

The effect of cellulose degradation products on thorium sorption onto hematite: studies of a model ternary system

G. M. N. BASTON, M. M. COWPER, T. G. HEATH, T. A. MARSHALL AND S. W. SWANTON*

AMEC[†], B150, Thomson Avenue, Harwell, Didcot, Oxfordshire OX11 0QB, UK

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ABSTRACT

Cellulose degradation products (CDPs) can complex with radioelements causing solubility enhancement and sorption reduction, effects which are detrimental to the containment of radionuclides in the near field of a geological disposal facility and surrounding geosphere. Isosaccharinic acid (ISA) is the principal component of CDPs formed under the alkaline anaerobic conditions of a cement-based near field and appears to be largely responsible for the impact of CDPs on radionuclide solubility and sorption under near-field conditions. However, the situation appears to be more complicated under near-neutral pH geosphere conditions.

A combined experimental and modelling study was undertaken to compare the impact of a CDP leachate to ISA in a simple model ternary sorption system consisting of hematite as a single mineral substrate, thorium as the radioelement and ISA or a CDP leachate as the complexant. Thorium sorbs strongly to hematite. A triple layer model for thorium sorption to hematite was refined to fit to the experimental data in the absence of ISA or CDP leachate; the effect of ISA on thorium sorption was then predicted.

In the presence of CDP leachate, a significant reduction in thorium sorption was observed from pH 6 to 12 in good agreement with model predictions based on a high concentration of ISA. However, only a limited impact of ISA on thorium sorption was observed at pH 6 to 12, in contrast to predictions. The effects of ISA could be accounted for by assuming the formation of a ternary thorium–ISA–surface complex. The model has yet to be extended to the more complex CDP systems. Differences in the thorium speciation in solution due to the formation of a ternary calcium–thorium–ISA complex in the CDP leachate, which is absent from solutions with ISA only, provides the most likely explanation for the differences observed experimentally.

KEYWORDS: cellulose degradation products, hematite, isosaccharinic acid, organic complexants, sorption, surface complexation model, thorium.

Introduction

SORPTION of radionuclides onto near-field and geosphere materials is a key mechanism for retarding radionuclide migration from a geological disposal facility (GDF) for higher activity radioactive wastes (Nuclear Decommissioning

Authority, 2010). Potentially, one of the most significant detrimental processes that may reduce the extent of radionuclide sorption is the formation of complexes with organic compounds that may be present in the groundwater or released from a GDF containing long-lived intermediate-level and some low-level wastes (ILW/LLW). Volumetrically, the most important potential sources of organic complexants within a GDF will be cellulosic materials such as paper, wood and cloth present in some ILW. The chemical degradation of cellulosic materials is well

* E-mail: steve.swanton@amec.com

[†] Formerly Serco

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established under the alkaline conditions relevant to a cement-based ILW/LLW near-field concept (Knill and Kennedy, 2003). The resulting degradation products have been shown to complex some radionuclides, causing large solubility enhancements in the near field, and a reduction in sorption in both the near field and the geosphere (Heath and Williams, 2005).

Isosaccharinic acid (ISA) has been identified as a major product of the alkaline anaerobic degradation of cellulose (Machell and Richards, 1960), and it appears to be largely responsible for the impact of cellulose degradation products (CDPs) on radionuclide solubility and sorption under cementitious near-field conditions (e.g. Heath and Williams, 2005; Van Loon and Glaus, 1998). Under the near-neutral pH conditions typical of the geosphere, however, the situation is more complicated. In general, the reduction in sorption of radionuclides to geological materials tends to be greater in the presence of CDPs than in the presence of ISA alone (Knight, 2006). This observation is indicative of the presence of additional complexants that may lower sorption more in the presence of CDPs than ISA. In addition, in some experiments apparent enhancement of radionuclide sorption has been observed in the presence of CDPs and/or ISA onto certain rock types (Knight, 2006). The discrepancies between the effects of ISA and CDPs under geosphere conditions are difficult to explain (Heath and Williams, 2005). Therefore, the aim of the present study was to develop a clearer conceptual understanding of the effects of these complexants under near-neutral conditions.

The approach adopted was to characterize the behaviour of a simple model ternary system and to compare the behaviour of that system with the effects of a CDP leachate prepared by the alkaline anaerobic degradation of paper tissues. The ternary system consisted of hematite as the single mineral substrate (an important sorbing mineral), thorium as the radioelement (non-redox sensitive) and ISA as the complexant. A combined experimental and modelling study was undertaken which consisted of (1) the development of an initial model based on literature data, to predict the extent of sorption under the conditions of the planned experiments; (2) an experimental programme to study the interactions in the ternary system; (3) comparison of the experimental data with the earlier model predictions; and (4) refinement of the model to take account of the new experimental data.

Experimental

Full experimental details are reported elsewhere (Cowper *et al.*, 2012) and are summarized below.

Materials

The synthetic hematite selected was 99.99% purity powder (Acros Organics). Two batches of material were supplied with BET surface areas of $5.58 \pm 0.02 \text{ m}^2 \text{ g}^{-1}$ (batch H1) and $13.6 \pm 0.02 \text{ m}^2 \text{ g}^{-1}$ (batch H2). The ^{228}Th and ^{232}Th were supplied by AEA Technology Nuclear Science, Harwell. A batch of the α -(erythro-) isomer of ISA in the lactone form was provided by AEA Technology (unless otherwise qualified, the abbreviation ISA refers to the α -isomer in this paper). The ^{14}C -labelled ISA was supplied by Amersham International. For the preparation of CDP leachates, 5 g of calcium hydroxide, 20 g Kimwipe tissues and 500 cm^3 of 0.1 mol dm^{-3} sodium hydroxide were heated inside each of five stainless steel canisters at 80°C for 30 days. The leachate was separated from any solid material using pre-treated $0.45 \mu\text{m}$ filter units (Nalgene Filtration Products). Preparation and all handling of the CDP leachates were undertaken in a nitrogen-atmosphere glove box.

The total organic carbon (TOC) content of the CDP leachates was typically about 2000 mg dm^{-3} and the pH was 12.8. The leachate contained about $9 \times 10^{-2} \text{ mol dm}^{-3}$ sodium, $6 \times 10^{-3} \text{ mol dm}^{-3}$ calcium, $5 \times 10^{-5} \text{ mol dm}^{-3}$ potassium and $2 \times 10^{-6} \text{ mol dm}^{-3}$ iron. High-performance liquid chromatography (HPLC) analysis of the CDP leachate was undertaken using an Agilent LC28 equipped with a 1090 series diode array UV detector; separation was carried out using a Waters Resolve C18 column with 0.1 mol dm^{-3} potassium dihydrogen orthophosphate solution adjusted to pH 3.2 as the mobile phase. Detector response was calibrated using standard solutions of α -ISA between 10^{-4} and $10^{-2} \text{ mol dm}^{-3}$ at pH 12. The α - and β -isomers of ISA eluted as a single broad peak with a combined concentration in each batch of $1.9 \times 10^{-2} \text{ mol dm}^{-3}$. Formic, acetic and lactic acids were tentatively identified based on standard additions; other unidentified components were also present.

Batch sorption experiments

Sorption experiments onto hematite were undertaken to investigate the following interactions as a function of pH: (1) ISA sorption as a function of

ISA concentration; (2) CDP sorption as a function of CDP leachate concentration; (3) thorium sorption; (4) thorium sorption in the presence of ISA; and (5) thorium sorption in the presence of a CDP leachate.

All work was undertaken in a nitrogen-atmosphere glove box to exclude carbon dioxide. Sorption experiments were undertaken at a liquid volume (cm^3) to solid mass (g) ratio of 50:1. The background electrolyte in all experiments was 0.1 mol dm^{-3} NaCl solution except for those with undiluted CDP leachate.

An initial study investigated the sorption of ISA at three concentrations (10^{-2} , 10^{-3} and $10^{-4} \text{ mol dm}^{-3}$) at pH 10 and 12, and CDP leachates at two concentrations (2000 and 200 mg TOC dm^{-3}) to hematite (batch H1) at six pH values: pH 6, 7, 8, 9, 10 and 12. To study ISA sorption at lower concentrations, ^{14}C -labelled ISA was used in subsequent experiments onto hematite from batch H2 at the six pH values. The ISA concentrations used were 2×10^{-3} , 2×10^{-5} , and $2 \times 10^{-7} \text{ mol dm}^{-3}$. After equilibration for at least one month, samples of the solution phase were filtered through pre-conditioned 30,000 nominal molecular weight cut-off (NMWCO) ultra-filters (Millipore TTK). The ^{14}C was determined by liquid scintillation counting.

Experiments with thorium using a mixture of $^{228}\text{Th}/^{232}\text{Th}$ were undertaken at pH 6, 9 and 12 in quadruplicate using fresh hematite, batch H2, that had not been in contact with water. In addition, duplicate experiments for thorium only were undertaken at each pH using hematite batch H1 pre-equilibrated with 0.1 mol dm^{-3} NaCl solutions at the three pH values. The target initial thorium concentration was $\sim 3 \times 10^{-11} \text{ mol dm}^{-3}$, about one order of magnitude below the solubility limit for thorium in the pH range from 6 to 12 (Neck *et al.*, 2003). Thorium solutions were prepared in 0.1 mol dm^{-3} NaCl solution with or without ISA or CDP leachate at the required pH before addition to the hematite. After two months, samples of the aqueous phase were taken from each experiment, filtered through pre-conditioned 30,000 NMWCO filters and acidified with dilute nitric acid. After sampling and pH measurement, each vessel was emptied, washed with demineralized water to remove remaining solid and leached with 25% nitric acid for several days to recover any thorium associated with the vessel walls; ^{228}Th was determined by alpha spectrometry.

Values for the sorption distribution ratio, R_D , were calculated for each experiment using the equation:

$$R_D = V(C_o - C_w - C_t)/mC_t$$

where V is the solution volume equilibrated with mass, m , of hematite; C_o is the initial concentration; C_w is the concentration of radionuclide sorbed to the vessel walls; and C_t is the final measured radionuclide concentration.

Modelling

Thermodynamic modelling was applied in the sorption model development using the geochemical speciation programs *PHREEQC* version 2.12 and *HARPHRO* (Haworth *et al.*, 1995) version 2.0. *HARPHRO* has been verified against *PHREEQC*, and against other programs under international projects (Read and Falck, 1996). Thermodynamic data were taken from the *HATCHES* database (Bond *et al.*, 1997) version NEA17. However, data for aqueous thorium complexes including ISA complexes were reviewed as part of this work and the selected values are given in Table 1. This work was performed before publication of the OECD/NEA data review for thorium (Rand *et al.*, 2008).

Experimental data for sorption onto single mineral phases are commonly interpreted using thermodynamic sorption models, with the implicit assumption that the experiments have reached equilibrium. For mineral phases with no ion-exchange capacity, thermodynamic surface complexation models are commonly applied. These include electrostatic models such as the diffuse-layer model (DLM) (Dzombak and Morel, 1995) and the triple-layer model (TLM) (Davies and Leckie, 1978), which account for the electrostatic interactions of sorbing ions with a charged surface. In this study literature-based models were developed using the DLM and TLM approaches.

Results and discussion

Initial Modelling

The first stage of this study involved the development of a sorption model for thorium onto hematite in the presence of ISA, which consisted of the development of literature-based models by the fitting of published experimental data and application of selected thermodynamic data given in Table 1; and the subsequent

TABLE 1. Summary of selected thermodynamic data for thorium used in sorption modelling calculations.

Equilibrium	log K°	Reference
$\text{Th}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{Th}(\text{OH})^{3+} + \text{H}^+$	-2.20	1
$\text{Th}^{4+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Th}(\text{OH})_2^{2+} + 2\text{H}^+$	-6.60	1
$\text{Th}^{4+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Th}(\text{OH})_3^+ + 3\text{H}^+$	-11.40	1
$\text{Th}^{4+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Th}(\text{OH})_4 + 4\text{H}^+$	-17.00	1
$2\text{Th}^{4+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Th}_2(\text{OH})_2^{6+} + 2\text{H}^+$	-5.70	2
$4\text{Th}^{4+} + 8\text{H}_2\text{O} \rightleftharpoons \text{Th}_4(\text{OH})_8^{8+} + 8\text{H}^+$	-20.40	2
$4\text{Th}^{4+} + 12\text{H}_2\text{O} \rightleftharpoons \text{Th}_4(\text{OH})_{12}^{4+} + 12\text{H}^+$	-26.70	2
$6\text{Th}^{4+} + 15\text{H}_2\text{O} \rightleftharpoons \text{Th}_6(\text{OH})_{15}^{9+} + 15\text{H}^+$	-34.00	2
$\text{Th}^{4+} + \text{ISA}^- \rightleftharpoons \text{Th}(\text{H}_{-3}\text{ISA}) + 3\text{H}^+$	-4.27	3
$\text{Th}^{4+} + \text{ISA}^- \rightleftharpoons \text{Th}(\text{H}_{-4}\text{ISA})^- + 4\text{H}^+$	-11.60	4

References used in the table are as follows: (1) Altmaier *et al.* (2006); (2) Neck *et al.* (2002); (3) Rai *et al.* (2003), value for $\text{Np}(\text{H}_{-3}\text{ISA})^-$ used as analogue for Th; (4) *HATCHES* database (Bond *et al.*, 1997) value selected for version NEA17 (Baston *et al.*, 2008) derived from Vercammen *et al.* (2001), but corrected for ionic strength differences and the change to log K for the $\text{Th}(\text{OH})_{4(\text{aq})}$ species to the value above.

The notation H_{-n} denotes that n hydroxyl protons have been displaced during complexation.

prediction of thorium sorption behaviour under the range of conditions studied experimentally.

Four models were investigated and predictions of thorium sorption were made under the chemical conditions applied in the experimental study as follows:

(1) TLM case 1, based on a reported surface model and surface complexation reaction and log K_s (Murphy *et al.*, 1999);

(2) TLM case 2, based on a reported surface model and site density (Murphy *et al.*, 1999) and fitting of experimental thorium sorption data reported elsewhere (Cromières *et al.*, 1998);

(3) TLM case 3, based on a reported surface model (Murphy *et al.*, 1999), fitting of experimental thorium sorption data reported elsewhere (Cromières *et al.* 1998) and applying a site density from the latter reference;

(4) DLM, based on reported experimental data and diffuse-layer model (Cromières *et al.*, 1998).

Thermodynamic data that were applied in the sorption model calculations are given in Table 1. The simplest model with the fewest thorium sorption parameters is TLM case 1 as it is based on the formation of only one thorium surface complex. It also gave the best agreement between model predictions and experimental data (Fig. 1). For these reasons, only TLM case 1 was taken forward for further investigation and model refinement using the new experimental data.

Separate predictions were made for each batch of hematite, under the conditions of relevance to the experiments in which they were studied. Details of the original predictive model for TLM case 1 are given in Table 2.

Experimental results: ISA and CDP sorption onto hematite

The experimental results summarized here are presented in full in Cowper *et al.* (2012). At the higher ISA concentrations of 10^{-2} , 10^{-3} and 10^{-4} mol dm^{-3} , no changes in solution concentrations of ISA were detectable by TOC or HPLC measurements after contact with hematite for 30 days. This was the case at both pH 10 and 12. These results were interpreted in terms of the sorption of only a small fraction of added ISA with the majority of the ISA remaining in solution. Similar results were obtained in experiments with CDP leachates at ~ 2000 and ~ 200 mg dm^{-3} TOC at all six pH values studied (6–12). It is considered that the range of concentrations amenable to study by the current HPLC methods using UV detection is probably too high ($\geq 10^{-4}$ mol dm^{-3}) to allow differences in sorption behaviour of CDP components to hematite to be distinguished due to the small fraction of CDP components sorbing at these concentrations.

THORIUM SORPTION ONTO HEMATITE

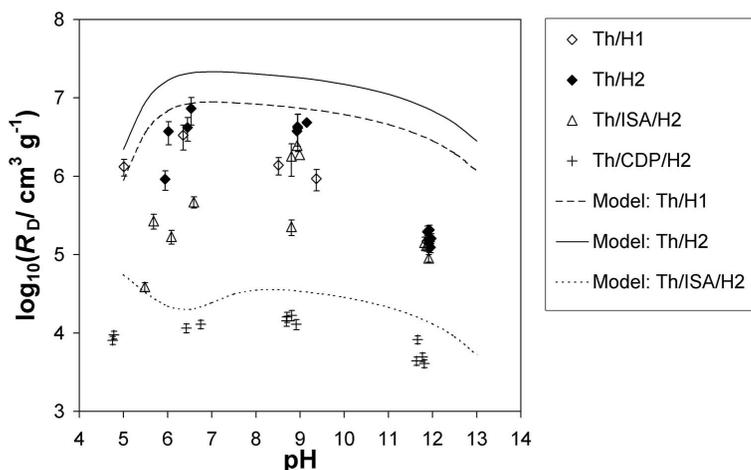


FIG. 1. Comparison of model TLM case 1 predictions with experimental data (uncertainties $\pm 2\sigma$). Hematite specific surface areas: $5.6 \text{ m}^2 \text{ g}^{-1}$ (batch H1); $13.6 \text{ m}^2 \text{ g}^{-1}$ (batch H2). Data at pH 9 with no error bars are minimum values; ISA concentration $0.002 \text{ mol dm}^{-3}$, CDP leachate $200 \text{ mg TOC dm}^{-3}$.

TABLE 2. Original and refitted model details for TLM case 1 applied under experimental conditions.

Equilibrium	Original model	Refitted model*
Surface complexation parameters ($\log K_s$)		
<i>Surface (de)protonation (inner-sphere)</i>		
$>\text{SOH} + \text{H}^+ \rightleftharpoons >\text{SOH}_2^+$	8.25	8.25
$>\text{SOH} \rightleftharpoons >\text{SO}^- + \text{H}^+$	-10.25	-10.25
<i>Electrolyte ML (outer-sphere)</i>		
$>\text{SOH} + \text{H}^+ + \text{L}^- \rightleftharpoons >\text{SOH}_2-\text{L}$	10.18	10.18
$>\text{SOH} + \text{M}^+ \rightleftharpoons >\text{SO}-\text{M} + \text{H}^+$	-8.46	-8.46
<i>ISA sorption</i>		
$>\text{SOH} + \text{ISA}^- \rightleftharpoons \text{SOHISA}^-$ (inner-sphere)	-1.00	removed
$>\text{SOH} + \text{H}^+ + \text{ISA}^- \rightleftharpoons \text{SOH}_2\text{ISA}$ (outer-sphere)		12.80
<i>Th sorption (inner-sphere)</i>		
$>\text{SOH} + \text{Th}^{4+} \rightleftharpoons >\text{SOHTh}^{4+}$	28.90	28.15
$>\text{SOH} + \text{Th}^{4+} + \text{H}_2\text{O} \rightleftharpoons >\text{SOThOH}^{2+} + 2\text{H}^+$	-	-
$>\text{SOH} + \text{Th}^{4+} + 4\text{H}_2\text{O} \rightleftharpoons >\text{SOTh(OH)}_4^- + 5\text{H}^+$	-	-
<i>Ternary >SOH - ISA - Th complex (outer-sphere)</i>		
$>\text{SOH} + \text{ISA}^- + \text{Th}^{4+} \rightleftharpoons >\text{SOH}_2(\text{ISAH}_{-4})\text{Th} + 3\text{H}^+$		6.00
Physical parameters		
Inner-layer capacitance (F m^{-2})	1.4	1.4
Outer-layer capacitance (F m^{-2})	0.2	0.2
Site density (sites nm^{-2})	2.31	2.31
Surface area ($\text{m}^2 \text{ g}^{-1}$) (hematite batch H1)	5.6	5.6
Surface area ($\text{m}^2 \text{ g}^{-1}$) (hematite batch H2)	13.6	13.6

* New or refitted parameters are in bold.

The original and refitted models both applied the thermodynamic data on aqueous thorium species listed in Table 1. The surface reaction and thorium sorption $\log K_s$ for the original model were taken from Murphy *et al.* (1999). The ISA sorption $\log K_s$ for the original model was derived from fitting of data for the sorption of lactate on goethite (Filius *et al.*, 1997) in the absence of data for ISA sorption on hematite.

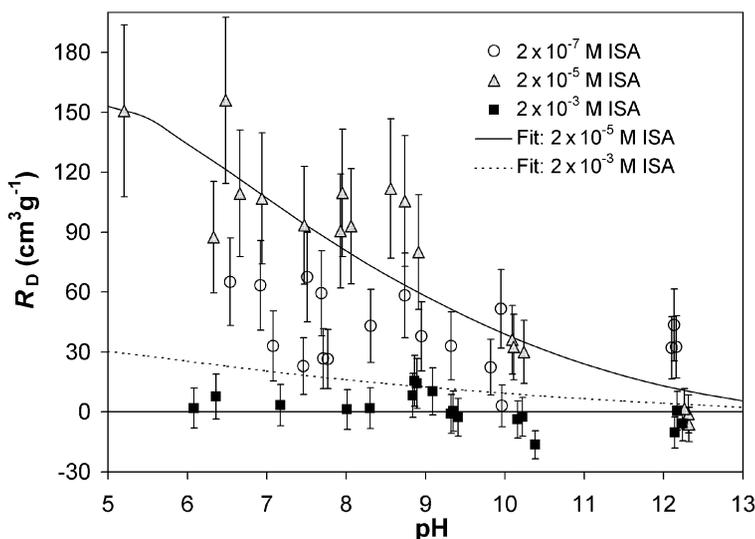


FIG. 2. The TLM case 1 revised model fit to experimental data for ^{14}C -labelled ISA sorption onto hematite (uncertainties $\pm 2\sigma$). Hematite specific surface area: $13.6 \text{ m}^2 \text{ g}^{-1}$ (batch H2); M denotes mol dm^{-3} . One fitted parameter value for outersphere complex: $\log K_s\{\text{>SOH} + \text{H}^+ + \text{ISA}^- \rightleftharpoons \text{>SOH}_2\text{ISA}\} = 12.8$.

At the ISA concentrations of 2×10^{-3} , 2×10^{-5} and $2 \times 10^{-7} \text{ mol dm}^{-3}$ studied with ^{14}C -labelled ISA, the following trends were noted (Fig. 2).

(1) Sorption of ISA at an initial concentration of $2 \times 10^{-3} \text{ mol dm}^{-3}$ ISA was weak at all pH values; R_D values were less than $10 \text{ cm}^3 \text{ g}^{-1}$ (more than 80% of the ISA remained in the solution phase).

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

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

Qualitatively, the trends in R_D values for ISA with pH and ISA concentration are consistent with expectations that at higher ISA concentrations the sorption isotherm becomes non-linear (and R_D values decrease) due to saturation of surface sites with sorbed ISA and that ISA will sorb more strongly at pH values below the point

of zero charge (about pH 8–9) where iron surface sites become net positively charged.

However, the R_D values for the lowest ISA concentration are lower than expected and differ from the second trend. This may be due a greater sensitivity at lower concentrations to minor processes or the presence of impurities in the experimental system. One possibility is the presence of small amounts of extractable ferric iron from the hematite that may be complexed by low levels of ISA and so compete with surface complexation reactions at low ISA concentrations.

Experimental results: thorium sorption onto hematite

The results of the thorium sorption experiments are shown in Fig. 1 and are reported in full elsewhere (Cowper *et al.*, 2012). In the absence of organic complexants, sorption of thorium was strong at all three pH values. The R_D values for thorium were $\geq 4 \times 10^6 \text{ cm}^3 \text{ g}^{-1}$ at pH ~9 and varied from $9 \times 10^5 \text{ cm}^3 \text{ g}^{-1}$ to $7 \times 10^6 \text{ cm}^3 \text{ g}^{-1}$ at pH ~6. The R_D values at pH 12 were about one order of magnitude lower, ranging from 1×10^5 to $2 \times 10^5 \text{ cm}^3 \text{ g}^{-1}$.

The presence of $2 \times 10^{-3} \text{ mol dm}^{-3}$ ISA appears to have a negligible effect on thorium sorption at pH 12 but reduces sorption by up to an

order of magnitude at pH 5.5–6.6. 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 CDP leachate (at 200 mg dm^{-3} TOC) has a much more significant effect on thorium sorption than ISA alone in all three pH ranges studied. At pH 4.7–6.8 and pH~9, sorption is reduced by about two orders of magnitude compared to the baseline case. A reduction of at least one order of magnitude is observed at pH 12.

Thus the significant effect of CDP leachate on thorium sorption to hematite cannot be reproduced by the presence of ISA alone either at near-neutral pH (as expected) or alkaline pH values (unexpectedly). The findings at near-neutral pH are consistent with previous results for CDP leachates obtained on the Nirex programme, showing that under these conditions CDPs have greater effects on radionuclide sorption than ISA alone (Knight, 2006).

Comparison of TLM case 1 with new experimental data: effect of ISA on thorium sorption

The agreement between the modelling predictions and the experimental data for TLM case 1 (Fig. 1) was better than for any other of the sorption models. For thorium sorption to hematite (batches H1 and H2) in the absence of ISA or CDPs, the predicted sorption is generally overestimated by a factor of around three to six at pH values around 6 and 9; and by at least an order of magnitude at around pH 12.

The predicted effect of ISA on thorium sorption is to reduce the thorium R_D value by about a factor of ~1000 due to strong complexation in solution (except around pH 6 where the decrease is smaller). However, the experimental data show a smaller effect of ISA in reducing thorium sorption than predicted across the pH range studied and no significant effect around pH 12. In contrast, the data for the sorption of thorium from the CDP leachate (at 200 mg dm^{-3} TOC) is similar to the predicted effect of ISA. The total ISA concentration in this leachate ($1.9 \times 10^{-3} \text{ mol dm}^{-3}$) is similar to that used in the α -ISA experiments.

Refinements to the TLM case 1 sorption model were made to improve the fit to the experimental data. Comparisons between the experimental data and revised TLM case 1 models are shown in Figs 2 and 3 (in the case of Fig. 2, the anomalous

ISA sorption data at the lowest ISA concentration were omitted from the model fits).

By comparing the experimental data and the TLM case 1 model predictions, two possible interpretations of the experimental data for the effects of ISA were developed. In the first interpretation, the revised TLM case 1 model summarized in Table 2 is applicable. Sorption of ISA to hematite is pH-dependent and increases with decreasing pH; there is strong complexation of thorium by ISA in solution. A reasonable overall fit to the complete set of thorium sorption data could be obtained, as shown in Fig. 3, by assuming the formation of a ternary surface complex consisting of a surface group, thorium ion and ISA ligand. However, this cannot explain the significant effect of the CDP leachate (see below).

Secondly, partial degradation of the ISA used in the thorium sorption experiments could potentially explain the poor agreement between the experimental data and the TLM case 1 model predictions. In this interpretation the ISA is weakly sorbing but forms strong complexes with thorium in solution. However, degradation of ISA leads to a smaller effect in reducing thorium sorption compared to the higher ISA concentration used in the model. Conversely, CDP is assumed to maintain a high concentration of strong organic complexant including ISA. This interpretation is currently considered less likely because separate tests on ISA solutions stored up to four months at high pH have indicated no significant degradation (Cowper *et al.*, 2012).

There are, however, significant uncertainties concerning the stability constants used in the models to predict thorium complexation by ISA in solution. If these stability constants are too high, the effect of ISA on thorium sorption may be overestimated. In particular, this may be the case in the lower pH range studied, where the stability constant for the predicted major species $\text{Th}(\text{H}_3\text{ISA})$, is derived by analogy with the corresponding $\text{Np}(\text{IV})$ complex (see Table 1). Experimental data at pH 8 and derived stability constants (Allard and Ekberg, 2006) suggest a lower stability for thorium–ISA complexes in this pH region when applied to an ISA concentration of $2 \times 10^{-3} \text{ mol dm}^{-3}$. Their interpretation of the data in terms of complexes of the form $\text{Th}(\text{ISA})_p^{(4-p)-}$ ($p = 1$ to 3) implies a rapid decrease in the stability of these complexes at higher pH values. However, no pH-dependent data or spectroscopic information is available to confirm that no hydroxyl proton displacement occurs.

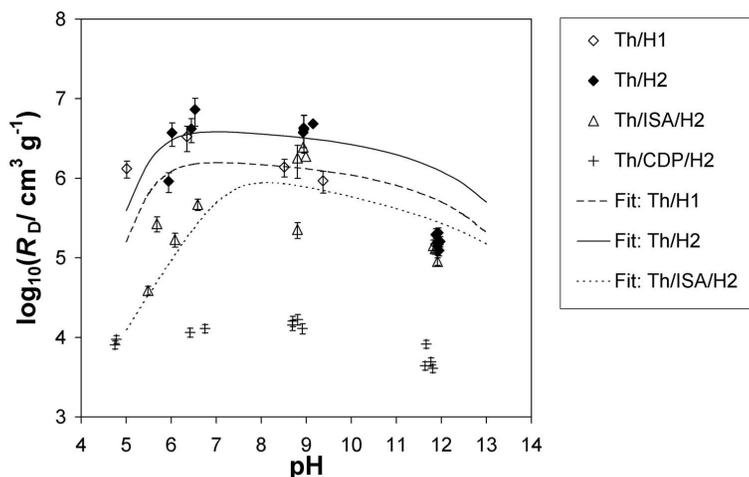


FIG. 3. The TLM case 1 revised model fit to experimental data for thorium sorption onto hematite (experimental uncertainties $\pm 2\sigma$, 2 adjusted parameters as in Table 2). Hematite specific surface areas: $5.6 \text{ m}^2 \text{ g}^{-1}$ (batch H1); $13.6 \text{ m}^2 \text{ g}^{-1}$ (batch H2). Data at pH 9 are minimum values; ISA concentration $0.002 \text{ mol dm}^{-3}$; CDP leachate $200 \text{ mg TOC dm}^{-3}$. Two fitted parameter values: $\log K_s\{\text{>SOH} + \text{Th}^{4+} \rightleftharpoons \text{>SOHTh}^{4+}\} = 28.15$; $\log K_s\{\text{>SOH} + \text{ISA}^- + \text{Th}^{4+} \rightleftharpoons \text{>SOH}_2\text{-(ISAH}_4\text{)Th} + 3\text{H}^+\} = 6.00$.

In the higher pH range the stability constant for the $\text{Th}(\text{H}_4\text{ISA})^-$ data was derived from experiments at pH 13.3 (Vercammen *et al.*, 2001) and successfully applied to model some limited thorium solubility data at pH 12 (Baston *et al.*, 2008). Therefore, the absence of any observed effect of ISA on thorium sorption around pH 12 in the current study appears to be inconsistent with the experimental data from the two earlier high pH solubility studies (in which strong complexation effects were observed). The two interpretations of the thorium sorption data described above would overcome this inconsistency, either by assuming that ISA degrades, or assuming that thorium sorption reduction by complexation in solution is balanced by a sorption enhancement due to the assumed Th–ISA–hematite ternary surface complex. Neither interpretation can be claimed to have been definitively demonstrated based on the current data.

Comparison of ISA and CDP effects on thorium sorption

Compared with the effect of ISA on thorium sorption, the sorption reduction effect of CDP leachate is much more significant, as shown in Fig. 1. It is emphasized that there was a significant difference in the aqueous chemistry

between these two sets of experiments. In the case of the ISA experiments, the electrolyte used was sodium chloride, whereas for the CDP leachate the major cation is calcium, resulting from the conditions of the cellulose degradation. At high pH and in the presence of calcium ions, strong evidence for the formation of ternary calcium–thorium–ISA complexes has been reported (Vercammen *et al.*, 1999, 2001). Applied to this study, such complexes may be formed only in the CDP leachate experiments, leading to increased partitioning of thorium into solution and significant reduction in sorption. This difference in thorium speciation in solution is considered to be the most probable explanation for the differences observed between the effects of ISA alone and the CDP leachate at high pH. It may also explain the differences at lower pH values although these lie outside the range of pH values in which ternary calcium–thorium–ISA complexes were studied (pH 10.7–13.3). Given the high concentration of organic species in the CDP leachate even at tenfold dilution, it is also possible that other ligands may contribute to thorium complexation and/or that competition for sorption sites may be involved. However, these alternative explanations are considered less likely to be the major cause of the observed differences between CDP leachate and ISA.

Further experimental and modelling work is required to test the above hypothesis.

Summary and conclusions

The presence of CDP leachate (at $\sim 200 \text{ mg dm}^{-3}$ TOC) has a significant effect on thorium sorption to hematite. At pH 4.7–6.8 and pH ~ 9 , thorium sorption is reduced by about two orders of magnitude in the presence of CDP compared to the baseline case; a reduction of at least one order of magnitude is observed at pH 12. In contrast, the presence of $2 \times 10^{-3} \text{ mol dm}^{-3}$ ISA appears to have a much smaller effect than CDP on thorium sorption; ISA has a negligible effect on thorium sorption to hematite at pH 12 but reduces sorption by up to an order of magnitude at pH 5.5 to 6.6. The results are consistent with previous findings that the presence of ISA alone does not appear to account for the effects of CDPs in reducing radionuclide sorption under near-neutral pH conditions. The findings at pH 12 for the effects of ISA were unexpected.

Application of a selected model to predict the extent of thorium sorption, in the absence of organics, gave reasonable agreement with the experimental data reported here. However, the predicted strong effect of ISA in reducing sorption at high pH was not observed experimentally. Refinement of the model was made to allow the formation of a ternary surface complex consisting of a surface group, thorium ion and ISA ligand. This gave a much improved fit to the experimental data obtained in the presence of ISA.

At the present stage of model development, there are uncertainties concerning the surface model of the hematite sample selected and the strength of thorium–ISA complexation in solution, particularly at neutral pH, that may impact on the modelling predictions. The model has yet to be extended to the more complex CDP leachate systems.

At high pH, the most likely explanation for the differences between the observed sorption of thorium in the presence of ISA and the CDP leachate is the formation of ternary calcium–thorium–ISA complexes in the latter system. By extension, the same explanation could be applied to the difference at neutral pH, but these conditions lie outside the range for which such complexes have been studied. Alternative explanations, including the presence of other complexants and/or additional processes, such as competition for surface sorption sites, are

considered less likely to be responsible for controlling thorium sorption behaviour in the presence of the CDP leachate.

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References

- Allard, S. and Ekberg, C. (2006) Complexing properties of α -isosaccharinate: thorium. *Radiochimica Acta*, **94**, 537–540.
- Altmaier, M., Neck, V., Denecke, M.A., Yin, R. and Fanghänel, Th. (2006) Solubility of $\text{ThO}_2 \cdot x\text{H}_2\text{O}$ and the formation of ternary Th(IV) hydroxide–carbonate complexes in NaHCO_3 – NaCO_3 solutions containing 0–4 M NaCl. *Radiochimica Acta*, **94**, 495–500.
- Baston, G.M.N., Heath, T.G. and Hunter, F.M.I. (2008) *Summary of Additions and Amendments to Data in the HATCHES Chemical Thermodynamic Database 2002 to 2007*. Serco Assurance Report SA/ENV-0934.
- Bond, K.A., Heath, T.G. and Tweed, C.J. (1997) *HATCHES: A Referenced Thermodynamic Database for Chemical Equilibrium Studies*. Nirex Report NSS/R379.
- Cowper, M.M., Marshall, T.A. and Swanton, S.W. (2012) *Sorption Detriments in the Geosphere: The Effect of Cellulose Degradation Products. Phase 1 Experimental Study*. Serco Report SA/ENV/0958 Issue 2.
- Cromières, L., Moulin, V., Fourest, B., Guilaumont, R. and Giffaut, E. (1998) Sorption of thorium onto hematite colloids. *Radiochimica Acta*, **82**, 249–255.
- Davies, J.A. and Leckie, J.O. (1978) Surface ionisation and complexation at the oxide/water interface. II. Surface properties of amorphous iron oxyhydroxide and adsorption of metal ions. *Journal of Colloid and Interface Science*, **67**, 90–107.
- Dzombak, D.A. and Morel, F.M.M. (1990) *Surface Complexation Modelling: Hydrous Ferric Oxide*. J. Wiley and Sons, New York.
- Filius, J.D., Hiemstra, T. and van Reimsdijk, W.H. (1997) Adsorption of small weak organic acids on goethite: modelling of mechanisms. *Journal of Colloid and Interface Science*, **195**, 368–380.
- Haworth, A., Heath, T.G. and Tweed, C.J. (1995) *HARPHRO: A Computer Program for Geochemical Modelling*. Nirex Report NSS/R380.

- Heath, T.G. and Williams, S.J. (2005) *Effects of Organic Complexants and Their Treatment in Performance Assessments*. Serco Assurance Report SA/ENV-0726.
- Knight, J.L. (2006) *FUNMIG – Review of ‘Anomalous’ Sorption Results from Nirex Commissioned Data*. Nirex Technical Note Document Reference 6492490.
- Knill, C.J. and Kennedy, J.F. (2003) Degradation of cellulose under alkaline conditions. *Carbohydrate Polymers*, **51**, 281–329.
- Machell, G. and Richards, G.N. (1960) Mechanism of saccharinic acid formation. Part 1. Competing reactions in the alkaline degradation of 4-O-methyl-D-glucose, maltose, amylose and cellulose. *Journal Chemical Society*, 1924–1931.
- Murphy, R.J., Lenhart, J.J. and Honeyman, B.D. (1999) The sorption of thorium(IV) and uranium(VI) to hematite in the presence of natural organic matter. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **157**, 47–62.
- Neck, V., Müller, R., Bouby, M., Altmaier, M., Rothe, J., Denecke, M.A. and Kim, J.I. (2002) Solubility of amorphous Th(IV) hydroxide – application of LIBD to determine the solubility product and EXAFS for aqueous speciation. *Radiochimica Acta*, **90**, 485–494.
- Neck, V., Altmaier, M., Müller, R., Brauer, A., Fanghänel, Th. and Kim, J.I. (2003) Solubility of crystalline thorium dioxide. *Radiochimica Acta*, **91**, 253–262.
- Nuclear Decommissioning Authority (2010) *Geological Disposal: Radionuclide Behaviour Status Report*. NDA Report NDA/RWMD/034.
- Rai, D., Hess, N.J., Xia, Y., Rao, L., Cho, H.M., Moore, R.C. and Van Loon, L.R. (2003) Comprehensive thermodynamic model applicable to highly acidic to basic conditions for isosaccharinate reactions with Ca(II) and Np(IV). *Journal of Solution Chemistry*, **32**, 665–689.
- Rand, M., Fuger, J., Grenthe, I., Neck, V. and Rai, D. (2008) *Chemical Thermodynamics Volume 11. Chemical Thermodynamics of Thorium*. OECD Publications, Paris.
- Read, D. and Falck, W.E. (editors) (1996) *CHEMVAL 2: A Coordinated Research Initiative for Evaluating and Enhancing Chemical Models in Radiological Risk Assessment*. Rep. EUR 16648, Office for Official Publications of the European Communities, Luxembourg.
- Van Loon, L.R. and Glaus, M.A. (1998) *Experimental and Theoretical Studies on Alkaline Degradation of Cellulose and its Impact on the Sorption of Radionuclides*. Nagra Technical Report NTB 97-04. Nagra, Wettingen, Switzerland.
- Vercammen, K., Glaus, M.A. and Van Loon, L.R. (1999) Evidence for the existence of complexes between Th(IV) and α -isosaccharinic acid under alkaline conditions. *Radiochimica Acta*, **84**, 221–224.
- Vercammen, K., Glaus, M.A. and Van Loon, L.R. (2001) Complexation of Th(IV) and Eu(III) by α -isosaccharinic acid under alkaline conditions. *Radiochimica Acta*, **89**, 393–401.

The Nirex, Nuclear Decommissioning Authority and Serco Reports listed above are available from the NDA bibliography.