Sorption detriments in the geosphere: the effect of cellulose degradation products. Phase 1 Experimental study

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Preface

This report has been prepared by Serco Technical Consulting Services under contract to the NDA and previously under contract to Nirex. It formed part of an ongoing programme of research originally commissioned by Nirex to underpin the long-term safety of a geological disposal facility for higher-active radioactive wastes. Before it was published, Nirex was subsumed into the NDA. However, references to Nirex in the text have been retained as they are appropriate for the period when this research was being performed. The report has been reviewed by the NDA, but the views expressed and conclusions drawn in the report are those of Serco Technical Consulting Services and do not necessarily represent those of the NDA.

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Executive Summary

The treatment of detriments to radionuclide sorption in the geosphere has been identified as a key uncertainty in performance assessments for a geological disposal facility (GDF). Potentially the most significant detrimental process affecting radionuclide chemistry is the formation of complexes with organic compounds that may be present in the groundwater (such as natural humic substances) or released from a GDF. Volumetrically, the most important potential sources of organic complexants within a GDF will be cellulosic materials such as paper, wood and cloth present in the wastes. Cellulosic materials have been shown to degrade under the alkaline conditions relevant to cement-based GDF concepts, and the resulting degradation products to complex some radionuclides, causing solubility enhancement in the near field and sorption reduction in both the near field and the geosphere. Historically, a significant amount of work had been undertaken to study the effects of cellulose degradation products (CDPs) on the sorption of a number of radionuclides onto a range of rock types.

To simulate the effect of CDPs on geosphere sorption, experimental studies have been undertaken previously using so-called ‘authentic’ cellulose degradation products (ACDP) produced by the alkaline anaerobic degradation of tissues in the presence of cementitious materials (in particular, Nirex Reference Vault Backfill, NRVB) with typically a 10% solid loading of organic material (compared with cementitious solids), conditions designed to simulate degradation in a GDF. Iso-saccharinic acid (ISA) has been identified as a major component of ACDP that appears to account for the effects of ACDP on sorption reduction and solubility enhancement under alkaline, near-field conditions. Under the near-neutral pH conditions typical of the geosphere, however, the situation is more complicated. In general, sorption in the presence of ISA tends to be higher than sorption in the presence of ACDP (i.e. ACDP has a greater effect in reducing radionuclide sorption than ISA). This observation is indicative of the presence of additional complexants and or other processes in the presence of ACDP that may lower sorption more than ISA alone. In addition, in some experiments apparent enhancement of radionuclide sorption has been observed in the presence of ACDP and/or ISA onto certain rock types. The discrepancies between the effects of ISA and ACDP under geosphere conditions are difficult to explain with current knowledge. Therefore, there is a need to develop a clearer conceptual understanding of the effects of these organic complexants on radioelement sorption to mineral surfaces under near-neutral conditions.

This report describes the results from a package of experimental work designed to provide initial characterisation of a simple model ternary system to investigate the effects of organic complexants on the sorption of radioelements to mineral surfaces. The model ternary system selected for study consisted of haematite as the single mineral substrate, thorium as the radioelement and ISA as the complexant with sodium chloride as the background electrolyte. The design of this experimental work programme was driven by the data requirements for thermodynamic modelling, the results of which have been reported separately.

Sorption experiments have been undertaken to investigate the following interactions in the ternary system:

- ISA sorption to haematite as a function of ISA concentration and pH;
- thorium sorption to haematite as a function of pH; and
- thorium sorption to haematite in the presence of ISA as a function of pH.

In addition, sorption experiments have been carried out in parallel with a CDP leachate to compare its impact on thorium sorption to that of ISA. All experiments have been undertaken under a nitrogen atmosphere to exclude carbon dioxide.
For the purposes of this study, CDP leachates have been prepared using a new generic recipe in which cellulosic material (paper tissues) has been degraded for 30 days under alkaline anaerobic conditions at 80°C in the presence of calcium but excluding the NRVB used in previous degradations to generate ACDP. HPLC analysis of CDP leachates prepared in this study found that they contain two major components: the isomers of ISA and a second component that has yet to be identified; plus a number of minor components. The maximum amount of ISA present in leachates prepared in the presence of calcium hydroxide is estimated to be $\approx 1.9 \times 10^{-2}$ mol dm$^{-3}$, about an order of magnitude higher than estimated previously for ACDPs prepared in the presence of bulk NRVB. This difference is thought to arise due to sorption of ISA to the NRVB in degradations undertaken by the previous method. Differences in composition between the new CDP leachate and ACDP leachates prepared in the presence of bulk NRVB have yet to be fully investigated.

No detectable changes in solutions concentrations of either ISA or CDP leachate components were detectable by TOC or HPLC measurements after contact with haematite for 30 days in initial sorption experiments with relatively high concentrations of organic complexants. It is considered that the range of concentrations amenable to study by the current HPLC method using UV detection is probably too high to allow differences in sorption behaviour of CDP components to haematite to be distinguished.

The results of the ISA sorption experiments onto haematite containing C-14 labelled ISA to measure ISA sorption at lower ISA concentrations show the following trends.

- ISA sorption to haematite at an initial concentration of $2 \times 10^{-3}$ mol dm$^{-3}$ ISA was weak at all pH values; measured sorption distribution ratios ($R_D$ values) were less than 10 cm$^3$ g$^{-1}$.

- At a lower initial concentration of $2 \times 10^{-5}$ mol dm$^{-3}$ ISA sorption of ISA at pH 12 was also very weak, but a significant increase in $R_D$ values was measured with decreasing pH; $R_D$ values increased from <10 cm$^3$ g$^{-1}$ at pH 12 to about 100 cm$^3$ g$^{-1}$ at pH 7 to 9.

- At $2 \times 10^{-7}$ mol dm$^{-3}$ ISA (initial) sorption of ISA to haematite at pH 12 was stronger than at higher ISA concentrations with a mean $R_D$ value of about 36 cm$^3$ g$^{-1}$. There was no significant increase in ISA sorption observed across the pH range 6.5 to 12. Measured $R_D$ values in this pH range varied from 22 ± 14 to 68 ± 22 cm$^3$ g$^{-1}$.

Qualitatively, the trends in measured $R_D$ values for ISA onto haematite with pH and ISA concentration at the two higher ISA concentrations used are consistent with expectations that:

- iso-saccharinate will sorb more strongly to haematite at pH values below the point of zero charge (about pH 8-9) where iron surface sites on the haematite become net positively charged, and

- at the higher ISA concentrations the sorption isotherm becomes non-linear (and $R_D$ values decrease) due to saturation of surface sites with sorbed ISA.

However, the results for the lowest ISA concentrations differ from these trends. This may be due a greater sensitivity at lower concentrations to the presence of impurities in the experimental system.

In the absence of organic complexants, sorption of thorium onto haematite has been measured to be strong at all three pH values considered. Measured $R_D$ values for thorium were $\geq 4 \times 10^{6}$ cm$^3$ g$^{-1}$ at pH ~9 and varied from $9 \times 10^{5}$ cm$^3$ g$^{-1}$ to $7 \times 10^{5}$ cm$^3$ g$^{-1}$ at pH~6. Measured $R_D$ values at pH 12 were about one order of magnitude lower ranging from 1-2 $10^5$ cm$^3$ g$^{-1}$. The overall trends in the $R_D$ values for thorium onto haematite measured in the present study are broadly consistent with data reported in the literature, although $R_D$ values are higher than in comparable studies undertaken under aerobic conditions.

The presence of $2 \times 10^{-3}$ mol dm$^{-3}$ ISA appears to have a negligible effect on thorium sorption to haematite at pH 12 but to reduce sorption by up to an order of magnitude at pH 5.5 to 6.6.
Owing to the spread of the data it is unclear whether there is also a smaller reduction in thorium sorption at pH 9.

The presence of 10% CDP leachate (i.e. a ten-fold dilution of the leachate originally prepared) has a much more significant effect on thorium sorption than ISA alone at all three pH ranges studied; at pH 4.7 to 6.8 and pH ~9, sorption to haematite is reduced by about 2 orders of magnitude compared to the baseline case. A reduction of at least one order of magnitude is observed at pH 12.

Thus, ISA does not appear to provide an adequate model for the effects of CDP on thorium sorption to haematite either at near-neutral (as expected) or alkaline pH values (which was not). The findings at near-neutral pH are consistent with previous results for ACDPs obtained on the Nirex programme, showing that under these conditions ACDPs have greater effects on radionuclide sorption than ISA alone. In addition the new CDP has a detrimental effect on thorium sorption to haematite at pH 12. Given the relatively weak effect of ISA, it would appear that the presence of other complexants or additional processes, rather than ISA, are responsible for controlling thorium sorption behaviour to haematite in the presence of the new CDP leachate.

Overall, the chosen model ternary system haematite-thorium-ISA does not appear to be as well-suited as expected as a basis for on-going development of a thermodynamic model of ternary system interactions owing to the limited impact of ISA on thorium sorption in this system. In addition there are uncertainties concerning sorption reversibility and the attainment of thermodynamic equilibrium for this system over experimental timescales. The impact of CDP leachate in reducing thorium sorption to haematite appears to be significant, however. Clearly more understanding is required concerning the presence of additional complexants and/or the operation of other processes (e.g. possible competition for surface sites by calcium ions) that control thorium sorption in the presence of the new CDP leachate.

This report was prepared by Serco Technical Consulting Services under contract to NDA RWMD (and previously to United Kingdom Nirex Limited (Nirex)). The main technical work reported here was carried out in the period July 2006 to March 2007 and the report is based upon, and solely refers to, information available at that time. The work forms part of the NDA RWMD Research Programme. The information has been verified under arrangements established by Serco Technical Consulting Services. These arrangements have been approved by NDA RWMD and are consistent with ISO 9001.

The views expressed and conclusions reached are those of Serco Technical Consulting Services and do not necessarily represent those of NDA RWMD.
Contents

1 Introduction 11

2 Design of the Phase 1 Programme 13
   2.1 Modelling approach 13
   2.2 Methodology 13
   2.3 Choice of ternary system 14
   2.4 Choice of cellulose degradation conditions 15
   2.5 Choice of Phase 1 experiments 16

3 Materials 17
   3.1 Haematite 17
   3.2 ISA 17
   3.3 Thorium 17

4 Preparation of cellulose degradation product leachate 18
   4.1 Degradation procedure 18
   4.2 Analytical methods 18
   4.3 Analytical results 19

5 Sorption Experiments 21
   5.1 Sorption of ISA and CDP onto haematite 21
   5.2 Sorption of C-14 labelled ISA onto haematite 24
   5.3 Effect of organic complexants on thorium sorption onto haematite 25
   5.4 Radiochemical Analysis 26
   5.5 Calculation of $R_D$ values 26
   5.6 pH Measurement 27

6 Results 27
   6.1 Sorption of ISA and CDP onto haematite 27
   6.2 Sorption of C-14-labelled ISA onto haematite 28
   6.3 Sorption of thorium onto haematite in the presence and absence of ISA or CDP 29
7 Discussion

7.1 Cellulose degradation product leachate

7.2 Sorption of ISA onto haematite

7.3 Sorption of CDP onto haematite

7.4 Sorption of thorium onto haematite

7.5 Sorption of thorium onto haematite in the presence of organic complexants

7.6 Suitability of the model ternary system: haematite-thorium-ISA

8 Conclusions

9 Acknowledgements

10 References

Tables

Figures
1 Introduction

The Nuclear Decommissioning Authority (NDA) has established the Radioactive Waste Management Directorate (RWMD) to manage the delivery of geological disposal for higher activity radioactive wastes, as required under UK Government policy published in the Managing Radioactive Waste Safely (MRWS) White Paper. A Disposal System Safety Case (DSSC) considers the safety of radioactive waste transport to a geological disposal facility (GDF), the safety of the construction and operation of a GDF, and the safety of the facility in the very long term, after it has been sealed and closed. A DSSC is in the early stages of development, because a site and design have not yet been chosen. At the current stage of the programme, NDA RWMD are examining a wide range of potentially suitable disposal concepts so that a well-informed assessment of options can be carried out at appropriate decision points in the implementation programme.

Prior to being subsumed into the NDA, Nirex had developed a deep underground geological disposal facility (GDF) concept for ILW and LLW that would make use of a combination of engineered and natural barriers [1]. Physical containment of radionuclides would be achieved by immobilisation and packaging of wastes in steel or concrete containers. Geological isolation would be achieved by emplacement of the waste packages in vaults excavated deep underground within a suitable geological environment. Chemical conditioning would be provided by backfilling the vaults with a cementitious material (Nirex Reference Vault Backfill, NRVB, a mix of Portland cement, limestone flour and lime [2]) after all the waste has been emplaced in the GDF, and at a time determined by future generations.

Research in support of a GDF concept is carried out under the NDA RWMD (formerly Nirex) research programme and includes experimental and modelling studies. Part of the programme is concerned with processes that would occur in the geosphere or ‘far field’, the geological environment surrounding the GDF. Work under the Nirex programme included experimental and modelling studies of the sorption of radionuclides onto both site-specific materials [e.g. 3, 4, 5, 6] and single mineral samples [e.g. 7, 8, 9] as these are an important input to the elicitation of data for post-closure performance assessments [10, 11, 12].

The treatment of detriments to radionuclide sorption in the geosphere has been identified as a key uncertainty in GDF performance assessments [13]. Consequently, a work programme to address how best to treat these detriments in future performance assessments was started in 2002/2003. Following a Peer Preview meeting at Nirex in November 2002, a strategy for addressing detriments to radionuclide sorption in the geosphere was formulated [14] and an outline work programme was prepared that included treatment of the effects of organic complexants [15]. During 2003 and 2004 an experimental study was undertaken to investigate the effects on radionuclide sorption of two specific types of organic complexants that were considered a high priority at that time (namely picolinate and degradation products from anion exchange resins (AERDP)) [16]. During 2004/05, the potential effects of light non-aqueous phase liquids on the sorption properties of rock were investigated [17].

Volumetrically, the most important potential sources of organic complexants within a GDF will be cellulosic materials such as paper, wood and cloth present in the wastes. Cellulosic materials have been shown to degrade under the alkaline conditions relevant to a GDF, and the resulting degradation products to complex some radionuclides, causing solubility enhancement in the near field and sorption reduction in both the near field and the geosphere [18]. A significant amount of work was undertaken previously on the Nirex research programme to study the effects of cellulose degradation products (CDPs) on the sorption of a number of radionuclides onto a range of rock types [e.g. 19–25]. These studies were undertaken in support of the site investigations of a number of UK sites (primarily Sellafield) during the 1990s.
To simulate the effect of CDP on geosphere sorption, experimental studies have been undertaken using three complexant materials: so-called ‘authentic’ cellulose degradation products (ACDP) produced by the alkaline degradation of tissues in the presence of cementitious materials; iso-saccharinic acid (ISA) and gluconate. The term ‘authentic’ was used on the former Nirex programme to describe CDPs produced in the presence of cementitious materials, in particular the Nirex Reference Vault Backfill (NRVB) under conditions designed to simulate the degradation of cellulosic materials in a GDF. In this report the term ACDP will be reserved for CDP leachates prepared in the presence of bulk cement; it is not applied to the CDP leachates prepared in this work in the presence of calcium hydroxide.

ISA has been identified as a major product of the alkaline anaerobic degradation of cellulose [26], and has been shown to give a significant enhancement in plutonium solubility under near-field conditions [18]. Gluconate is a readily-available polyhydroxy-carboxylate that was used as an analogue of the simple products from the degradation of cellulose (although it is not expected to be present in wastes).

Under alkaline, near-field conditions, it appears that the effects of ACDP on sorption reduction and solubility enhancement can be accounted for by the presence of ISA. Under the near-neutral pH conditions typical of the geosphere, however, the situation is more complicated. In general, sorption in the presence of ISA tends to be higher than sorption in the presence of ACDP [27] (i.e. ACDP has a greater effect in reducing radionuclide sorption than ISA). This observation is indicative of the presence of additional complexants that may lower sorption more in the presence of ACDP than ISA alone. In addition, in some experiments apparent enhancement of radionuclide sorption has been observed in the presence of ACDP and/or ISA onto certain rock types [27]. The discrepancies between the effects of ISA and ACDP under geosphere conditions are difficult to explain with current knowledge [18]. Therefore, there is a need to develop a clearer conceptual understanding of the effects of these organic complexants on radionuclide sorption to mineral surfaces under near-neutral conditions.

Following discussions with Nirex on 30 June 2006, an initial package of work was agreed as part of a multi-year programme to address the potential effects of cellulosic degradation products on radionuclide sorption in the geosphere. This work programme was based on the strategy and work programme that were formulated in 2002/03 [14], which remained largely valid, although some significant progress has been made in understanding the behaviour in ternary systems over the intervening 3 years (from e.g. the European FUNMIG project [28]). The work programme includes both experimental and thermodynamic modelling components.

The overall objectives of the work programme are to:

1) Develop a conceptual model of radionuclide-solid-complexant interactions through study of a suitable model ternary system (this includes the possibility of sorption enhancement under some conditions);

2) Understand better the impact of CDP on radionuclide sorption in the geosphere and whether ISA is an adequate model for CDP or whether additional components of the CDP (as yet unidentified) need to be included in the conceptual model.

The design of the experimental component of the work programme has been driven by the data requirements for thermodynamic modelling. The modelling strategy and the choice of the ternary system for use in the study are discussed in Section 2 of this report.

The particular objectives of the initial package of experimental work described in this report were to:

- Prepare CDP and understand the composition in terms of ISA and other components;
- Perform initial characterisation of the chosen ternary system: radionuclide – substrate-ISA/CDP:
o Scope the impacts of ISA and CDP on radioelement sorption behaviour onto a model substrate at 6 pH values;
o Scope the interactions of ISA and CDP with the model substrate as a function of concentration at 3 pH values;
• Assess the suitability of the proposed ternary system for more detailed mechanistic study;
• Assess how well ISA represents CDP for the ternary system under study.

The results of a thermodynamic modelling study to develop a thermodynamic sorption model of the selected ternary system are described separately [29].

The remainder of the report is structured as follows. The design of the Phase 1 experimental programme is discussed in detail in Section 2. The materials used are described in Section 3; Section 4 describes the preparation and analysis of the CDP leachates. The experimental procedures for the batch sorption experiments are described in Section 5, the results are presented in Section 6 and discussed in Section 7; conclusions are drawn in Section 8.

This report was prepared by Serco Technical Consulting Services under contract to NDA RWMD (and formerly to United Kingdom Nirex Limited (Nirex)). The main technical work reported here was carried out in the period July 2006 to March 2007 and the report is based upon, and solely refers to, information available at that time. The information has been verified under arrangements established by Serco Technical Consulting Services. These arrangements have been approved by NDA RWMD and are consistent with ISO 9001.

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2 Design of the Phase 1 Programme

2.1 Modelling approach

Experimental data for sorption of radioelements onto single mineral phases are often interpreted using thermodynamic sorption models. Implicit to this approach is the assumption that the experiments have reached thermodynamic equilibrium. For mineral phases with no ion exchange capacity, thermodynamic surface complexation models are often applied. These include non-electrostatic models in which the electrostatic interaction of sorbing ions with the charged surface is neglected, and electrostatic models such as the diffuse layer model (DLM) [30] and the triple layer model (TLM) [31] which account for such interactions. As part of the Phase 1 programme models using the DLM and TLM approaches have been developed for the ternary system under study. The development of these models is reported separately [29].

2.2 Methodology

The effect of organic complexants on the sorption of radionuclides is potentially a complicated issue involving a wide range of processes. When the effect of a multi-component mixture of organics, such as CDP, is considered, the level of complexity is increased further by the large number of potential interactions of the various CDP components with the radioelement and with surface sorption sites. The range of potential interactions are summarised schematically in Figure 1. The radioelement (M)-ISA-sorbent system is represented by processes (1) to (4). Additional processes arising from other complexing components (X) and non-complexing components (N) of CDP are represented by processes (5) to (8). Previous radioelement sorption experiments undertaken in the presence of a complexant have measured only the loss
of the metal M from solution. Figure 1 shows that this measurement might be dependent on a number of competing reactions, (1) to (8), which have not been distinguished in NDA RWMD or Nirex research to date. Therefore, to gain a fundamental understanding of the chemistry of rock-radioelement-complexant interactions it is necessary to obtain information not only on the direct effects of the organic complexant on radioelement sorption but also to investigate the associated processes in separate experiments where practicable. Owing to the level of complexity involved, the experimental system selected for study needs to be kept as simple as possible. In particular, this means using a single mineral as the substrate and a simple (1:1) electrolyte as the solution phase.

The overall approach adopted in the programme has been first to build up an overall thermodynamic model for the effects of ISA on radioelement sorption after an understanding of the individual processes has been developed. These processes include:

- speciation of radioelement in solution;
- complexation of radioelement in solution by ISA;
- surface reactions of mineral phase;
- dissolution of mineral phase and effect of ISA;
- sorption of ISA;
- sorption of radioelement in absence of ISA;
- sorption of radioelement in the presence of ISA.

The experimental programme was carefully designed to give information not only on the direct effect of the organic complexant on radionuclide sorption, but also to investigate a number of the associated binary processes identified above.

The strategy for thermodynamic modelling has been to:

- develop literature-based DLM and TLM models based on fitting published experimental data and available thermodynamic data;
- predict the impact of ISA on radionuclide sorption in the ternary system;
- compare the predictions with the experimental data obtained in the current study;
- and refine the models based on model fits to the new experimental data.

2.3 Choice of ternary system

Following recommendations in reference [15], it was agreed with Nirex staff to use haematite as the single mineral substrate and sodium chloride as the electrolyte in the present study.

In natural systems, iron oxides and oxyhydroxides are known to act as important sinks for trace elements [32, 33]. It is believed that they play an important role in controlling sorption behaviour for many metal ions. Therefore, an iron oxide, haematite (α-Fe₂O₃) has been selected as the sorbent phase. Haematite is not common as a primary mineral in igneous rocks, but may form as an alteration product of iron-bearing minerals [34]. It is a common mineral in sedimentary rocks (and their metamorphosed equivalents), soils and mineral deposits.

It was agreed that a high purity synthetic haematite will be used from the same source (initially from the same batch) that was used previously to study the impacts of picolinate and AERDP [16]. A synthetic haematite was chosen in preference to a natural sample to ensure that sorption is measured onto a single mineral phase free from minor mineral contaminants.

Based on the strategy developed in reference [14], the priority radioelements on the basis of performance assessment considerations were identified as: uranium, thorium, neptunium, radium and lead. Plutonium was also included and nickel also considered (as both model element and radioelement, with long-lived radionuclide, Ni-59). The radioelements proposed for study previously in reference [15], were plutonium and nickel. Following discussions with Nirex and Loughborough University it was agreed to start the current work programme using thorium.
Thorium was chosen because it has several advantages over some of the other radioelements considered:

- some data are already available for thorium-ISA complexation [35];
- thorium has both long-lived (Th-232) and short-lived (Th-228) isotopes (unlike neptunium for example) so that a wide range of amounts of thorium can be used in experiments;
- thorium is present in only the +4 oxidation state in aqueous systems and no redox control is required.

It was agreed to carry out all experiments under anaerobic conditions in a nitrogen (or argon) atmosphere to ensure low carbon dioxide concentrations. Although no redox control is required with thorium, carbonate complexation may be a complication, particularly at alkaline pH values if experiments are undertaken in air.

### 2.4 Choice of cellulose degradation conditions

Previous studies of the impact of ACDP on radioelement sorption in the geosphere undertaken on the Nirex programme have used leachates produced by the degradation of cellulose at elevated temperature (usually 80°C) in the presence of water and crushed cement. In the earliest experiments, ACDP was prepared under aerobic alkaline conditions (references [20, 21, 22, 23]) but in reference [36] both aerobically- and anaerobically-prepared leachates were used. The cement used in initial degradations was an OPC/BFS mix to represent a grout that might be used to encapsulate cellulose-containing wastes in waste containers. Given the uncertainties concerning the composition of encapsulation materials that may be used by waste producers to package cellulose-containing wastes, in later studies [24, 25], NRVB was chosen as the cement material that would best simulate near-field chemical conditions in the GDF. Thus, the ACDP leachates produced were regarded as providing ‘authentic’ materials for use in data gathering studies that were directly relevant to the NDA RWMD disposal concept (the PGRC).

Many of the degradations contained a 10% loading of organic material to OPC/BFS or NRVB (that is, a mass ratio of cement to organic material of 9:1) although lower loadings down to 0.1% have also been degraded. Most of these studies used sources of cellulose in the form of paper tissues. In some experiments wood was used for comparison purposes (e.g. reference [19]). A liquid to total solid ratio of 2.5 became established as part of a standard recipe from the early 1990s onwards [e.g. 37, 38].

A temperature of 80°C was chosen initially to provide an accelerated rate of degradation compared with ambient temperature. (Information on the maximum temperature of the GDF was not available at the time the choice was made.) This temperature is now expected to be the maximum allowed short-term temperature for current GDF concepts [39]. Radioelement solubility and sorption data have been determined in samples of leachates removed from these degradations experiments, allowed to cool to room temperature and phase separated by filtration.

In view of the generic nature of the work programme, the need was identified to use a more generic recipe for CDP preparation. It was felt that the degradation of cellulosic materials in the presence of NRVB was too specific to the then Nirex disposal concept, that the CDP could not easily be reproduced elsewhere and, therefore, that the results obtained with these materials were not amenable to direct comparison with the results obtained on other programmes.

In work undertaken on the Swiss programme by the Paul Scherrer Institute (PSI), a more generic recipe for the degradation of cellulosic materials has been used [40]. The degradation of a number of different forms of cellulosic materials was investigated under conditions...
representing those of the early stage of cement degradation in a GDF\(^1\). The artificial cement pore water composition selected (denoted ACW-1) was a mixed sodium and potassium hydroxide solution which was saturated with respect to calcium hydroxide. The composition of ACW-1 with respect to its main constituents was as follows:

\[
\begin{align*}
\text{Na:} & \quad 0.114 \text{ mol dm}^{-3} \\
\text{Ca:} & \quad 0.0023 \text{ mol dm}^{-3} \\
\text{K:} & \quad 0.18 \text{ mol dm}^{-3} \\
\text{pH:} & \quad 13.3
\end{align*}
\]

For the PSI degradation experiments, a solution containing the required amounts of sodium and potassium hydroxides was used in the presence of an excess of calcium hydroxide solid. The solid calcium hydroxide was left in contact with the solution to ensure that saturation with portlandite was maintained throughout the degradation process.

For the current programme, where the intention was to keep the system as simple as possible, it was agreed with Nirex to use only sodium hydroxide to represent the alkali metal hydroxides in the porewater of a grouted wasteform. A concentration of 0.1 mol dm\(^{-3}\) was chosen. 10 g of calcium hydroxide solid were used per litre of sodium hydroxide solution as per the recipe used in reference \([40]\).

In common with preparations of ACDP leachates undertaken previously for Nirex, it was agreed that paper tissues would be used as the source of cellulosic material. A batch of Kimwipe® (Kimberly Clarke) tissues was obtained and set aside for this purpose.

### 2.5 Choice of Phase 1 experiments

The design of the Phase 1 experimental programme was based on recommendations in references \([14]\) and \([15]\) with the aim of building understanding of a number of the individual binary process identified in Figure 1.

The following programme of experiments was agreed with Nirex:

1) Preparation of CDP leachates using the new recipe and their initial characterisation in terms of ISA and other components by total organic carbon (TOC) and high performance liquid chromatography (HPLC). In particular, an intention was to measure a component ‘fingerprint’ for CDP by HPLC.

2) Batch sorption experiments to study the sorption of ISA onto haematite as a function of ISA concentration and pH. At the outset, the extent of sorption of ISA to haematite was not known. Therefore initial experiments were undertaken at relatively high concentrations of ISA (10\(^{-4}\), 10\(^{-3}\) and 10\(^{-2}\) mol dm\(^{-3}\)) that would be comparable with concentrations of ISA (and ACDP) used in previous experiments to study the impact of ISA (and ACDP) on radioelement sorption. The pH range of interest was from pH 6 to 12 covering the range of pH that may occur between the GDF near field and the undisturbed geosphere. It was agreed to undertake experiments at 6 nominal pH values in this range: pH 6, 7, 8, 9, 10 and 12. Analysis of the solutions after equilibration with haematite included analysis for iron to investigate possible dissolution of the haematite in the presence of ISA.

3) Batch sorption experiments in parallel to study the sorption of the CDP onto haematite at 6 pH values (6, 7, 8, 9, 10, 12) using ‘as-prepared’ CDP and at 10-fold dilution for comparison with ISA. Analysis of the solutions after contact with the haematite included (i) HPLC to look for changes in the amounts of CDP components in solution to identify sorbing components and (ii) analysis for dissolved iron.

\(^1\) PSI investigated cellulose degradation under anaerobic conditions at a temperature of 25 ± 2°C that were considered to be appropriate for the Swiss LLW/ILW disposal concept. Degradation times varied between 1 week and 4 years.
4) Further batch sorption experiments to study the sorption of ISA onto haematite as a function of pH and at lower ISA concentrations using C-14-labelled ISA.

5) Batch sorption experiments on the sorption of thorium to haematite in the presence and absence of organic complexants at 3 values of pH: 6, 9 and 12. Experiments were carried out in parallel with ISA and CDP to compare their impacts on thorium sorption to haematite.

A summary of the sorption experiments is given in Table 1

3 Materials

3.1 Haematite

The synthetic haematite selected for use in this study was a 99.999% purity 5.24 g cm\(^{-3}\) 100 mesh (particle size nominally <150 µm) ferric oxide powder supplied through Acros Organics. Two batches of material were used that were found to have been prepared by different manufacturers and which differed slightly in their surface area and trace element compositions. Both materials were confirmed to be haematite by X-ray powder diffraction. Fe and O were the only elements detected by Energy Dispersive X-ray analysis (EDX) confirming that no minor mineral components were present.

Material from the first batch of haematite (Lot A0182079) had been used for a previous study of the effect of organic complexants on radioelement sorption under geosphere conditions \[16\]. The surface area of this powder had previously been measured to be 5.58 ± 0.02 m\(^2\) g\(^{-1}\) by the multi-point BET nitrogen adsorption method. The BET surface area of the second batch powder (Lot A0228333) was measured to be 13.6 ± 0.1 m\(^2\) g\(^{-1}\). Two electron micrographs of the second powder are shown in Figure 2. The powder consists of aggregates of smaller particles with a grain size less than a few µm. Image analysis found that the majority of particles were less than 1 µm\(^2\) in cross-sectional area.

3.2 ISA

Iso-saccharinic acid was used from a batch of the α- (erythro-) isomer in the lactone form identified as PDR7A Batch 1 and dated 28 October 1992.

C-14- labelled ISA was supplied by Amersham International in solid form (37 MBq). A stock solution was prepared by dissolving the solid in 5 cm\(^3\) of 0.01 mol dm\(^{-3}\) hydrochloric acid.

3.3 Thorium

Th-228 and Th-232 were supplied by AEA Technology Nuclear Science, Harwell. Th-228 was obtained in the form of a stock solution in 2 mol dm\(^{-3}\) nitric acid. Th-232 was obtained as thorium nitrate pentahydrate.
4 Preparation of cellulose degradation product leachate

4.1 Degradation procedure

Two batches of CDP leachate have been prepared according to the recipe described above, without the presence of NRVB. The degradations and all liquid handling were undertaken under anaerobic conditions in a nitrogen atmosphere glovebox.

5g of calcium hydroxide and 20g Kimwipe® tissues were placed inside each of five stainless steel canisters. 500 cm$^3$ of 0.1 mol dm$^{-3}$ sodium hydroxide solution prepared in nitrogen-sparged demineralised water were added to each container to give a liquid to cellulose ratio of 25:1. The canisters were then sealed, placed in an oven within the glovebox and heated at 80°C for 30 days.

At the end of one month, the canisters were removed from the oven, cooled and the leachate was separated from any solid material by filtration through a 500 cm$^3$ 0.45 μm pore size polyethylysulphone (PES) membrane filter unit, (Nalgene Filtration Products). Each filter unit was pre-treated with about 50 cm$^3$ of leachate before filtered leachate was collected. Samples of the filtrate were retained and frozen for possible later analysis by HPLC, if required; the bulk filtrates were then combined. Two batches were produced in identical fashion yielding a total of approximately 4.5 dm$^3$ of CDP leachate.

Samples of the two CDP batches were taken for TOC analysis and for component analysis by HPLC at Loughborough University. Further analyses for major metal ion content (Ca, Fe, Na and K) were undertaken on samples from Batch II. In addition, the effect of filtration through a 30,000 nominal molecular weight cut-off filter was investigated on Batch II samples.

Prior to the start of batch sorption experiments, the bulk CDP leachate from Batch I was stored in a nitrogen atmosphere glovebox at room temperature in PTFE containers. Subsequently, the remaining volume of Batch I and the Batch II leachate were sealed with PTFE tape and then transferred to a refrigerator for longer-term storage at <5°C.

4.2 Analytical methods

4.2.1 Metals analysis and total organic carbon

Analyses of the CDP leachates were undertaken by Alcontrol Geochem, Chester, using laboratory methods accredited to ISO 17025 (with the exception of sodium and potassium analyses).

Total organic carbon (TOC) present in the sample was measured by oxidation to carbon dioxide with sodium persulphate at 100°C. The total mass of carbon dioxide released was measured with a non-dispersive infra-red detector. Before TOC analysis, the sample was acidified and purged to remove inorganic carbon (carbonates).

Calcium and iron concentrations were measured by inductively coupled plasma-mass spectrometry (ICP-MS) and sodium and potassium concentrations by flame photometry.

4.2.2 High performance liquid chromatography

HPLC separation and analysis of the CDP was undertaken using an Agilent LC28 HPLC with a 1090 series diode array detector. The separation was undertaken using a Waters Resolve C18 5μm 30 × 300 mm column with 0.1 mol dm$^{-3}$ potassium dihydrogen orthophosphate solution,
adjusted to a pH of 3.2 with orthophosphoric acid, as the mobile phase. Runs were undertaken under isocratic conditions at a flow rate of 0.7 cm$^3$ per minute. For each sample studied, measurements were run in triplicate with an injection volume of 20 mm$^3$. Detection was undertaken at a wavelength of 210 nm; chromatograms were recorded electronically for a period of 20 minutes per run. Component peak retention times and areas (by integration between manually selected time limits) were measured.

The column and mobile phase were the same as those used previously on the Nirex programme to resolve ACDP components [37], based on a method developed originally by Dickerson [41].

Standard solutions of $\alpha$-ISA were prepared at concentrations of $10^{-4}$, $5 \times 10^{-4}$, $10^{-3}$ and $10^{-2}$ mol dm$^{-3}$ at a pH value of about 12 in a sodium hydroxide solution. This was to ensure that the injected ISA was in the open chain rather than the lactone form. Triplicate runs were undertaken using the ISA standard solutions both before and after a batch of sample runs.

The tentative identification of a number of possible simple carboxylic acid components of the CDP leachate, formic acid, lactic acid and acetic acid, was made by the method of standard addition. These three compounds had been tentatively identified previously as being present in ACDP leachates [37]. A 1 mm$^3$ aliquot of formic acid was added to a 10 cm$^3$ sample of a CDP leachate solution derived from batch I and three samples were taken for analysis by HPLC; this process was repeated for lactic acid and then acetic acid.

### 4.3 Analytical results

#### 4.3.1 Metal analyses and total organic carbon

The results of TOC and elemental analyses on the CDP are summarised in Table 2. The TOC values for both batches are similar and about 2000 mg dm$^{-3}$ carbon. It is notable that the CDP contains about $1.8 \times 10^{-6}$ mol dm$^{-3}$ of iron, leached from the stainless steel containers and/or from the paper tissues. Filtration of the CDP through a 30,000 NMWCO filter had no apparent effect on either the TOC or the elemental composition indicating that the CDP does not contain any significant concentration of higher molecular weight (colloidal) species. The final pH of each batch was about 12.8.

The TOC values indicate a carbon concentration in the leachate of about 0.16 mol dm$^{-3}$. If all of this carbon was present as ISA (with molecular formula $C_6H_{12}O_6$), this concentration would be equivalent to an ISA concentration of the order $3 \times 10^{-2}$ mol dm$^{-3}$.

The TOC results in Table 2 compare with a value of 2080 mg dm$^{-3}$ carbon measured for a CDP prepared previously in the presence of excess Ca(OH)$_2$ rather than NRVB [42].

If it assumed that the tissues used for the degradations are composed of 100% cellulose, which has the molecular formula $(C_6H_{10}O_5)_n$, then the TOC data implies that approximately 11% of the cellulose has degraded to form soluble products.

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2 The solution used was from an experiment in which the CDP leachate had been equilibrated with haematite for 34 days at pH ~6. However, only a very small fraction of the CDP components were removed by sorption to the haematite as confirmed by the HPLC analysis. See sub-section 6.1.1 for further details.

3 In the preparation described in reference [42], a 10% solid loading of cellulose was used. The recipe comprised: 10 g of tissues : 90 g Ca(OH)$_2$ solid : 250 cm$^3$ of demineralised water. The cellulose was degraded anaerobically for 52 days at 80°C.

4 It is possible that some products may be solubility-limited (e.g. by forming calcium salts of low solubility) or be retained by sorption to the calcium hydroxide present.
4.3.2 HPLC Results

Typical traces for a CDP component analysis by HPLC are shown in Figure 3, in which results for the two batches of CDP are compared (batch I in red; batch II in blue) with data for a standard $10^{-2}$ mol dm$^{-3}$ solution of $\alpha$-ISA in the open chain form. The chromatograph of $\alpha$-ISA has a single major peak at a retention time of about 3.6 minutes (note that an injection peak is observed at about 3.0 minutes).

The component fingerprints for the two CDP batches are very similar. The CDP leachates show two principal peaks: one at 3.6 minutes attributable to ISA and a second at 4.4 minutes, which has yet to be identified. The peak observed at 3.6 minutes for the CDP leachates is noticeably broader than the equivalent peak in the $\alpha$-ISA solution and has a shoulder with a shorter retention time.

Degradation of cellulosic materials in the presence of calcium is known to yield both the $\alpha$- and $\beta$-(threo)- isomers of ISA in roughly equal proportions as the major products \[43\]. Previous studies by HPLC onto a similar Waters Resolve C18 column, have shown that the $\alpha$- and $\beta$-isomers of ISA have similar retention times but that a mixture of pure isomers can be distinguished at lower column temperatures (~13.4°C), where the $\beta$-isomer appears slightly before the $\alpha$- isomer. The broadness of the chromatographic peak measured at 3.6 minutes for the CDP is ascribed to the presence of both $\alpha$- and $\beta$-ISA. In addition, at least one additional component with slightly shorter retention time than ISA appears to be present. This peak was more clearly resolved in later measurements (see Section 6.1).

Comparison of the areas for the 3.6 minute peaks suggests that if the peak arose purely from ISA, its concentration in the CDP leachates would be up to about $1.9 \times 10^{-2}$ mol dm$^{-3}$. This is about one order of magnitude higher than the ISA concentrations considered to be present in ACDPs used previously on the Nirex programme (which were prepared in the presence of NRVB). For example, a total ISA concentration of $2.6 \times 10^{-3}$ mol dm$^{-3}$ was measured by Hurdus and Pilkington by spectrophotometric assay \[37\]. The above figure should be regarded as a maximum value for ISA given that the envelope of the 3.6 minute peak could include non-ISA components.

In addition to the two principal peaks, at least seven minor component peaks or shoulders were identified in the chromatograms as seen in Figure 3 and listed in Table 3\[5\]. Standard additions of formic acid, lactic acid and acetic acid gave enhanced peaks at 3.48, 4.28\[6\] and 4.76 minutes respectively, which provide tentative identification of three minor components as shown in Figure 4.

Further analysis of fractions containing these components would be required, e.g. by liquid-chromatography-mass spectrometry (LC-MS), to confirm the presence of these components.

Later HPLC measurements on a fresh solution of the lactone form of $\alpha$-ISA (in which a new column with different retention time was used) confirmed that the second major component of the ACDP leachates was not the lactone form of $\alpha$-ISA (see Section 6.1).

The close agreement between the HPLC traces for the two batches of CDP gives confidence that the degradation procedure is reproducible.

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\[5\] In addition, there is a strong, negative peak in the chromatogram of CDP samples at just over 5 minutes. Such a peak may indicate the presence of a solute with a lower UV absorbance at 210 nm than the mobile phase. This feature has not been observed previously in liquid chromatograms of CDPs. Further investigation of the origin of this peak has been beyond the scope of this study.

\[6\] It should be noted that a slight shift in retention time of the unidentified peak was observed to ~4.4 minutes in later chromatograms and this peak is distinct from the 4.28 minute peak tentatively ascribed to lactic acid, as seen in Figure 4.
5 Sorption Experiments

5.1 Sorption of ISA and CDP onto haematite

All sorption experiments were undertaken at room temperature under anaerobic conditions in a nitrogen atmosphere glovebox. Several series of batch sorption experiments were set up to measure the sorption of ISA and CDP onto haematite as a function of organic complexant concentration and pH. The experiments were also designed to measure the solubility of iron(III) from dissolution of the haematite solid phase under the varying experimental conditions. In addition, the experiments were undertaken at concentrations of the organic complexants (greater than or equal to $10^{-4}$ mol dm$^{-3}$ ISA) that were sufficiently high to allow the equilibrated solutions to be studied by HPLC. The intention here was to investigate whether CDP components that were preferentially sorbed onto the haematite could be identified from changes in the fingerprint of the CDP components.

The following series of batch sorption experiments were set up in triplicate for one month’s equilibration in a nitrogen atmosphere glovebox.

- Sorption of ISA at 3 concentrations ($10^{-2}$, $10^{-3}$ and $10^{-4}$ mol dm$^{-3}$) in the presence of haematite in 0.1 mol dm$^{-3}$ NaCl solutions at 6 pH values: pH 6, 7, 8, 9, 10 and 12;
- Sorption of CDP, as prepared and after a ten-fold dilution (referred to as 10% CDP below), in the presence of haematite in 0.1 mol dm$^{-3}$ NaCl solutions at 6 pH values: pH 6, 7, 8, 9, 10 and 12;
- Blank experiments in which haematite was contacted with 0.1 mol dm$^{-3}$ NaCl solutions without any organic complexants at 6 pH values: pH 6, 7, 8, 9, 10 and 12.

A number of additional experiments were set up with ISA at a concentration of $10^{-3}$ mol dm$^{-3}$ at pH values of 6, 9 and 12 to allow the extent of sorption with equilibration time to be followed.

All solution handling was undertaken in a nitrogen atmosphere glovebox and solutions were prepared using nitrogen-sparged demineralised water.

The ISA solutions were prepared from an original 0.011 mol dm$^{-3}$ stock solution that was prepared by dissolving solid α-ISA in the lactone form in 0.1 mol dm$^{-3}$ NaCl solution. A sufficient volume of each ISA solution was prepared by dilution with 0.1 mol dm$^{-3}$ NaCl solution and the pH was adjusted to the required value by the addition of an appropriate volume of NaOH solution.

CDP leachate from Batch I was used. For sorption experiments with the ‘as-prepared’ CDP, portions of the leachate were adjusted (from pH ~12.8) to the required pH by the addition of hydrochloric acid solution. No additional sodium chloride electrolyte was added to these experiments. For experiments with 10% CDP, portions of the leachate were diluted with 0.1 mol dm$^{-3}$ NaCl solution and the pH values adjusted to the required values by addition of hydrochloric acid solution.

Sorption experiments were undertaken at a liquid to solid ratio of 50 to 1 in triplicate, with a fourth tube set aside for pH measurements. 0.8g of haematite was weighed out into 120 screw-capped 50 cm$^3$ centrifuge tubes. For each combination of ISA or CDP, organic concentration and pH, a 10 cm$^3$ aliquot of the ISA or CDP-containing solution was taken and filtered through a pre-conditioned 0.45 μm syringe filter (Millipore Millex) into a glass sample vial to measure the initial TOC concentration of the ISA or CDP (C$_o$) in the experiments. 40 cm$^3$ of the solution was then filtered through the 0.45 μm Millex filter into each of four tubes containing haematite. A second sample of the initial ISA or CDP solution was then taken for a duplicate C$_o$ TOC measurement.
The centrifuge tubes were shaken well to mix. The pH was measured in the pH tube from each set and was corrected to the required pH (6, 7, 8, 9, 10 or 12), by the addition of 0.1 or 1.0 mol dm\(^{-3}\) sodium hydroxide solution or hydrochloric acid. An equivalent volume of sodium hydroxide solution or hydrochloric acid was then added to the three other tubes in the set. The samples were re-shaken and left to equilibrate.

In addition to the sorption experiments with organic complexants, a series of triplicate blank experiments were prepared in which 0.8g of haematite were contacted with 40 cm\(^3\) of 0.1 mol dm\(^{-3}\) NaCl solution adjusted to pH values of 6, 7, 8, 9, 10 or 12. These experiments were designed to measure the dissolution of iron(III) from the haematite solid phase in the absence of the organic complexants.

Samples of the ISA and CDP solutions at each concentration and pH value were set aside in the glovebox under the same conditions as the sorption experiments as controls to test whether any degradation of the organic complexants (e.g. due to microbial activity) occurred over the duration of the sorption experiments.

(a) pH buffering of ISA sorption experiments

The pH of each experiment was re-measured after two week’s equilibration to check whether significant drift of the pH had occurred from the target value and to make any necessary adjustments. In almost all of the experiments with ISA with a target pH at or below pH 10, a significant drift of the pH to lower values by over one unit was observed. In the case of the experiments at the highest ISA concentration at pH 6, 7, 8 and 9, the pH had fallen to values of about 4. With the exception of the ISA experiments at pH 10, further slow but significant pH buffering to lower values was observed despite repeated adjustments of the pH back to the target values with the addition of sodium hydroxide solution.

The blank experiments with haematite were not affected in this way, nor were the experiments with CDP at all target pH values or with ISA at pH 12. In general, these experiments appeared to show pH drift towards the expected point of zero charge (PZC) of the haematite between pH 8 and 9 (i.e. experiments at pH 6, 7 and 8 tended to show an upward drift of pH values).

The pH drift observed in the experiments with ISA is attributable to the use of ISA solid in the lactone form, which is favoured in solution under acid conditions, to prepare the initial ISA stock solutions. ISA lactone undergoes slow hydrolysis to the open chain, acid form at higher pH with an estimated half-life for the ring opening reaction of about 16 hours, based on a first-order rate constant of 4.85 \(10^{-3}\) min\(^{-1}\) given in reference [44]. Dissociation of the acid form then leads to a drop in pH. Being a weak acid, the open chain form of ISA will then act as a pH buffer.

It appears that the ISA solutions were not allowed to equilibrate for long enough before the start of the experiments, so that a significant proportion of the ISA lactone remained in the lower pH solutions\(^7\). Subsequent ring-opening of the lactone would explain the pH-buffering observed. For this reason it was not possible to maintain the experiments at nominal pH values less than 10 at the required pH values; they consistently drifted down to pH 5 or less. Therefore, the experiments at nominal pH values of 6-9 were terminated.

Experiments with ISA at higher pH values (10 and 12) were not affected in this way owing to the higher initial pH. The experiments containing CDP leachate were also unaffected as the CDP

\(^7\) Previous work undertaken on the Nirex programme had suggested that at near-neutral pH and in the presence of a phosphate buffer, ring opening of ISA lactone to the open chain form occurred rapidly and was nearly complete within a few minutes [25]. However, the methodology used in that earlier study, in which samples were frozen and defrosted prior to HPLC analysis, appears to be misleading in terms of the timescale over which the ring-opening reaction occurred, since the reaction would have continued in the samples during the freezing and defrosting periods and during any subsequent delay prior to analysis.
was prepared under alkaline conditions; the ISA present was in the open chain form, as indicated by the HPLC analysis.

(b) Final Sampling

After at least one month’s equilibration, the remaining sorption experiments were sampled and filtered through 30,000 NMWCO filters (Millipore TTK). The filters were washed using 2 cm$^3$ of demineralised water and then pre-conditioned with 2 cm$^3$ of the solution to be sampled. These filtrates were discarded. Two samples were collected from each experiment (tubes B, C and D), one of 20 cm$^3$ for final TOC (C$_f$) and one of 14 cm$^3$ for iron concentration measurement by ICP-MS, prior to final pH measurements.

Two of the three tubes from each set of haematite blank experiments (with no added ISA or CDPs) at all 6 nominal pH values were sampled in the same way as above for iron analysis by ICP-MS only.

Iron and TOC analyses were undertaken by Alcontrol Geochem, Chester, using the methods outlined in sub-Section 4.2.1.

The fourth tube (tube A) from each set of sorption experiments was sampled in a similar way as above for analysis by HPLC using the methods described previously. Two batches of samples were sent to Loughborough University for analysis. For the first batch, the A-tube experiments with ISA solutions (at all three concentrations) and CDP leachate (100%) were sampled after 34-36 days equilibration and were refrigerated prior to analysis by HPLC within 13 days of sampling.

A second batch of samples was collected for HPLC analysis after about 12 weeks equilibration. The A-tube experiments with 10% CDP solutions at the 6 nominal pH values were sampled after 84 days equilibration and those from additional sorption experiments with $10^{-3}$ mol dm$^{-3}$ ISA solutions at nominal pH values of 6, 9 and 12 after 82 days. These samples were refrigerated and analysed 8 days after sampling.

In addition, the second batch included the control samples of the CDP leachate and 10% CDP solutions at nominal pH values of 6, 9 and 12 that had been stored in the nitrogen atmosphere for 42 days and 82 days respectively prior to refrigeration and analysis, which was after a total of 90 days.

5.1.1 High performance liquid chromatography

HPLC separation and analysis was undertaken using the methods outlined in sub-Section 4.2.2. Two sets of samples were supplied to Loughborough University, which were analysed on different Waters Resolve C18 columns. Unfortunately, these columns differed in the extent to which the CDP components were separated and retained so that the two sets of results cannot be compared directly. Separation of components was improved and retention times were somewhat longer for samples from the second set that were analysed using a newer column.

The following samples were supplied to Loughborough University for HPLC analysis.

Set 1:

- CDP leachate samples from Batches I and II;
- $10^{-2}$ mol dm$^{-3}$ ISA in 0.1 mol dm$^{-3}$ NaCl stock solution at pH ~10;
- A-tubes from 100% CDP-haematite batch sorption experiments, post equilibration for 5 weeks and 30,000 NMWCO-filtered;
- A-tubes from pH 10 and pH 12 ISA-haematite batch sorption experiments at $10^{-2}$, $10^{-3}$ and $10^{-4}$ mol dm$^{-3}$ concentrations of ISA, post equilibration for 5 weeks and 30,000 NMWCO-filtered.
Set 2:

- A-tubes from 10% CDP-haematite batch sorption experiments, post equilibration for 84 days, 30,000 NMWCO-filtered;
- $10^{-3}$ mol dm$^{-3}$ ISA 82-day equilibration experiment samples at pH 6, 9 & 12, 30,000 NMWCO-filtered;
- 100% CDP Blank samples at pH 6, 9 & 12, after equilibration for 42 days;
- 10% CDP Blank samples at pH 6, 9 & 12, after equilibration for 82 days;
- Deionised water, 30,000 NMWCO-filtered;
- $\alpha$-ISA lactone sample PRD 7A (solid).

5.2 Sorption of C-14 labelled ISA onto haematite

Following the termination of the sorption experiments with ISA at near-neutral pH values described above, further batch sorption experiments were undertaken with ISA but extending to lower ISA concentrations and with the addition of C-14 labelled ISA to improve the accuracy and lower the limits of detection for analysis.

Three initial ISA concentrations were chosen ($2 \times 10^{-3}$, $2 \times 10^{-5}$ and $2 \times 10^{-7}$ mol dm$^{-3}$) to span a range in initial concentration that is similar to that used previously in ISA sorption experiments onto samples of crushed rock [24]. The six target pH values of 6, 7, 8, 9, 10 and 12, and the background electrolyte (0.1 mol dm$^{-3}$ sodium chloride solution) were the same as in the previous suite of experiments.

A stock solution of $10^{-2}$ mol dm$^{-3}$ $\alpha$-ISA in the open chain form was prepared by dissolving $\alpha$-ISA lactone in demineralised water, adjusting the pH to 12 by the addition of sodium hydroxide solution and allowing the solution to equilibrate (at a temperature below 5°C) for over one week.

Solutions of ISA at concentrations of $2 \times 10^{-3}$, $2 \times 10^{-5}$ and $1.6 \times 10^{-7}$ mol dm$^{-3}$ were prepared by successive dilutions of the initial stock solution with 0.1 mol dm$^{-3}$ NaCl solution. An aliquot of C-14 labelled ISA solution was then added to each of the three solutions to give a C-14 activity of about 92 Bq cm$^{-3}$ (equivalent to $4 \times 10^{-8}$ mol dm$^{-3}$ C-14-ISA).

Sorption experiments were undertaken at a liquid to solid ratio of 50:1 using 0.6g of haematite per tube from the second batch of material. Each set of experiments was undertaken in triplicate with an additional tube (A tube) set up for measurement of pH and pH adjustment (which was then applied to the other 3 tubes). The experiments were set up in a similar manner to the previous experiments with two $C_0$ samples taken per set (these were acidified with nitric acid).

The batches were left to equilibrate for between 48 and 50 days prior to sampling, with occasional pH-checking of the A-tube.

The solution phase of each experiment was separated by filtration through pre-conditioned 30,000 NMWCO filters (Millipore TTK) prior to analysis. The filters were washed using 2 cm$^3$ of demineralised water and then pre-conditioned with 2 cm$^3$ of the solution to be sampled. These filtrates were discarded. An 18 cm$^3$ sample was filtered from each experiment (tubes B, C and D) and acidified with 1cm$^3$ of 1mol dm$^{-3}$ hydrochloric acid. The pH value of the remaining solution was then measured. Finally each tube was emptied, rinsed with demineralised water and then leached with 40 cm$^3$ 25% HNO$_3$ for over 18 hours, to recover ISA sorbed to the vessel walls.

C-14 analysis of the solution phase and wall wash samples by direct liquid scintillation counting (LSC) was undertaken by NIRAS.
5.3 Effect of organic complexants on thorium sorption onto haematite

The following sets of quadruplicate batch sorption experiments with thorium were undertaken in a nitrogen atmosphere glovebox:

- Sorption of thorium onto haematite in the absence of organic complexants in 0.1 mol dm\(^{-3}\) NaCl solutions at 3 pH values: pH 6, 9 and 12;
- Sorption of thorium onto haematite in 0.1 mol dm\(^{-3}\) NaCl solutions containing 2 \(10^{-3}\) mol dm\(^{-3}\) ISA at 3 pH values: pH 6, 9 and 12;
- Sorption of thorium onto haematite in a 1 part in 10 dilution of CDP in 0.1 mol dm\(^{-3}\) NaCl solutions at 3 pH values: pH 6, 9 and 12.

For the experiments with ISA and CDP, the complexant concentrations were chosen such that the ISA concentrations would be similar to those considered to be present in ACDP leachates (prepared in the presence of bulk NRVB) used previously in radionuclide sorption experiments onto crushed rock on the Nirex programme [e.g. 22-24]. To enable comparison with previous results, a 2 \(10^{-3}\) mol dm\(^{-3}\) solution of ISA and a 1 in 10 dilution of CDP leachate (from batch II) were used for the ISA and CDP ternary experiments with thorium, respectively.

The haematite used in the batch sorption experiments was fresh material (from batch II) that had not been in contact with solution. An additional set of duplicate thorium sorption experiments was set up, without organics, using haematite that had been pre-equilibrated with 0.1 mol dm\(^{-3}\) NaCl solutions at pH values of 6, 9 and 12. These additional experiments were undertaken owing to concerns that the surface of the haematite, as-supplied, (which is a high density material, apparently prepared at high temperature) may not be fully hydroxylated, which may affect the number and nature of surface sites available for sorption.

The haematite used in these additional experiments was material from batch I which had been used in previous blank experiments, run in duplicate, to measure iron solubility in 0.1 mol dm\(^{-3}\) NaCl solution as a function of pH (see sub-section 5.1). The tubes were centrifuged at 4200 rpm for 10 minutes to sediment the haematite; the solution phase was then removed.

The target thorium concentration for the experiments was \(\sim 3 \times 10^{-11}\) mol dm\(^{-3}\), about one order of magnitude below the solubility limit for thorium in water in the pH range from 6 to 12 [see e.g. 45]. A mixed thorium-228 and thorium-232 stock solution in 0.01 mol dm\(^{-3}\) hydrochloric acid was prepared containing 1.32 \(10^{-8}\) mol dm\(^{-3}\) Th-232 and 18,140 Bq cm\(^{-3}\) Th-228 (2.6 \(10^{-9}\) mol dm\(^{-3}\) thorium) with a total thorium concentration of 1.58 \(10^{-8}\) mol dm\(^{-3}\). This solution was diluted by a factor of 500 for use in the batch sorption experiments.

Batch sorption experiments were undertaken at a liquid to solid ratio of 50:1. Experiments were undertaken in quadruplicate with a fifth sample (tube A) for intermediate pH checking and adjustment.

Each set of experiments was set up in the following manner. The required amount of thorium stock solution was added to a volume of 0.1 mol dm\(^{-3}\) sodium chloride solution (with or without added ISA or CDP) and the pH was adjusted to the required value by addition of small volumes of 0.1 and 0.01 mol dm\(^{-3}\) sodium hydroxide solutions. To remove any particulate thorium hydroxide generated during either thorium or alkali addition, the solution was pre-filtered through a 0.45 μm syringe filter (Millipore Millex) before use in the experiments. First, 10 cm\(^3\) of the solution was used to pre-condition the 0.45 μm filter and this was discarded to waste. A 5 cm\(^3\) aliquot of the solution was then filtered directly into a vial containing 1 cm\(^3\) of 50% nitric acid, to measure the initial thorium concentration (C\(_0\)). 30 cm\(^3\) of solution was then filtered into each of centrifuge tubes containing 0.6g haematite (batch II). In addition, for the thorium-only experiments, 40 cm\(^3\) of solution were added to the two tubes containing the 0.8 g of pre-equilibrated haematite (from batch I). Finally a second 5 cm\(^3\) aliquot of the solution was taken and acidified as a second C\(_0\) sample.
The experiments were left to equilibrate for between 43 and 49 days with intermediate pH checking (using tube A) and pH adjustment as described previously. After 2 months, 20 cm$^3$ samples of the aqueous phase were taken from each experiment, filtered through washed and pre-conditioned 30,000 NMWCO filters (Millipore TTK) and then acidified with 2 cm$^3$ 4 mol dm$^{-3}$ nitric acid. Each filter was washed with 2 cm$^3$ demineralised water and then pre-conditioned with 4 cm$^3$ of the solution to be filtered. These filtrates were discarded. Samples B and D and C and E in each set were filtered using the same filter unit, with the described pre-treatment prior to sampling on both occasions. The pH of each experiment was measured after sampling.

After sampling, each experimental tubes was emptied, washed with demineralised water to remove any remaining solid phase and leached with 30 cm$^3$ of 25% nitric acid for several days to recover any radionuclide associated with the vessel walls. Wall wash samples were combined from tubes B and C and tubes D and E for analysis.

All solution phase and wall wash samples were analysed for Th-228 by alpha spectrometry.

5.4 Radiochemical Analysis

Radiochemical analyses were undertaken by NIRAS analytical services, Birchwood Park, Warrington.

Thorium-228 was isolated from the supplied solution by anion-exchange chromatography. The purified thorium was then electro-deposited onto a stainless steel disc to produce a uniform source. The electro-deposited sources were counted for an appropriate length of time using an Ortec Plus alpha spectrometer and the spectrum analysed using Ortec Maestro 32MCA emulator software. Thorium-229 was used as an internal standard for the procedure.

Carbon-14 analyses were undertaken by liquid scintillation counting. The counting efficiency was measured by standard addition using a certified carbon-14 solution ($^{14}$C-carbonate). However, some problems were encountered measuring the $C_o$ samples that were supplied to NIRAS in a higher concentration of nitric acid, leading to measured C-14 concentrations that were too high (up to 3 times higher than expected target activity). For these samples, matrix effects on counting efficiency appeared to be different for the organic C-14-ISA compared to the inorganic $^{14}$C-carbonate standard$^8$. Neutralisation of the supplied solutions with sodium hydroxide prior to measurement was found to improve but not entirely mitigate the problem. Where possible the $C_o$ measurements were repeated and the spread of $C_o$ values was reduced significantly. $C_t$ samples that were supplied in more dilute hydrochloric acid were not subject to matrix effects in this way.

5.5 Calculation of $R_D$ values

Values for the sorption distribution ratio, $R_D$, of each radionuclide onto the haematite were calculated for each experiment using the equation:

$$R_D = \frac{V}{m} \left( \frac{C_o - C_w - C_t}{C_t} \right),$$

where: $V$ is the solution volume (cm$^3$) equilibrated with mass, $m$, of mineral (g); $C_o$ is the initial concentration of radionuclide; $C_w$ is the concentration of radionuclide sorbed to the walls of the container; and $C_t$ is the final measured radionuclide concentration (all concentrations Bq cm$^{-3}$).

$^8$ Loss of C-14 standard as $^{14}$CO$_2$ is also suspected.
In general, the experimental uncertainties in the measured $R_D$ values are based on the analytical errors in measured radionuclide concentrations, which include counting errors and errors associated with internal calibration with yield tracers. The quoted errors are two sigma.

In the case of the C-14 ISA experiments, where the initial C-14 activities in all of the experiments were expected to be similar, the spread of the measured $C_0$ results (even after pre-neutralisation to reduce the matrix effects) remained unsatisfactorily large (nearly a factor of two) and there were some experimental sets for which it had not been possible to repeat the $C_0$ measurements. Therefore the $C_0$ results were screened and a common mean $C_0$ value for all datasets was calculated from those measurements that were within 30% of the expected value. The calculated mean of 107.9 Bq cm$^{-3}$ has a two sigma uncertainty of nearly 20% which introduces a significant uncertainty into the calculated $R_D$ values for C-14 ISA.

5.6 pH Measurement

pH measurements were made using a Whatman PHA 2000 pH meter or a Phillips PW 9420 meter and a Russell combination pH/reference electrode (pH range 0 to 14) (type CWL/DJ/S7), and calibrated using pH 7 and 10 buffers (as required by the in-built calibration procedure for the Whatman meter) supplied by Whatman. The response was then checked against a pH 13 buffer.

6 Results

6.1 Sorption of ISA and CDP onto haematite

6.1.1 TOC and HPLC

The TOC results for the sorption experiments with ISA at the three initial concentrations and at pH values of 10 and 12 are presented in Table 4 and shown in Figure 5, in which the TOC values for the three experimental tubes are compared with the two $C_0$ values. At the two higher ISA concentrations ($10^{-2}$ and $10^{-3}$ mol dm$^{-3}$) there is no distinguishable difference between the initial and final TOC concentrations measured within experimental error. Therefore, the extent of sorption of ISA to the haematite at pH 10 and at pH 12 at these ISA concentrations is low.

At $10^{-4}$ mol dm$^{-3}$ ISA (TOC = 8 mg dm$^{-3}$), the final TOC concentrations were all found to be higher than the initial concentrations. This is attributed to the presence of additional organic material in the final solutions that had been leached from the 30,000 NMWCO filters. Separate tests have shown that about 10 mg dm$^{-3}$ TOC of organic material is leached from the 30,000 NMWCO filters when 30 cm$^3$ of demineralised water is passed through.

The results of the sorption experiments with CDP are summarised in a similar way in Figure 6. In common with the results for ISA, there is no distinguishable difference between the initial and final TOC concentrations measured within experimental error at any of the 6 pH values or at either CDP concentration studied.

The findings of the TOC measurements are supported by quantitative analysis of the A-tube samples by HPLC. The A-tube samples from the ISA sorption experiments at pH 10 and 12 and those from the CDP experiments with 100% CDP at different pH values show no major differences in peak areas for the major peaks at 3.6 and 4.4 minute peaks. These results confirm that sorption of ISA and the major CDP components onto the haematite is weak under the conditions studied.
In a similar way, the 6 A-tube samples from the sorption experiments with 10% CDP leachate showed no significant differences in measured peak areas after contact with haematite for 84 days at the different pH values. This is illustrated in Figure 7, which compares the measured peak areas for the solutions after contact with haematite at the 6 nominal pH values with results from control samples that were equilibrated under the nitrogen atmosphere but in the absence of haematite. These samples were analysed using the second HPLC column on which the major peak arising from ISA at ~3.6 minutes was shifted to 4.25 minutes and the second, unidentified component peak at ~4.4 minutes was shifted to 5.9 minutes.

Comparison of the chromatographs of the CDP leachates with a freshly-prepared solution of α-ISA lactone confirmed that the second major peak (5.9 minutes on column 2) was not the lactone form of ISA (Figure 8). The lactone peak appears at ~5.2 minutes on column 2. Although there was evidence for the ISA lactone in a 10⁻³ mol dm⁻³ ISA solution after contact with haematite for 82 days due to the presence of a second peak at ~5.3 minutes retention, there was no equivalent peak in the CDP leachates equilibrated at lower pH values. The closest peak at ~5.0 minutes retention time appears to be pH-independent which is not consistent with the ISA lactone.

On the basis of the HPLC results outlined above, there was little evidence for any chemical or microbiological degradation of ISA or CDP leachates in the nitrogen atmosphere over the 3-month timescale of the sorption experiments.

6.1.2 Dissolution of iron(III) in the presence and absence of organic complexants

The dissolution of iron from the surface of the haematite in the presence and absence of the organic complexants was also measured by ICP-MS (Table 4, Table 5 and Table 6). No iron was detectable in the blank experiments without added organics at any of the 6 pH values studied. The limit of detection was about 20 ppb or ~4 10⁻⁷ mol dm⁻³.

Iron was not detectable in the majority of the experiments with ISA at pH 10 and 12 (Table 4) except for two anomalously high measurements at final pH values of 8.3 and 10.1 at different ISA concentrations.

Some iron is already present in the CDP leachates, with a typical measured concentration of 2 10⁻⁶ mol dm⁻³ in Batch II (Table 2). An apparent enhancement in the dissolved iron concentration was noted in the presence of the as-prepared CDP at low pH (6) and high pH (10 and 12), with mean concentrations of 5-6 10⁻⁶ mol dm⁻³ (Table 5). For the 10% CDP solution, measured iron concentrations were, in general, close to the limit of detection except at pH 9.8-9.9 where the mean concentration was about 8 10⁻⁷ mol dm⁻³ (Table 6). These results suggest that some component(s) of CDP other than ISA may enhance the dissolution of iron from the haematite surface at high pH.

Some initial thermodynamic modelling of haematite solubility and iron speciation over the pH range of interest in the presence of ISA predicts that even at an ISA concentration of 10⁻² mol dm⁻³, the solubility of iron will remain below 10⁻⁸ mol dm⁻³ and thus below the limit of detection of ICP-MS as applied in these experiments [29].

6.2 Sorption of C-14-labelled ISA onto haematite

The results of the binary sorption experiments with C-14-labelled ISA onto haematite at three initial concentrations and at five nominal pH values are given in and are compared in Figure 9. The uncertainty in the initial ISA concentrations used to calculate the R_D values is reflected in the size of the error bars on the data.

ISA sorption to haematite at an initial concentration of 2 10⁻³ mol dm⁻³ ISA (Table 9) was weak at all pH values. In general, measured R_D values were less than 10 cm³ g⁻¹. The results at pH 10 and 12 were consistent with the previous measurements presented in Table 4. At a
lower initial concentration of $2 \times 10^{-5}$ mol dm$^{-3}$ ISA (Table 8), sorption of ISA at pH 12 was also very weak, but a significant increase in $R_0$ values was measured with decreasing pH. $R_0$ values increased from $<10$ cm$^3$ g$^{-1}$ at pH 12 to about 100 cm$^3$ g$^{-1}$ at pH 7 to 9.

The experiments at $2 \times 10^{-7}$ mol dm$^{-3}$ ISA gave somewhat different results (Table 7). Sorption of ISA to the haematite at pH 12 was stronger than at higher ISA concentrations with a mean $R_0$ value of about 36 cm$^3$ g$^{-1}$. However, there was no significant increase in ISA sorption observed across the pH range 6.5 to 12. Measured $R_0$ values in this pH range varied from $22 \pm 14$ to $68 \pm 22$ cm$^3$ g$^{-1}$ (excluding one anomalously low result at pH 10).

It would be expected that ISA sorption at the lowest ISA concentration would be comparable to or greater than that at $2 \times 10^{-5}$ mol dm$^{-3}$ ISA. If sorption at these two concentrations is described by a linear sorption isotherm, where $R_0$ is constant with ISA concentration, then the results at the two concentrations should be the same; otherwise the $R_0$ values would be expected to be greater for the lower ISA concentration. Clearly from Figure 9, neither of these expected trends is observed. Given the low concentration of $2 \times 10^{-7}$ mol dm$^{-3}$ ISA, it is more likely these results are affected by minor processes or impurities in the system. One possibility for the unexpectedly low sorption (relative to the $2 \times 10^{-5}$ mol dm$^{-3}$ ISA data) is that there is a small amount of readily extractable ferric iron associated with haematite that is complexed by low levels of ISA in solution.

### 6.3 Sorption of thorium onto haematite in the presence and absence of ISA or CDP

The results of the binary and ternary sorption experiments with thorium onto haematite at three nominal pH values are presented in and shown in Figure 10.

In all of the experiments, sorption of thorium to haematite is measured to be strong. In the absence of organic complexants (baseline case, fresh haematite), measured $R_0$ values at pH 12 range from $1.2-2.1 \times 10^5$ cm$^3$ g$^{-1}$ (Table 10). Thorium sorption at the lower pH values is about one order of magnitude stronger; at pH ~9 final solution concentrations of thorium are close to the limit of detection (and were below LoD in two cases) indicating $R_0$ values of $4 \times 10^5$ cm$^3$ g$^{-1}$ or higher. In the lowest final pH range 5.9-6.5, the $R_0$ values varied from $9 \times 10^5$ cm$^3$ g$^{-1}$ to $7 \times 10^6$ cm$^3$ g$^{-1}$. The results from experiments undertaken on pre-equilibrated haematite (Table 11) are consistent with those on the fresh material, considering that the experiments were undertaken using lower surface area haematite material from Batch I. There are some additional uncertainties with the absolute values for $R_0$ in these experiments in that the value for the solid to liquid ratio is not known accurately because existing experiments were re-used.

The presence of $2 \times 10^{-3}$ mol dm$^{-3}$ ISA appears to have a negligible effect on thorium sorption at pH 12 but to reduce sorption by up to an order of magnitude at (final) pH 5.5 to 6.6 (Table 12). The picture at pH 9 is less clear as two of the four final thorium concentrations are below the limit of detection but one is an order of magnitude higher.

The presence of 10 % CDP has a much more significant effect on thorium sorption; at pH 4.7 to 6.8 and pH ~9, sorption to haematite is reduced by about 2 orders of magnitude compared to the baseline case (Table 13). A reduction of at least one order of magnitude is observed at pH 12.
7 Discussion

7.1 Cellulose degradation product leachate

In the current study, two batches of CDP leachate have been prepared using a new generic recipe, which simulates the chemical conditions in the near-field porewater of a cementitious GDF but in the absence of bulk cementitious backfill or grout material. TOC and HPLC analyses have confirmed that the two batches are very similar in composition, confirming that the degradation process is reproducible.

7.1.1 Identification of CDP components

HPLC analysis has shown that the CDP leachates contain at least two major components and at least seven minor components, as listed in Table 3. The first major peak in the chromatogram coincides with that for the straight-chain form of the α-(erythro-)isomer of ISA (Figure 3) but is significantly broader, with a possible shoulder at shorter retention times, indicating the presence of additional components.

Degradation of cellulosic materials in the presence of calcium is known to yield both the α- and β-(threo)-isomers of ISA in roughly equal proportions as the major products [46]. In that study, four other acids have been tentatively identified as components of ACDP on the basis of their HPLC retention times: formic, lactic, acetic and 2-hydroxybutanoic acids.

Previous studies by HPLC onto a similar Waters Resolve C18 column, have shown that the α- and β-isomers of ISA have similar retention times but that a mixture of pure isomers can be distinguished at lower column temperatures (~13.4°C), where the β-isomer appears slightly before the α-isomer.

The appearance of the chromatographic peak at 3.6 minutes in this study is consistent with the presence of both α- and β-ISA. The presence of additional components with similar retention time, which has been suggested previously for ACDP [46], cannot be ruled out at this stage, however.

Some further investigations have been carried out by Loughborough University in an attempt to identify the second major component of the CDP, which gives rise to the peak at 4.4 minute retention time [47]. HPLC analysis has confirmed that it is not the lactone form of α-ISA (or the β-lactone which appear to have similar retention time [46]). Fractions containing the two main components of the CDP have been collected and analysed using a number of physical analysis techniques including proton nuclear magnetic resonance (NMR), liquid chromatography-mass spectrometry (LC-MS), infra-red (IR) and ultraviolet (UV) spectrosocopies. Results obtained to date indicate that the compounds present in the two peaks are very similar. The fractions have almost identical mass, IR and UV spectra, although some differences are observed in the proton NMR spectra. At this stage, these differences in the NMR are thought to arise from the presence of small amounts of other compounds present in the fractions as the peaks were not fully resolved.

7.1.2 ISA concentrations in CDP leachates

It is notable that the estimated maximum concentration of ISA measured in the CDP leachates generated in this study is about $1.9 \times 10^{-2}$ mol dm$^{-3}$, which is about 1 order of magnitude higher than concentrations considered previously in ACDP prepared in the presence of bulk NRVB, where a much higher solid content was used. TOC concentrations of about 2000 mg dm$^{-3}$ carbon, similar to those measured in the present study, were reported in a previous study in which tissues were degraded in the presence of bulk calcium hydroxide rather than NRVB [40].
The total concentration of ISA in ACDP produced by the standard recipe has been measured to be $2.6 \times 10^{-3}$ mol dm$^{-3}$ using a 2-thiobarbituric acid spectrophotometric assay [37]. In a separate study the total concentration of ISA plus lactone form was measured by HPLC to be $6 \pm 1 \times 10^{-4}$ mol dm$^{-3}$ in an ACDP leachate [37]. In general, it has been considered that the ISA concentration in ACDP is of the order of $10^{-3}$ mol dm$^{-3}$; an ISA concentration of $2 \times 10^{-3}$ mol dm$^{-3}$ has frequently been used in sorption studies on the Nirex programme as a simulant for ACDP [e.g. 24].

The most likely explanation for the higher ISA concentration in the CDP leachate prepared in this study compared to ACDP is that a significant amount of ISA is lost by sorption to NRVB in the preparation of ACDP leachate.

The sorption of ISA onto NRVB was studied previously on the Nirex programme [48, 49]. In saline NRVB-equilibrated waters, measured $R_D$ values for ISA onto NRVB were about $30 \text{ cm}^3 \text{ g}^{-1}$ at initial ISA concentrations in the range $10^{-6}$ to $10^{-4}$ mol dm$^{-3}$ ISA, but fell to $24 \text{ cm}^3 \text{ g}^{-1}$ at $10^{-3}$ mol dm$^{-3}$ ISA (initial) and $7 \text{ cm}^3 \text{ g}^{-1}$ at $10^{-2}$ mol dm$^{-3}$ ISA [49]. These measurements were all made at a liquid to solid ratio of 5:1. In non-saline NRVB equilibrated water, sorption measurements at a liquid to solid ratio of 5:1 and an initial ISA concentration of $10^{-2}$ mol dm$^{-3}$ ISA gave somewhat higher $R_D$ values of $\sim 59 \text{ cm}^3 \text{ g}^{-1}$ [48].

In ACDP preparations using the standard recipe with a solid to liquid ratio of 2.5 to 1 and under non-saline conditions, an $R_D$ value of $25 \text{ cm}^3 \text{ g}^{-1}$ for ISA sorption onto the NRVB would reduce the solution concentration of ISA in the leachate by a factor of 10 compared to the total amount of ISA generated. Some sorption of ISA may occur to the calcium hydroxide used in the new generic recipe. However, the similarity of TOC values measured here with those measured in a CDP leachate prepared in the presence of bulk calcium hydroxide [42], suggests that sorption to calcium hydroxide is much less significant than sorption to NRVB. In addition, given the much smaller amount of solid used, sorption to calcium hydroxide would have a much smaller effect on the final ISA concentration. The observed differences in ISA concentrations between the new CDP leachate and ACDP are consistent with levels of sorption measured previously for ISA sorption to NRVB [49, 48].

It is also noted that in a previous study of the rate of degradation of tissues in the presence of calcium hydroxide, it was estimated that about 6.3% of the initial mass of cellulose was degraded to soluble products over a period of 27 days at $80^\circ\text{C}$ in a nitrogen atmosphere [49]. This rate is lower but broadly comparable with the 11% degradation estimated over 30 days in the current study when taking into account the differences in the way the experiments were undertaken. Both estimates consider soluble products only and specifically exclude any ISA sorbed to the calcium hydroxide solid.

### 7.1.3 Stability of ISA/ACDP solutions

The observed stability of the ISA and CDP leachate solutions used in this study when stored under a nitrogen atmosphere at room temperature over the three-month timescale of the experiments is consistent with previous findings on the Nirex programme.

The alkaline degradation of ISA was studied in reference [48]. Some evidence for the chemical degradation of ISA was observed, but this was only significant after heating for one year at $80^\circ\text{C}$ in the presence of oxygen. Only about 5% degradation of ISA was observed over 10 months at

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9 In these degradation tests, 2.7g of Kimwipe® tissues, 10g of calcium hydroxide and initially 385 cm$^3$ of de-ionised water were placed in glass Duran bottles and heated at $80^\circ\text{C}$ for 113 days in an oven inside a nitrogen-atmosphere glovebox. The bottles were periodically removed from the oven and cooled to allow ~15 cm$^3$ samples of the aqueous solution to be taken for TOC analysis. The sample volumes removed were not replaced.
room temperature under air or oxygen and only a small amount of degradation was observed over one year at 80°C in nitrogen.

### 7.2 Sorption of ISA onto haematite

The results of the ISA sorption experiments onto haematite show the following trends (Figure 5):

- ISA sorption onto haematite at an initial concentration of $2 \times 10^{-3}$ mol dm$^{-3}$ ISA was weak at all pH values; measured $R_0$ values were less than 10 cm$^3$ g$^{-1}$.
- At a lower initial concentration of $2 \times 10^{-5}$ mol dm$^{-3}$ ISA, sorption of ISA at pH 12 was also very weak, but a significant increase in $R_0$ values was measured with decreasing pH; $R_0$ values increased from <10 cm$^3$ g$^{-1}$ at pH 12 to about 100 cm$^3$ g$^{-1}$ at pH 7 to 9.
- At $2 \times 10^{-7}$ mol dm$^{-3}$ ISA (initial) sorption of ISA to haematite at pH 12 was stronger than at higher ISA concentrations with a mean $R_0$ value of about 36 cm$^3$ g$^{-1}$. There was no significant increase in ISA sorption observed across the pH range 6.5 to 12. Measured $R_0$ values in this pH range varied from 22 ± 14 to 68 ± 22 cm$^3$ g$^{-1}$.

Qualitatively, the trends in measured $R_0$ values for ISA onto haematite with pH and ISA concentration at the two higher ISA concentrations used are consistent with expectations that:

- iso-saccharinate will sorb more strongly to haematite at pH values below the point of zero charge (about pH 8-9) where iron surface sites on the haematite become net positively charged, and
- at the higher ISA concentrations the sorption isotherm becomes non-linear (and $R_0$ values decrease) due to saturation of surface sites with sorbed ISA.

However, the results for the lowest ISA concentrations differ from these trends.

No sorption data for ISA onto haematite (or other iron oxides) have been found in the literature. However, a study was undertaken for Nirex during the late 1990s in which the sorption of ISA onto site-specific rock samples was investigated [24]. The findings of the present study appear to be broadly in agreement with trends observed in that previous study, the results of which are summarised in Table 14. In that study, the sorption of organic degradation products and ISA (and their effects on thorium sorption) were investigated onto wall rock and fracture infill materials from the BVG$^{10}$ at Sellafield. The fracture infill material consisted of haematite, calcite and dolomite as the predominant minerals; the wall rock is composed predominantly of quartz and mica with some haematite. Samples of these materials were aged by contact with an evolved near-field porewater at 70°C for 4 months to simulate conditions in the alkaline disturbed zone of the geosphere surrounding a cementitious GDF.

ISA was found to sorb relatively weakly to both the unreacted and reacted materials at high ISA concentrations ($R_0 \leq 10$ cm$^3$ g$^{-1}$ for concentrations $\geq 2 \times 10^{-4}$ mol dm$^{-3}$). Sorption to the reacted wall rock at pH ~10 was also weak down to low concentrations of ISA ($\leq 2 \times 10^{-7}$ mol dm$^{-3}$). However, higher $R_0$ values were measured for the ISA under near-neutral conditions (pH 7-8) at lower ISA concentrations ($\leq 2 \times 10^{-5}$ mol dm$^{-3}$) onto unreacted wall rock and fracture infill materials. The reasons for these last observations were not discussed in reference [24], but they indicate non-linearity of the ISA sorption isotherms at higher ISA concentrations, broadly in agreement with the findings of the present study. Interpretation of the effects of pH on ISA sorption is more difficult from the data in reference [24], owing to the use of altered materials for higher pH experiments. In common with the present study, the effect of ISA concentration on ISA sorption to geological materials in reference [24] is greater at lower pH values, although, given the use of altered materials in the higher pH experiments, it is not clear that ISA concentration is the only factor.

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$^{10}$ Borrowdale Volcanics Group
In the dataset presented in reference [24], there is no indication for different behaviour in the experiments at an initial ISA concentration of $2 \times 10^{-7}$ mol dm$^{-3}$. In the present study, it is likely that results at the lowest ISA concentration are affected more by minor processes or impurities in the system. As noted previously, one possibility for the unexpectedly low sorption (relative to the of $2 \times 10^{-5}$ mol dm$^{-3}$) ISA data) is that there is a small amount of readily extractable ferric iron associated with haematite that is complexed by low levels of ISA in solution. This would effectively compete with the process of surface complex formation to reduce measured $R_D$ values.

7.3 Sorption of CDP onto haematite

Owing to the high concentrations of organic complexants used in the batch experiments to study the sorption of CDP components onto haematite, measured sorption has been weak. There are no consistent, distinguishable differences between the initial and final TOC solution phase concentrations measured within experimental error at any of the six pH values or at either CDP concentration studied. These findings are confirmed by the HPLC results.

Comparison of the chromatograms for the CDP solutions after contact with haematite at the 6 pH values has shown no significant changes in the fingerprints of the CDP components that might identify preferentially sorbing components at the CDP concentrations studied. This is not surprising given that sorption is weak under the conditions studied.

For differences in component sorption to be distinguishable by HPLC, significant sorption of these components needs to occur over concentrations ranges that are amenable to measurement. For ISA, the lowest working concentration is about $10^{-4}$ mol dm$^{-3}$, which is only a factor of 10-20 below the ISA concentrations in the 10% CDP leachate solutions studied here. Working in the same CDP concentration range, it may be possible to increase the amount of CDPs removed from solution (by sorption) to measurable amounts by using significantly lower water to solid ratios than in the current experiments. However, in general, it is considered that the range of concentrations amenable to study by the current HPLC method using UV detection is probably too high to be able to distinguish differences in sorption behaviour of CDP components.

7.4 Sorption of thorium onto haematite

In this study, in the absence of organic complexants, sorption of thorium onto haematite has been measured to be very strong at all three pH values considered (Table 10). Measured $R_D$ values for thorium were $\geq 4 \times 10^4$ cm$^3$ g$^{-1}$ at pH ~9 and varied from $9 \times 10^3$ cm$^3$ g$^{-1}$ to $7 \times 10^6$ cm$^3$ g$^{-1}$ at pH~6. Measured $R_D$ values at pH 12 were about one order of magnitude lower ranging from 1-2 $\times 10^5$ cm$^3$ g$^{-1}$. These values can be compared with the results of previous batch studies of thorium sorption onto haematite undertaken on the Nirex programme [7, 50] and with studies undertaken elsewhere [51, 52, 53].

Previous work on the Nirex programme was concerned with investigating controls on thorium sorption under geosphere conditions, in particular the effects of pH and carbonate and calcium ion concentrations (acting as complexing ions and competing ions for surface sites respectively). Sorption was studied onto crushed samples of a natural haematite kidney ore with BET surface areas in the range 3.6 to 6.8 m$^2$ g$^{-1}$. 0.1 mol dm$^{-3}$ sodium nitrate or sodium chloride was used as the background electrolyte. The highest reported thorium $R_D$ values were $9 \times 10^6$ cm$^3$ g$^{-1}$ measured at pH 10 at the lowest added calcium concentration (10$^{-5}$ mol dm$^{-3}$) under a nitrogen atmosphere (negligible CO$_2$) [50]. Thorium $R_D$ values under similar conditions at pH 7 and 12 were reported to be ~300 cm$^3$ g$^{-1}$ and ~3700 cm$^3$ g$^{-1}$ respectively [7].

At alkaline pH values, above the point of zero charge of haematite, thorium sorption was found to be sensitive to the concentration of calcium ions in solution. The presence of 0.1 mol dm$^{-3}$ calcium at pH 9.5 to 10.1 was found to reduce the $R_D$ values for thorium by up to 2 orders of
magnitude to $\sim 10^3 \text{ cm}^3 \text{ g}^{-1}$ [50]. Similar trends were reported at pH 12 in reference [7], but thorium sorption was insensitive to the calcium concentration at pH 7 with measured $R_0$ values of $\sim 300 \text{ cm}^3 \text{ g}^{-1}$ at up to $10^{-2} \text{ mol dm}^{-2}$ calcium.

In reference [50], thorium sorption was found to be more sensitive to the effects of carbonate at low pH than at high pH. Experiments carried out in air were found to give lower $R_0$ values by up to an order of magnitude at pH 7 compared to those under a nitrogen atmosphere as total dissolved carbonate concentration was increased from $10^{-8}$ to $10^{-4} \text{ mol dm}^{-3}$. Sorption was found to be less sensitive to carbonate concentration at pH $\sim 10$ with measured $R_0$ values in the range $2-7 \times 10^3 \text{ cm}^3 \text{ g}^{-1}$; owing to the uncertainties in the data it is not possible to draw firm conclusions as to whether or not sorption was reduced.

While the high $R_0$ values measured for thorium to haematite at pH 9 and the observed decrease in values at pH 12 in the present study are broadly consistent with the trends of the previous results given the very low calcium and carbonate concentrations in the experiments and the higher surface area of the haematite substrate\(^{11}\), the high $R_0$ values measured for thorium at pH $\sim 6$ in the present study are not.

The results of three studies reported in the open literature [51, 52, 53] are more directly comparable with those from the current study as all three were undertaken using monodispersed colloidal sols of synthetic haematite with surface areas in the range $10-20 \text{ m}^2 \text{ g}^{-1}$ (comparable with the second batch of haematite). Reported sorption experiments were undertaken over the pH range 1 to 10.3 but generally at significantly higher liquid to solid ratios than in the present study (from 50 to 3370 mg dm\(^{-3}\) haematite) with sodium perchlorate as the background electrolyte. In none of these studies was atmospheric CO\(_2\) excluded from the experiments.

In references [51] and [52] thorium sorption data are presented as plots of the fraction of thorium sorbed against pH only. Above pH 3.5 all the experimental data points reported by Murphy et al. [51] are at 100% thorium sorption to the accuracy that can be read from their graph. This hides the actual pH dependence of their data across the pH region of greatest interest in this study. Assuming that at least 99% of the added thorium is sorbed, the plot suggests $R_0$ values $\geq 3 \times 10^4 \text{ cm}^3 \text{ g}^{-1}$ at pH values from 3.5 to 8.5. Working at lower solid concentrations (115 mg dm\(^{-3}\) haematite), Quigley et al.’s plot [52] shows fractions of thorium sorbed between 96% and 99% over the pH range from 5 to 10 (with one lower value of 88% at pH 6), but with no clear trends indicative of a pH dependence in $R_0$ values over this range. Between pH 6 and 10, the $R_0$ values are inferred to range from 2 to $9 \times 10^5 \text{ cm}^3 \text{ g}^{-1}$.

Cromieres et al. [53] report log $R_0$ values increasing from about 4.7±0.2 at pH 6.5 to 5.7±0.2 at pH 10.3. This corresponds to a range from $3 \times 10^4 \text{ cm}^3 \text{ g}^{-1}$ (minimum at pH 6.5) to $8 \times 10^5 \text{ cm}^3 \text{ g}^{-1}$ (maximum at pH 10.3). This trend with pH for experiments in air is consistent with that reported in the Nirex study [50] but with $R_0$ values that are about two orders of magnitude higher. The latter is due, at least in part, to the higher surface area of the colloidal haematite sample.

The $R_0$ values measured at pH 6 and 9 in the present study are up to one order of magnitude higher than the ranges inferred from references [52] and [53] and are more consistent with the trends observed in these data. The effect of carbonate on thorium sorption to haematite at high pH values is currently unclear. However, the exclusion of carbonate in the present study may contribute to the stronger thorium sorption observed. Another possible factor is that relatively short equilibration times of $\sim 24$ hours were used by Quigley et al. and Cromieres et al. compared to the 43 to 49 days’ equilibrations in the current study. It is possible therefore that sorption equilibrium may not have been fully achieved. Quigley et al. [52] provide evidence that

\(^{11}\) This author notes that the haematite kidney ore was reported to contain some quartz impurity that may account for its lower than expected measured point of zero charge [50]. This finding suggests that a significant fraction of the available surface area may be quartz rather than haematite, to which thorium sorption is expected to be weaker.
reversible sorption equilibrium had not been achieved over the timescale of their experiments, due to differences between thorium sorption and desorption behaviour over timescales of up to four days. Unfortunately their study was not extended to longer equilibration times. Finally, it is noted that in experiments with very high liquid to solid ratios (such as those described above), the results may be more susceptible to the effects of impurities that will be present at low concentrations in the reagents used and which may act to reduce thorium sorption by competing for available surface sites or by complexation.

In summary, the overall trends in the $R_0$ values for thorium onto haematite measured in the present study are broadly consistent with data reported previously, although $R_0$ values are significantly higher than in comparable studies by at least one order of magnitude. Such high values are thought to arise due to the high purity and relatively high surface area of the synthetic haematite particles, the exclusion of carbonate, the low levels of calcium present in the experiments and possibly the use of lower liquid to solid ratios and of longer equilibration times.

7.5 Sorption of thorium onto haematite in the presence of organic complexants

The results of the thorium sorption experiments onto haematite in the presence of organic complexants show the following (Figure 10).

- The presence of $2 \times 10^{-3}$ mol dm$^{-3}$ ISA appears to have a negligible effect on thorium sorption at pH 12 but to reduce sorption by up to an order of magnitude at pH 5.5 to 6.6. There may also be a smaller reduction in thorium sorption at pH 9 although it isn’t possible to draw firm conclusions.

- The presence of 10% CDP has a much more significant effect on thorium sorption than ISA alone at all three pH ranges studied; at pH 4.7 to 6.8 and pH ~9, sorption to haematite is reduced by about 2 orders of magnitude compared to the baseline case. A reduction of at least one order of magnitude is observed at pH 12.

A significant amount of work has been undertaken previously on the Nirex programme to investigate the effects of CDPs, gluconate and/or ISA on the sorption of radioelements (principally thorium, uranium(IV), uranium(VI) and plutonium) to geological materials. A number of studies have investigated sorption of thorium onto a variety of rock types in the presence or absence of ACDP [20, 21, 22] but in only one study have the effects of ISA and ACDP been compared on the same materials [24]. These materials consisted of fracture mineral assemblages (FMAs) and wall rock from the BVG at Sellafield both as supplied and after hydrothermal ageing under strongly alkaline conditions (the nature of these materials has been discussed previously in sub-section 7.2). Thorium was found to be moderately sorbing to these materials; hydrothermal treatment had little effect on thorium sorption in the absence of organic species. On all four materials, thorium sorption was reduced by about a factor of 2 in the presence of organic species, but there was no apparent correlation with ISA concentration over the range $2 \times 10^{-7}$ to $2 \times 10^{-3}$ mol dm$^{-3}$ or the presence of ACDP (experiments at pH 7-8 for FMAs or pH 10 for reacted wall rock). The exception to this was that the mean $R_0$ value onto unreacted wall rock at pH ~7 was reduced from 450 cm$^3$ g$^{-1}$ to 20 cm$^3$ g$^{-1}$ in the presence of ACDP leachate. This compares with a mean $R_0$ value of 160 cm$^3$ g$^{-1}$ in the presence of $2 \times 10^{-3}$ mol dm$^{-3}$ ISA. The wall rock is composed predominantly of quartz and mica with some haematite.

In an earlier study, thorium sorption to haematised and unhaematised tuff samples from the BVG at Sellafield was found to be unaffected by the presence of ACDP leachate at pH 8 or pH 12 [21]. Sorption of thorium onto St Bees Sandstone was reduced by a factor 3-4 at pH 8 and pH 12 in experiments undertaken at a liquid to solid ratio of 50:1 [22]. However, some small apparent increases in sorption were observed in experiments at liquid to solid ratios of 5:1. A small apparent increase in thorium sorption in the presence of an ACDP was also
observed onto London Clay at a pH of 11.0 to 11.5 whereas a reduction (up to a factor of 2) was observed onto Caithness Flagstones under similar conditions [20].

The 10% CDP leachate used in the present study was found to have a more significant effect in reducing thorium sorption onto haematite at all three pH values than has been observed previously for the impact of ACDPs on thorium sorption to most of the geological materials studied. This is perhaps not surprising given the heterogeneous nature of the geological materials which will contain a variety of mineral surfaces that differ in their sorbent properties. The major exception to this is the case of unreacted wall rock studied in reference [24] where the ACDP was found to have a significantly greater effect on thorium sorption than $2 \times 10^{-3}$ mol dm$^{-3}$ ISA. This result is one of a number of examples from the Nirex programme where the effect of ACDP on radionuclide sorption at near-neutral pH is found to be significantly greater than the impact of ISA at a concentration that is considered to be representative of ISA components of the ACDP. Other examples include plutonium onto three BVG tuffs [25, 36] and uranium(IV) onto BVG tuff [36]. Uranium(IV) sorption onto a red eutaxitic tuff was reduced to similar extent (by two orders of magnitude) by ACDP and $2 \times 10^{-3}$ mol dm$^{-3}$ ISA at pH 7 [36].

These observations have been interpreted as being consistent with the presence of additional complexants in CDPs and/or processes that lower sorption in the presence of CDPs compared to ISA under near-neutral pH conditions [27]. The results of the present study provide further support for this view. In addition, the greater effect of CDP on thorium sorption than ISA at pH 12 was an unexpected result because, in general, ISA has been considered to be a good model for ACDP as a whole at high pH (i.e. in terms of both solubility enhancement and sorption reduction).

The results of the thorium sorption experiments are contrary to initial modelling predictions described elsewhere [29], which suggest reduction in thorium sorption in the presence of $2 \times 10^{-3}$ mol dm$^{-3}$ ISA by up to three orders of magnitude across the pH range from 6 to 12. The modelling predictions are based on existing complexation data for thorium with ISA and models for the surface properties of haematite and thorium-haematite sorption based on literature data applied using both triple layer and diffuse layer surface complexation models.

One possible explanation for the experimental data is that ISA present in the thorium sorption experiments had undergone partial degradation. However this is considered unlikely, on the basis of the results of the blank experiments undertaken previously during this study.

A second possibility is that complexation of thorium by ISA is much weaker than suggested by previous results. A recent study of the solubility of thorium in the presence of ISA at pH 12 found only a very small increase in thorium solubility in the presence of $2 \times 10^{-3}$ mol dm$^{-3}$ ISA [54], contrary to previous results [55]. Given differences in the experimental methodology between the two studies (the recent study was carried out by the under-saturation method while data in reference [55] was measured by the over-saturation method) and the results of Reiller et al. [56] who found that the extent of thorium sorption in the presence of humic acid was strongly dependent on the order of the addition of the thorium and humic acid to the system, further investigations are on-going on the NDA programme to investigate the possible impact of the methodology on measured thorium solubility. The results of these studies should help to clarify the understanding of ISA-thorium complexation.

The effect of CDP on thorium sorption was significant across the full pH range studied, which implies that there are additional thorium-complexing components present in CDP and/or other processes operating that contribute to a reduction in thorium sorption. Given the relatively weak effect of ISA, it would appear that these other complexants or processes, rather than ISA, are responsible for controlling thorium sorption behaviour to haematite in the presence of the new CDP. A second major component (in addition to ISA) has been observed in the CDP by HPLC, that has yet to be identified and which could potentially also act as a complexant for thorium. Further work is required to identify the nature of this material and its potential complexing ability.
One potentially significant difference between the CDP and ISA solutions used in the ternary sorption experiments is that the CDP leachate contains calcium, which will be present at only trace levels in the ISA solutions. As described above, previous studies undertaken on the Nirex programme have shown that calcium can compete with thorium for surface sorption sites on haematite, reducing thorium $R_D$ values at pHs above the point of zero charge of haematite [7, 50]. The CDP prepared in the current study contained about 6 $10^{-3}$ mol dm$^{-3}$ calcium (Table 2); this was diluted by a factor of 10 for use in thorium sorption experiments. A calcium concentration of $10^{-3}$ mol dm$^{-3}$ was found to reduce the sorption of thorium to haematite kidney ore by a factor of about 5 (compared to $10^{-5}$ mol dm$^{-3}$ calcium) at pH 12 [7]; a calcium concentration of $5 \times 10^{-4}$ mol dm$^{-3}$ was found to reduce thorium sorption by at least a factor of 2 to 3 at pH 10 [50]. Although significant complexation of calcium to CDP components is anticipated in the ternary system experiments, it is also possible that the calcium may compete with thorium for surface sorption sites thereby contributing to the observed reduction of thorium sorption in the presence of 10% CDP solution at pH 9 and 12. Further understanding is required of the possible impact of calcium on radioelement sorption in the presence of CDP.

7.6 Suitability of the model ternary system: haematite-thorium-ISA

One objective of the current study has been to consider the suitability of the chosen ternary system (haematite-thorium-ISA) for more detailed mechanistic study and as a basis for model development. The modelling approach is based on a number of important assumptions:

- that ISA will have an effect on sorption of thorium to haematite over the pH range of interest (i.e. pH 6 to 12);
- that ISA is an appropriate model for the behaviour of CDP in controlling thorium sorption, at least in the alkaline pH range; and
- that thermodynamic equilibrium is achieved in the binary and ternary system sorption experiments and that sorption of complexant or radionuclide species to the substrate is reversible over the experimental timescales.

Given the relatively weak effect of ISA on thorium sorption to haematite, which is only significant at lower pH, the chosen system does not appear to be as suitable as expected as a model ternary system for more detailed mechanistic study and as the basis for model development. In addition, ISA does not appear to provide an adequate model for the effects of CDP on thorium sorption to haematite. In contrast to ISA, the effect of CDP on thorium sorption was significant across the full pH range studied. Given the relatively weak effect of ISA, it would appear that the presence of other complexants or additional processes, rather than ISA, are responsible for controlling thorium sorption behaviour to haematite in the presence of the new CDP.

An important finding from the literature during the course of this work has been that two papers concerned with thorium sorption onto haematite indicated that, in this case, sorption may not be reversible over the time scales of the experiments performed. Quigley et al. [52] found significant differences between their measured values determined in sorption and desorption experiments over four days. Reiller et al. [56] found that the extent of thorium sorption in the presence of humic acid was strongly dependent on the order of addition of the thorium and humic acid to the system. If failure to reach equilibrium is generally the case for the thorium-haematite system over accessible timescales, then the justification for applying thermodynamic models would be removed. This could be tested by performing equivalent sorption and desorption experiments or investigating the addition order of thorium and CDP or ISA under conditions similar to those in the present study.

Overall, the chosen model ternary system haematite-thorium-ISA does not appear to be as well-suited as expected as a basis for on-going development of a thermodynamic model of ternary system interactions owing to the limited impact of ISA on thorium sorption in this system and uncertainties concerning sorption reversibility and the attainment of thermodynamic equilibrium.
for this system over experimental timescales. The impact of CDP leachate in reducing thorium sorption to haematite appears to be significant, however. Clearly more understanding is required concerning the presence of additional complexants and/or the operation of other processes (e.g. possible competition for surface sites by calcium ions) that control thorium sorption in the presence of the new CDP leachate.

8 Conclusions

This report describes the results from a package of experimental work designed to provide initial characterisation of a model ternary system to investigate the effects of organic complexants on the sorption of radionuclides to mineral surfaces. The model ternary system selected for study consisted of haematite as the single mineral substrate, thorium as the radionuclide and ISA (a major degradation product of cellulose under alkaline anaerobic conditions). The design of this experimental work programme was driven by the data requirements for thermodynamic modelling, the results of which have been reported separately [29].

Sorption experiments have been undertaken to investigate the following interactions in the ternary system:

- ISA sorption to haematite as a function of ISA concentration and pH;
- thorium sorption to haematite as a function of pH; and
- thorium sorption to haematite in the presence of ISA as a function of pH.

In addition, sorption experiments have been carried in parallel with CDP leachate (prepared by a new, more generic recipe) to compare its impact on thorium sorption to that of ISA.

The most important experimental findings of this study are that:

- The presence of $2 \times 10^{-3}$ mol dm$^{-3}$ ISA appears to have a negligible effect on thorium sorption to haematite at pH 12 but to reduce sorption by up to an order of magnitude at pH 5.5 to 6.6.
- The presence of a 10% CDP leachate has a much more significant effect on thorium sorption than ISA alone at all three pH ranges studied; at pH 4.7 to 6.8 and pH ~9, sorption to haematite is reduced by about 2 orders of magnitude compared to the baseline case. A reduction of at least one order of magnitude is observed at pH 12.

The main conclusions of this study are as follows.

ISA does not appear to provide an adequate model for the effects of CDP on thorium sorption to haematite either at near-neutral (as expected) or alkaline pH values (which was not). The findings at near-neutral pH are consistent with previous results for ACDPs obtained on the Nirex programme, showing that under these conditions ACDPs have greater effects on radionuclide sorption than ISA alone. In addition the ACDP has a detrimental effect on thorium sorption to haematite at pH 12. Given the relatively weak effect of ISA, it would appear that the presence of other complexants or additional processes, rather than ISA, are responsible for controlling thorium sorption behaviour to haematite in the presence of the new CDP leachate.

Overall, the chosen model ternary system haematite-thorium-ISA does not appear to be as well-suited as expected as a basis for ongoing development of a thermodynamic model of ternary system interactions owing to the limited impact of ISA on thorium sorption in this system. In addition there are uncertainties concerning sorption reversibility and the attainment of thermodynamic equilibrium for this system over experimental timescales. The impact of CDP leachate in reducing thorium sorption to haematite appears to be significant, however. Clearly more understanding is required concerning the presence of additional complexants and/or the operation of other processes (e.g. possible competition for surface sites by calcium ions) that control thorium sorption in the presence of the new CDP leachate.
9 Acknowledgements

The authors thank Mr Graham Baston of Serco TCS for assistance with the C-14-ISA sorption experiments and Miss Charlotte Heath of Loughborough University for undertaking the HPLC analyses. The radiochemical analyses were undertaken by NIRAS part of AMEC-NNC and TOC and inorganic analyses by Alcontrol, Chester. Mr Frank Cullen and Dr Alison Crossley of the Oxford University Materials Characterisation Service are thanked for the BET and SEM analyses of the haematite powders.

10 References


25  J.A. Berry, K.A. Bond, K.A. Boult, *Effects of organic materials at different concentrations on the sorption of uranium (VI) and plutonium onto a sample of tuff from the Borrowdale Volcanic Group, Sellafield, Borehole 2 (~526.8 mBRT)*, AEA Technology Report AEAT/R/ENV/0207, 2001.


28  For further details please visit: [http://www.funmig.com](http://www.funmig.com).


47 P. Warwick, Personal communication to S.W. Swanton, February 2007.


<table>
<thead>
<tr>
<th>Sorbate/ sorbent</th>
<th>pH values</th>
<th>organic concentration</th>
<th>duration</th>
<th>comment</th>
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<tbody>
<tr>
<td>ISA/ haematite</td>
<td>6,7,8,9,10,12</td>
<td>$10^{-4}$, $10^{-3}$, $10^{-2}$ M</td>
<td>1 month</td>
<td>Fe analysis after equilibration</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TOC analysis before and after equilibration</td>
</tr>
<tr>
<td>Blank/ haematite</td>
<td>6,7,8,9,10,12</td>
<td>-</td>
<td>1 month</td>
<td>Fe analysis in absence of organics</td>
</tr>
<tr>
<td>CDP/ haematite</td>
<td>6,7,8,9,10,12</td>
<td>As prepared, 10-fold dilution</td>
<td>1 month</td>
<td>HPLC, Fe analysis after equilibration, TOC analysis before and after equilibration</td>
</tr>
<tr>
<td>C-14 ISA/ haematite</td>
<td>6,7,8,9,10,12</td>
<td>$2 \times 10^{-3}$, $2 \times 10^{-5}$, $2 \times 10^{-7}$ M</td>
<td>48-50 days</td>
<td></td>
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<td>Th/ haematite</td>
<td></td>
<td></td>
<td></td>
<td>43-49 days</td>
</tr>
<tr>
<td>with ISA</td>
<td>6,9,12</td>
<td>$2 \times 10^{-3}$ M</td>
<td></td>
<td></td>
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<tr>
<td>with CDP</td>
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<td>10-fold dilution</td>
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<td>no organic (1)</td>
<td>6,9,12</td>
<td>-</td>
<td></td>
<td></td>
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<tr>
<td>no organic (2)</td>
<td>6,9,12</td>
<td>-</td>
<td></td>
<td>Th sorption from NaCl solution pre-equilibrated with haematite</td>
</tr>
</tbody>
</table>

General conditions: solid liquid ratio = 50 cm$^3$ g$^{-1}$, nitrogen atmosphere glovebox, phase separation by 30,000 nominal molecular cut off filtration, ambient temperature. Experiments generally performed in quadruplicate (with one tube used for pH monitoring), except "Th/ haematite no organic (2)" performed in duplicate.
Table 2  Results of elemental and TOC analyses of CDP leachate solutions from batches I and II

<table>
<thead>
<tr>
<th>Sample</th>
<th>Filtration</th>
<th>TOC (mg dm(^{-3}))</th>
<th>Ca (mol dm(^{-3}))</th>
<th>Fe (mol dm(^{-3}))</th>
<th>Na (mol dm(^{-3}))</th>
<th>K (mol dm(^{-3}))</th>
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<tr>
<td>CDP Batch I</td>
<td>0.45 µm</td>
<td>2080</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>CDP Batch II sample 1</td>
<td>0.45 µm</td>
<td>-</td>
<td>6.5 (10^{-3})</td>
<td>5.4 (10^{-7})</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CDP Batch II</td>
<td>0.45 µm A</td>
<td>2250</td>
<td>6.4 (10^{-3})</td>
<td>1.7 (10^{-6})</td>
<td>8.3 (10^{-2})</td>
<td>4.6 (10^{-5})</td>
</tr>
<tr>
<td>CDP Batch II</td>
<td>0.45 µm B</td>
<td>1860</td>
<td>6.2 (10^{-3})</td>
<td>1.8 (10^{-6})</td>
<td>8.5 (10^{-2})</td>
<td>4.3 (10^{-5})</td>
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<tr>
<td>CDP Batch II</td>
<td>30k MWCO A</td>
<td>2450</td>
<td>6.1 (10^{-3})</td>
<td>1.9 (10^{-6})</td>
<td>8.6 (10^{-2})</td>
<td>5.1 (10^{-5})</td>
</tr>
<tr>
<td>CDP Batch II</td>
<td>30k MWCO B</td>
<td>2030</td>
<td>6.6 (10^{-3})</td>
<td>1.9 (10^{-6})</td>
<td>8.8 (10^{-2})</td>
<td>5.4 (10^{-5})</td>
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<tr>
<td>Limit of Detection</td>
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<td>1</td>
<td>1.0 (10^{-7})</td>
<td>1.0 (10^{-7})</td>
<td>1.0 (10^{-6})</td>
<td>5.0 (10^{-6})</td>
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Table 3  Retention times and relative peak areas for the CDP Batch I components analysed by HPLC on a Waters Resolve C18 column compared with 0.011 mol dm\(^{-3}\) α-ISA.

<table>
<thead>
<tr>
<th>Peak no.</th>
<th>Mean retention time (min)</th>
<th>Mean relative area (mAU×s)</th>
<th>Mean fractional area</th>
<th>Comment</th>
<th>Possible identification of component</th>
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<td>Compound</td>
<td>Mean retention time (min)</td>
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<tr>
<td></td>
<td>Injection peak</td>
<td>Injection peak</td>
<td></td>
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<td></td>
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<tr>
<td></td>
<td>α- and β-ISA (open chain)</td>
<td>Mean retention time (min)</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Formic acid</td>
<td>Injection peak</td>
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<tr>
<td></td>
<td>Lactic acid</td>
<td>Injection peak</td>
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<tr>
<td></td>
<td>Acetic acid</td>
<td>Injection peak</td>
<td></td>
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</tr>
</tbody>
</table>

CDP Batch I

1  3.036  68.9  -  Injection peak
2  3.145  45.8  0.04  Shoulder
3  3.387  14.3  0.01  Shoulder
4  3.583  675.5  0.57  Formic acid  3.48
5  3.947  14.2  0.01  α- and β-ISA
6  4.331  310.8  0.26  (open chain)  3.60
7  4.472  20.0  0.02  Lactic acid  4.28
8  4.734  33.7  0.03  Shoulder
9  7.011  37.4  0.03  Acetic acid  4.76
10 11.480  31.6  0.03  Injection peak

0.011 mol dm\(^{-3}\) α-ISA

1  3.039  21.7  -  Injection peak
2  3.603  413.6  1.0
Table 4  Results of batch sorption experiments with ISA onto haematite

<table>
<thead>
<tr>
<th>Experiment ID</th>
<th>Elapsed Time (days)</th>
<th>Final pH</th>
<th>Initial TOC (mg dm(^{-3}))</th>
<th>Final TOC (mg dm(^{-3}))</th>
<th>Fe (mol dm(^{-3}))</th>
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<tr>
<td>ISA (10^{-2}) M</td>
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<tr>
<td>pH 10 B</td>
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<td>9.94</td>
<td>840</td>
<td>1180</td>
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<td>pH 10 C</td>
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<td>1220</td>
<td>&lt; 5.4 (10^{-7})</td>
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<td>pH 10 D</td>
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<td>8.30</td>
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<td>2.0 (10^{-6})</td>
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<tr>
<td>pH 12 B</td>
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<td>11.97</td>
<td>870</td>
<td>830</td>
<td>&lt; 5.4 (10^{-7})</td>
</tr>
<tr>
<td>pH 12 C</td>
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<td>11.96</td>
<td>NDP</td>
<td>NDP</td>
<td>&lt; 5.4 (10^{-7})</td>
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<tr>
<td>pH 12 D</td>
<td>36</td>
<td>11.96</td>
<td>NDP</td>
<td>NDP</td>
<td>&lt; 5.4 (10^{-7})</td>
</tr>
<tr>
<td>ISA (10^{-3}) M</td>
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<td></td>
</tr>
<tr>
<td>pH 10 B</td>
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<td>67</td>
<td>68</td>
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<td></td>
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<td>pH 12 B</td>
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<td>pH 12 C</td>
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<td>pH 12 D</td>
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<td>71</td>
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<td>ISA (10^{-4}) M</td>
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<td>pH 10 B</td>
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<td>22</td>
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<td>pH 12 C</td>
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</tr>
<tr>
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<td>12.17</td>
<td>22</td>
<td>22</td>
<td>&lt; 5.4 (10^{-7})</td>
</tr>
</tbody>
</table>

NDP = no determination possible
Table 5  Sorption of cellulose degradation products from undiluted leachate onto haematite

<table>
<thead>
<tr>
<th>Experiment ID</th>
<th>Elapsed Time (days)</th>
<th>Final pH</th>
<th>Initial TOC (mg dm$^{-3}$)</th>
<th>Final TOC (mg dm$^{-3}$)</th>
<th>Fe (mol dm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 6 B</td>
<td>34</td>
<td>6.4</td>
<td>2320</td>
<td>2270</td>
<td>3.9 $10^{-6}$</td>
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<tr>
<td>pH 6 C</td>
<td>34</td>
<td>6.4</td>
<td>2420</td>
<td>4.7 $10^{-6}$</td>
<td></td>
</tr>
<tr>
<td>pH 6 D</td>
<td>34</td>
<td>6.4</td>
<td>2360</td>
<td>6.1 $10^{-6}$</td>
<td></td>
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<tr>
<td>pH 7 B</td>
<td>35</td>
<td>7.2</td>
<td>2290</td>
<td>2280</td>
<td>1.1 $10^{-6}$</td>
</tr>
<tr>
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<td>7.2</td>
<td>2420</td>
<td>2100</td>
<td>2.5 $10^{-6}$</td>
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<tr>
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<td>7.1</td>
<td>2160</td>
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<td>2280</td>
<td>2050</td>
<td>2.7 $10^{-6}$</td>
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<td>35</td>
<td>8.0</td>
<td>2180</td>
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<td>8.0</td>
<td>2210</td>
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<td>1870</td>
<td>2310</td>
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</tr>
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<td>8.9</td>
<td>2110</td>
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<td>8.9</td>
<td>2110</td>
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<td>1760</td>
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<tr>
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<td>10.0</td>
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<tr>
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<td>2210</td>
<td>2010</td>
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</tr>
<tr>
<td>pH 12 C</td>
<td>36</td>
<td>12.07</td>
<td>2090</td>
<td>6.3 $10^{-6}$</td>
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</tr>
<tr>
<td>pH 12 D</td>
<td>36</td>
<td>12.10</td>
<td>2060</td>
<td>5.0 $10^{-6}$</td>
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</table>
Table 6  Sorption of cellulose degradation products onto haematite from 10% CDP (i.e. after ten-fold dilution of original leachate)

<table>
<thead>
<tr>
<th>Experiment ID</th>
<th>Elapsed Time (days)</th>
<th>Final pH</th>
<th>Initial TOC (mg dm(^{-3}))</th>
<th>Final TOC (mg dm(^{-3}))</th>
<th>Fe (mol dm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 6 B</td>
<td>33</td>
<td>7.2</td>
<td>230</td>
<td>240</td>
<td>&lt; 5.4 (10^{-7})</td>
</tr>
<tr>
<td>pH 6 C</td>
<td>33</td>
<td>7.0</td>
<td>200</td>
<td>240</td>
<td>5.4 (10^{-7})</td>
</tr>
<tr>
<td>pH 6 D</td>
<td>33</td>
<td>7.0</td>
<td>220</td>
<td>240</td>
<td>&lt; 5.4 (10^{-7})</td>
</tr>
<tr>
<td>pH 7 B</td>
<td>34</td>
<td>7.5</td>
<td>250</td>
<td>120</td>
<td>&lt; 5.4 (10^{-7})</td>
</tr>
<tr>
<td>pH 7 C</td>
<td>34</td>
<td>7.5</td>
<td>170</td>
<td>240</td>
<td>5.4 (10^{-7})</td>
</tr>
<tr>
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<td>34</td>
<td>7.3</td>
<td>340</td>
<td>240</td>
<td>&lt; 5.4 (10^{-7})</td>
</tr>
<tr>
<td>pH 8 B</td>
<td>35</td>
<td>7.9</td>
<td>240</td>
<td>220</td>
<td>&lt; 5.4 (10^{-7})</td>
</tr>
<tr>
<td>pH 8 C</td>
<td>35</td>
<td>8.0</td>
<td>210</td>
<td>220</td>
<td>&lt; 5.4 (10^{-7})</td>
</tr>
<tr>
<td>pH 8 D</td>
<td>35</td>
<td>7.6</td>
<td>220</td>
<td>240</td>
<td>&lt; 5.4 (10^{-7})</td>
</tr>
<tr>
<td>pH 9 B</td>
<td>35</td>
<td>8.8</td>
<td>180</td>
<td>110</td>
<td>&lt; 5.4 (10^{-7})</td>
</tr>
<tr>
<td>pH 9 C</td>
<td>35</td>
<td>8.7</td>
<td>220</td>
<td>240</td>
<td>2.3 (10^{-6})</td>
</tr>
<tr>
<td>pH 9 D</td>
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<td>8.8</td>
<td>210</td>
<td>220</td>
<td>&lt; 5.4 (10^{-7})</td>
</tr>
<tr>
<td>pH 10 B</td>
<td>35</td>
<td>9.9</td>
<td>240</td>
<td>220</td>
<td>1.1 (10^{-6})</td>
</tr>
<tr>
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<td>35</td>
<td>9.8</td>
<td>210</td>
<td>240</td>
<td>9.0 (10^{-7})</td>
</tr>
<tr>
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<td>9.9</td>
<td>210</td>
<td>220</td>
<td>3.6 (10^{-7})</td>
</tr>
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<td>12.1</td>
<td>250</td>
<td>220</td>
<td>5.4 (10^{-7})</td>
</tr>
<tr>
<td>pH 12 C</td>
<td>36</td>
<td>12.0</td>
<td>240</td>
<td>220</td>
<td>5.4 (10^{-7})</td>
</tr>
<tr>
<td>pH 12 D</td>
<td>36</td>
<td>12.0</td>
<td>250</td>
<td>220</td>
<td>&lt; 5.4 (10^{-7})</td>
</tr>
</tbody>
</table>
Table 7  Sorption of C-14 labelled ISA onto haematite at an ISA concentration of $2 \times 10^{-7}$ mol dm$^{-3}$

<table>
<thead>
<tr>
<th>Experiment ID</th>
<th>Elapsed Time (days)</th>
<th>Final pH</th>
<th>Initial C-14 activity (Bq cm$^{-3}$)</th>
<th>C-14 lost to vessel walls (%)</th>
<th>Final C-14 activity (Bq cm$^{-3}$)</th>
<th>Distribution Ratio, $R_D$ (cm$^3$ g$^{-1}$)*</th>
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</thead>
<tbody>
<tr>
<td>2 $\times 10^{-7}$ mol dm$^{-3}$ ISA</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 6 B</td>
<td>50</td>
<td>7.5</td>
<td>$107.9 \pm 20.4$</td>
<td>nm</td>
<td>$45.6 \pm 2.1$</td>
<td>$68 \pm 22$</td>
</tr>
<tr>
<td>pH 6 C</td>
<td>50</td>
<td>6.9</td>
<td>$3.8$</td>
<td>$45.5 \pm 2.1$</td>
<td>$63 \pm 22$</td>
<td></td>
</tr>
<tr>
<td>pH 6 D</td>
<td>50</td>
<td>6.5</td>
<td>nm</td>
<td>$46.6 \pm 2.1$</td>
<td>$65 \pm 22$</td>
<td></td>
</tr>
<tr>
<td>pH 7 B</td>
<td>49</td>
<td>8.3</td>
<td>$107.9 \pm 20.4$</td>
<td>$2.7$</td>
<td>$56.5 \pm 2.7$</td>
<td>$43 \pm 18$</td>
</tr>
<tr>
<td>pH 7 C</td>
<td>49</td>
<td>7.7</td>
<td>$2.5$</td>
<td>$47.5 \pm 2.2$</td>
<td>$59 \pm 21$</td>
<td></td>
</tr>
<tr>
<td>pH 7 D</td>
<td>49</td>
<td>7.1</td>
<td>$10.9$</td>
<td>$57.4 \pm 2.7$</td>
<td>$33 \pm 18$</td>
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<tr>
<td>pH 8 B</td>
<td>49</td>
<td>7.7</td>
<td>$107.9 \pm 20.4$</td>
<td>$2.5$</td>
<td>$68.4 \pm 3.5$</td>
<td>$27 \pm 15$</td>
</tr>
<tr>
<td>pH 8 C</td>
<td>49</td>
<td>7.8</td>
<td>$1.2$</td>
<td>$69.6 \pm 3.6$</td>
<td>$26 \pm 15$</td>
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<td>pH 8 D</td>
<td>49</td>
<td>7.5</td>
<td>$1.6$</td>
<td>$72.6 \pm 3.8$</td>
<td>$23 \pm 14$</td>
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</tr>
<tr>
<td>pH 9 B</td>
<td>49</td>
<td>9.3</td>
<td>$107.9 \pm 20.4$</td>
<td>$7.3$</td>
<td>$59.9 \pm 3.0$</td>
<td>$33 \pm 17$</td>
</tr>
<tr>
<td>pH 9 C</td>
<td>49</td>
<td>9.0</td>
<td>$2.8$</td>
<td>$59.6 \pm 3.0$</td>
<td>$38 \pm 17$</td>
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<tr>
<td>pH 9 D</td>
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<td>8.7</td>
<td>$3.0$</td>
<td>$47.9 \pm 2.2$</td>
<td>$58 \pm 21$</td>
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</tr>
<tr>
<td>Experiment ID</td>
<td>Elapsed Time (days)</td>
<td>Final pH</td>
<td>Initial C-14 activity (Bq cm(^{-3}))</td>
<td>C-14 lost to vessel walls (%)</td>
<td>Final C-14 activity (Bq cm(^{-3}))</td>
<td>Distribution Ratio, (R_D) (cm(^3) g(^{-1})) *</td>
</tr>
<tr>
<td>---------------</td>
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<td>----------</td>
<td>----------------------------------------</td>
<td>-----------------------------</td>
<td>----------------------------------------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>pH 10 B</td>
<td>46</td>
<td>9.8</td>
<td>107.9 ± 20.4</td>
<td>1.9</td>
<td>72.8 ± 3.4</td>
<td>22 ± 14</td>
</tr>
<tr>
<td>pH 10 C</td>
<td>46</td>
<td>10.0</td>
<td></td>
<td>1.9</td>
<td>99.8 ± 5.1</td>
<td>3 ± 11</td>
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<td>pH 10 D</td>
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<td>10.0</td>
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<td>1.5</td>
<td>52.3 ± 2.3</td>
<td>52 ± 20</td>
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<td>pH 12 B</td>
<td>45</td>
<td>12.1</td>
<td>107.9 ± 20.4</td>
<td>0.5</td>
<td>57.1 ± 3.3</td>
<td>44 ± 18</td>
</tr>
<tr>
<td>pH 12 C</td>
<td>45</td>
<td>12.1</td>
<td></td>
<td>0.2</td>
<td>65.2 ± 2.7</td>
<td>32 ± 16</td>
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<tr>
<td>pH 12 D</td>
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<td>12.2</td>
<td></td>
<td>0.4</td>
<td>64.5 ± 2.7</td>
<td>33 ± 16</td>
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</tbody>
</table>

Nm = not measured

Experiments were undertaken at a liquid to solid ratio of 50:1.

* The ±2σ uncertainties are based on the combination of the uncertainties in the counting statistics.
### Table 8  Sorption of C-14 labelled ISA onto haematite at an ISA concentration of $2 \times 10^{-5}$ mol dm$^{-3}$

<table>
<thead>
<tr>
<th>Experiment ID</th>
<th>Elapsed Time (days)</th>
<th>Final pH</th>
<th>Initial C-14 activity (Bq cm$^{-3}$)</th>
<th>C-14 lost to vessel walls (%)</th>
<th>Final C-14 activity (Bq cm$^{-3}$)</th>
<th>Distribution Ratio, $R_D$ (cm$^3$ g$^{-1}$)</th>
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<tbody>
<tr>
<td>$2 \times 10^{-5}$ mol dm$^{-3}$ ISA</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 6 B</td>
<td>49</td>
<td>6.5</td>
<td>$107.9 \pm 20.4$</td>
<td>4.9</td>
<td>$24.9 \pm 1.2$</td>
<td>$156 \pm 42$</td>
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<td>49</td>
<td>5.2</td>
<td></td>
<td>11.0</td>
<td>$23.9 \pm 1.0$</td>
<td>$151 \pm 43$</td>
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<td></td>
<td>6.2</td>
<td>$36.5 \pm 1.7$</td>
<td>$88 \pm 28$</td>
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<tr>
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<td>6.9</td>
<td>$107.9 \pm 20.4$</td>
<td>8.0</td>
<td>$32.0 \pm 1.5$</td>
<td>$107 \pm 33$</td>
</tr>
<tr>
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<td>$109 \pm 32$</td>
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<td>5.5</td>
<td>$35.3 \pm 1.7$</td>
<td>$93 \pm 29$</td>
</tr>
<tr>
<td>pH 8 C</td>
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<td>7.9</td>
<td></td>
<td>6.2</td>
<td>$35.6 \pm 1.7$</td>
<td>$91 \pm 29$</td>
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<tr>
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<td></td>
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<td>$32.2 \pm 1.5$</td>
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<tr>
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<td>11.5</td>
<td>$29.3 \pm 1.4$</td>
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<td>8.7</td>
<td></td>
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<td>$106 \pm 33$</td>
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<tr>
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<td></td>
<td>13.2</td>
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<td>$80 \pm 29$</td>
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<tr>
<td>Experiment ID</td>
<td>Elapsed Time (days)</td>
<td>Final pH</td>
<td>Initial C-14 activity (Bq cm(^{-3}))</td>
<td>C-14 lost to vessel walls (%)</td>
<td>Final C-14 activity (Bq cm(^{-3}))</td>
<td>Distribution Ratio, (R_D) (cm(^3) g(^{-1})) (^*)</td>
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<tr>
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<td>-------------------------------</td>
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</tr>
<tr>
<td>pH 10 B</td>
<td>50</td>
<td>10.1</td>
<td>107.9 ± 20.4</td>
<td>4.8</td>
<td>59.2 ± 2.9</td>
<td>36 ± 17</td>
</tr>
<tr>
<td>pH 10 C</td>
<td>50</td>
<td>10.2</td>
<td>107.9 ± 20.4</td>
<td>3.8</td>
<td>64.5 ± 3.2</td>
<td>30 ± 16</td>
</tr>
<tr>
<td>pH 10 D</td>
<td>50</td>
<td>10.1</td>
<td>107.9 ± 20.4</td>
<td>3.8</td>
<td>62.2 ± 3.0</td>
<td>33 ± 16</td>
</tr>
<tr>
<td>pH 12 B</td>
<td>50</td>
<td>12.3</td>
<td>107.9 ± 20.4</td>
<td>1.2</td>
<td>122.0 ± 6.2</td>
<td>-6 ± 9</td>
</tr>
<tr>
<td>pH 12 C</td>
<td>50</td>
<td>12.3</td>
<td>107.9 ± 20.4</td>
<td>0.2</td>
<td>110.1 ± 5.4</td>
<td>-1 ± 9</td>
</tr>
<tr>
<td>pH 12 D</td>
<td>50</td>
<td>12.3</td>
<td>107.9 ± 20.4</td>
<td>0.2</td>
<td>104.4 ± 5.1</td>
<td>2 ± 10</td>
</tr>
</tbody>
</table>

Experiments were undertaken at a liquid to solid ratio of 50:1.

* The ±2\(\sigma\) uncertainties are based on the combination of the uncertainties in the counting statistics.
### Table 9  Sorption of C-14 labelled ISA onto haematite at an ISA concentration of 2 \(10^{-3}\) mol dm\(^{-3}\)

<table>
<thead>
<tr>
<th>Experiment ID</th>
<th>Elapsed Time (days)</th>
<th>Final pH</th>
<th>Initial C-14 activity (Bq cm(^{-3}))</th>
<th>C-14 lost to vessel walls (%)</th>
<th>Final C-14 activity (Bq cm(^{-3}))</th>
<th>Distribution Ratio, (R_D) (cm(^3) g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 (10^{-3}) mol dm(^{-3}) ISA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 6 B</td>
<td>44</td>
<td>8.3</td>
<td>107.9 ± 20.4</td>
<td>1.8</td>
<td>102.1 ± 4.6</td>
<td>2 ± 10</td>
</tr>
<tr>
<td>pH 6 C</td>
<td>44</td>
<td>6.4</td>
<td></td>
<td>0.2</td>
<td>93.6 ± 4.2</td>
<td>8 ± 11</td>
</tr>
<tr>
<td>pH 6 D</td>
<td>44</td>
<td>6.1</td>
<td></td>
<td>0.2</td>
<td>103.6 ± 4.8</td>
<td>2 ± 10</td>
</tr>
<tr>
<td>pH 7 B</td>
<td>44</td>
<td>7.2</td>
<td>107.9 ± 20.4</td>
<td>0.5</td>
<td>100.6 ± 4.6</td>
<td>3 ± 10</td>
</tr>
<tr>
<td>pH 7 C</td>
<td>44</td>
<td>8.0</td>
<td></td>
<td>0.2</td>
<td>105.1 ± 4.9</td>
<td>1 ± 10</td>
</tr>
<tr>
<td>pH 7 D</td>
<td>44</td>
<td>8.8</td>
<td></td>
<td>0.2</td>
<td>92.0 ± 4.1</td>
<td>8 ± 11</td>
</tr>
<tr>
<td>pH 8 B</td>
<td>44</td>
<td>9.1</td>
<td>107.9 ± 20.4</td>
<td>1.2</td>
<td>88.5 ± 3.9</td>
<td>10 ± 12</td>
</tr>
<tr>
<td>pH 8 C</td>
<td>44</td>
<td>8.9</td>
<td></td>
<td>1.2</td>
<td>83.0 ± 3.6</td>
<td>14 ± 13</td>
</tr>
<tr>
<td>pH 8 D</td>
<td>44</td>
<td>8.9</td>
<td></td>
<td>1.1</td>
<td>81.5 ± 3.5</td>
<td>16 ± 13</td>
</tr>
<tr>
<td>pH 9 B</td>
<td>45</td>
<td>9.4</td>
<td>107.9 ± 20.4</td>
<td>0.8</td>
<td>112.9 ± 5.3</td>
<td>-3 ± 9</td>
</tr>
<tr>
<td>pH 9 C</td>
<td>45</td>
<td>9.3</td>
<td></td>
<td>4.2</td>
<td>105.6 ± 4.9</td>
<td>-1 ± 10</td>
</tr>
<tr>
<td>pH 9 D</td>
<td>45</td>
<td>9.4</td>
<td></td>
<td>0.9</td>
<td>106.0 ± 4.9</td>
<td>0 ± 10</td>
</tr>
<tr>
<td>Experiment ID</td>
<td>Elapsed Time (days)</td>
<td>Final pH</td>
<td>Initial C-14 activity (Bq cm(^{-3}))</td>
<td>C-14 lost to vessel walls (%)</td>
<td>Final C-14 activity (Bq cm(^{-3}))</td>
<td>Distribution Ratio, (R_D) (cm(^3) g(^{-1}))^*</td>
</tr>
<tr>
<td>--------------</td>
<td>---------------------</td>
<td>----------</td>
<td>---------------------------------------</td>
<td>-------------------------------</td>
<td>--------------------------------------</td>
<td>----------------------------------------</td>
</tr>
<tr>
<td>pH 10 B</td>
<td>45</td>
<td>10.4</td>
<td>107.9 ± 20.4</td>
<td>2.0</td>
<td>157.1 ± 8.0</td>
<td>-16 ± 7</td>
</tr>
<tr>
<td>pH 10 C</td>
<td>45</td>
<td>10.2</td>
<td>2.8</td>
<td>110.3 ± 5.1</td>
<td>-2 ± 10</td>
<td></td>
</tr>
<tr>
<td>pH 10 D</td>
<td>45</td>
<td>10.2</td>
<td>2.9</td>
<td>113.4 ± 5.2</td>
<td>-4 ± 9</td>
<td></td>
</tr>
<tr>
<td>pH 12 B</td>
<td>48</td>
<td>12.1</td>
<td>107.9 ± 20.4</td>
<td>0.7</td>
<td>135.5 ± 6.3</td>
<td>-10 ± 8</td>
</tr>
<tr>
<td>pH 12 C</td>
<td>48</td>
<td>12.2</td>
<td>0.6</td>
<td>121.5 ± 5.5</td>
<td>-6 ± 9</td>
<td></td>
</tr>
<tr>
<td>pH 12 D</td>
<td>48</td>
<td>12.2</td>
<td>0.6</td>
<td>106.1 ± 4.6</td>
<td>1 ± 10</td>
<td></td>
</tr>
</tbody>
</table>

Experiments were undertaken at a liquid to solid ratio of 50:1.

The ±2\(\sigma\) uncertainties are based on the combination of the uncertainties in the counting statistics.
Table 10  Thorium sorption onto haematite in the absence of any organic complexants

<table>
<thead>
<tr>
<th>Experiment ID</th>
<th>Elapsed Time (days)</th>
<th>Final pH</th>
<th>Initial Th-228 activity (Bq cm(^{-3}))</th>
<th>Th-228 lost to vessel walls (%)</th>
<th>Final Th-228 activity (Bq cm(^{-3}))</th>
<th>Distribution Ratio, (R_D) (cm(^3) g(^{-1}))(^*)</th>
<th>Mean Distribution Ratio, (R_D) (cm(^3) g(^{-1}))(^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 6 B</td>
<td>46</td>
<td>6.5</td>
<td>20.22 ± 1.71</td>
<td>11</td>
<td>2.13 ± 0.68 (10^{-4})</td>
<td>4.20 ± 1.40 (10^{6})</td>
<td>4.05 ± 1.69 (10^{6})</td>
</tr>
<tr>
<td>pH 6 C</td>
<td>46</td>
<td>6.0</td>
<td></td>
<td>11</td>
<td>2.43 ± 0.76 (10^{-4})</td>
<td>3.75 ± 1.22 (10^{6})</td>
<td></td>
</tr>
<tr>
<td>pH 6 D</td>
<td>46</td>
<td>6.5</td>
<td></td>
<td>9</td>
<td>1.27 ± 0.47 (10^{-4})</td>
<td>7.32 ± 2.82 (10^{6})</td>
<td></td>
</tr>
<tr>
<td>pH 6 E</td>
<td>46</td>
<td>5.9</td>
<td></td>
<td>9</td>
<td>1.01 ± 0.26 (10^{-3})</td>
<td>9.15 ± 2.53 (10^{5})</td>
<td></td>
</tr>
<tr>
<td>pH 9 B</td>
<td>43</td>
<td>9.2</td>
<td>20.34 ± 1.66</td>
<td>12</td>
<td>&lt;1.9 (10^{-4})</td>
<td>&gt;4.9 (10^{6})</td>
<td>&gt;4.3 (10^{6})</td>
</tr>
<tr>
<td>pH 9 C</td>
<td>43</td>
<td>9.0</td>
<td></td>
<td>12</td>
<td>2.19 ± 1.08 (10^{-4})</td>
<td>4.14 ± 2.80 (10^{6})</td>
<td></td>
</tr>
<tr>
<td>pH 9 D</td>
<td>43</td>
<td>8.9</td>
<td></td>
<td>11</td>
<td>&lt;2.4 (10^{-4})</td>
<td>&gt;3.8 (10^{6})</td>
<td></td>
</tr>
<tr>
<td>pH 9 E</td>
<td>43</td>
<td>8.9</td>
<td></td>
<td>11</td>
<td>2.13 ± 0.09 (10^{-4})</td>
<td>4.28 ± 1.85 (10^{6})</td>
<td></td>
</tr>
<tr>
<td>pH 12 B</td>
<td>43</td>
<td>11.9</td>
<td>17.34 ± 1.81</td>
<td>11</td>
<td>3.94 ± 0.57 (10^{-3})</td>
<td>1.95 ± 0.37 (10^{5})</td>
<td>1.72 ± 0.28 (10^{6})</td>
</tr>
<tr>
<td>pH 12 C</td>
<td>43</td>
<td>11.9</td>
<td></td>
<td>11</td>
<td>3.72 ± 0.33 (10^{-3})</td>
<td>2.07 ± 0.31 (10^{5})</td>
<td></td>
</tr>
<tr>
<td>pH 12 D</td>
<td>43</td>
<td>12.0</td>
<td></td>
<td>14</td>
<td>4.60 ± 0.39 (10^{-3})</td>
<td>1.61 ± 0.24 (10^{5})</td>
<td></td>
</tr>
<tr>
<td>pH 12 E</td>
<td>43</td>
<td>12.0</td>
<td></td>
<td>14</td>
<td>6.00 ± 0.45 (10^{-3})</td>
<td>1.24 ± 0.18 (10^{5})</td>
<td></td>
</tr>
</tbody>
</table>

Experiments were undertaken at a liquid to solid ratio of 50:1.

- The ±2\(\sigma\) uncertainties are based on the combination of the uncertainties in the counting statistics.
Table 11  Thorium sorption onto pre-equilibrated haematite in the absence of any organic complexants

<table>
<thead>
<tr>
<th>Experiment ID</th>
<th>Elapsed Time (days)</th>
<th>Final pH</th>
<th>Initial Th-228 activity (Bq cm(^{-3}))</th>
<th>Th-228 lost to vessel walls (%)</th>
<th>Final Th-228 activity (Bq cm(^{-3}))</th>
<th>Distribution Ratio, (R_D) (cm(^3) g(^{-1}))*</th>
<th>Mean Distribution Ratio, (R_D) (cm(^3) g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 6 A</td>
<td>46</td>
<td>5.0</td>
<td>20.22 ± 1.71</td>
<td>15</td>
<td>6.49 ± 1.43 (10^4)</td>
<td>1.32 ± 0.32 (10^6)</td>
<td>1.17 ± 0.61 (10^6)</td>
</tr>
<tr>
<td>pH 6 B</td>
<td>47</td>
<td>6.4</td>
<td></td>
<td>15</td>
<td>2.57 ± 0.87 (10^4)</td>
<td>3.34 ± 1.17 (10^6)</td>
<td></td>
</tr>
<tr>
<td>pH 9 A</td>
<td>46</td>
<td>8.5</td>
<td>20.34 ± 1.66</td>
<td>16</td>
<td>6.16 ± 1.43 (10^4)</td>
<td>1.38 ± 0.35 (10^5)</td>
<td>5.79 ± 2.25 (10^5)</td>
</tr>
<tr>
<td>pH 9 B</td>
<td>47</td>
<td>9.4</td>
<td></td>
<td>16</td>
<td>9.13 ± 2.64 (10^4)</td>
<td>9.34 ± 2.85 (10^5)</td>
<td></td>
</tr>
<tr>
<td>pH 12 A</td>
<td>46</td>
<td>11.9</td>
<td>17.34 ± 1.81</td>
<td>11</td>
<td>5.96 ± 0.75 (10^3)</td>
<td>1.29 ± 0.22 (10^5)</td>
<td>6.93 ± 1.68 (10^4)</td>
</tr>
<tr>
<td>pH 12 B</td>
<td>46</td>
<td>11.9</td>
<td></td>
<td>11</td>
<td>5.20 ± 0.64 (10^3)</td>
<td>1.48 ± 0.25 (10^5)</td>
<td></td>
</tr>
</tbody>
</table>

Experiments were undertaken at a liquid to solid ratio of 50:1.

* The \(±2σ\) uncertainties are based on the combination of the uncertainties in the counting statistics.
Table 12  Thorium sorption onto haematite in the presence of ISA at 2 \(10^{-3}\) mol dm\(^{-3}\)

<table>
<thead>
<tr>
<th>Experiment ID</th>
<th>Elapsed Time (days)</th>
<th>Final pH</th>
<th>Initial Th-228 activity (Bq cm(^{-3}))</th>
<th>Th-228 lost to vessel walls (%)</th>
<th>Final Th-228 activity (Bq cm(^{-3}))</th>
<th>Distribution Ratio, (R_D) (cm(^3) g(^{-1}))(\times)10(^5)</th>
<th>Mean Distribution Ratio, (R_D) (cm(^3) g(^{-1}))(\times)10(^5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 6 B</td>
<td>48</td>
<td>6.6</td>
<td>21.78 ± 1.66</td>
<td>5</td>
<td>2.22 ± 0.31 10(^{-3})</td>
<td>4.70 ± 0.75 10(^5)</td>
<td>2.37 ± 0.50 10(^6)</td>
</tr>
<tr>
<td>pH 6 C</td>
<td>48</td>
<td>5.7</td>
<td>5</td>
<td>3.88 ± 0.77 10(^{-3})</td>
<td>2.69 ± 0.58 10(^5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 6 D</td>
<td>48</td>
<td>6.1</td>
<td>6.06 ± 1.10 10(^{-3})</td>
<td>6</td>
<td>6.19 ± 0.34 10(^5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 6 E</td>
<td>48</td>
<td>5.5</td>
<td>2.64 ± 0.26 10(^{-2})</td>
<td>6</td>
<td>3.88 ± 0.39 10(^4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 9 B</td>
<td>47</td>
<td>8.8</td>
<td>23.10 ± 1.82</td>
<td>10</td>
<td>5.83 ± 2.53 10(^{-4})</td>
<td>1.79 ± 0.79 10(^6)</td>
<td>&gt;1.59 10(^6)</td>
</tr>
<tr>
<td>pH 9 C</td>
<td>47</td>
<td>8.8</td>
<td>4.62 ± 0.96 10(^{-3})</td>
<td>10</td>
<td>2.26 ± 0.51 10(^5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 9 D</td>
<td>48</td>
<td>9.0</td>
<td>&lt;5.6 10(^{-4})</td>
<td>9</td>
<td>&gt;1.9 10(^6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 9 E</td>
<td>48</td>
<td>8.9</td>
<td>&lt;4.3 10(^{-4})</td>
<td>9</td>
<td>&gt;2.5 10(^6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 12 B</td>
<td>47</td>
<td>11.8</td>
<td>22.50 ± 1.74</td>
<td>11</td>
<td>6.96 ± 1.08 10(^{-3})</td>
<td>1.42 ± 0.25 10(^5)</td>
<td>1.33 ± 0.23 10(^6)</td>
</tr>
<tr>
<td>pH 12 C</td>
<td>47</td>
<td>11.9</td>
<td>5.96 ± 1.01 10(^{-3})</td>
<td>11</td>
<td>1.69 ± 0.32 10(^5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 12 D</td>
<td>47</td>
<td>11.9</td>
<td>8.40 ± 1.07 10(^{-3})</td>
<td>3</td>
<td>1.30 ± 0.20 10(^5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH 12 E</td>
<td>47</td>
<td>11.9</td>
<td>1.21 ± 0.10 10(^{-2})</td>
<td>3</td>
<td>9.02 ± 0.72 10(^4)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Experiments were undertaken at a liquid to solid ratio of 50:1.

* The ±2\(\sigma\) uncertainties are based on the combination of the uncertainties in the counting statistics.
Table 13  Thorium sorption onto haematite in the presence of 10% CDP (i.e. after ten-fold dilution of original leachate)

<table>
<thead>
<tr>
<th>Experiment ID</th>
<th>Elapsed Time (days)</th>
<th>Final pH</th>
<th>Initial Th-228 activity (Bq cm(^{-3}))</th>
<th>Th-228 lost to vessel walls (%)</th>
<th>Final Th-228 activity (Bq cm(^{-3}))</th>
<th>Distribution Ratio, (R_D) (cm(^3) g(^{-1}))*</th>
<th>Mean Distribution Ratio, (R_D) (cm(^3) g(^{-1}))*</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 6 B</td>
<td>48</td>
<td>6.8</td>
<td>17.88 ± 1.53</td>
<td>20</td>
<td>5.59 ± 0.31 (10^{-2})</td>
<td>1.29 ± 0.16 (10^{4})</td>
<td>1.05 ± 0.12 (10^{4})</td>
</tr>
<tr>
<td>pH 6 C</td>
<td>48</td>
<td>4.8</td>
<td></td>
<td>20</td>
<td>8.94 ± 0.47 (10^{-2})</td>
<td>8.07 ± 0.10 (10^{3})</td>
<td></td>
</tr>
<tr>
<td>pH 6 D</td>
<td>49</td>
<td>4.8</td>
<td></td>
<td>15</td>
<td>8.16 ± 0.44 (10^{-2})</td>
<td>9.45 ± 1.08 (10^{3})</td>
<td></td>
</tr>
<tr>
<td>pH 6 E</td>
<td>49</td>
<td>6.4</td>
<td></td>
<td>15</td>
<td>6.69 ± 0.54 (10^{-2})</td>
<td>1.15 ± 0.09 (10^{4})</td>
<td></td>
</tr>
<tr>
<td>pH 9 B</td>
<td>49</td>
<td>8.9</td>
<td>20.34 ± 2.03</td>
<td>18</td>
<td>6.49 ± 0.53 (10^{-2})</td>
<td>1.29 ± 0.19 (10^{4})</td>
<td>1.50 ± 0.21 (10^{4})</td>
</tr>
<tr>
<td>pH 9 C</td>
<td>49</td>
<td>8.8</td>
<td></td>
<td>18</td>
<td>4.99 ± 0.43 (10^{-2})</td>
<td>1.68 ± 0.25 (10^{4})</td>
<td></td>
</tr>
<tr>
<td>pH 9 D</td>
<td>49</td>
<td>8.7</td>
<td></td>
<td>16</td>
<td>5.39 ± 0.49 (10^{-2})</td>
<td>1.60 ± 0.24 (10^{4})</td>
<td></td>
</tr>
<tr>
<td>pH 9 E</td>
<td>49</td>
<td>8.7</td>
<td></td>
<td>16</td>
<td>6.04 ± 0.51 (10^{-2})</td>
<td>1.43 ± 0.12 (10^{4})</td>
<td></td>
</tr>
<tr>
<td>pH 12 B</td>
<td>48</td>
<td>11.7</td>
<td>21.36 ± 1.72</td>
<td>3</td>
<td>1.25 ± 0.10 (10^{-1})</td>
<td>8.22 ± 0.94 (10^{3})</td>
<td>5.41 ± 0.63 (10^{3})</td>
</tr>
<tr>
<td>pH 12 C</td>
<td>48</td>
<td>11.6</td>
<td></td>
<td>3</td>
<td>2.32 ± 0.20 (10^{-1})</td>
<td>4.40 ± 0.53 (10^{3})</td>
<td></td>
</tr>
<tr>
<td>pH 12 D</td>
<td>48</td>
<td>11.8</td>
<td></td>
<td>4</td>
<td>2.48 ± 0.20 (10^{-1})</td>
<td>4.08 ± 0.48 (10^{3})</td>
<td></td>
</tr>
<tr>
<td>pH 12 E</td>
<td>48</td>
<td>11.8</td>
<td></td>
<td>4</td>
<td>2.05 ± 0.18 (10^{-1})</td>
<td>4.94 ± 0.43 (10^{3})</td>
<td></td>
</tr>
</tbody>
</table>

Experiments were undertaken at a liquid to solid ratio of 50:1.

* The ±2σ uncertainties are based on the combination of the uncertainties in the counting statistics.
Table 14  Summary of the effects of initial iso-saccharinate concentration on iso-saccharinate sorption (from reference [24])

<table>
<thead>
<tr>
<th></th>
<th>pH Range</th>
<th>2 $10^{-3}$ M ISA</th>
<th>2 $10^{-4}$ M ISA</th>
<th>2 $10^{-5}$ M ISA</th>
<th>2 $10^{-7}$ M ISA</th>
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<td>Reacted Fracture</td>
<td>7.7</td>
<td>6</td>
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<td>Mineral Assemblages</td>
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<td>10.0 – 10.4</td>
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<td>4</td>
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<td>8</td>
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<td>Unreacted Fracture</td>
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<td>Mineral Assemblages</td>
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<td>Unreacted Wall Rock</td>
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<td>10</td>
<td>100</td>
<td>160</td>
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</table>

Water:rock ratio:- 50:1
These experiments were conducted in the presence of thorium, $\sim 2 \times 10^{-11}$ M.

In the above table the initial ISA concentrations are given, for ease of comparison.

Wall rock: major components: quartz and mica; minor components: albite and dolomite with some chlorite and haematite present
Fracture Mineral assemblages: major components: calcite, dolomite and haematite.
Figure 1  Schematic representation of processes that influence the impact of cellulose degradation products on radionuclide sorption

M metal
X complexing component of CDP
N non complexing component of CDP
Figure 2  Scanning electron micrographs of haematite powder from the second batch of material used (Lot A0228333); scale bars read: (a) 90 µm; and (b) 20 µm
Figure 3  High Performance Liquid Chromatographs of the 2 batches of CDP compared to a 0.011 mol dm$^{-3}$ solution of α-ISA (straight chain form)
Figure 4  
Tentative identification of three CDP components by HPLC by the method of sequential standard addition; α-ISA in open chain form included for comparison.
Figure 5  Comparison of initial and final TOC concentrations for sorption experiments with haematite and ISA

![Graph showing comparison of initial and final TOC concentrations for sorption experiments with haematite and ISA](image-url)
Figure 6  Comparison of initial and final TOC concentrations for sorption experiments with haematite and CDP leachate
Figure 7  Comparison of measured chromatogram peak areas for solutions of 10% CDP leachate after contact with haematite for 84 days and for control samples equilibrated for 82 days in the absence of haematite at pH 6 and 12
Figure 8  Comparison of chromatograms for ISA solutions in lactone and open chain forms with CDP leachates and ISA solutions equilibrated at pH 6 for over 80 days.
Figure 9  Measured sorption distribution ratios for C-14 labelled ISA onto haematite (batch II) as a function of ISA concentration and pH.
Figure 10  Measured sorption distribution ratios for thorium sorption onto haematite as a function of pH in the absence and presence of organic complexants derived from cellulosic materials (background electrolyte 0.1 mol dm\(^{-3}\) NaCl solution)

Points marked as \(\times\) or \(\times\) are greater than values

Error bars on points around pH 12 are excluded for clarity