The effect of α -isosaccharinic acid on the stability of and Th(IV) uptake by hardened cement paste

By E. Wieland*, J. Tits, J. P. Dobler and P. Spieler

Paul Scherrer Institut, Waste Management Laboratory, CH-5232 Villigen PSI, Switzerland

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Summary. The effect of α -isosaccharinic acid (ISA) on Th(IV) uptake by hardened cement paste (HCP) has been investigated under alkaline conditions (pH 13.3). Prior to performing the uptake studies the stability of HCP was determined in the presence of ISA. It was observed that the formation of Ca-ISA complexes in solution enhances portlandite solubility. The fraction of portlandite dissolved from the HCP matrix depends on the solid to liquid (S/L) ratio of the system and the ISA concentration in solution. Th(IV) uptake by HCP was found to be reduced above an aqueous ISA concentration of about 10^{-4} M. Reduction of Th(IV) uptake can be modelled taking into account the formation of a Th : ISA : Ca = 1 : 2 : 1 complex in solution. It is indicated that the formation of ternary Th(IV)-ISA complexes may be important in cement systems. The final interpretation of the data however fails due to the large uncertainties in the distribution ratios measured in the absence of ISA.

Introduction

Cementitious materials are commonly used world-wide in immobilisation strategies for the disposal of short-lived low- and intermediate-level (L/ILW) and long-lived intermediate-level (LL-ILW) radioactive wastes. Cement is an important component of the near-field of a repository because it is used to solidify and surround the waste materials and to build the engineered barrier system. The immobilisation of safety-relevant radionuclides by hardened cement paste (HCP) is an important aspect of performance assessment (PA) studies where it is considered that the solubility and interaction of radionuclides with the cement matrix determine the source term for radionuclide migration into the host rock.

The immobilisation potential of HCP originates from its selective binding properties for cations and anions present in the waste matrix, *e.g.*, see reviews in [1–4]. Earlier studies indicate a strong uptake of Th(IV) by cementitious materials [5–7 and references therein]. Recent studies have supported this finding and, in the absence of complexing ligands, sorption values were found to be $\geq 1 \text{ m}^3 \text{ kg}^{-1}$ [8, 9]. In addition,

it was shown that complexing ligands present in the cement pore water, namely products of cellulose degradation and cement additives, may exert an effect on Th(IV) uptake by cementitious and naturally occurring solid materials [8–12]. The objectives of the experiments described here were to investigate the effect of α -isosaccharinic acid (ISA) on the stability of HCP and on Th(IV) uptake by HCP under conditions relevant to the near-field of a repository for radioactive waste. ISA has been reported to be the main product in the degradation of cellulosic material under alkaline conditions [13, 14], and moreover, it forms stable complexes namely with tri- and tetravalent nuclides [15, 16]. Th(IV) is often chosen to be representative of a major group of the safety-relevant radionuclides present in the waste matrix, *i.e.*, the tetravalent actinides.

Materials and methods

A crushed material prepared from hardened cement paste (HCP) was employed in the experiments. Commercial sulphate-resisting cement (Type CPA 55 HTS, Lafarge, France), denoted as HTS (Haute Teneur en Silice), was used to manufacture the cement paste as described by Sarott *et al.* [17]. The crushed material was prepared from bulk samples by grinding in a mortar under CO_2 free conditions and sieving the material to collect the size fractions $< 70 \mu\text{m}$. The N_2 -BET surface area of the powder was determined to be $46 \pm 4 \text{ m}^2 \text{ g}^{-1}$.

Synthesis and analytical determination of α -ISA in alkaline solutions are described in detail by Van Loon and Glaus [23]. For this work, ISA stock solutions of 0.1 M and 10^{-3} M were prepared and diluted to obtain the required initial concentrations in the experiments. Aqueous ISA concentrations were estimated based on previously published sorption isotherms for ISA [22, 23] and checked on a few samples.

Prior to the uptake studies, stability tests with HCP were carried out for the relevant experimental system, *i.e.*, HCP powder in contact with artificial cement pore water (ACW) containing ISA. For this, HCP powder was immersed in ACW with increasing ISA concentrations at a solid to liquid (S/L) ratio of $1.25 \times 10^{-2} \text{ kg L}^{-1}$. The suspensions were equilibrated for at least 30 days. Kinetic tests showed that 30 days was the minimum time required to

* Author for correspondence (E-mail: erich.wieland@psi.ch).

reach equilibrium in stability tests [19]. Thereafter, solid and liquid phases were separated by centrifugation (60 min at 95 000 g). Aliquots were withdrawn from the supernatant, acidified and analysed by ICP-OES for the important cement-derived elements Na, K, Ca, Al, Si and S.

For the uptake studies, cement suspensions were prepared by contacting HCP powder with ACW. The preparation of the ACW is described in an earlier publication [9]. The resulting pH was 13.3, ionic strength was 0.3 M and the total carbonate concentration was at a level corresponding to saturation with respect to CaCO_3 (1.2×10^{-4} M). Batch-type uptake studies were conducted using the method reported by Wieland *et al.* [9]. In contrast to the earlier study, the S/L ratios of the suspensions were increased to 10^{-4} kg L⁻¹ and 5×10^{-3} kg L⁻¹ to minimise possible uncertainties associated with the very low solid content used in the previous experiments. The cement suspensions were pre-equilibrated for at least 14 days prior to adding the radiotracer.

Partitioning of Th(IV) between the solid and liquid phase was determined using ^{228}Th tracer (γ -emitter, $t_{1/2} = 1.91$ y) purchased from CIS Medipro AG, Teufen, Switzerland and carrier-free ^{234}Th tracer (β -emitter, $t_{1/2} = 24.1$ d) prepared according to a slightly modified version of the ion exchange method described by Dyrssen [20]. Activity measurements were carried out using a Packard Cobra 5003 auto gamma counter for ^{228}Th assay, and a Canberra Packard Tri-carb 2250 CA liquid scintillation counter for ^{234}Th assay. Prior to ^{228}Th activity measurements, suspensions and solutions were stored for at least one month to allow secular equilibrium with the daughters to be established. Note that Th(IV) tracer solutions were found to be stable up to total concentrations of approximately 10^{-9} M [12]. In this work Th(IV) concentrations used were $\leq 10^{-10}$ M.

The partitioning of the tracers was quantified in terms of a distribution ratio (R_d value), which is defined as follows:

$$R_d = \frac{A_s}{A_l} = \left(\frac{A_{\text{input}} - A_{\text{wall}} - A_l}{A_l} \right) \cdot \left(\frac{V}{m} \right) = \left(\frac{A_{\text{susp}} - A_l}{A_l} \right) \cdot \left(\frac{V}{m} \right) \quad [\text{m}^3 \text{kg}^{-1}]. \quad (1)$$

A_s and A_l denote radionuclide activities measured on the solid and in solution, respectively, at equilibrium in counts per minute (cpm) [cpm kg^{-1} and cpm m^{-3}]. V and m denote the volume of ACW [m^3] and the mass of HCP [kg], respectively. The difference between total activity of the sus-

pension (A_{susp}) and the activity of the supernatant solution after centrifugation (A_l) was taken as measure of the tracer activity on the solid. A_{susp} is the total activity of the suspension prior to separating solid and liquid phases [cpm m^{-3}]. A_{input} and A_{wall} denote the activities [cpm m^{-3}] added to the system and sorbed on the walls of the polyallomere centrifuge tubes, which were used for the experiments. In the case of ^{228}Th A_{susp} was determined directly in aliquots taken from the cement suspension. In the case of ^{234}Th , however, A_{wall} was determined separately as follows: At the end of each uptake experiment solid and liquid phases were discarded, the tubes rinsed with water and filled with 1 M HCl to desorb Th(IV) from the walls. ^{234}Th activities were determined in the acid extracts after equilibration for one day.

Results

Stability of HCP

Recent studies by Vercammen *et al.* [21] showed that Ca may form complexes with ISA under alkaline conditions. Thus, Ca complexation by ISA was suggested to promote the leaching of Ca from Ca containing phases in the HCP matrix. Measuring the Ca concentration in ACW at increasing ISA concentrations allowed us to determine the stability of HCP. Fig. 1 shows that Ca concentrations were enhanced in the HCP suspensions at aqueous ISA concentrations above about 10^{-3} M under the given experimental conditions (S/L ratio = 1.25×10^{-2} kg L⁻¹). This indicates dissolution of Ca containing cement phases in the presence of ISA. Further analysis of the data showed that the effect of ISA on the total Ca concentration in solution ($[\text{Ca}]_{\text{tot}}^{\text{sol}}$) can be modelled assuming portlandite dissolution and Ca-ISA complex formation:

$$[\text{Ca}]_{\text{tot}}^{\text{sol}} = \frac{K_s [\text{H}^+]^2}{(K_w)^2} \left(1 + \frac{K_{11}}{[\text{H}^+]} + [\text{ISA}^-] \times \left(\frac{K_{\text{CaISA}^0}}{[\text{H}^+]} + K_{\text{CaISA}^+} \right) \right) [\text{M}]. \quad (2)$$

Calculations were based on the chemical equilibria and thermodynamic constants listed in Table 1. Fig. 1 reveals good agreement between experimental data and thermodynamic calculations. The difference between model calculations and experimental data is attributed to uncertainties associated with the thermodynamic constants and the experimental data.

Table 1. Conditional thermodynamic constants for solubility and speciation calculations ($I = 0.3$, $T = 25^\circ\text{C}$).

Solids	$\log K_s$ ($I = 0.3$) ^a	Chemical equilibrium	Reference
CaCO_3	-7.17	$\text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$	Hummel <i>et al.</i> [26]
Ca(OH)_2	-4.31	$\text{Ca(OH)}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$	Hummel <i>et al.</i> [26]
Species	$\log K$ ($I = 0.3$) ^a	Chemical equilibrium	Reference
CaOH^+	-13.07	$\text{Ca}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{CaOH}^+ + \text{H}^+$	Hummel <i>et al.</i> [26]
Ca(ISA)^0	-10.99	$\text{Ca}^{2+} + \text{ISA}^- \rightleftharpoons \text{Ca(ISA-H)}^0 + \text{H}^+$	Vercammen <i>et al.</i> [21]
Ca(ISA)^+	1.12	$\text{Ca}^{2+} + \text{ISA}^- \rightleftharpoons \text{Ca(ISA)}^+$	Vercammen <i>et al.</i> [21]

a: The thermodynamic constants ($\log K^0$ and $\log K_{s,0}^0$) were taken from the references listed in the table and corrected for ionic strength $I = 0.3$ M using the Davies equation.

Fig. 1. Dependence of the Ca concentration in ACW on the aqueous ISA concentration. Predictions are made on the assumption that the free Ca concentration is controlled by portlandite solubility. Ca speciation at pH = 13.3 is dominated by the first hydrolysis product and the formation of Ca-ISA complexes.

Uptake of Th(IV) by HCP in the absence and presence of ISA

Complex formation in solution and uptake of Th(IV) by HCP are considered to be competing reactions. In the absence of ISA and under the given experimental conditions, *i.e.*, high pH and low CO_3^{2-} and Cl^- concentrations, OH^- is the only relevant complexing ligand in solution. In general, hydrolysis reactions of a metal cation M^{z+} are given by:

With this, the distribution ratio defined in Eq. (1) can be rewritten as:

$$R_d^0 = \frac{\{\text{M}_s\}}{[\text{M}^{z+}] \left(1 + \sum_m \beta_m^{\text{OH}} \cdot [\text{OH}^-]^m \right)} \quad [\text{m}^3 \text{ kg}^{-1}]. \quad (4)$$

$\{\text{M}_s\}$ denotes the concentration of Th(IV) sorbed $[\text{mol kg}^{-1}]$; $[\text{M}^{z+}]$ is the free metal concentration in solution; R_d^0 denotes the distribution ratio determined in the absence of ISA.

Experimental data on the effect of ISA on Th(IV) uptake by HCP are shown in Fig. 2. Th(IV) uptake was found to be dependent on the aqueous ISA concentration. Reduction of the Th(IV) uptake in the presence of ISA is attributed to the formation of Th(IV)-ISA complexes in solution. In an earlier study the effect of ISA on Th(IV) and Eu(III) uptake by cement has already been suggested [9]. Nevertheless, interpretation of the data at that time was limited due to missing thermodynamic information on Th(IV)-ISA complex formation. According to Vercammen *et al.* [16] a Th : ISA : Ca = 1 : 2 : 1 solution complex is formed under the conditions relevant to this study. Consideration of the stabilising effect of Ca^{2+} on Th(IV)-ISA complexes is necessary based on the experimental results published by these authors [15, 16].

Fig. 2. Effect of α -isosaccharinic acid on Th(IV) uptake by cement. Measurements were carried out on cement systems with different S/L ratios. Predictions are based on Eq. (6) assuming $R_d^0 = 350 \text{ m}^3 \text{ kg}^{-1}$ and $R_d^0 = 6000 \text{ m}^3 \text{ kg}^{-1}$.

The reaction schemes proposed by Vercammen *et al.* [16] and by Tits *et al.* [12] can be applied to cement systems. Taking into account Th(IV)-ISA complex formation in solution, the distribution ratio R_d can be written as:

$$R_d = \frac{\{\text{M}_s\}}{[\text{M}^{z+}] \left(1 + \sum_m \beta_m^{\text{OH}} \cdot [\text{OH}^-]^m + \beta_{\text{ThISA}} \cdot \frac{[\text{H}_4\text{ISA}^-]^2 [\text{Ca}^{2+}]}{[\text{H}^+]^4} \right)} \quad [\text{m}^3 \text{ kg}^{-1}]. \quad (5)$$

Note that the concentrations of free and sorbed metal species are different in the absence and presence of ISA. However, assuming linear sorption for which $\{\text{M}_s\}/[\text{M}^{z+}] = \{\text{M}_s\}/[\text{M}^{z+}]$ holds, Eqs. (2) and (3) can be combined and re-written in the logarithmic form to yield:

$$\log R_d = \log R_d^0 - \log \left(1 + \frac{\beta_{\text{ThISA}} [\text{Ca}^{2+}]}{A [\text{H}^+]^4} [\text{H}_4\text{ISA}^-]^2 \right) \quad [\text{m}^3 \text{ kg}^{-1}], \quad (6)$$

where

$$A \cong 1 + \beta_4^{\text{OH}} [\text{OH}^-]^4. \quad (7)$$

Fig. 2 shows predictions of the effect of ISA on Th(IV) uptake. The relevant reaction stoichiometries of Th(IV)-ISA complex formation and Th(IV) hydrolysis including the corresponding thermodynamic constants are listed in Table 2. Note that the distribution ratios are plotted as a function of the aqueous ISA concentration. The latter was estimated based on the total ISA concentration added and published sorption isotherms for ISA [22, 23]. Fig. 2 reveals that predictions of the effect of ISA based on Eq. (6) and interpretation of the data are dependent on the R_d^0 value, *i.e.*, the distribution ratio of Th(IV) determined in the absence of ISA. The following discussion will be based on predictions made using $R_d^0 = 350 \text{ m}^3 \text{ kg}^{-1}$ (solid line) and $R_d^0 = 6000 \text{ m}^3 \text{ kg}^{-1}$ (broken line).

Table 2. Relevant conditional complexation constants for aqueous Th(IV) complexes under alkaline conditions ($I = 0.3$, $T = 25^\circ\text{C}$).

Chemical equilibrium	$\log \beta$ ($I = 0.3$) ^a	Reference
$\text{Th}^{4+} + 4\text{OH}^- \rightleftharpoons \text{Th}(\text{OH})_4(\text{aq})$	34.9	Hummel <i>et al.</i> [26]
$\text{Th}^{4+} + 2\text{H}_4\text{ISA}^- + \text{Ca}^{2+} \rightleftharpoons \text{Th}(\text{H}_2\text{ISA})_2\text{Ca} + 4\text{H}^+$	$-(7.4 \pm 0.3)$	Tits <i>et al.</i> [12]

a: The thermodynamic complexation constants $\log \beta^0$ were taken from the references listed in the table and corrected for ionic strength $I = 0.3$ M using the Davies equation.

Discussion

Investigations of the stability of HCP powder in ACW in the presence of ISA were performed to assess changes in the chemical composition of the cement suspensions and to define appropriate experimental conditions for uptake studies. Dissolution of HCP in the presence of ISA was found to limit the “experimental window” for uptake studies. The present assessment is based on the assumption that a maximum of 20 wt. % of portlandite is allowed to dissolve without altering the cement matrix significantly and causing artefacts in the uptake experiments. On this assumption, a HCP loss of a maximum of 5 wt. % can be accepted, taking into account the weight content of portlandite in the cement matrix (range 20 to 25 wt. %). Note however that the limit is arbitrarily chosen. The effect of ISA on the Ca concentration in HCP suspensions can be predicted assuming portlandite solubility and the formation of aqueous Ca-ISA complexes (Fig. 1). This effect can be quantified taking into account the quantity of HCP in the system and the total ISA concentration added. Based on the above assumptions, it was estimated that the aqueous ISA concentration was allowed to be at most 10^{-3} M at a S/L ratio of 10^{-4} kg L⁻¹ and at most 5×10^{-2} M at a S/L ratio of 5×10^{-3} kg L⁻¹. Note that the maximum ISA concentration in the cement pore water at pH 13.3 was determined to be 4.4×10^{-2} M [24]. Based on these findings, maximum ISA concentrations have been considered in the uptake experiments according to the S/L ratios and the free ISA concentrations of the suspensions.

Fast kinetics was found to be characteristic for Th(IV) uptake by HCP [9]. The earlier study showed that equilibrium was reached within less than two days in the presence and absence of ISA. Studies on Th(IV) uptake by CSH phases corroborate fast uptake kinetics in cementitious systems [11, 25]. Note that CSH phases are expected to be important sorbing phases for Th(IV) in the cement matrix, primarily due to their abundance (~ 50 wt. %) and their high sorption capacity. In all cases R_d values ≥ 100 m³ kg⁻¹ have been reported indicating strong uptake of Th(IV) by HCP at pH 13.3.

The influence of α -ISA on Th(IV) uptake by feldspar was recently investigated by Van Loon and Glaus [23] and Van Loon *et al.* [10]. Tits *et al.* [12] studied the effect of α -ISA on Th(IV) uptake by calcite. In all these studies a significant effect of ISA on Th(IV) uptake was observed above $[\text{ISA}]_{\text{aq}} \sim 10^{-5}$ M. In this study, however, a reduction in the Th(IV) uptake by HCP was found to be significant only above $[\text{ISA}]_{\text{aq}} \sim 10^{-4}$ M, taking into account uncertainties on the distribution ratios in the absence of ISA (shaded area in Fig. 2). Van Loon *et al.* [10] and Tits *et al.* [12] modelled the effect of ISA on Th(IV)

uptake by considering Th(IV)-ISA complex formation in solution according to the stoichiometries proposed by Vercammen *et al.* [16]. It is worth mentioning that the determination of the stoichiometric coefficients and the stability constants $\beta_{\text{Th-ISA}}$ is dependent on the assumptions made concerning the relevant hydrolysis products for Th(IV) at high pH as well as the corresponding hydrolysis constants [16]. Our data interpretation is based on the assumption that $\text{Th}(\text{OH})_4$ is the dominant hydrolysis product at pH 13.3 and on a set of self-consistent thermodynamic constants reported by Hummel *et al.* [26]. With this, the stability constants, $\beta_{\text{Th-ISA}}$, for the Th(IV)-ISA complex, which were deduced from the data published by Vercammen *et al.* [16] and Tits *et al.* [12], are found to be consistent using the hydrolysis product and constant listed in Table 2, *i.e.*, ($\log \beta_{\text{Th-ISA}}^{0.3}$): $-(7.4 \pm 0.1)$ [16] and $-(7.4 \pm 0.3)$ [12]).

Reduction of Th(IV) uptake by HCP in the presence of ISA can be modelled using the complexation scheme previously reported [12, 16] and assuming $R_d^0 = 6000$ m³ kg⁻¹ (dashed line). In this case, sorption reduction due to the presence of ISA can be attributed to the formation of Th(IV)-ISA complexes in solution. Note that a R_d^0 value ≥ 1000 m³ kg⁻¹ is supported from uptake measurements carried out at a S/L ratio = 10^{-5} kg L⁻¹ [9]. Nevertheless, the effect of ISA on Th(IV) uptake is overestimated if the distribution ratio in the absence of ISA is taken to be lower, *i.e.*, $R_d^0 = 350$ m³ kg⁻¹ (solid line in Fig. 2). A R_d value ranging from 100 m³ kg⁻¹ to 1000 m³ kg⁻¹ is indicated from measurements at S/L ratios $\geq 10^{-4}$ kg L⁻¹. Moreover, studies of Th(IV) uptake by CSH phases corroborate a R_d^0 value in this range [11, 25]. On this assumption, however, the formation of ternary Th(IV)-ISA complexes at the HCP-ACW interface is necessary to explain the discrepancy between the predicted ISA effect (solid line in Fig. 2) and the experimental data. The formation of ternary Th(IV)-ISA complexes implies that aqueous Th(IV)-ISA complexes may sorb onto the HCP surface and, therefore, enhance the overall Th(IV) uptake. Note that ISA was found to strongly sorb on HCP and CSH phases [22], which certainly justifies consideration of ternary complex formation in cement systems. Nevertheless, uncertainties in the R_d^0 value are too large to enable a final mechanistic interpretation of the ISA effect on Th(IV) uptake to be made based on the currently available data. Precise measurements of the distribution ratio for Th(IV) are needed, but constrained by the following experimental conditions: a) High activities (or concentrations, respectively) are required to reduce the sources of error caused by radio assay to a statistically acceptable level [12]. Note that Th(IV) tracer solutions are stable up to a maximum concentration of 10^{-9} M, which limits the concentration range for tracer studies. b) The very low solid concentrations required in

these experiments raises questions concerning the preparation of representative HCP samples and the stability of the material at low S/L ratios. The reasons for the observed variations in the R_d^0 value in the absence of ISA are unclear at present. It appears, however, that precise measurements of the distribution ratio in the absence of ISA and at S/L ratios $\leq 10^{-4}$ kg L $^{-1}$ are needed for a more detailed interpretation of the data.

Nevertheless, the actual knowledge on the overall effect of ISA on Th(IV) uptake allows us to already assess its impact on radionuclide mobility in a cementitious near-field. A lower bound value for the distribution ratio of Th(IV) in the absence of ISA is assumed, i.e., $R_d^0 = 100$ m 3 kg $^{-1}$. With this, a reduction of Th(IV) uptake by HCP in the presence of ISA is expected only at $[ISA]_{aq} > 10^{-4}$ M based on the experimental data displayed in Fig. 2. The ISA concentration in the pore water of the cementitious near-field was reported to depend on the amount of cellulose in the repository, the extent of degradation, the stability of ISA, the formation of sparingly soluble solids and the sorption of ISA [23]. The main process regulating the concentration of ISA in the cement pore water however is ISA sorption on HCP. For example, estimates made for the present design of the Swiss ILW repository showed that the ISA concentration in the pore water is expected to be, at a maximum, $\sim 3 \times 10^{-6}$ M if the total cellulose inventory (~ 500 kg) degrades and ISA is allowed to sorb on HCP [27]. The ISA concentration in the pore water is expected to be $\sim 3 \times 10^{-7}$ M for a more realistic case, where only 10% of the cellulose inventory degrades and ISA sorption is allowed. The experimental data clearly indicate that no significant effect of ISA on Th(IV) uptake by HCP is anticipated at these concentration levels.

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