. In all these systems virtually no ferrihydrite was remaining after the full 8 weeks ageing. These data were fit using the following first-order rate equation:

\[ [\text{Fh}]_t = [\text{Fh}]_0 e^{-kt} \]

Where \([\text{Fh}]_t\) is the fraction of ferrihydrite remaining after time \(t\), \([\text{Fh}]_0\) is the initial fraction of ferrihydrite, \(k\) is the rate constant, and \(t\) is time. In contrast, second- and zeroth-order rate equations failed to give acceptable fits. The first-order model should actually be considered pseudo first-order since only formation of the crystalline end product is considered, not the concentration changes in all the
relevant chemical phases (Shaw et al., 2005). The rate constants \(k\) obtained for the pure Fe nitrate, sulfate, boric acid and 1 ppm phosphate systems were similar and almost within error of one another (Table 1), indicating minimal effect of these added species on the kinetics of transformation.

![Figure 2: Change in fraction of ferrihydrite present as a function of ageing time, as determined by oxalate extraction experiments. Error bars represent the standard deviation based on triplicate measurements of the iron concentration via the ferrozine method. Note that some error bars are concealed by the symbols.](image)

**Table 1:** First-order reaction rate constants calculated by fitting oxalate extraction data with standard errors in parenthesis (calculated in the fitting routine in Origin Pro using the Levenberg-Marquardt Algorithm).

<table>
<thead>
<tr>
<th>Experimental system</th>
<th>([\text{Fh}]_0)</th>
<th>(k) (days(^{-1}))</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Fe nitrate</td>
<td>0.99 (0.14)</td>
<td>0.062 (0.04)</td>
<td>0.96</td>
</tr>
<tr>
<td>Sulfate</td>
<td>1.01 (0.19)</td>
<td>0.071 (0.03)</td>
<td>0.95</td>
</tr>
<tr>
<td>Boric acid</td>
<td>1.00 (0.07)</td>
<td>0.068 (0.02)</td>
<td>0.99</td>
</tr>
<tr>
<td>Phosphate (1 ppm)</td>
<td>1.02 (0.08)</td>
<td>0.073 (0.03)</td>
<td>0.99</td>
</tr>
</tbody>
</table>
To test the effect of different transformation pH conditions on the composition of the conversion products, ageing experiments were also conducted at an effluent treatment endpoint pH of 9.5. XRD indicates that hematite is again the dominant conversion product in all systems except phosphate (100 ppm), where transformation is again entirely inhibited during the 8 weeks ageing period (Figure 3). Goethite peaks are significantly more intense in the pure Fe nitrate and sulfate systems when aged at pH 9.5 compared to pH 9. Indeed, Rietveld analysis indicated 28% and 39% goethite in the 8 weeks aged pure Fe nitrate and sulfate systems respectively (Figure S1), while no goethite was again detected in the boric acid system.

Figure 3: X-ray diffraction (XRD) patterns collected as a function of ageing time for samples aged at an initial pH of 9.5.

Changes in the floc with ageing time were also monitored using TEM (Figure 4). In all systems, the fresh floc was composed of nanoparticulate ferrihydrite (~ 3 nm
diameter) aggregated into large structures (Weatherill et al., 2017). A gradual conversion of the nanoparticulate ferrihydrite into larger crystalline particles was observed with ageing time in the pure Fe nitrate, sulfate and boric acid systems, in agreement with XRD and oxalate extraction results. For example, Figure 4D-G shows TEM images and SAED patterns collected on floc from the boric acid system at each ageing time. In the 1 week aged sample, aggregates of ferrihydrite were observed along with numerous darker particles within the aggregate interior of up to ~120 nm diameter which are presumably hematite particles, with the SAED pattern showing diffraction spots confirming crystallinity. In the 4 weeks sample, clear and distinct hematite particles surrounded by unconverted ferrihydrite were observed, while in the 8 weeks sample only crystalline hematite particles were observed, confirming full transformation of the ferrihydrite after 8 weeks, in agreement with the oxalate extraction data (Figure 2). For the phosphate systems, only nanoparticulate ferrihydrite was observed throughout the 8 weeks ageing period in the 100 and 10 ppm systems, while full transformation to hematite was observed after 8 weeks in the 1 ppm system, again in agreement with oxalate extraction results.

In all the experimental systems, the predominant crystallites were high sphericity hematite particles with average diameters of ~120 nm and a relatively monodisperse size distribution. Hematite particles observed after ageing for 1 week were the same size (~120 nm) as those observed after 8 weeks (Figure S2). This indicates that during transformation beyond 1 week, the remaining ferrihydrite transforms to form new hematite particles, rather than contributing to growth of existing hematite particles. Hematite particles in the 1 ppm phosphate system (Figure 4J) were slightly more elongated compared to the other systems. Interestingly, high magnification TEM images appear to show sub-structure in the hematite particles, indicating they are formed from smaller particulates of various sizes (Figure S2). In addition to hematite, a smaller population of goethite particles, which were distinguished by their acicular morphology, were observed in the pure Fe nitrate and sulfate systems. Relatively more goethite was observed in the samples aged at initial pH pH 9.5 compared to pH 9 in the pure Fe nitrate system (Figure 4B & C), consistent with XRD data. Most of the acicular goethite particles exhibited epitaxial growth on the hematite crystals, which is possible due to these two compounds possessing similar interplanar spacings (Atkinson et al., 1968; Barrón et al., 1997). A very small amount of goethite was also
observed in the 8 week aged boric acid sample (Figure S2), but its presence was minimal compared to the sulfate and pure Fe nitrate systems.

**Figure 4:** Transmission electron microscopy (TEM) images of the iron oxyhydroxide floc isolated at different ageing times and from different systems. A) Pure Fe nitrate system, fresh, pH 9, with inset showing higher magnification image where the individual ~ 3 nm diameter ferrihydrite nanoparticles can be observed. B) Pure Fe nitrate system, 8 weeks, pH 9. C) Pure Fe nitrate system, 8 weeks, pH 9.5. D – G) Boric acid system, fresh to 8 weeks, pH 9. C) Pure Fe nitrate system, 8 weeks, pH 9.5. D – G) Boric acid system, fresh to 8 weeks, pH 9, with insets showing selected area electron diffraction (SAED) patterns collected on the shown areas. H – J) Phosphate systems (100, 10 and 1 ppm), 8 weeks, pH 9, with insets showing SAED patterns collected on the shown areas.
6.4.2. Solution analysis

Figure S3 shows aqueous concentrations of phosphorus \([P_{(aq)}]\), sulphur \([S_{(aq)}]\), and boron \([B_{(aq)}]\) in the initial effluent simulants before reaction (pH 0.1) and after reaction for the pH 9 experiments as a function of ageing time. In the phosphate system (100 ppm), practically all the \([P_{(aq)}]\) was removed from solution after reaction. Our previous work showed this was predominantly due to phosphate adsorption to the ferrihydrite floc surface (Weatherill et al., 2017). With subsequent ageing, ~10% of the \([P_{(aq)}]\) was re-released into solution (Figure S3), indicating a small amount of phosphate desorption. In the sulfate system, almost all the \([S_{(aq)}]\) was present in solution after the reaction and subsequent ageing, indicating minimal interaction of sulfate with the solid phase at pH 9. In the boric acid system, ~15% of the \([B_{(aq)}]\) was removed from solution after the reaction, primarily due to boric acid adsorption to the ferrihydrite floc (IR results below and Weatherill et al. (2016)). \([B_{(aq)}]\) remained suppressed throughout the ageing period indicating continued boric acid adsorption.

Figure S4 shows the pH evolution with time in each system. For the experiments with an initial pH of 9, the pH tended to decrease with ageing time in all except the boric acid system which instead had a relatively stable pH, only exhibiting a modest increase in pH over the 8 weeks ageing. The pKa of boric acid is 9.24 and therefore this species acts as an effective buffer at around pH 9, explaining the more stable pH. For the other systems which exhibited a decrease in pH, this does not appear to be a direct result of the ferrihydrite transformation since pH decrease was also observed in the 100 ppm and 10 ppm phosphate system where no transformation occurred. For the experiments aged at an initial pH of 9.5, the pH exhibited a small increase after 1 week ageing followed by a decrease back to almost pH 9.5 with further ageing (Figure S4).

6.4.3. Ion-solid phase interactions

Figure 5 shows infrared spectra collected on the solid phase as a function of ageing time in each system. Spectra of fresh, 1, 4 and 8 weeks aged solids are shown for samples aged at pH 9, while only the end-point 8 week spectra are shown for the samples aged at pH 9.5. A peak centered at 1620 – 1645 cm\(^{-1}\) was present in all systems attributable to sorbed water (Russell, 1979). The IR spectra collected on fresh solids in the pure Fe nitrate and sulfate systems exhibit absorption features consistent with
adsorbed carbonate (CO$_3^{2-}$) and/or bicarbonate (HCO$_3^-$) (Su and Suarez, 1995), i.e., sharp peaks centred at 1475 and 1352 cm$^{-1}$, a broad peak centred at $\sim$ 915 cm$^{-1}$, and a small shoulder peak at 1075 cm$^{-1}$. These features became less prominent with ageing time, indicating progressive desorption of (bi)carbonate, while absorption peaks centered at $\sim$ 1390 and 1340 cm$^{-1}$, attributable to nitrate (Harrison and Berkheiser, 1982), became increasingly prominent. This trend of (bi)carbonate desorption and nitrate adsorption with ageing time was also evident in the boric acid system, although spectra were more complex due to some overlap with boric acid absorption peaks. In contrast, in the 100 ppm phosphate system, carbonate and nitrate absorption was suppressed in both the fresh and aged samples (Figure 5). In the pH 9.5 spectra, carbonate and nitrate adsorption peaks were not prominent in any of the systems, which was likely due to increased negative surface charge on the solid phase at this higher pH causing increased electrostatic repulsion between the solid and these anions (Harrison and Berkheiser, 1982).

Spectra from the sulfate system exhibited no evidence for sulfate sorption, consistent with the solution data (Figure S3), the expected adsorption edge of sulfate on ferrihydrite (Fukushi et al., 2013), and our previous publication where we showed that sulfate adsorbs to the solid ferrihydrite phase only below pH 7.5.

In the 100 ppm phosphate system, IR absorption peaks between 1080 and 840 cm$^{-1}$ were a clear indication of phosphate adsorption to the solid phase, consistent with [P(aq)] removal observed in the solution data (Figure S3). The structure of the absorption peaks indicate multiple phosphate inner sphere sorption complexes, likely including a mix of bidentate and monodentate surface complexes (Arai and Sparks, 2001; Antelo et al., 2010). These IR spectra exhibited minimal changes during the ageing period and between the pH 9 and pH 9.5 samples, suggesting there were no significant changes in the phosphate interactions. Figure S5 shows infrared spectra collected on the lower concentration 10 and 1 ppm phosphate systems. For 10 ppm phosphate, both adsorbed phosphate and carbonate were observed throughout the ageing period, indicating that carbonate adsorption was not suppressed at this lower phosphate concentration unlike in the 100 ppm phosphate system. Interestingly, the carbonate did not desorb during the 8 week ageing period, unlike in the other systems. In the 1 ppm phosphate system, phosphate adsorption was not evidenced, possibly due to its concentration being below detection limit. Instead, the 1 ppm
phosphate spectra were very similar to the pure Fe nitrate and sulfate system spectra (Figure 5), with carbonate adsorption occurring initially followed by desorption and then adsorption of nitrate with ageing time.

In the boric acid system, the fresh spectra showed absorption peaks at ~ 1390, 1330 and 1250 cm\(^{-1}\) (B-O \(v_1\) vibrations) and a shoulder peak at ~ 985 cm\(^{-1}\) (B-O \(v_1\) vibration), indicative of a mix of inner and outer sphere boric acid adsorption (Su and Suarez, 1995; Peak et al., 2003). Additionally, a shoulder peak at 1465 cm\(^{-1}\) indicated adsorbed carbonate, and therefore carbonate will also be contributing to the absorption bands in the 1390 – 1330 region since carbonate should also absorb at ~ 1350 cm\(^{-1}\). It is possible borate (B(OH)\(_4\)) may additionally be adsorbed, but the expected borate absorption region at ~ 935 cm\(^{-1}\) (Peak et al., 2003) was obscured by the broad adsorption centered at 915 cm\(^{-1}\) which is attributable to carbonate. Boric acid adsorption peaks (including the peak at 1250 cm\(^{-1}\) which is solely attributable to boric acid) were still present after 8 weeks ageing in both the pH 9 and 9.5 samples, indicating continued association of boric acid with the solid phase after crystallization, in line with the solution data (collected for the pH 9 experiment only) (Figure S3). Meanwhile, the peak at 1465 cm\(^{-1}\) diminishes after 4 weeks ageing, indicating desorption of carbonate.

In the pure Fe nitrate and sulfate systems, sharp absorption peaks at 890 and 800/795 cm\(^{-1}\) which are characteristic of goethite (Cambier, 1986) were present in the aged samples spectra, confirming that measurable goethite forms in these systems alongside hematite. These peaks were significantly stronger for the pH 9.5 sample than the pH 9 sample, consistent with more goethite formation in these systems at the higher pH (XRD, Figure 3). Very weak goethite peaks were also observed in the boric acid system, indicating a small but detectable amount of goethite. We note that IR is significantly more sensitive to the presence of small amounts of goethite than XRD (Cornell and Schwertmann, 2003). Absorption peaks indicative of hematite are expected at lower wavenumbers (<650 cm\(^{-1}\)) than those measured here (Žic et al., 2007).
Figure 5: ATR-FTIR spectra collected on the solid phase isolated at different ageing times in the A) pure Fe nitrate system, B) sulfate system, C) phosphate 100 ppm system, and D) boric acid system. For the samples aged at pH 9, the fresh, 1 week, 4 weeks and 8 weeks aged spectra are shown, while for the samples aged at pH 9.5, only the end point 8 weeks aged spectra is shown.
6.4.4. Floc volume and sedimentation kinetics

Sedimentation kinetics of the solid phase in fresh and 8 week aged samples at pH 9 were monitored by measuring the change in light absorbance as sedimentation was allowed to occur. The resulting sedimentation curves (Figure 6) were highly reproducible, based on three repeat runs for each system. For the fresh samples, the sedimentation curves were subdivided into three major regions (Figure S6, Supporting Information). In region (i) absorption was relatively constant or, in the phosphate (100 ppm) and sulfate systems, was increasing. This presumably represents an induction period in which the freshly dispersed aggregates lost their kinetic energy and re-flocculated. In region (ii), a large decrease in absorption was observed indicating rapid sedimentation. Lastly in region (iii) a more gradual decrease in absorption was observed, representing slower sedimentation of the smaller/less dense aggregates. Longer induction times were observed in region (i) in the phosphate system and, to a lesser extent, sulfate system, which was likely due to an electrostatic repulsion effect of these negative anions with the iron oxyhydroxide aggregates, which are expected to be negatively charged at pH 9 according to the expected PZC of ferrihydrite and hematite (Cornell and Schwertmann, 2003). This effect is more pronounced for the phosphate system, which can be attributed to the higher negative charge on phosphate than sulfate and also the strong interactions between phosphate and the Fe phase at pH 9 (IR, Figure 5).

Significant changes were observed between the fresh and 8 week sedimentation curves in the pure Fe nitrate, sulfate, and boric acid systems, reflective of the ferrihydrite transformation processes observed in these systems. The 8 week curves for these systems exhibited only two regions: (i) an initial induction region where absorption was effectively constant, attributable to particles losing their kinetic energy before sedimentation, and (ii) a region characterised by a gradual decrease in absorption due to particle sedimentation. Similar to the fresh samples, the induction period was slightly longer in the sulfate system than the pure Fe nitrate and boric acid systems. Sedimentation was significantly slower in these aged samples, even though hematite is more dense than ferrihydrite (5.3 vs. 4.0 g cm\(^{-3}\) respectively (Cornell and Schwertmann, 2003)). This likely reflects the reduced tendency of hematite to aggregate into an extensive floc compared to ferrihydrite, as evidenced in TEM images (Figure 5) and also from visual observation during sedimentation (Figure S7). In the phosphate system, changes between fresh and 8 week aged sample were less
significant, in agreement with the lack of change in the mineralogy of these samples with time. The initial induction period was slightly shorter in the 8 week sample however, perhaps reflecting a reduced electrostatic repulsive effect of the phosphate due to desorption of ~10% of the phosphate with ageing (Figure S3).

**Figure 6:** Sedimentation curves obtained by measuring the change in absorbance at 508 nm of A) fresh samples and B) 8 weeks aged samples. Data are plotted as a ratio of the absorbance (A) over the initial absorbance at time 0 (A0).

In the pure Fe nitrate, sulfate and boric acid systems, an order of magnitude decrease in the settleable solids volume was observed over the 8 weeks ageing period (Figure 7). This decrease closely followed the decrease in percentage ferrihydrite remaining in these systems (Figure 2). In contrast, no decrease in settleable solids volume was observed in the 100 ppm phosphate system, corresponding to the inhibition of ferrihydrite transformation in this system. Interestingly, the initial volumes of ferrihydrite flocs in the sulfate and phosphate flocs were higher than those in the pure Fe nitrate and boric acid systems, which may be due to electrostatic repulsions in the former systems resulting in a less dense floc. Nevertheless, upon ageing, the floc volume in the sulfate system decreased to a similar value to that in the pure Fe nitrate and boric acid systems (Figure 7), indicating that the impact of sulfate on
secondary waste volumes in this system should be minimal as long as transformation is allowed to occur.

![Figure 7: Changes in the volume of settleable solids with ageing time, measured for 50 ml of the slurry.](image)

### 6.5. Discussion

Complete transformation of ferrihydrite to crystalline phases occurred within 8 weeks (56 days) in all experimental systems for ageing at pH 9 and 40 °C, except for the 100 and 10 ppm phosphate systems. Baltpurvins et al. (1996) previously reported that full ferrihydrite transformation occurred within 246 days when aged at pH 9 and 20 °C in a nitrate solution. The faster transformation time in the present study can be attributed to the higher temperature utilised (40 °C vs 20 °C) which is representative of plant conditions (Das et al., 2011). Additionally, the ferrihydrite slurries in the present study had particularly high ionic strengths of ~ 1.5 M (relevant to effluent treatment), with Brinza et al. (2015) reporting that ferrihydrite transformation to hematite was 30% faster at higher ionic strength (0.7 M compared to 0.1 M) in their experiments performed at pH 8.

Hematite was the dominant transformation product in all systems, in line with previous studies which have shown hematite formation is favoured at pH close to the point of zero charge of ferrihydrite (~ pH 7 – 10), i.e. when ferrihydrite is most
insoluble (Schwertmann and Murad, 1983; Baltpurvins et al., 1996). However, ageing at the slightly higher pH of 9.5 in this study was enough to induce considerable goethite formation in the pure Fe nitrate (~ 28 % goethite) and sulfate (~ 43 % goethite) systems, with a smaller amount of goethite (~ 5 %) also present in these systems when aged at pH 9. This demonstrates the high pH sensitivity of the transformation products and highlights the need for strict pH control of floc slurries in order for floc transformations to be predictable. In contrast, goethite formation was suppressed in the boric acid system, which may be due to the presence of adsorbed boric acid (IR results, Figure 5). The presence of adsorbed ions including silicate (Francisco et al., 2016), oxalate (Fischer and Schwertmann, 1975), and phosphate (Galvez et al., 1999) has previously been reported to lead to an increase in the proportion of hematite relative to goethite (Cornell, 1987a), although this effect has not been observed for boric acid. The preferential formation of hematite over goethite is considered to be due to a dual effect of the adsorbed species: the adsorbed species can firstly act as a template for hematite formation (Cornell, 1987a) and can secondly inhibit Fe dissolution (Biber et al., 1994) and therefore the supply of dissolved ferric species necessary for goethite nucleation. It is specifically ions which adsorb as binuclear complexes, and therefore bind two Fe atoms, which inhibit dissolution of the solid Fe phase because the simultaneous dissolution of two Fe-centres is energetically unfavourable (Biber et al., 1994). Likewise, it is binuclear adsorption complexes which have the potential to act as templates for hematite formation, by inducing ordering and therefore hematite nucleation within ferrihydrite aggregates (Fischer and Schwertmann, 1975; Cornell, 1987a). Therefore, while the exact adsorption mechanism of boric acid and its anion borate B(OH)₄⁻ on ferrihydrite is currently unclear (Su and Suarez, 1995; Peak et al., 2003), the hematite promotion/goethite suppression effect observed in this study would indicate the presence of binuclear boric acid complexes. Indeed, Peak et al. (2003) reported that binuclear adsorption complexes of boric acid and borate were the most likely mechanisms of boric acid adsorption to ferrihydrite, as based on their infrared spectroscopy study.

In the 100 and 10 ppm phosphate systems (P/Fe ratios 15% and 1.5% respectively), strong adsorption of phosphate to the ferrihydrite floc was observed throughout the 8 weeks ageing period and ferrihydrite transformation was completely suppressed. Galvez et al. (1999) similarly reported that at P/Fe as low as 1.5% ferrihydrite
transformation was suppressed when ageing at pH 9 and 50 °C, while Paige et al. (1997) reported that 1% P/Fe retarded ferrihydrite transformation by a factor of 20 when aged at pH 12 and 60 °C. Phosphate likely has a twofold effect on inhibiting ferrihydrite transformation. Firstly, phosphate adsorbs predominantly as a bidentate complex and therefore inhibits goethite nucleation as discussed above. Secondly, adsorbed phosphate can cause electrostatic repulsion between ferrihydrite particles, thereby inhibiting their close contact and transformation to hematite (Cornell, 1987a; Galvez et al., 1999).

FTIR results (Figure 5 & S5) showed that carbonate was adsorbed to the floc in all the experimental systems except the 100 ppm added phosphate system in which carbonate adsorption was suppressed. Although carbonate was not directly added to the experimental solutions, ingress of atmospheric carbon dioxide to the solutions is expected under the open atmospheric conditions, and was not controlled in order to maintain relevance to the EARP process. While carbonate may influence the adsorption behaviour of individual anions (Wijnja and Schulthess, 2002), FTIR results indicated carbonate desorbed upon ageing and therefore the presence of carbonate probably had minimal impact on the ageing process. Additionally, due to using a consistent methodology, carbonate was expected to be present in similar concentrations in each system and therefore the differences observed between systems are unlikely to be a result of varying carbonate concentrations.

The detailed mechanisms by which ferrihydrite crystallises to hematite and goethite are not fully resolved. For hematite, there is evidence that the transformation proceeds via an intermediate phase which forms within the ferrihydrite aggregates via dehydration before rapid transformation and growth to hematite (Combes et al., 1990; Michel et al., 2010; Gutiérrez et al., 2016). Recent evidence suggests hematite growth is not a monomer-by-monomer process but is a particle-mediated process whereby small hematite particles nucleate within the ferrihydrite aggregates followed by crystallisation into larger hematite particles, likely by orientated attachment. Interestingly, in the present study, close-up TEM images reveal microstructure within the ~ 120 nm hematite particles (Figure S2), suggesting they are formed from aggregates of smaller particles and providing further evidence for a particle-mediated formation process.
Hematite particle morphology is sensitive to the conditions of formation (Wang et al., 2008; Faivre, 2016). For example, Wang et al. (2008) were able to prepare a range of hematite morphologies, including with cubic, spherical, sheetlike and hexagonal structures, by only varying the nucleation rate, Fe$^{3+}$ concentration, and ageing time. In the present study, hematite morphologies were largely consistent between the systems, with high sphericity particles of ~ 120 nm diameter forming in each system, indicating minimal effect of the added species. However, the hematite particles in the 1 ppm phosphate system tended to be slightly more elongated, which is consistent with previous studies which report phosphate promoting ellipsoid morphology (Morales et al., 1992; Reeves and Mann, 1997; Galvez et al., 1999).

The effect of ferrihydrite crystallisation on the settleable solids volume and settling kinetics were also similar in each system. Ferrihydrite crystallisation resulted in an order of magnitude decrease in settleable solids volume, highlighting the benefit of ferrihydrite floc crystallisation in regards to secondary waste minimisation. However, the sedimentation kinetics were slower in the crystallised floc (Figure 6), which may have an impact on treatment schemes which use a sedimentation step to isolate the solid phase from solution. Interestingly, operational experience at EARP has found that the crystalline phases generally filter better, with higher dewatering factors achieved in shorter amounts of time. A further potential benefit of ferrihydrite crystallisation is that the contaminants associated with the ferrihydrite floc can become incorporated into the crystalline phase during crystallisation, thereby reducing contaminant lability and the likelihood of leaching to the environment upon final disposal of the wasteform (Marshall et al., 2014a, 2014b, 2015; Bots et al., 2016). Clearly, further work is required to determine the extent of contaminant incorporation in EARP-relevant flocs.

Notably, no decrease in the volume of settleable solids was observed in phosphate systems where transformation was completely inhibited. Therefore, to ensure secondary waste minimisation and other benefits associated with crystallisation, it may be beneficial to limit phosphate in acidic effluent feeds before treatment. This could potentially be achieved by chemical precipitation of phosphate, which would require dosing with cationic species that readily form an insoluble phase with phosphate at low pH before iron oxyhydroxide precipitation. In some industries, calcium is used to remove phosphate from wastewater by the precipitation of
hydroxylapatite \( \text{(Ca}_{10} \text{(PO}_4)_6 \text{(OH)}_2) \) (Yeoman et al., 1988), but this only occurs at high pH (> pH 8) and is therefore not suitable for phosphate removal in iron oxyhydroxide floculation processes. Using higher charge cations which have low solubility even at low pH could be an option. For example, zirconium (Zr\(^{4+}\)) has low solubility at low pH and can precipitate as both zirconium oxides or zirconium phosphates; precipitation of zirconium phosphate will result in direct removal of phosphate from solution, while precipitation of zirconium oxides can remove phosphate via surface adsorption of phosphate (Su et al., 2013).

### 6.6. Conclusions

Ferrihydrite floc prepared in a process designed to mimic effluent treatment processes was aged in the presence of different added species and its transformation was monitored. When aged at pH 9 and 40 °C, ferrihydrite transformed predominantly to high sphericity hematite particles of ~ 120 nm diameter, with full ferrihydrite transformation occurring within 8 weeks ageing. This was observed for a pure Fe nitrate system and also systems with added sulfate or boric acid. This transformation to hematite was accompanied by an order of magnitude decrease in the settleable solids volume, representing a significant benefit for minimisation of waste volumes. In contrast, ferrihydrite transformation was completely inhibited within the 8 weeks ageing period in systems with added phosphate (100 and 10 ppm), with phosphate strongly adsorbed to the ferrihydrite floc throughout the ageing period and no decrease in the volume of settleable solids observed. However, decreasing the phosphate concentration to 1 ppm was sufficient to allow full transformation to hematite to occur within 8 weeks. Ageing the floc at the slightly higher pH of 9.5 induced significant formation of acicular goethite in the pure Fe nitrate and sulfate systems (28% and 39% goethite respectively), while goethite formation was suppressed in the boric acid system with only hematite once again formed. Overall, these data are useful for helping predict the transformation behaviour of ferrihydrite floc relevant to effluent treatment processes and the subsequent effect this will have on waste volumes and floc processing.
Supporting Information for Chapter 6:
Ferrihydrite Transformation in the Presence of Sulfate, Phosphate and Boric acid: Relevance to Radioactive Effluent Treatment

Additional figures

**Figure S1**: Rietveld refinement fits of XRD patterns to determine relative proportions of hematite and goethite. A) Pure Fe nitrate system, pH 9.5, 8 weeks aged. B) Sulfate system, pH 9.5, 8 weeks aged
**Figure S2:** Transmission electron microscopy (TEM) images of the iron oxyhydroxide floc isolated at different ageing times and from different systems. A – C) Pure Fe nitrate system, 1 – 8 weeks, pH 9. Note that the hematite particle sizes are approximately the same throughout the ageing period. D) Boric acid system, 4 weeks, pH 9. Inset shows selected area diffraction (SAED) pattern collected on the shown area. E) Boric acid
system, 8 weeks, pH 9. F) Sulfate system, 1 week, pH 9. Inset shows SAED pattern collected on the shown area. In images A), C), D) and E), the hematite particles appear to have particulate character.

Figure S3: Change in A) phosphorus concentration in the 100 ppm phosphate system, B) sulfur in the sulfate system, and C) boron in the boric acid system. Concentrations of all species were determined by ICP-AES. Concentrations of the species at pH 9 (after the ferrihydrite formation reaction) were adjusted for dilution from addition of the NaOH during the reaction.
Figure S4: Change in pH of the floc slurry during ageing. A) Pure Fe nitrate, sulfate and boric acid experiments with an initial pH of 9. B) Phosphate experiments with an initial pH of 9. C) Pure Fe nitrate, sulfate, boric acid, and phosphate (100 ppm) experiments with an initial pH of 9.5.
**Figure S5**: ATR-FTIR spectra collected on the solid phase isolated at different ageing times in the A) 10 ppm phosphate system and B) 1 ppm phosphate system.

**Figure S6**: Reproduction of sedimentation curves from the pure ferric nitrate system (Figure 6 from the main paper) with the different regions labelled (details in the main paper text).
Figure S7: Photos of floc during sedimentation in the A) pure Fe nitrate system, B) sulfate system, C) phosphate (100 ppm) system, and D) boric acid (150 ppm) system. The photos were taken in the same cuvettes used to collect the sedimentation curves data (Figure 6, main paper).
CHAPTER 7
Conclusions and Future Work Directions

7.1. Conclusions

The aim of this project was to characterise the iron oxyhydroxide floc formation processes relevant to the Enhanced Actinide Removal Plant (EARP) at Sellafield, with a view to provide scientific underpinning of this vital radionuclide removal treatment process. Additionally, ageing-induced transformations of the floc were investigated, since this has important implications for the processing of the floc and its behaviour as a wasteform.

Although iron oxyhydroxide formation and ageing have been widely investigated, these processes have proven to be highly complex and variable. Therefore, investigation of these processes under conditions specific to EARP is highly important in order to gain fundamental understanding of EARP and enable enhanced control over the process. Additionally, the fundamental iron oxyhydroxide formation process remains unresolved, particularly the role of intermediate species, and the work in this thesis contributes to this general area.

Here, the EARP process was mimicked in the laboratory in a highly controlled environment using a batch reactor chemostat system and EARP effluent simulants. Formation of the iron oxyhydroxide floc was characterised throughout the neutralisation reaction at both the nanoscale and macroscale via state-of-the-art techniques. Floc formation in a pure ferric nitrate system was investigated (Chapter 4), as well as in systems with added sulfate, phosphate and boric acid (inorganic chemical species relevant to EARP operation) (Chapter 5). Produced flocs were subsequently aged in different chemical environments in order to explore floc transformation pathways (Chapter 6).

Chapter 4 investigated iron oxyhydroxide formation under EARP-like conditions in a “pure” ferric nitrate system, i.e. where the EARP effluent simulant was composed only of ferric nitrate dissolved in nitric acid. Using in situ time-resolved SAXS in combination with ex situ TEM, XRD and solution analysis, it was shown that Fe₉ Keggin clusters (radius ~ 0.45 nm) initially form in solution at pH 0.12–1.5, and
were persistent for at least 18 days if left at low (undersaturated) pH conditions (pH 0.5 and 1.5). The Fe\textsubscript{13} clusters began to aggregate as the pH increased above 1, initially forming highly linear mass fractal structures. Above ~ pH 2, densification of the aggregates occurred in conjunction with precipitation of low molecular weight Fe(III) species to form mass fractal aggregates of ~ 3 nm ferrihydrite nanoparticles in which the Fe\textsubscript{13} Keggin motif was preserved. SAXS analysis suggested the ferrihydrite nanoparticles consist of an Fe\textsubscript{13} core surrounded by an Fe-depleted, hydrous shell (~ 1 nm thick) and supporting the surface depleted model of ferrihydrite (Hiemstra, 2013; Hiemstra and Zhao, 2016; Wang \textit{et al.}, 2016b). In our experiments, we propose that the Fe\textsubscript{13} clusters form in localised areas where the strong base was added (dropwise) to the acidified ferric nitrate solution. This has also been observed in formation of Al\textsubscript{13} clusters in aqueous aluminium systems (Bertsch, 1986; Kloprogge \textit{et al.}, 1992a).

Overall, this research presents the first direct evidence for the role of Fe\textsubscript{13} clusters in the pathway of ferrihydrite formation during base hydrolysis, showing clear structural continuity from isolated Fe\textsubscript{13} Keggins to the ferrihydrite particle structure. Additionally, this research shows that the low pH, undersaturated regime in the EARP process (i.e. before mass precipitation of iron, < pH 2.5) is not solely dominated by Fe-monomers, with unequivocal evidence for cluster formation and aggregation occurring, with important implications for the EARP process.

Chapter 5 extended the experiments of Chapter 4 to systems with additional species added to the effluent simulants. Specifically, the effects of added sulfate, phosphate and boric acid were investigated, since these can all be present in EARP effluent in significant and variable concentrations. In each of these additional systems, it was found that the floc was again composed of mass fractal aggregates of ~ 3 nm ferrihydrite nanoparticles which also form via an Fe\textsubscript{13} Keggin cluster pathway. The pH at which initial aggregation of the Fe\textsubscript{13} clusters occurred varied between the systems, indicating different interactions of the added species with the clusters. Aggregation was promoted in the phosphate system, with aggregation occurring > pH 0.5, compared to > pH 1 in the pure Fe nitrate system, with this effect likely due to phosphate bridging between clusters and/or a charge compensation effect. In contrast, aggregation was delayed in the sulfate and boric acid systems, indicating their ability to stabilise Fe\textsubscript{13} clusters, possibly due to their ability to form hydrogen bonds with Fe(III) at low pH. The resulting ferrihydrite nanoparticles were again shown to have a core-shell structure whereby the shell was more disordered and
hydrous compared to the Fe\textsubscript{13} core, with pair distribution function (PDF) analysis showing that the ordered range of the nanoparticles was $\sim 1$ nm; consistent with an ordered Fe\textsubscript{13} Keggin core and disordered shell. Infrared spectroscopy provided further insight into the mechanisms of phosphate, sulfate and boric acid interactions during the hydrolysis process, with both inner and outer sphere adsorption observed for different species. Overall, these results confirm the ability of Fe\textsubscript{13} Keggin clusters to act as a pre-nucleation intermediate to ferrihydrite formation, even in the presence of strong complexing species such as phosphate and sulfate.

In Chapter 6, ageing of the ferrihydrite floc in the presence of the different added species was investigated. When aged at pH 9 and 40 °C, the ferrihydrite floc transformed predominantly to highly spherical hematite particles of $\sim 120$ nm diameter, with full ferrihydrite transformation occurring within 8 weeks ageing. This was observed for a pure Fe nitrate system and also systems with added sulfate or boric acid, and was accompanied by an order of magnitude decrease in the settleable solids volume, representing a significant benefit for minimisation of waste volumes. Notably, transformation to hematite also resulted in slower settling kinetics of the floc, which was reflective of the reduced tendency of hematite to aggregate into large flocs compared to ferrihydrite. In contrast, in systems with added phosphate (100 and 10 ppm phosphate) ferrihydrite transformation was completely inhibited within the 8 weeks ageing period, with phosphate strongly retained on the floc throughout the ageing period and no decrease in the volume of settleable solids observed. However, decreasing the initial phosphate concentration to 1 ppm was sufficient to allow full transformation to hematite to occur within 8 weeks. Ageing the floc at the slightly higher pH of 9.5 induced significant formation of acicular goethite in the pure Fe nitrate and sulfate systems (28% and 39% goethite respectively), while goethite formation was suppressed in the boric acid system with essentially only hematite once again formed. Overall, these data are useful for helping predict the transformation behaviour of ferrihydrite floc relevant to effluent treatment processes and the subsequent effect this will have on waste volumes and floc processing.
7.2. Future work directions

i) Iron oxyhydroxide formation and ageing using more complex effluent simulants.

Due to the complexity of iron oxyhydroxide formation, experiments utilising simplified EARP effluent simulants in this project were essential in characterising the fundamental floc formation process in EARP and resolving the impact of adding particular species. Understanding these baseline systems provides strong scientific underpinning to the EARP system and a firm foundation from which to build up complexity in the simulant. Additional experiments using more complex EARP effluent simulants which contain multiple added components would be beneficial for building on the findings of this project and gaining further underpinning understanding of the EARP process.

ii) Effects of POCO decontamination agents.

After ~ 2020 when fuel reprocessing ends at Sellafield, post operational clean out (POCO) of the Magnox and THORP reprocessing plants and of associated downstream plants will occur. This will involve the use of decontamination agents including EDTA, citrate and oxalate, which will then be present in EARP effluent feeds. These species are likely to influence the EARP process. EDTA is a well-known metal complexing agent and therefore may affect iron precipitation and decontamination factors (Kari and Giger, 1996). Citrate has previously been shown to impair polymerisation of Fe(O, OH)$_6$ octahedra and decrease ferrihydrite particle sizes (Mikutta et al., 2010). Additionally, both citrate and oxalate are reported to have significant effects on ferrihydrite transformation: citrate slows transformation and promotes hematite formation over goethite (Cornell and Schwertmann, 1979), while oxalate accelerates hematite nucleation from ferrihydrite (Fischer and Schwertmann, 1975). Given the significant impacts these species may have on the EARP process, it is essential to build on the work in this thesis to investigate the effects of these species on the iron oxyhydroxide floc formation process and floc ageing.

iii) Effect of initial pH on floc formation processes.

The Fe$_{13}$ cluster pathway by which the ferrihydrite floc forms, as characterised in Chapters 4 & 5, is likely induced by localised formation of the Fe$_{13}$ clusters at the points of inhomogeneous pH where the strong NaOH base is added to the acidified ferric nitrate effluent (Chapter 4), analogous to Al$_{13}$ formation (Bertsch, 1986;
Kloprogge et al., 1992a). The clusters form rapidly after addition of the NaOH at pH as low as 0.15 and are stabilised at low pH, with clusters still detected in pH 0.5 and 1.5 solution after 18 days (Chapter 4 & 5). The initial pH of EARP effluent is variable and can sometimes be closer to pH 1–2; it is unclear whether the Fe$_3$ cluster pathway would still occur in such effluents. In fact, based on the results of this project, the pH of some effluent feeds to EARP were lowered to see if this improved DFs and this led to an improvement in americium DFs on plant. It was inferred that this may be due to an influence of cluster formation at low pH. Follow on research questions from these observations are:

- Does the Fe$_3$ cluster precursor pathway to ferrihydrite floc still occur in less acidic effluents?
- If not, is the improvement in the americium DF, which was induced by increasing effluent acidity, due to promoting a Fe$_3$ cluster pathway to floc formation?

Interestingly, for treatment processes using aluminium as the coagulant and flocculant, it has been found that Al$_{13}$ cluster species are the most effective and stable polymeric Al species in wastewater treatment (Jiang and Graham, 1998; Gao et al., 2005). For example, Gao et al. (2005) found that polyaluminium chloride coagulants with greater amounts of Al$_{13}$ species had greater charge-neutralising ability and resulted in higher humic acid and colour removal when treating both synthetic and actual surface water samples. These observations clearly lead to the question, could Fe$_3$ species have a similar effect in promoting more effective contaminant removal?

iv) Effect of floc properties on filterability.

Dewatering of the floc by ultrafiltration to create a compact wasteform suitable for cementation is a vital step in the EARP process. The generation of flocs which dewater quickly and efficiently provides great economic advantage both in regards to speed of processing and volume of waste to be treated. While this project characterised some important floc properties which determine filtration performance, such as particles sizes and floc fractal dimension, the focus of this project was on floc formation not ultrafiltration. Future work could focus on factors which influence the filterability of the floc. In particular, ageing induced transformation of the floc is expected to have a major effect on filtration performance since this results in a
fundamental change in the mineralogy and therefore floc properties (particle size, density, aggregate structure etc.). Indeed, Chapter 6 showed that transformation of the ferrihydrite floc to crystalline phases resulted in significantly smaller solid volumes and slower settling kinetics. While plant experience suggests crystallised flocs dewater more quickly and efficiently, more work is required in this area on optimisation and quantification. Recently, a non-radioactive rig scale facility mimicking the EARP process, including both the floc formation and ultrafiltration steps, has been completed at the National Nuclear Laboratory, Workington and will be used for filterability investigations, with work from this PhD being used directly to inform the study programme.

v) Effects of non-radioactive species on radionuclide uptake.

In this project, the interactions of select non-radioactive species with the iron oxyhydroxide floc during formation were investigated. Sulfate, phosphate, boric acid, nitrate and carbonate all exhibited adsorption behaviour on the ferrihydrite floc. This may potentially have an impact on radionuclide decontamination factors: for example, radionuclide adsorption may decrease due to competition from the non-radioactive species, or alternatively radionuclide adsorption may be promoted by the formation of ternary adsorption complexes. Phosphate is of particular interest because our experiments showed that almost all the added phosphate was strongly adsorbed to the floc at the final pH of 9 and out-competed carbonate for adsorption. Interestingly, it has previously been reported that the presence of phosphate increases uptake of uranium on ferrihydrite via the formation of ternary surface complexes (Payne et al., 1996), and uptake of strontium on ferric hydroxide floc has also been shown to increase in the presence of phosphate (Bull, 1974). However, the effect on other radionuclides, particularly other anionic species such as pertechnetate ($\text{TcO}_4^-$), has not been widely studied.
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Appendix 1

Exploratory work investigating phosphate removal from effluent simulants using zirconium

Rationale

In Chapter 6 we showed that the presence of phosphate in effluent simulants at concentrations ≥ 10 ppm caused inhibition of ferrihydrite floc transformation to more crystalline phases within the measured 8 week period. This was due to strong adsorption of phosphate to the ferrihydrite floc at the end point pH (pH 9 and 9.5).

Operational experience on the EARP plant suggests that formation of a more crystalline floc is beneficial since these flocs generally filter better, with higher dewatering factors achieved in shorter amounts of time. Therefore, it may be desirable to remove phosphate from effluent feeds before base treatment in order to ensure floc crystallisation can take place within an appropriate timeframe.

In this exploratory work, it was hypothesised that zirconium (Zr) added to the effluent simulant before base treatment may precipitate phosphate out of solution as zirconium phosphate, since these phases are known to be highly insoluble even at low pH (Alberti and Torracca, 1968). This would render the phosphate unavailable to adsorb to the floc, thereby allowing ferrihydrite floc transformation to occur.

Experimental

0.167 g of Zr(OH)₄ was added to 65 ml of conc HNO₃ and gently heated on a hot plate with stirring to promote dissolution of the Zr(OH)₄. Once almost all the Zr(OH)₄ had appeared to dissolve, the solution was diluted to 1 M HNO₃ with DI water and Fe(NO₃)₃.9H₂O was added to give a Fe(III) concentration of 7.16 mM / 400 ppm. The Zr concentration was calculated to be ~ 1 mM / 96 ppm. NaH₂PO₄ was then added to the solution to give a phosphate concentration of 1.05 mM / 100 ppm. This solution was used as the effluent simulant. Filtered solution samples (0.22 µm PES filter) were taken for ICP-AES analysis immediately before and 5 min after addition of the NaH₂PO₄.
400 mL of the prepared effluent simulant was used in a standard NaOH base titration experiment (Chapter 3, section 3.2.4.). After the end point pH 9 was reached, the flocculated slurry was allowed to stand for 10 min, followed by taking a filtered solution sample (0.22 µm PES) for ICP-AES. 100 ml of the slurry was taken and the solid centrifuged down and washed x3 with DI water before drying overnight in the oven at 40 °C. The remainder of the slurry was left in the oven at 40 °C to age, with filtered solution samples taken for ICP-AES after 2 and 8 weeks ageing. After 8 weeks ageing, the solid was isolated by centrifuging, washed 3x with DI water and dried overnight in the oven at 40 °C. The fresh and 8 week aged dried samples were ground to a powder and analysed using XRD (Bruker D8 Advance Diffractometer, Chapter 3, section 3.3.1.).

**Thermodynamic calculations (PHREEQC)**

The PHREEQC model of the iron oxyhydroxide synthesis procedure (Chapter 3, Section 3.6.) was run with the inclusion of 100 ppm phosphate and 100 ppm Zr in the initial effluent simulant solution. All the Zr solid phases (Figure 2) available in the SIT database were allowed to precipitate during the model run.

**Results and Discussion**

**Thermodynamic calculations**

Below pH 9, Zr was predicted to be in the solid phase as a combination of ZrO$_2$ and Zr(HPO$_4$)$_2$ (Figure 1 and 2). With increasing pH, the proportion of Zr as ZrO$_2$ relative to Zr(HPO$_4$)$_2$ increased, with Zr predicted to be present entirely as ZrO$_2$ above ~ pH 7.8. Subsequently, above pH 9, rapid dissolution of ZrO$_2$ was predicted and the Zr was released into solution.

Related to this, phosphate is predicted to be entirely in the solid phase as Zr(HPO$_4$)$_2$ until ~ pH 6.5, above which the Zr(HPO$_4$)$_2$ begins to dissolve and phosphate is released to solution. We note that Zr(OH)$_4$, which was the compound used to add Zr to the effluent simulant, is undersaturated at pH 0.1 and would therefore be expected to dissolve.
**Figure 1:** Predicted changes in concentrations of dissolved iron (Fe), phosphorus (P), and zirconium (Zr) during the base titration of acidic effluent simulant, as based on thermodynamic calculations performed in PHREEQC.

**Figure 2:** Predicted amounts of solid Zr phases during the base titration of acidic effluent simulant, as based on thermodynamic calculations performed in PHREEQC.
ICP-AES

Solution analysis of dissolved Zr, phosphate and Fe are shown in Figures 3 and 4. In the pH 0.1 effluent simulant before phosphate addition, the Zr concentration was ~ 64 ppm. In contrast, calculations based on the amount of Zr(OH)$_4$ added to the simulant suggest the concentration should be 96 ppm if all the Zr(OH)$_4$ dissolved. This suggests that some of the Zr re-precipitated as another phase, or not all the Zr(OH)$_4$ was dissolved initially. Indeed, thermodynamic calculations suggest ZrO$_2$ is oversaturated in the initial pH 0.1 effluent (Figure 2), and therefore some Zr may have precipitated as ZrO$_2$. In particular, this may have occurred when the conc HNO$_3$ – Zr solution was diluted to make the 1 M HNO$_3$ effluent.

The dissolved Zr concentration decreased significantly to ~ 1 ppm after addition of NaH$_2$PO$_4$ to the pH 0.1 effluent simulant. The measured concentration of phosphate was ~ 8 ppm, despite enough NaH$_2$PO$_4$ added to give 100 ppm phosphate. This suggests that addition of the NaH$_2$PO$_4$ resulted in precipitation of zirconium phosphate, which is consistent with visual observations of formation of a white precipitate upon addition of the NaH$_2$PO$_4$ and thermodynamic calculations showing Zr(HPO$_4$)$_2$ was oversaturated in this solution (Figure 2). The amount of Zr precipitated was 0.27 mM compared to 0.39 mM for phosphate. While this stoichiometry is approximately consistent with the formation of Zr(HPO$_4$)$_2$ which has a Zr:PO$_4$ ratio of 1:2, a greater amount of Zr is precipitated than required for precipitation of all the phosphate, suggesting some ZrO$_2$ precipitation may also occur.

After the base titration reaction to form the iron oxyhydroxide floc, the Zr and phosphate concentrations in solution were below detection limit (Figure 3). Zr remained below detection limit for the 8 week ageing period, while a very small amount of phosphate (< 1 ppm) was present after 8 weeks ageing. This is in contrast to the thermodynamic calculations which predict Zr and phosphate to be entirely in solution at pH 9. However, we note that the thermodynamic calculations do not include adsorption processes which may remove these species from solution.

The Fe concentration in the pH 0.1 effluent was approximately the same before and after addition of the NaH$_2$PO$_4$ (Figure 4), confirming no formation of solid Fe phases in the initial effluent before base addition. After the base titration, Fe concentration was below detection limit, consistent with formation of an iron oxyhydroxide floc.
**Figure 3:** Zr and phosphate concentrations in solution samples measured by ICP-AES. Note: phosphate concentration was measured as dissolved phosphorous.

**Figure 4:** Fe concentrations in solution samples measured by ICP-AES.
**Powder XRD**

XRD analysis of the solid phase (Figure 5) shows that it was composed of 2-line ferrihydrite – both immediately after formation and after 8 weeks ageing. Therefore, transformation of the ferrihydrite floc was entirely inhibited within the 8 week ageing period, similar to results presented in Chapter 6 for effluents with 10 and 100 ppm added phosphate. Interestingly, no solid Zr phases were detected in the XRD, indicating that they had either dissolved during the base addition (as predicted in the thermodynamic calculations (Figure 2)) or were present below detection limit.

![Figure 5: Powder XRD patterns collected on the solid phase – immediately after formation and after 8 weeks ageing.](image)

**Conclusions**

The data presented here indicate that addition of phosphate to acidic effluent simulants containing dissolved Zr results in a significant proportion of the phosphate (~ 90 % in this experiment) not being present in the aqueous phase. This is likely due to precipitation of Zr(HPO$_4$)$_2$.

However, after the base titration reaction, XRD analysis of the final solid phase at pH 9 shows only the presence of 2-line ferrihydrite. This indicates that Zr(HPO$_4$)$_2$ and other Zr solid phases present (i.e. ZrO$_2$) dissolve with the increase in pH (as predicted in thermodynamic calculations) or are present below detection limit of the XRD.
Interestingly, the Zr solution concentration is below detection limit at pH 9, indicating no dissolved Zr is present. Therefore, if the solid Zr phases did dissolve, the Zr may have been removed from solution by adsorption to the ferrihydrite floc.

The presence of the Zr did not prevent the phosphate from inhibiting the transformation of the ferrihydrite floc. This may be because the precipitated Zr(HPO$_4$)$_2$ had dissolved by pH 9, allowing the phosphate to adsorb to the ferrihydrite floc. Alternatively, there may have been enough residual phosphate in the initial pH 0.1 effluent to adsorb to the ferrihydrite floc and inhibit transformation. Indeed, there was ~ 8 ppm dissolved phosphate in the pH 0.1 effluent used in this experiment; and Chapter 6 showed that 10 ppm phosphate in the effluent simulant was enough to inhibit transformation of the ferrihydrite floc within the 8 weeks ageing period.

**References**

Appendix 2

Conference Presentations

Oral presentations

- **Sellafield Day**, the University of Manchester, 16\(^{th}\) Feb 2017.
- **SEES Postgraduate Research Conference**, the University of Manchester, 2\(^{nd}\) Dec 2016.
- **Ninth International Conference on Nuclear and Radiochemistry**, Helsinki, Finland, 29\(^{th}\) Aug – 2\(^{nd}\) Sept 2016.
- **Environmental Mineralogy Group: Research in Progress Meeting**, the University of Bristol, 19\(^{th}\) June 2016.
- **Sellafield Day**, the University of Manchester, 27\(^{th}\) Jan 2016.
- **Dalton Day**, the University of Manchester, 27\(^{th}\) Nov 2015.
- **Goldschmidt**, Prague, Czech Republic, 17\(^{th}\) – 21\(^{st}\) Aug 2015.
- **Mineralogical Society’s joint Environmental Mineralogy and Geomicrobiology Research in Progress Meeting**, the University of Leeds, 24\(^{th}\) June 2015.
- **Sellafield Day**, the University of Manchester, 12\(^{th}\) Jan 2015.
- **Research Frontiers in Decommissioning and Radioactive Waste Management**, the University of Lancaster, 12\(^{th}\) Nov 2014.

Poster presentations

- **SEAES Postgraduate Research Conference**, the University of Manchester, 2\(^{nd}\) Dec 2014.