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Selection of reduction factors and speciation calculations

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Summary

In the context of expanding the disposal facilities of low- and intermediate-level waste in the final repository at Forsmark (SFR), the long-term performance of the repository is analysed in the SR-PSU safety analysis. Key parameters feeding into these analyses include distribution coefficients (K_d values) for the uptake of all relevant radionuclides by cement-based materials in the Silo and vaults of the SFR facility. Different types of wastes in SFR contain organic substances (ligands) that can form stable aqueous complexes with many of the relevant radionuclides, which may cause a decrease of radionuclide uptake. In addition, organic ligands may also be present in the form of concrete admixtures.

The present report provide key values for quantifying the potential decrease of radionuclide uptake due to the presence of organic ligands, and discusses the underlying evidence for the selection of these values:

- No-effect concentrations define the lowest organic ligand concentration below which no influence on radionuclide uptake can be observed.
- Uptake reduction factors quantify the reduction of radionuclide uptake in the presence of organic ligands with respect to the uptake in an organic-free system.

The organic ligands considered in this context include isosaccharinate (ISA), EDTA, NTA, gluconate, citrate, oxalate, and degradation products of a UP2 filter aid.

Contents

1 Introduction and objectives

In the context of expanding the disposal facilities of low- and intermediate-level waste in the final repository at Forsmark (SFR), the long-term performance of the repository is analysed in the SR-PSU safety analysis. To this end, important processes and key input parameters for safety analysis modelling need to be defined and quantified.

Among others, these key parameters include distribution coefficients (K_d values[1]) quantifying the uptake of all relevant radionuclides by cement-based materials in various compartments of the SFR facility. Different types of wastes in SFR contain organic substances (ligands) that can form stable aqueous complexes with many of the relevant radionuclides, which may cause a decrease of radionuclide uptake. In addition, organic ligands may also be present in the form of concrete admixtures.

The goal of this report is to provide key values for quantifying the potential decrease of radionuclide uptake due to the presence of organic ligands, and to discuss the underlying evidence for the selection of these values.

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[1] As explained in detail in /SKB 2014b/, uptake processes in hydrated cement systems may include various incorporation processes in addition to surface adsorption. Therefore, the more general term 'uptake' is preferred over 'sorption'. For reasons of simplicity, the term 'K_d' is retained in the sense of a solid/liquid distribution coefficient, without making any implications regarding the nature or reversibility of the uptake process.

2 System overview

A definition of the system and a discussion of the relevant processes is given in the SR-PSU waste process and data reports (SKB 2014a, b). Briefly, the main issues related to the definition of uptake reduction factors are summarised here.

In SKB (2014a), solid/liquid distribution ratios (K_d values) quantifying the uptake of radionuclides by the cementitious materials are proposed. Cement-based materials are an important component in the Silo as well as in the BMA and BTF storage vaults of SFR. Note that the recommended uptake values in SKB (2014a) are generic in that they refer to radionuclide uptake by typical hydrated cement paste (HCP) in contact with cement-equilibrated porewater. Minor differences in concrete or grout formulation are not taken into account.

In SKB (2014a), the following states of evolution of cementitious systems are considered, defined by the following chemical conditions. These conditions are matched in the speciation calculations in Appendix 1, except state IIIb where porewater with lower pH (porewater D) had been used.

- State I correspond to fresh hydrated cement paste. High concentrations of alkalis are still present, giving $pH \geq 13$ and elevated Na/K but low Ca(II) concentrations in the pore solution.
- State II is characterised by equilibrium with portlandite and $pH \approx 12.5$. Dissolved Ca(II) is relatively high.
- In state III, most Ca(II) has been leached, portlandite disappears and the Ca/Si ratio of the CSH minerals starts to decrease continuously from about 1.5 to about 0.9 (when C/S reaches a value of about 0.8, roughly the C/S ratio of the mineral tobermorite, the CSH phases dissolve completely). Because state III is relatively variable in terms of mineralogical and solution composition, conditions for the beginning and end of this state were considered separately as follows in SKB (2014a):
- State IIIa: CSH with a C/S ratio not much lower than 1.5, presence of Ca-aluminates, pH 12.
- State IIIb: CSH with a lower C/S ratio (approaching $C/S \approx 1$), absence of Ca-aluminates, pH 10.5.

In addition, the pore solutions may contain organic ligands stemming from the waste or originally added as part of concrete or grout formulations. The organic ligands considered relevant for SFR include:

- isosaccharinate (ISA),
- ethylene diamine tetraacetate (EDTA),
- nitrilo triacetate (NTA),
- gluconate (GLU),
- citrate (CIT),
- oxalate (OX),
- degradation products of UP2 filter aid (UP2).

Concentrations to be expected in the relevant parts of SFR are given in Keith-Roach et al. (2014).

3 Uptake reduction by organic ligands

3.1 Approach

The potential decrease of radionuclide uptake by organic ligands is characterised by two values:

- No-effect concentrations define the lowest organic ligand concentration below which no influence on radionuclide uptake can be observed.
- Uptake reduction factors quantify the reduction of radionuclide uptake in the presence of organic ligands with respect to the uptake in an organic-free system.

As far as possible, these values were evaluated on the basis of experimental evidence directly applicable to the ternary HCP-radionuclide-organics system. In case of lacking data, chemical analogue information was used. Priority was given to data sources according to the following considerations:

- Establishment of a well-defined reference value: Considering the uncertainties in radionuclide uptake values (SKB 2014a), it is not always straightforward to distinguish effects of organic ligands from normal scatter of the data. It is therefore important to have enough good quality uptake data measured for the same system in the absence of organic ligands.
- For the same reason, data sets including a range of ligand concentrations are much preferred over single point measurements. Ideally, data describing a trend of uptake as a function of organic ligand concentration are available. Such data allow to quantify the influence of the organic ligand at different concentration levels and to evaluate the uncertainty of individual data points in comparison to overall trends. Single point measurements can be valuable indications of an effect, but are difficult to use for quantitative estimates.
- As ISA results from cellulose degradation, some studies used solutions of cellulose degradation products. Experiments with actual ISA are clearly preferable, due to the ill-defined nature of the cellulose solutions.
- Studies were preferred that paid attention to or discussed experimental windows in terms of radionuclide uptake and stability of HCP in the presence of high ligand concentrations.
- Where no direct experimental data were found, the use of chemical analogies was preferred over estimations based on speciation. For several radionuclides, the results of speciation calculations are compared with reduction effects. These cases show that aqueous speciation is valuable for qualitative comparisons, but that it is not directly applicable to the quantification of reduction effects, as the HCP-bound functional groups or sites are very important. These can presently not be included in speciation models due to missing constants for the various surface- or solid-interactions.
- Similarly, the use of chemical analogue data from a well-characterised system can be preferable to ill-defined data obtained for the radionuclide of interest.

A general overview of the pertinent literature is given in SKB (2014b); important aspects related to the reduction of radionuclide uptake are repeated in the present report. New literature, as far as available, is integrated.

The estimation of no-effect concentrations and uptake reduction factors is discussed below for each radionuclide. The proposed values are summarised in tables at the end of Section 3.2.

- In most cases, realistic or best-estimate values are proposed. Depending on the available data, these are often based on a conservative (cautious) approach.
- As much of the information is only available for ISA, the values proposed for the effects by ISA are given in a separate table (Table 3-1).
- Table 3-2 summarises the values for all other organic ligands. In many cases, these are based on ISA by analogy. Values for specific ligands other than ISA are correspondingly marked in the table.
- In a few cases, actual conservative (pessimistic) values are proposed. These are given in Table 3-3.

3.2 Uptake reduction factors for relevant radionuclides

3.2.1 Carbon and Calcium isotopes

Inorganic carbon as well as Ca are main constituents of various minerals making up the matrix of cementitious materials. Accordingly, the uptake of radioactive isotopes will be controlled by the exchange with stable isotopes rather than by chemical reactions. It is expected that this isotopic exchange process is not influenced by the presence of organic ligands under relevant conditions. Accordingly, a sorption reduction factor of 1 is recommended.

In theory, high organic ligand concentrations could lead to an increased solubility of calcite and hydrated cement phases, which in turn could have an influence on the isotopic exchange process. However, such conditions would impair the stability of the cementitious matrix and are not seen as relevant.

^{14}C in organic form is expected to exist either as methane or in the form of other simple organic compounds. As zero sorption is assumed for organic ^{14}C (SKB 2014a), any possible sorption reduction is not relevant and no reduction factor is assigned.

3.2.2 Halogens

The relevant forms of halogen elements are chloride and iodide (SKB 2014b). No information was found in the literature on the influence of organic complexing agents on the uptake of either by cementitious materials. Based on the properties of the relevant organic ligands, no formation of aqueous complexes with chloride and iodide is expected. Theoretically, organic acid anions could interfere with purely electrostatic uptake processes of chloride or iodide, but this is considered insignificant in view of the much higher concentrations of OH^- and stable chloride anions in the relevant porewaters.

3.2.3 Caesium

No significant complexation of Cs(I) by the organic ligands considered here is expected. The available sorption data regarding the effects of gluconate and ISA on Cs(I) uptake by HCP (Bradbury and Van Loon 1998, Holgersson et al. 1998) show that the uptake of Cs(I) is not affected by the presence of organics under realistic conditions. Accordingly, a reduction factor of 1 is assigned.

3.2.4 Alkaline earth elements

Most of the organic compounds considered here are known to form fairly stable aqueous complexes with Ca(II) ions. In Appendix 1 the speciation of ISA and EDTA in the various porewaters is calculated. EDTA is predicted to exist under all conditions entirely as $Ca(EDTA)^{2-}$ species, at a total EDTA concentration of 1.1×10^{-6} M. The calculations for ISA were performed using the high ISA concentration (0.023 M), but ISA a few to about 30% of ISA still exist as Ca(II)-species. Similar complexation properties are expected for the other ligands considered here.

Similar interactions as for Ca(II) can be expected for Sr(II) and other alkaline earth elements. The only dataset directly applicable to an evaluation of reduction factors is given in Wieland et al. (2000). They observed no measurable effect on Sr(II) uptake on HCP in the presence of ISA at equilibrium concentrations up to 1 mM. At higher ISA concentrations, Sr(II) uptake seemed to increase slightly and only started to decrease at ISA concentrations > 10 mM. Based on these findings, the following values are proposed:

- For ISA, 10 mM is proposed as no-effect concentration, considering the uncertainties in the uptake values. This value is also proposed for the other organic ligands.
- For organic ligand concentrations > 10 mM, an uptake reduction factor of 10 is proposed for each 10-fold increase in dissolved ligand concentration.
- By analogy, the same no-effect concentrations and reduction factors are proposed for Ra(II) and Ba(II).

3.2.5 Silver

No quantitative information regarding the influence of organic ligands on the sorption of silver in cement-based systems was found. With regard to a possible effect of the relevant ligands, it is known (Hart 2005) that a soft metal ion like Ag(I) tends to form complexes with soft ligands, such as the N-containing EDTA and NTA. The speciation calculations presented in Appendix 1, using the dissolved EDTA concentration realistically to be expected, showed no influence of EDTA on Ag(I) speciation. Therefore, no realistic value for a sorption reduction factor is proposed.

However, to take into account possible higher concentrations of organic ligands, an arbitrary, conservative reduction factor of 100 (constant) is recommended for N-containing ligands (EDTA, NTA). As the complexation of Ag(I) by EDTA is approximately comparable to the complexation of Ca(II) or weaker (see Appendix 1), this factor is only applied to EDTA and NTA concentrations above the dissolved Ca(II) concentration (see also Chapter 2).

No effect is expected for the organic O-ligands (hydroxo-carboxylic acids, see SKB 2014b). To acknowledge the lack of direct information, a conservative constant factor of 10 is assigned arbitrarily for all organic ligand concentrations > 10 mM.

3.2.6 Cadmium

No data regarding the influence of organic ligands on the uptake processes of Cd(II) could be found. In general, formation of aqueous metal-organic complexes should be expected for Cd(II). Considering the soft chemical character of Cd(II), EDTA and NTA could be particularly important.

The results of the speciation calculations in Appendix 1 are approximately consistent with that general assessment. Even at a low concentration of EDTA (1.1×10^{-6} M), Cd(II) exists in the form of an EDTA-complex to 42% in state IIIa and to 100% under conditions of porewater D. Under the high-pH conditions of states I and II, no Cd(II)-EDTA complexes are predicted. At high ISA concentrations, approximately 20–30% of total dissolved Cd is complexed by ISA (except in state IIIa). When the low ISA concentration is used in the speciation calculations, no Cd(II)-ISA complexes are predicted.

In SKB (2014a), the uptake of Cd(II) by HCP in the absence of organic ligands is estimated based on analogy with the uptake of Pb(II). While Ni(II) is considered a more suitable analogue, Pb(II) was used due to the particular uptake mechanism (isotopic exchange) of Ni(II). For the present purpose, some evidence is available regarding the influence of organic ligands on Ni(II) uptake by Ni-free model minerals (i.e. in a situation where Ni is taken up by sorption rather than by isotopic exchange). Based on the information given in the section on Ni and Co, the following values are proposed:

- A no-effect concentration of 10 mM is selected on the basis of the results by Van Loon and Glaus (1998).
- No data directly applicable to defining a reduction factor are available. As an arbitrary but conservative choice, the same factor as for trivalent actinides is proposed.

3.2.7 Palladium

No relevant experimental data could be found. Therefore, the approach of Ochs et al. (2011) was followed (as in the definition of K_d in an organic-free system (SKB 2014a)) and Pb(II) was used as analogue.

3.2.8 Nickel and cobalt

All available evidence suggest that the interaction of radioactive Ni- and Co-isotopes with cement systems occurs through isotopic exchange rather than any form of chemical uptake (SKB 2014a, b, Wieland and Van Loon 2002, Wieland 2014, Wang et al. 2009). Accordingly, any influence of organic complexing agents should be limited to the influence on the solubility (or accessibility) of the respective solid phases (probably layered double hydroxides (Wieland 2014, Wang et al. 2009)). Relevant experimental solubility measurements or thermodynamic data for a quantitative assessment are not available. However, evidence from experiments of Ni(II) partitioning in relevant systems in the presence of organic complexing agents clearly shows the absence of significant effects at relevant ligand concentrations.

Glaus and Van Loon (2004) noted that various organic compounds had a much weaker influence on apparent Ni(II) uptake by HCP in comparison to Eu(III) and Th(IV). They further point out that contrary to expectations, compounds with additional N-functional groups did not influence Ni(II) more strongly than those without. Wieland et al. (2000) determined that ISA had no influence on Ni(II) uptake up to a concentration of about 1 mM, Holgersson et al. (1998) observed a corresponding value of 5 mM ISA. At higher ISA concentrations, the effects of ISA seem not conclusive: Wieland et al. (2000) observed enhancement or reduction at different elevated ISA concentrations. Holgersson et al. (2011) also found no evidence for a reduction of Co(II) uptake by HCP in the presence of ISA, EDTA and citrate within the concentration range investigated (0.26 mM to 4.2 mM for all compounds).

Information on the influence of organic ligands on Ni(II) uptake is also available from presumably Ni-free systems where isotopic exchange should not be relevant and partitioning of Ni(II) can be expected to be dominated by chemical processes. Bradbury and Van Loon (1998) showed that gluconate does not influence Ni(II) uptake on CSH-phases at gluconate concentrations below 10^{-4} M, but did not investigate the effect of higher gluconate concentrations. To determine the effect of aqueous Ni(II)-ISA complex formation in the absence of ISA sorption reactions, Van Loon and Glaus (1998) compared Ni(II) sorption on feldspar as a function of ISA concentration. Ni(II) sorption was only significantly reduced at dissolved ISA concentrations > 0.01 M. As no sorption of ISA takes place in this system, their data should reflect a worst-case situation in terms of competition by aqueous complexation.

It is proposed to treat the influence of organic ligands as follows:

- Based on the nature of isotopic exchange and on the additional evidence discussed above, no effects of organic ligands are expected for the partitioning of radioactive Ni isotopes. A realistic reduction factor of 1 is proposed.
- To acknowledge the observations discussed above, an additional conservative reduction factor of 10 (constant value) is assigned to organic ligand concentrations above 5 mM.
- SKB (2014a, b) and Wieland (2014) propose on the basis of good evidence that the partitioning of radioactive Co isotopes also takes place through isotopic exchange. Accordingly, it is proposed to treat Co(II) in the same manner as Ni(II) with regard to effects of organic ligands.

3.2.9 Trivalent actinide and lanthanide elements, actinium

The influence of organic ligands relevant for cementitious systems, and especially of ISA, on the behaviour of elements belonging to this group is comparatively well studied. Based on their hard cation character, significant complexation with the relevant organic ligands can be expected. The literature overview given in SKB (2014b) indicates that in particular ISA may be important in influencing the uptake of these elements.

In Appendix 1 speciation calculations for Am(III) and Eu(III) in the presence of the two ISA-concentrations given in Keith-Roach et al. (2014) are performed. The results for states I-IIIa indicate that at high ISA concentrations, the speciation of both elements is completely dominated by a mixed hydroxo-ISA complex ($Am(OH)_3(ISAH_2)^-$, $Eu(OH)_3(ISAH_2)^-$). At pH < 10 (porewater D), these complexes are still dominant.

At the more realistic lower ISA concentration, the mixed hydroxo-ISA complexes make up about 30% of Eu(III) and < 15% of Am(III) species in states I-IIIa. At the lower pH of porewater D, it is predicted that the speciation of Am(III) and Eu(III) is not influenced by ISA.

ISA

The effect of ISA on the uptake of lanthanide elements was investigated in several studies. Depending on the range of conditions (especially ISA concentration) considered and on how carefully the experimental conditions were chosen, some results can be used directly to evaluate the effects in the ternary system HCP-radionuclide-ISA. In other cases, the scope was too limited or conditions not entirely appropriate; these studies are also discussed but are not used in the definition of uptake reduction factors.

- The effect of ISA on Eu(III) uptake was investigated by Van Loon and Glaus (1998) and Wieland et al. (1998). Both studies give consistent results, indicating that ISA concentrations below 1 mM do not have a significant influence on Eu(III) uptake.
- The recent report of Wieland (2014) presents a number of datasets obtained for the uptake of Eu(III) by HCP and by CSH as a function of ISA concentration (Figure 3-1). The experiments were performed at pH 13.3 and in the presence of up to 0.04 M ISA; i.e. under conditions where significant complexation of Eu(III) by ISA can be expected. Reportedly, extra care was taken to choose combinations of solid/liquid ratio and Eu(III) as well as ISA concentration that would provide a sufficient experimental window for determining uptake in the ternary system and at the same time prevent the dissolution of the solid at elevated ISA concentrations.
- Data on Eu(III) uptake as a function of ISA concentration as given in Bradbury and Van Loon (1998) are also shown in Figure 3-1. Note that these data are largely identical with the data by Wieland et al. (1998). They differ in absolute values from the data by Wieland (2014), but show a nearly identical trend regarding the effect of ISA. Considering the low solid/water ratio (10 mg/L) used in these experiments and the discussion given in Wieland (2014) on the experimental window in the presence of elevated ISA, the data by Wieland (2014) are viewed as more reliable.
- Dario et al. (2004a) measured Eu(III) sorption on HCP and TiO_2 in the presence of ISA. Their results are not entirely conclusive, because they used only ISA concentrations in the range of 0.1–10 mM. However, the results obtained with HCP and TiO_2 are consistent and it appears from the available data a slight reduction effect may already be possible at 0.1 mM ISA. Whether this is significant in comparison to the uncertainty of the sorption measurements is difficult to see on the basis of the graphs provided in Dario et al. (2004a).
- Holgersson et al. (1998) investigated the effect of isosaccharinate on promethium (PmIII) uptake in cement systems. They observed transient effects, which are not straightforward to interpret.

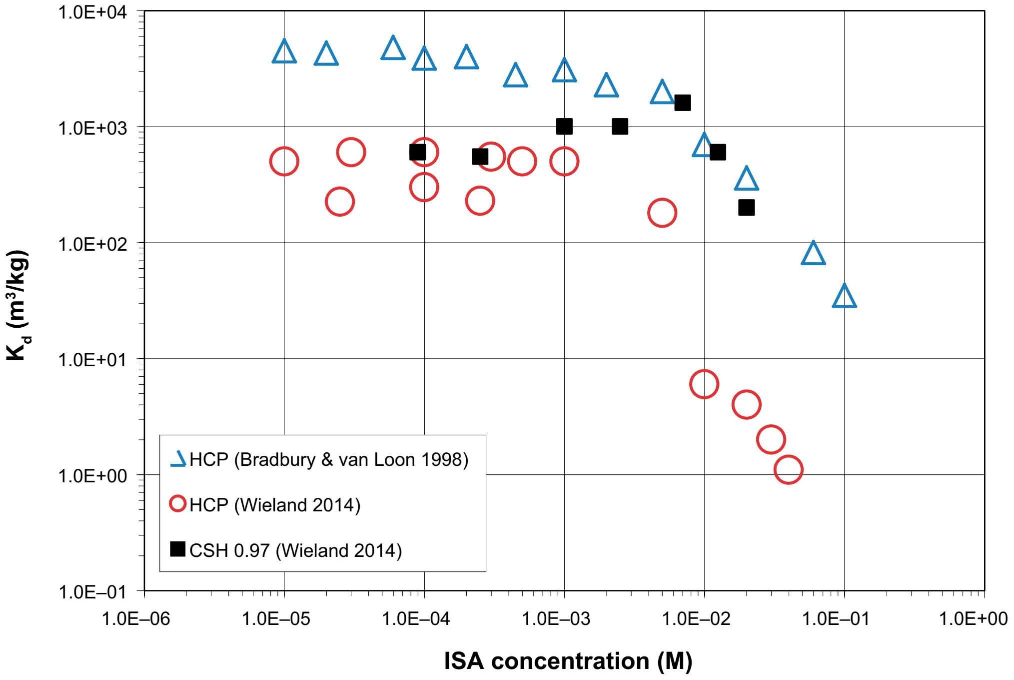


Figure 3-1. *Uptake of Eu(III) by HCP and by CSH as a function of ISA concentration.*

No direct information on the influence of ISA on the uptake of trivalent actinides or of actinium by HCP was found. Bradbury and Van Loon (1998) report that no influence of 1×10^{-3} M ISA on Am(III) uptake by HCP was observed (without providing further details and referring to an internal PSI report). To relate findings of Eu(III) in HCP systems to trivalent actinides, additional results for calcite and speciation information can be drawn upon. Both lines of evidence show that uptake reduction observed for Eu(III) applies to Am(III), and by analogy to other trivalent actinides:

- The speciation calculations presented in Appendix 1 indicate that the aqueous complexation by ISA is at least as strong in case of Eu(III) as in case of Am(III).
- Tits et al. (2005) observed the same effect of ISA for Eu(III) and Am(III) uptake by calcite (decrease of uptake at ISA concentrations above 10^{-5} M).

Uptake reduction factors for trivalent actinides, lanthanides and actinium are therefore based on the effects observed in case of Eu(III) (Figure 3-1):

- Considering an uncertainty of about an order of magnitude for the uptake values of Eu(III) measured in the ISA-free systems, a no-effect concentration of 1×10^{-3} M is proposed.
- For ISA concentrations > 1×10^{-3} M, an uptake reduction factor of 10 is proposed for each 10-fold increase in dissolved ISA concentration. This is based on the downward slope of the data shown in Figure 3-1.
- Note that the data in Figure 3-1 reflect all relevant processes in the ternary Eu(III)-ISA-HCP system, i.e. uptake of Eu(III) not complexed by ISA as well as any possible uptake of Eu(III)-ISA species, reduction of Eu uptake by competition of dissolved ISA for Eu.

Gluconate

Wieland (2014) also report several datasets on the effect of gluconate that had not been previously published. These include the uptake of Eu(III) by HCP and CSH as a function of gluconate concentration. It appears from these data that gluconate actually leads to a reduction of trivalent actinide/lanthanide uptake at lower concentrations than ISA. This is consistent with the observations by Tits et al. (2002, 2005), who found that gluconate leads to a reduction of Eu(III) and Th(IV) uptake by calcite at lower concentrations than ISA. Note that uptake reduction effects occur at significantly lower organics concentrations in case of calcite than in case of CSH or HCP. The reasons for this are not clear, but could be related to the more pronounced formation of ternary complexes in case of the HCP minerals.

Bradbury and Van Loon (1998) estimated that gluconate at dissolved concentrations < 1×10^{-4} M would not influence radionuclide uptake on HCP. This estimate was based on a limited set of in-house data regarding the uptake of Cs(I), Sr(II), Ni(II), Eu(III) and Th(IV) by CSH phases.

Dario et al. (2004a) report some measurements of Eu(III) uptake by HCP at different concentrations of gluconate. While their data show considerable scatter and provide little information regarding Eu uptake at gluconate concentrations < 1 μM, it seems fairly clear that gluconate leads to a reduction of Eu(III) sorption at fairly low concentrations (≈ 10 μM) in their experiments.

The proposed reduction factor is evaluated from the data given in Wieland (2014):

- Considering again an uncertainty of about an order of magnitude for the uptake values of Eu(III) measured in the absence of ISA, a reduction in uptake becomes significant at dissolved gluconate concentrations in the range of 1×10^{-5} to 1×10^{-4} M. A no-effect concentration of 1×10^{-5} M is proposed.
- Taking into account the Eu(III) uptake values corresponding to the range of 1×10^{-5} to 1×10^{-2} M gluconate, an uptake reduction factor of 10 is proposed for each 10-fold increase in dissolved gluconate concentration.

Other ligands

The effect of additional organic complexing agents potentially relevant for SFR was investigated by Dario et al. (2004a, b, c). In addition to HCP they used TiO_2 as a model solid to study the role of variable dissolved Ca(II) concentrations. The investigated organic compounds include EDTA, NTA, citrate, oxalate, a polycarboxylate (Glenium 51) and degradation products of a UP2 filter aid:

- EDTA and NTA: In the presence of EDTA alone (no Ca(II) added), Eu(III) sorption on TiO_2 started to decrease at micromolar concentrations of EDTA. When 2 mM Ca(II) was added to resemble cement systems, Eu(III) sorption decreased when the EDTA concentration exceeded about 1 mM. This was consistent with the results from the cement system and demonstrated competition between Ca(II) and Eu(III) ions for EDTA. This is consistent with the calculations results of Appendix 1 which show that EDTA exists nearly exclusively as $Ca(EDTA)^{2-}$ in HCP porewaters. In both HCP and TiO_2 systems initially containing about 2 mM dissolved Ca(II), Eu(III) sorption started to decrease once the concentration of EDTA started to exceed the dissolved Ca(II) concentration. A nearly identical picture was observed with NTA. Note that in case of HCP, but not in case of TiO_2, the dissolved Ca(II) concentration is buffered by portlandite; i.e. the final total dissolved Ca(II) concentration may not have been identical in the HCP and TiO_2 systems.
- Citrate, oxalate: The experiments by Dario et al. (2004a) indicate that Eu(III) uptake by HCP starts to be affected in the presence of about 1 mM citrate. No important effect of Ca(II) was observed. Oxalic acid showed no effect at concentrations up to 10 mM and may have precipitated as Ca-oxalate.
- Glenium 51: This polycarboxylate appears to lead to a reduction of Eu(III) sorption at a concentration of about 0.01% of the liquid phase, based on the measurements of Dario et al. (2004a, b).
- The degradation of a UP2 filter aid contained in some wastes and the effect of the resulting degradation products on Eu(III) uptake were also studied by Dario et al. (2004a, c). Their data show a reduction in Eu(III) uptake at a DOC concentration of about 1×10^{-4} M; this effect seems to be independent of the Ca(II) concentration in case of the TiO_2 sorbent. Approximately the same effect of UP2 filter aid degradation products on Eu(III) uptake by HCP was observed in later study by Duro et al. (2012). Most of their data were measured in the presence of degradation products obtained at 60°C. The few data measured in the presence of degradation products obtained at 25°C, are not conclusive, on the other hand: when pH during degradation was 13.4, a decrease of Eu(III) uptake is observed, whereas the material obtained at pH 12.5 shows no effect within the concentration range considered (up to ~ 7×10^{-4} M DOC). The authors themselves conclude that no significant effects should be expected up to 8 mg/L DOC under conditions relevant for SFR. It needs to be noted that the obtained degradation products in both studies are ill defined and their properties appear to depend significantly on the degradation conditions.

In summary, the evidence for these organic ligands is less systematic than in case of ISA, but the same general trends can be observed. Uptake reduction parameters are therefore defined as follows:

- A no-effect concentration of 1×10^{-3} M is proposed for all compounds. This is based on the evidence discussed above and on analogy with ISA, considering that ISA is a very effective complexing agent for trivalent actinides and lanthanides. While the data for the UP2 filter degradation products are not conclusive, an additional conservative no-effect concentration of 1×10^{-4} M is proposed.
- The reduction factor of 10 defined for ISA and gluconate is also proposed here.

3.2.10 Tetravalent actinide elements

Of all radionuclides, tetravalent actinides appear to be most affected by the presence of organic complexing agents (Wieland 2014, Bradbury and Van Loon 1998, Greenfield et al. 1992). Most of the available evidence concerns the effect of ISA on Th(IV) uptake. Much less data are available for the other relevant actinides (Pu, Np, U), due to the experimental difficulties related to maintaining the +IV oxidation state.

ISA

Similar to the trivalent actinides, tetravalent actinides can be expected to form strong complexes with ISA. This is confirmed by the speciation calculations discussed in Appendix 1.

- At high ISA concentration, Th(IV) is calculated to exist to > 90% as either $CaTh(OH)_4(ISAH_2)^+$ or as $Th(OH)_4(ISAH_2)_2^{2-}$ under all porewater conditions (the proportion of the complexes vary with pH and Ca(II) concentration). At the lower ISA concentration, complexation with ISA is only relevant for states I-IIIa; only the ISA-complex $CaTh(OH)_4(ISAH_2)^+$ is formed, which makes up about 15–58% of dissolved Th. Note that this refers to the calculations performed with the thermodynamic data selected as standerd for the present purpose (ThermoChimie, see Section A1.3.5. Alternative speciation information is discussed in Section A1.3.5.
- Pu(IV) is predicted to be even stronger complexed by ISA, with more than 99% in the form of $Pu(OH)_4(ISAH_2)_2^{2-}$ at high ISA concentration under all porewater conditions. At the lower ISA concentration, the same complex is formed and makes up about 15–25% of dissolved Pu(IV) in all porewaters.

Systematic data for the uptake of Th(IV) by HCP, CSH and CASH phases are given in Wieland et al. (2002) and Wieland (2014) as a function of ISA concentration. Their data are summarized in Figure 3-2. Further uptake studies of Th(IV) by Holgersson et al. (1998) and Wieland et al. (1998) on different HCP samples in the presence of ISA are consistent with these data. From the data of Holgersson et al. (1998) it also appears that the effect of ISA is time-dependent and is decreasing with long equilibration times (~2 months).

It should be mentioned that there are also experimental results that are not easy to interpret, especially from studies where only a few data were measured. Baker et al. (2002) measured the uptake of Th(IV) by Nirex Reference Vault Backfill (NRVB) in the presence of ISA. They obtained three K_d values which show about the same reduction effect with increasing ISA concentration as shown in Figure 3-2, but provide no reference values for uptake in the absence of ISA. A comparison with an uptake value given in Greenfield et al. (1997) in a similar system without ISA would indicate a clear reduction at the lowest ISA concentration used (0.1 mM), which does not agree with other studies. Wang et al. (2009) speculate that this may be related to different equilibration times used, but a clear explanation is lacking.

Further supporting evidence is given by the study of Van Loon and Glaus (1998) for the sorption of Th(IV) on feldspar at high pH as a function of ISA concentration. They selected feldspar to avoid sorption of ISA and observed the same trends and no-effect concentration as indicated by the data in Figure 3-2. As ISA is essentially not interacting with feldspar surfaces, their results should reflect the maximum sorption reduction effect due to the formation of dissolved Th-ISA complex species.

Data for other tetravalent actinides are sparse, and are seen as clearly less reliable than the data for Th(IV). On the basis of data by Baker et al. (2002) and Greenfield et al. (1997), Wang et al. (2009) discuss that the no-effect concentration may be lower for Pu(IV) than for Th(IV). However, in view of the significant uncertainty related to phase separation also mentioned by Wang et al. (2009), these data are not considered reliable.

Due to the relatively limited data available for cement systems and as a result of the uncertainty associated with a value for the baseline uptake of Th(IV), it is not straightforward to define the dissolved ISA concentration corresponding to the onset of a measurable reduction effect. Considering the uncertainty of the uptake values, it can be taken from Figure 3-2 that ISA appears to have no influence on the uptake of Th(IV) by HCP up to a dissolved concentration of at least 0.1 mM; this is also the interpretation of Wieland (2014). Van Loon and Glaus (1998) also estimated 0.1 mM as the minimum ISA concentration required to cause significant sorption reduction. Wieland et al. (1998, 2002) noted a definite decrease of Th(IV) uptake at ISA concentrations of about 0.5 mM, while Holgersson et al. (1998) saw no effect at 3 mM (however, these may be total rather than dissolved concentrations).

The reduction effect of ISA appears to be stronger for tetravalent actinides than for the trivalent elements discussed above. Figure 3-2 suggests that an increase of about an order of magnitude in dissolved ISA concentration leads to a decrease of Th(IV) uptake (expressed as a K_d value) by about two orders of magnitude. A logical explanation for this difference would be the formation of Eu(III)-ISA 1:1 complexes in comparison to Th(IV)-ISA 1:2 complexes (see Section A1.3). However, the presently available speciation information does allow to clearly determine at which ISA concentration a 1:2 complex with Th becomes relevant and whether the formation of such a complex would also depend on the dissolved Ca(II) concentration (see Section A1.3.5).

In summary, reliable experimental data regarding effects of organic ligands on the uptake of tetravalent actinides by HCP is limited to the system Th-ISA-HCP. Uptake reduction factors and no-effect concentrations are taken directly from the studies summarized in Figure 3-2. Data for the other tetravalent actinides are proposed in analogy to Th(IV).

- For Th(IV), a no-effect concentration of 1×10^{-4} M is proposed. Considering the uncertainty of the reference uptake value for ISA-free systems, this is considered a cautious estimate. Taking further into account the strong complexing ability of ISA, this value is also proposed for the other relevant ligands.
- For dissolved ISA concentrations above 1×10^{-4} M, an uptake reduction factor of 100 is proposed for each 10-fold increase in dissolved ISA concentration, based on the slope of the experimental data shown in Figure 3-2. By analogy, this value is used for all other tetravalent actinides.
- On the basis of tentative evidence, Wang et al. (2009) argue that the uptake reduction factor for Pu(IV) should be 1,000 at higher ISA concentrations, but admit that there are uncertainties regarding the oxidation state of Pu(IV) in the underlying data. On the other hand, Wieland (2014) does not distinguish between Pu(IV) and other tetravalent actinides. From the speciation results of Appendix 1 discussed above, the use of a reduction factor that is significantly different from that of Th(IV) does not seem warranted.

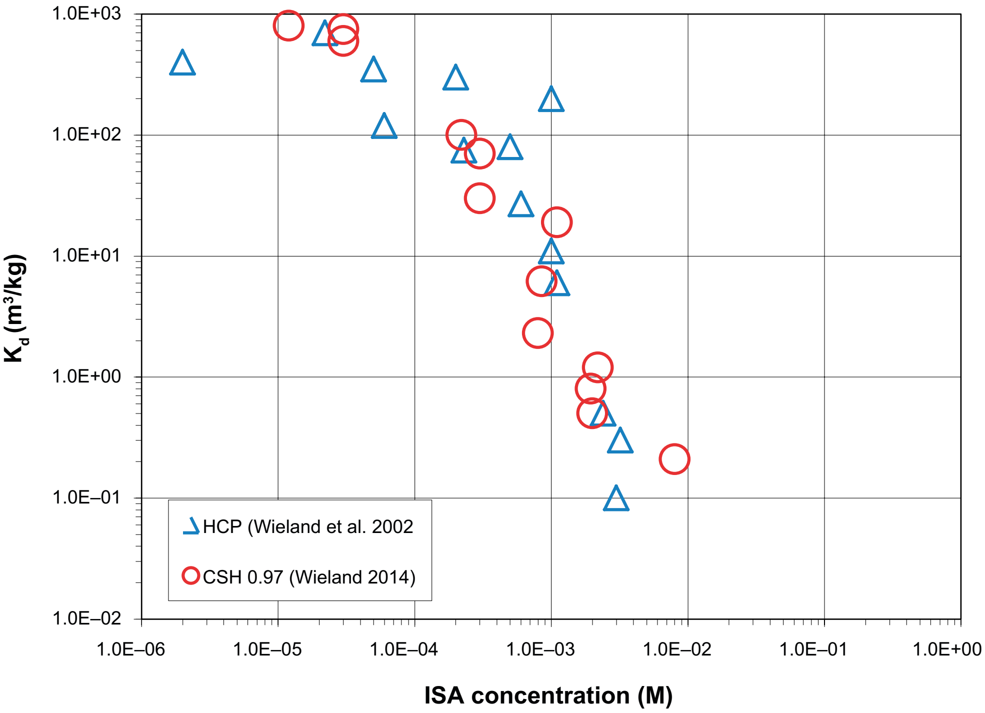


Figure 3-2. *Uptake of Th(IV) by HCP and by CSH as a function of ISA concentration.*

Gluconate

As for trivalent elements, Wieland (2014) provide as yet unpublished data regarding the effect of gluconate on Th(IV) uptake by HCP as well as CSH and CASH phases. Wieland (2014) gives no detailed evaluation, as no gluconate concentrations above 2×10^{-5} M are considered in the respective repository system. The given experimental data indicate no measurable effect of gluconate up to a dissolved concentration of 5×10^{-5} M gluconate. An effect is clearly visible at concentrations $> 1\times10^{-4}$ M gluconate, and the data measured within this concentration range are not conclusive. Values for the reduction effect are proposed as follows:

- As no-effect concentration, the values of 5×10^{-5} M gluconate discussed above is used. This value corresponds most closely to the experimental data for Th(IV) uptake by HCP given in Wieland (2014).
- An uptake reduction factor of 100 is taken directly from the experimental data in Wieland (2014) for each 10-fold increase in dissolved gluconate concentration.
- The proposed values are consistent with the values proposed for ISA and with the observations by Tits et al. (2002, 2005) that gluconate leads to a reduction of Th(IV) uptake by calcite at lower concentrations than ISA.

Other ligands

No data applicable to the other relevant organic ligands were found. The no-effect concentration as well as the uptake reduction factor proposed for ISA are also selected for these substances. Based on the strong complexing ability of ISA, this is a cautious approach.

3.2.11 Pentavalent actinide elements

No relevant information has been found for the pentavalent actinides. As a cautious approach it is proposed to use the same no-effect concentrations and uptake reduction factors for Np(V) and Pu(V) as for trivalent actinides and the same values for Pa(V) as for tetravalent actinides, respectively.

3.2.12 Hexavalent actinide elements

Very little information is available regarding the effects of the considered organic ligands on the uptake of hexavalent actinides on HCP. In Appendix 1 the speciation of U(VI) in the presence of high and low ISA concentrations is calculated. At the high concentration, U(VI) is predicted to exist nearly exclusively in the form of the $UO_2(OH)_4(ISAH_2)^{3-}$ complex in states I-IIIa. No complexation with ISA is predicted under the conditions of porewater D. On the other hand, at the lower ISA concentration, only about 16% of the total U(VI) are complexed by ISA under conditions corresponding to state I, no complexation by ISA is predicted for all other conditions. These results may be interpreted to indicate, as a first approximation, that the effect of ISA may be similar for U(VI) as for the reduced actinide species at least at fairly high ISA concentrations.

The only systematic work on the effect of organic ligands on hexavalent actinides appears to be the study of Pointeau et al. (2006b). They investigated the uptake of U(VI) by HCP as a function of ISA concentration (ranging over several orders of magnitude) under two sets of conditions corresponding approximately to states I and IIIa. Reduction effects are estimated from their data:

- Under state I conditions, no effect of ISA is visible at ISA concentrations below about 2×10^{-3} M. The data from the experiments corresponding roughly to state IIIa are less clear, but a reduction effect seems to occur at about 5×10^{-4} M ISA. This value is proposed as no-effect concentration for ISA.
- Similarly, the data of Pointeau et al. (2006b) indicated that the reduction effect may be much more pronounced under the conditions corresponding approximately to state IIIa. As a cautious approach, the proposed reduction factor is based on these data, giving an uptake reduction factor of 10 for each 10-fold increase in dissolved ISA concentration.
- In the absence of further reliable experimental data, these values are also proposed for Pu(VI). As a cautious approach, it is further proposed to use these values for the other relevant organic ligands.

3.2.13 Zirconium

In Ochs et al. (2011), very high reduction factors between ≈ 30–125 were estimated based on the experiments by Brownsword et al. (2002) (see also section on Pb). On the other hand, Wieland (2014) assigns the same values as for trivalent actinides, based on the assumption that complexation with organic ligands is less important for Zr(IV) than for Th(IV). However, the respective thermodynamic data are not established (Berner 2014). However, a fairly strong similarity between Zr(IV) and tetravalent actinides is accepted (Baes and Mesmer 1976, Berner 2014), and the analogy with Th(IV) is viewed as more reliable for the present purpose than the study by Brownsword et al. (2002). Thus, the values proposed for Th(IV) are also used for Zr(IV); this may be conservative in view of the evaluation by Wieland (2014).

3.2.14 Tin

No relevant information could be found. It is proposed to use chemical analogy with Th(IV).

3.2.15 Technetium

Tc(IV)

No relevant experimental data were found. It is proposed to rely on an analogy with Th(IV) as a first approximation.

Tc(VII)

A reduction factor of 1 is proposed for pertechnetate. This is based on the proposed uptake mechanism of oxo-anions (SKB 2014a, b) and following the argumentation given in the section on selenate.

3.2.16 Niobium

Wang et al. (2009) propose a reduction factor of 10 based on results from studies performed with 10% cellulose-loaded leachate. Considering the uncertainties involved in the respective system, this evidence is not considered to be directly applicable to the present purpose, and no realistic reduction factor is proposed.

However, the above results are accepted as qualitative evidence for an effect of organic ligands on Nb(V) uptake. Considering the strong hydrolysis of Nb(V) and the lack of any direct evidence, it is proposed to base the reduction factor and no-effect concentration for Nb(V) on analogy with Th(IV), as a quite conservative approach.

3.2.17 Selenium

Selenate

For the selenate anion, a specific uptake mechanism is proposed: the replacement of sulphate in ettringite (SKB 2014a, b). It is not expected that any of the relevant organic ligands are able to compete with Se(VI) for such specific sites. Complexation reactions are not relevant in this case as well. Thus, no effect of organic ligands on Se(VI) uptake is expected, and a reduction factor of 1 is proposed.

Selenite

Selenite is taken up by HCP stronger than selenate, and presumable by less specific mechanisms (SKB 2014b). On this basis, some type of organic anions for the same sinks in HCP would seem plausible. This type of mechanism would be consistent with the similar behaviour of selenite and the relevant organic ligand anions in terms of Ca(II) complexation and has been proposed by Pointeau et al. (2006a).

Their work represents the only investigation of the effect of organic ligands (EDTA, ISA, gluconate) on the uptake of selenite by fresh and degraded HCP. EDTA and ISA at a concentration of 2×10^{-3} M had a strong impact on Se(IV) uptake (decrease of K_d by one to two orders of magnitude, but only when HCP had been pre-equilibrated with the organics. Otherwise, no significant effect was observed.

Based on the indication of a possibly strong impact of organic anions and on the absence of systematic evidence, the following reduction factor and limiting concentrations are proposed:

- A clear no-effect concentration cannot be defined on the basis of the available data. Therefore, as a conservative approach, the lowest no-effect concentration observed for any of the radionuclides considered is adopted. Similarly, an arbitrary reduction factor of 10 is proposed.

Selenide

Zero uptake is assumed (SKB 2014a) in the absence of organic ligands.

3.2.18 Molybdenum

Only Mo(VI) is relevant. Based on the proposed uptake mechanism (SKB 2014a, b) and following the argumentation given in the section on selenate, a reduction factor of 1 is proposed for molybdenum.

3.2.19 Lead

Ochs et al. (2011) estimated reduction factors for the uptake of Pb(II) in the presence of ISA based on a study by Brownsword et al. (2002). These experiments were not carried out with ISA directly but with cellulose degradation products. Brownsword et al. (2002) observed a significant reduction of Pb(II) uptake in the presence of > 0.1% cellulose loading. The concentration of organics in the underlying experiments was not low enough to observe a no-effect level, however. To convert the cellulose loading to ISA concentrations, Ochs et al. (2011) used the procedure given in Wang et al. (2009). From this would follow that a constant reduction of uptake was observed at ISA levels in the range of 0.01 mM to 1 mM. Higher ISA concentrations apparently did not lead to a higher reduction in sorption.

In view of the uncertainties in the cellulose-loading to ISA conversion, and considering the effect of organic ligands on other elements, the assessment by Ochs et al. (2011) is seen as very conservative, but is partly accepted considering the lack of any other evidence.

- The no-effect level according to the calculations by Ochs et al. (2011) would be 0.01 mM ISA. Based on the observation that the lowest no-effect levels directly observed for any element considered for the present report is 0.1 mM, this is seen as too pessimistic and a value of 0.05 mM is proposed here.
- Ochs et al. (2011) propose an uptake reduction factor of 100. This is given as a constant value which is independent of the ISA concentration (when above the no-effect concentration). This is accepted for the present purpose.

3.2.20 Polonium

No relevant data for Po could be found. In SKB (2014a, b) it is argued that Se(IV) may be a possible chemical analogue for Po(IV) in terms of uptake by HCP. This is based on the position of Po in the periodic table as well as on earlier assessments by Bradbury and Baeyens (2003) and Yui et al. (1999) and the fact that Po(IV) and Se(IV) sorption on bentonite are approximately within the same order magnitude (SKB 2014a). Very recently, chemical analogy with Th(IV) rather than Se(IV) was considered for estimating solubility limits (Berner 2014). As this analogy still needs to be confirmed, and as its application to the uptake of Po(IV) by HCP would also warrant the selection of new K_d values for organic-free systems, it is not adopted here. For the present purpose, analogy with Se(IV) is proposed, which is consistent with the selection of the K_d value in SKB (2014a). In view of the above discussion, it should be kept in mind that analogy with Se(IV) may be very conservative.

Table 3-1. Limiting no-effect concentrations and uptake reduction factors for ISA (realistic values). Radionuclides where information only applies by analogy are indicated in italics. Reduction factors apply to all radionuclide uptake values (i.e. best estimate and upper/lower limits, see SKB 2014a).

Radionuclide (oxidation state)	no-effect concentration for ISA	reduction factor for ISA*
Ag(I)	no effect expected for ISA (see Table 3-3 for conservative values)	1
^{14}C, carbonate species	isotope exchange, no effects expected	1
^{14}C, CH_4, simple organics	not relevant: $K_d = 0$ assumed	not applicable
Ca(II), radioactive isotopes	no effects expected	1
Cd(II)	reduction expected for [ISA] > 10 mM	10
Cl(-I), I(-I)	no effects expected	1
Cs(I)	no effects expected	1
Eu(III), *Ac(III)*, *Am(III), Cm(III), Ho(III), Pu(III), Sm(III)*	reduction expected for [ISA] > 1 mM	10
Mo(VI), Se(VI), Tc(VII)	no effects expected	1
Nb(V)	no realistic value proposed for ISA, (conservative values: Table 3-3)	–
Ni(II), *Co(II)*	isotope exchange, no effects expected	1
Pb(II), *Pd(II)*	reduction expected for [ISA] > 0.05 mM	100, constant
Th(IV)*, Np(IV), Pu(IV), U(IV), Pa(IV), Tc(IV), Zr(IV), Sn(IV)*	reduction expected for [ISA] > 0.1 mM	100
Np(V), Pu(V)	reduction expected for [ISA] > 1 mM	10
Pa(V)	reduction expected for [ISA] > 0.1 mM	100
Se(-II)	not relevant: $K_d = 0$ assumed	not applicable
Se(IV), *Po(IV)*	reduction expected for [ISA] > 0.1 mM	10
Sr(II), *Ba(II), Ra(II)*	reduction expected for [ISA] > 10 mM	10
U(VI), *Pu(VI)*	reduction expected for [ISA] > 0.5 mM	10

* The proposed reduction factors will increase by a factor of 10 with each 10-fold increase of [ISA] above the indicated no-effect level, except for Pb/Pd. I.e. with an indicated no-effect of 1 mM [ISA] and a reduction factor of 10, sorption values are expected to be reduced by a factor of 10 between > 1 mM to 10 mM [ISA], and by a factor of 100 between > 10 mM to 100 mM [ISA], etc.

Table 3-2. Limiting no-effect concentrations and uptake reduction factors for organic ligands other than ISA (realistic estimate). Radionuclides where information only applies by analogy are indicated in italics, ORG stands for any of the ligands indicated in Chapter 2 (other than ISA or gluconate, where indicated). Reduction factors apply to all radionuclide uptake values (i.e. best estimate and upper/lower limits, see SKB 2014a).

Radionuclide (oxidation state)	no-effect concentration for other organics	reduction factor for other organics*
Ag(I)	no effect expected for ORG (see Table 3-3 for conservative values)	1
^{14}C, carbonate species	isotope exchange, no effects expected	1
^{14}C, CH_4, simple organics	not relevant: $K_d = 0$ assumed	not applicable
Ca(II), radioactive isotopes	no effects expected	1
Cd(II)	reduction expected for [ORG] > 10 mM	10
Cl(-I), I(-I)	no effects expected	1
Cs(I)	no effects expected	1
Eu(III), *Ac(III)*, *Am(III), Cm(III), Ho(III), Pu(III), Sm(III)*	reduction expected for [GLU] > 1×10^{-5} M [ORG] > 1 mM	10 10
Mo(VI), Se(VI), Tc(VII)	no effects expected	1
Nb(V)	no realistic value proposed for ORG, (conservative values: Table 3-3)	–
Ni(II), *Co(II)*	isotope exchange, no effects expected	1
Pb(II), *Pd(II)*	reduction expected for [ORG] > 0.05 mM	100 (constant)
Th(IV)*, Np(IV), Pu(IV), U(IV), Pa(IV), Tc(IV), Zr(IV), Sn(IV)*	reduction expected for [GLU] > 5×10^{-5} M [ORG] > 0.1 mM	100 100
Np(V), Pu(V)	reduction expected for [ORG] > 1 mM	10
Pa(V)	reduction expected for [ORG] > 0.1 mM	100
Se(-II)	not relevant: $K_d = 0$ assumed	not applicable
Se(IV), *Po(IV)*	reduction expected for [ORG] > 0.1 mM	10
Sr(II), *Ba(II), Ra(II)*	reduction expected for [ORG] > 10 mM	10
U(VI), *Pu(VI)*	reduction expected for [ORG] > 0.5 mM	10

* Except for Pb/Pd, reduction factors will increase by a factor of 10 with each 10-fold increase of [ORG] above the indicated no-effect level. i.e. with an indicated no-effect of 1 mM [ORG] and a reduction factor of 10, sorption values are expected to be reduced by a factor of 10 between > 1 mM to 10 mM [ORG], and by a factor of 100 between > 10 mM to 100 mM [ORG], etc.

Table 3-3. Additional, conservative limiting no-effect concentrations and uptake reduction factors. Radionuclides where information only applies by analogy are indicated in italics, ORG stands for any of the ligands indicated in Chapter 2. Reduction factors apply to all radionuclide uptake values (i.e. best estimate and upper/lower limits, see SKB 2014a).

Radionuclide (oxidation state)	no-effect concentration, conservative	reduction factor conservative*
Ag(I)	no effects for [EDTA, NTA] < [Ca(II)] no effects for other ligands < 10 mM	100 (constant) 10 (constant)
^{14}C, carbonate species	–	–
^{14}C, CH_4, organic acids	–	–
Ca(II), radioactive isotopes	–	–
Cd(II)	–	–
Cl(-I), I(-I)	–	–
Cs(I)	–	–
Eu(III), *Ac(III)*, *Am(III), Cm(III), Ho(III), Pu(III), Sm(III)*	reduction expected for [UP2] > 0.1 mM	10 (no additional conservative factor given)
Mo(VI), Se(VI), Tc(VII)	–	–
Nb(V)	reduction expected for [ORG] > 0.1 mM	100
Ni(II), *Co(II)*	reduction expected for [ORG] > 5 mM	10 (constant)
Pb(II), *Pd(II)*	–	–
Th*, Np(IV), Pu(IV), U(IV), Pa(IV), Tc(IV), Zr(IV), Sn(IV)*	–	–
Np(V), Pu(V), Pa(V)	–	–
Se(-II)	–	–
Se(IV), *Po(IV)*	–	–
Sr(II), *Ba(II), Ra(II)*	–	–
U(VI), *Pu(VI)*	–	–

* The reduction factor for Nb will increase by a factor of 10 with each 10-fold increase of [ORG] above the indicated no-effect level.

References

SKB's (Svensk Kärnbränslehantering AB) publications can be found at www.skb.se/publications.

Baes C E, Mesmer R E, 1976. The hydrolysis of cations. Malibar, FL: R.E. Krieger.

Baker S, Oliver P, McCrohon R, 2002. Near-field batch sorption studies – 1992 to 1998. AEAT/ERRA-0345, AEA Technology, UK.

Berner U, 2014. Solubility of radionuclides in a concrete environment for provisional safety analyses for SGT-E2. Nagra NTB 14-07, Nagra, Switzerland.

Bradbury M H, Baeyens B, 2003. Near-field sorption data bases for compacted MX-80 bentonite for performance assessment of high-level radioactive waste repository in Opalinus Clay host rock. Nagra NTB 02-19, Nagra, Switzerland.

Bradbury M H, Van Loon L R, 1998. Cementitious near-field sorption data bases for performance assessment of a L/ILW disposal facility in a Palfris Marl Host Rock, CEM-94: Update I, June 1997, PSI Bericht 98-01, Paul Scherrer Institute, Switzerland.

Brownsword M, Manning M C, Pilkington N J, Williams S J, 2002. The effect of cellulose degradation products on the solubility and sorption of zirconium and the sorption of lead under cementitious repository conditions. Report AEAT/R/ENV/0549, AEA Technology, UK.

Colàs E, 2014. Complexation of Th(IV) and U(VI) by polyhydroxy and polyamino carboxylic acids. PhD thesis. Universitat Politècnica de Catalunya.

Colàs E, Grivé M, Rojo I, Duro L, 2013. The effect of gluconate and EDTA on thorium solubility under simulated cement porewater conditions. Journal of Solution Chemistry 42, 1680–1690.

Cronstrand P, 2014. Evolution of pH in SFR 1. SKB R-14-01, Svensk Kärnbränslehantering AB.

Dario M, Molera M, Allard B, 2004a. Effect of organic ligands on the sorption of europium on TiO_2 and cement at high pH. SKB TR-04-04, Svensk Kärnbränslehantering AB.

Dario M, Molera M, Allard B, 2004b. Effect of cement additives on radionuclide mobility. In Oversby V M, Werme L O (eds). Scientific basis for nuclear waste management XXVII: symposium held in Kalmar, Sweden, 15–19 June 2003. Warrendale, PA: Materials Research Society. (Materials Research Society Symposium Proceedings 807), 639–644.

Dario M, Molera M, Allard B, 2004c. Effects of technical adsorbents and cleaning agents in a cement matrix – a case study. In Oversby V M, Werme L O (eds). Scientific basis for nuclear waste management XXVII: symposium held in Kalmar, Sweden, 15–19 June 2003. Warrendale, PA: Materials Research Society. (Materials Research Society Symposium Proceedings 807), 371–376.

Duro L, Grivé M, Gaona X, Bruno J, Andersson T, Borén H, Dario M, Allard B, Hagberg J, Källström K, 2012. Study the effect of the fibre mass UP2 degradation products on radionuclide mobilisation. SKB R-12-15, Svensk Kärnbränslehantering AB.

Evans N D M, 2003. Studies on metal α-isosaccharinic acid complexes. PhD thesis. Loughborough University.

Giffaut E, Grivé M, Blanc P, Vieillard P, Colàs E, Gailhanou H, Gaboreau S, Marty N, Madé B, Duro L, 2014. Andra thermodynamic data for performance assessment: ThermoChimie. Applied Geochemistry. doi: 10.1016/j.apgeochem.2014.05.007

Glaus M A, Van Loon L R, 2004. A generic procedure for the assessment of the effect of concrete admixtures on the retention behaviour of cement for radionuclides: Concept and case studies. PSI Bericht 04-02, Paul Scherrer Institute, Switzerland.

Greenfield B F, Moreton A D, Spindler M W, Williams S J, Woodwark D R, 1992. The effects of the degradation of organic materials in the near field of a radioactive waste disposal facility. In Sombret C G (ed). Scientific basis for nuclear waste management X: symposium held in Strasbourg, France, 4–7 November 1991. Pittsburgh, PA: Materials Research Society. (Materials Research Society Symposium Proceedings 257), 299–306.

Greenfield B F, Hurdus M H, Spindler M W, Thomason H P, 1997. The effects of the products from the anaerobic degradation of cellulose on the solubility and sorption of radioelements in the near field. Report NSS/R367, UK Nirex Ltd.

Grivé M, Colàs E, Duro L, 2011. A reappraisal on nickel complexes with hydroxycarboxylic ligands under alkaline conditions. 13th International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere, Beijing, 18–23 September 2011.

Hart J H, 2005. Ethylenediaminetetraacetic acid and related chelating agents. In Ullmann's encyclopedia of industrial chemistry. Weinheim: Wiley-VCH.

Holgersson S, Albinsson Y, Allard B, Borén, H, Pavasars I, Engkvist I, 1998. Effects of gluco-isosaccharinate on Cs, Ni, Pm, and Th sorption onto, and diffusion into cement. Radiochimica Acta 82, 393–398.

Holgersson S, Dubois I, Börstell L, 2011. Batch experiments of Cs, Co and Eu sorption onto cement with dissolved fibre mass UP2 in the liquid phase. SKB P-11-24, Svensk Kärnbränslehantering AB.

Hummel W, 1991. Thermodynamic data base for organic ligands. Report TM-41-91-43, Paul Scherrer Institute, Switzerland.

Keith-Roach M, Lindgren M, Källström K, 2014. Assessment of complexing agent concentrations in SFR. SKB R-14-03, Svensk Kärnbränslehantering AB.

Ochs M, Vielle-Petit L, Wang L, Mallants D, Leterme B, 2011. Additional sorption parameters for the cementitious barriers of a near-surface repository. NIROND-TR 2010–06 E, ONDRAF/NIRAS, Belgium.

Parkhurst D L, Appelo C A J, 2013. Description of input and examples for PHREEQC version 3: a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: Denver, CO: U.S. Geological Survey. (Techniques and Methods 6-A43)

Pointeau I, Hainos D, Coreau N, Reiller P, 2006a. Effect of organics on selenite uptake by cementitious materials. Waste Management 26, 733–740.

Pointeau I, Coreau N, Hainos D, Reiller P, 2006b. Effet des produits de dégradation de composés organiques présents dans les déchets B, vis-à-vis du comportement chimique des RN dans les milieux cimentaires. Rapport final, RT DPC-SECR 05-061 indice A, CEA, France. (In French.)

Sawyer D T, 1964. Metal-gluconate complexes. Chemical Reviews 64, 633–643.

Schubert J, Lindenbaum A, 1952. Stability of alkaline earth – organic acid complexes measured by ion exchange. Journal of the American Chemical Society 74, 3529–3532.

SKB, 2008. Safety analysis SFR 1. Long-term safety. SKB R-08-130, Svensk Kärnbränslehantering AB.

SKB, 2013. Låg- och medelaktivt avfall i SFR. Referensinventarium för avfall 2013. SKB R-13-37, Svensk Kärnbränslehantering AB. (In Swedish.)

SKB, 2014a. Data report for the safety assessment SR-PSU. SKB TR-14-10, Svensk Kärnbränslehantering AB.

SKB, 2014b. Waste form and packaging process report for the safety assessment SR-PSU. SKB TR-14-03, Svensk Kärnbränslehantering AB.

Smith R M, Martell A E, 2004. NIST critically selected stability constants of metal complexes database. Version 8.0. Texas A & M University.

Tits J, Wieland E, Bradbury M H, Ecker P, Schaible A, 2002. The uptake of Eu(III) and Th(IV) by calcite under hyperalkaline conditions. PSI Bericht 02-03, Paul Scherrer Institute, Switzerland.

Tits J, Wieland E, Bradbury M H, 2005. The effect of isosaccharinic acid and gluconic acid on the retention of Eu(III), Am(III) and Th(IV) by calcite. Applied Geochemistry 20, 2082–2096.

Van Loon L R, Glaus M A, 1998. Experimental and theoretical studies on alkaline degradation of cellulose and its impact on the sorption of radionuclides. Nagra NTB 97-04, Nagra, Switzerland.

Vercammen K, 2000. Complexation of calcium, thorium and europium by α-isosaccharinic acid under alkaline conditions. PhD thesis. Swiss Federal Institute Of Technology, Zurich.

Vercammen K, Glaus M A, Van Loon L R, 2001. Complexation of Th(IV) and Eu(III) by α-isosaccharinic acid under alkaline conditions. Radiochimica Acta 89, 393–401.

Wang L, Martens E, Jacques D, de Cannière P, Berry J, Mallants D, 2009. Review of sorption values for the cementitious near field of a near surface radioactive waste disposal facility. NIROND TR 2008-23E, ONDRAF/NIRAS, Belgium.

Warwick P, Evans N, Vines S, 2006. Studies on some divalent metal alpha-isosaccharinic acid complexes. Radiochimica Acta 94, 363–368.

Wieland E, 2014. Sorption data base for the cementitious near field of L/ILW and ILW repositories for provisional safety analyses for SGT-E2. Nagra NTB 14-08, Nagra, Switzerland.

Wieland E, Van Loon L, 2002. Cementitious near-field sorption data base for performance assessment of an ILW repository in Opalinus clay. PSI Bericht 03-06, Paul Scherrer Institute, Switzerland.

Wieland E, Tits J, Spieler P, Dobler J-P, 1998. Interaction of Eu(III) and Th(IV) with sulphate-resisting Portland cement. In McKinley I G, McCombie C (eds). Scientific basis for nuclear waste management XXI: symposium held in Davos, Switzerland, 23 September–3 October 1997. Warrendale, PA: Materials Research Society. (Materials Research Society Symposium Proceedings 506), 573–578.

Wieland E, Tits J, Spieler P, Dobler J-P, Scheidegger A M, 2000. Uptake of nickel and strontium by a sulphate-resisting Portland cement. In Rammlmair D, Mederer J, Oberthür T, Heimann R B, Pentinghaus H (eds). Applied mineralogy. Vol 2. Rotterdam: Balkema, 705–708.

Wieland E, Tits J, Dobler J-P, Spieler P, 2002. The effect of α-isosaccharinic acid on the stability of and Th(IV) uptake by hardened cement paste. Radiochimica Acta 90, 683–688.

Yui M, Azuma J, Shibata M, 1999. JNC thermodynamic database for performance assessment of high-level radioactive waste disposal system. JNC Technical Report TN8400 99-070, Japan Nuclear Cycle Development Institute.

Appendix 1

Organic ligand speciation in the context of SFR

Introduction and Objectives

Organic materials are present in the different types of waste disposed in SFR. Some of these organic materials (e.g. isosaccharinate (ISA) or EDTA) have high complexing affinities for radionuclides (RN).

In this chapter an answer is provided to the need of SKB to assess the influence of the organic ligands potentially present in SFR on the speciation of some RN of interest. Speciation calculations have been performed on representative cement porewaters for four cement degradation states after selecting a good thermodynamic dataset for the system of interest. Specifically, the final aim is to provide speciation calculations of the following systems:

- Am(III)-ISA.
- Eu(III)-ISA.
- Th(IV)-ISA.
- Pu(IV)-ISA.
- U(VI)-ISA.

In addition, preliminary calculations have been carried out in the systems:

- Ag(I)-EDTA.
- Cd(II)-ISA and Cd(II)-EDTA.
- Pb(II)-ISA.
- Sr(II)-ISA and Sr(II)-EDTA.

The speciation calculations have been carried out for four different porewaters, representative of four cement degradation states after selecting a good set of thermodynamic data for the system of interest.

A1.1 System definition

A1.1.1 SFR1 repository

The SFR1 repository at Forsmark in Sweden consists of one Silo and four vaults (BMA, 1BTF, 2BTF and BLA) with different designs to hold different types of waste.

Cement-based materials play an important role in Silo, BMA and BTF storage vaults, as conditioning matrix for the waste and as backfill and construction material. The presence of cement in those vaults results in an alkaline environment with large calcium concentrations. BLA vault does not contain cementitious materials as backfill or immobilization matrix and hence, its conditions are different from the other vaults.

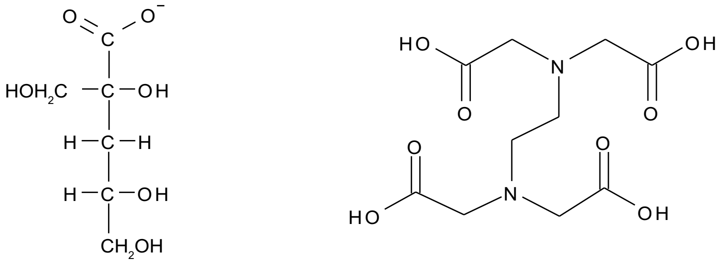
The vaults studied in the present work are SILO, 1BMA and 1BTF.

A1.1.2 Organic ligands

Operating waste in the repository contains different organic substances, whose composition and volumes may vary considerably. Knowledge of radionuclide complexation with those organic ligands is important because:

- complexation of a radionuclide tends to increase its solubility, and thus its mobility; and
- adsorption of metal ions on solid surfaces (such as cement) is significantly influenced by complex formation.

The main organic ligands of interest within this work are isosaccharinate (ISA) and ethylenediaminetetraacetate (EDTA) (Figure A1-1). Notice that, in the formulas, isosaccharinate ion will be written as “$ISAH_2^-$“, where “H_2” refers to the hydrogens of the secondary alcohol functions in the molecule.



ISA EDTA

Figure A1-1. *Isosaccharinate and EDTA chemical structures.*

The amount of organic ligands present in each repository vault is defined in Keith-Roach et al. (2014).

In Keith-Roach et al. (2014), concentrations of ISA in the vaults were calculated after 5,000 years of cellulose degradation, based on the predicted waste distribution at closure. The concentration of organic ligands used in the calculations reported in the present work, based on the information in Keith-Roach et al. (2014), are summarized in Table A1-1.

A1.1.3 Metals and Radionuclides

The radionuclides studied in this work are Am(III), Eu(III), Th(IV), Pu(IV) and U(VI). Preliminary scooping calculations have also been done for Ag(I), Cd(II), Pb(II) and Sr(II).

The inventory for those metals/radionuclides has been provided by SKB (SKB 2013). The inventory (Becquerels) has been recalculated to the corresponding radionuclide concentrations (mol/l) using the volumes reported in Keith-Roach et al. (2014). The concentrations used in the calculations reported in present work are summarized in Table A1-2.

Table A1-1. Concentrations of organic ligands used in the calculations in present work, from Keith-Roach et al. (2014).

	ISA concentration (M) Sorption(a)	EDTA concentration (M)
Silo vault	$3.8 \cdot 10^{-5}$	$5.2 \cdot 10^{-7}$
1BMA vault	$2.9 \cdot 10^{-4}$	$3.8 \cdot 10^{-6}$
1BTF vault	$4.5 \cdot 10^{-6}$	$1.3 \cdot 10^{-6}$

(a) ISA concentrations as reported in Keith-Roach et al. (2014). The concentrations were calculated taking into account that ISA sorbs onto hydrated cement.

Table A1-2. Concentrations (M) of metals and radionuclides used in the calculations in present work. In the case of Ag(I), Cd(II), Pb(II) and Sr(II), only preliminary/scoping calculations are done.

Metal/RN (M)	Silo vault	1BMA vault	1BTF vault
Am	$1.05 \cdot 10^{-7}$	$1.44 \cdot 10^{-10}$	$2.03 \cdot 10^{-11}$
Eu	$5.23 \cdot 10^{-11}$	$3.49 \cdot 10^{-12}$	$3.91 \cdot 10^{-13}$
Th (a)	$6.54 \cdot 10^{-9}$	$1.67 \cdot 10^{-9}$	$2.55 \cdot 10^{-10}$
Pu	$6.54 \cdot 10^{-9}$	$1.67 \cdot 10^{-9}$	$2.55 \cdot 10^{-10}$
U	$1.65 \cdot 10^{-6}$	$4.82 \cdot 10^{-7}$	$2.54 \cdot 10^{-5}$
Ag	$1.06 \cdot 10^{-9}$	$1.44 \cdot 10^{-10}$	$1.88 \cdot 10^{-11}$
Cd	$1.42 \cdot 10^{-12}$	$1.90 \cdot 10^{-13}$	$2.28 \cdot 10^{-14}$
Pb (b)	$7.67 \cdot 10^{-15}$	$1.38 \cdot 10^{-15}$	$1.14 \cdot 10^{-13}$
Sr	$1.09 \cdot 10^{-9}$	$2.67 \cdot 10^{-10}$	$3.07 \cdot 10^{-11}$

(a) Using the same concentration as Pu, see text.

(b) Calculated from ^{238}U, see text.

When concentrations for more than one isotope of the same radionuclide were provided in the inventory, the final concentration used in the calculations corresponds to the sum of all the isotopes available. For example: in the case of Plutonium, the concentration shown in Table A1-2 corresponds to the sum of concentrations for ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu provided in the inventory.

Thorium is not present in the inventory. Th is frequently used as an analogue to study the behaviour of other tetravalent elements such as Pu(IV). In fact, much of the data available regarding tetravalent elements complexation with organic ligands concerns Th(IV), due to the experimental difficulties associated with maintaining IV oxidation state for other elements. Because of this, thorium has been included in the calculations. The inventory of Pu has been used to provide a maximum value for possible Th concentrations in the calculations.

Lead is not present in the inventory but it is a daughter of ^{238}U. The concentration of this element has been calculated considering the decay chain of ^{238}U and assuming that all the decay chain is in secular equilibrium. This means that the activity of all the isotopes of the decay chain of ^{238}U have the same activity (Bq), including ^{210}Pb. Using the specific activity of ^{210}Pb, lead concentration is calculated. ^{214}Pb is also part of the decay chain of ^{238}U but under the assumed conditions, its concentration is negligible and has not been taken into account.

A1.1.4 Porewaters

The alkaline environment imposed by cement and concrete materials will evolve with time as those materials degrade. The different cement degradation stages will lead to different cement porewaters, with different pH and calcium concentrations. Those changes will affect the speciation of the analysed radionuclides.

The typical mineral evolution and the corresponding pH evolution for cement are reported in Cronstrand (2014). Initially, cement porewaters are characterised by high pH values and high Na and K concentrations, due to the dissolution of alkali oxides. As cement degrades, pH decreases and portlandite controls the pH at ≈12.6 and calcium concentration at $2\cdot10^{-2}$ M, whereas pH is typically decreasing during the decalcification of CSH in the interval 12–11. After CSH dissolution, pH drops to levels below 10, supported by remaining cement specific minerals or precipitated hydroxides.

In present work, four different cement porewaters have been selected to perform speciation calculations:

- **Porewater "A" (pH=13.06):** Reported in Cronstrand (2014). Corresponds to the initial composition of cement porewater assumed to be a mixture between pure concrete porewater and the temperate-preglacial water infiltrating in SFR, scaled to the fractional content of cement and concrete in the vaults.
- **Porewater "B" (pH=12.60):** Reported in SKB (2008). Corresponds to a leached cement porewater, representing a degradation state where highly soluble alkali hydroxides have been leached out and the pH is buffered by calcium hydroxide (portlandite).
- **Porewater "C" (pH=11.60):** Water composition calculated as a result of the dissolution of SFR concrete by fresh groundwater. At this stage, CSH dissolution dominates the porewater chemistry.
- **Porewater "D" (pH=9.66):** Water composition calculated as a result of the dissolution of SFR concrete by fresh groundwater. It corresponds to an advanced degradation state.

The chemical compositions of the four different cement porewaters studied are summarized in Table A1-3.

Table A1-3. Cement porewaters chemical compositions used in present work to perform speciation calculations.

Parameter	Porewater A pH=13.06	Porewater B pH=12.60	Porewater C pH=11.60	Porewater D pH=9.66
pH	13.06	12.60	11.60	9.66
Ca (M)	$1.48 \cdot 10^{-3}$	$2.00 \cdot 10^{-2}$	$2.59 \cdot 10^{-3}$	$4.57 \cdot 10^{-5}$
Al (M)	$9.66 \cdot 10^{-6}$	$2.00 \cdot 10^{-6}$	–	–
C (IV) (M)	$1.53 \cdot 10^{-3}$	–	$9.81 \cdot 10^{-6}$	$8.79 \cdot 10^{-4}$
Cl (M)	$1.61 \cdot 10^{-3}$	$2.00 \cdot 10^{-3}$	$5.36 \cdot 10^{-3}$	$5.36 \cdot 10^{-3}$
K (M)	$1.12 \cdot 10^{-1}$	$1.00 \cdot 10^{-4}$	$1.28 \cdot 10^{-4}$	$1.28 \cdot 10^{-4}$
Mg (M)	$1.48 \cdot 10^{-4}$	–	$1.23 \cdot 10^{-8}$	$3.01 \cdot 10^{-5}$
Na (M)	$5.01 \cdot 10^{-2}$	$3.00 \cdot 10^{-3}$	$7.83 \cdot 10^{-3}$	$7.83 \cdot 10^{-3}$
S (VI) (M)	$3.53 \cdot 10^{-4}$	$2.00 \cdot 10^{-5}$	$1.00 \cdot 10^{-3}$	$5.21 \cdot 10^{-4}$
Si (M)	$8.38 \cdot 10^{-5}$	$3.00 \cdot 10^{-6}$	$5.63 \cdot 10^{-4}$	$2.00 \cdot 10^{-4}$

A1.2 Methodology

The main objective of the present work is to calculate the speciation of the metal/radionuclides in the presence of organic ligands. As previously mentioned, only scoping calculations have been carried out for Ag(I), Cd(II), Pb(II) and Sr(II).

Speciation calculations have been carried out for 24 different cases, using the porewaters, the organic ligands inventories and the radionuclide inventories described in Section A1.1. In addition, speciation calculations for ISA and EDTA in the absence of radionuclides have also been done. The 24 cases are described in the appendix (Section A1.7).

Calculations were performed with PhreeqC (version 3.1.2; Parkhurst and Appelo 2013) using the thermodynamic database ThermoChimie (Version 9; Giffaut et al. 2014). Data not originally included in ThermoChimie have been added in order to perform the calculations. A summary of the added reactions and stability data is given in Section A1.6.

In some cases, metal/radionuclide solid phases (e.g. $ThO_2(s)$, $Pu(OH)_4(am)$) are slightly oversaturated. In those cases the oversaturated solid phases have been allowed to precipitate.

A1.3 Discussion on the obtained results

The results of the calculations for the 24 cases considered in present work are fully reported in the appendix (Appendix 4).

In this section, some of the results obtained in representative cases are discussed.

The concentrations provided in the table legend correspond to the aqueous ligand, metal or radionuclide concentration in solution. As mentioned in the methodology section, in some cases metal/radionuclide solid phases (e.g. $ThO_2(s)$, $Pu(OH)_4(am)$…) are slightly oversaturated. In those cases the oversaturated solid phases have been allowed to precipitate in the calculations; the aqueous concentration reported in the table legend does take into account the precipitation. Those cases are indicated by an "*" in the tables.

The percent values provided in the table correspond to the % of each species present in solution.

A1.3.1 Organic ligands speciation in the absence of metals/radionuclides

The speciation of organic ligands studied in present work (ISA and EDTA) in the absence of radionuclides/metals is shown in Table A1-4 and in Table A1-5.

ISA speciation is dominated by the anionic species $ISAH_2^-$. At high Ca(II) concentrations (porewater "B") calcium-isosaccharinate species are also significant.

EDTA speciation is dominated by the formation of $Ca(EDTA)^{2-}$.

A1.3.2 Radionuclide speciation in the SILO in the presence of ISA (considering ISA sorption)

Radionuclide and metal ion speciation in the SILO in the presence of ISA, with $[ISA]_T=3.8\cdot10^{-5}$ M (considering ISA sorption), are calculated in test cases 1, 2, 3 and 4. The results are summarized in the appendix (Section A1.8) and also in Table A1-6 and Table A1-7.

In the case of radionuclides, complexation with ISA dominates the speciation in most of the porewaters studied, except in the case of porewater at pH=9.66.

In the case of Cd, Pb and Sr, it must be noticed that the results are only preliminary as available thermodynamic data are scarce (see Section A1.6). Taking into account the results obtained, it might be suggested that the low ISA concentrations studied do not play a key role in the speciation of those elements.

A1.3.3 Radionuclide speciation in the BTF in the presence of ISA (considering ISA sorption)

Radionuclide and metal ion speciation in the BTF in the presence of ISA, with $[ISA]_T=4.5\cdot10^{-6}$ M (considering ISA sorption), are calculated in test cases 17, 18, 19 and 20. The results are summarized in the appendix (Section A1.8) and also in Table A1-8 and Table A1-9.

Under those conditions, RN-ISA species do play an important role on radionuclide speciation. However, as the ISA concentration ($4.5\cdot10^{-6}$ M) is lower than in the SILO ($3.8\cdot10^{-5}$ M, Section A1.3.2), radionuclide-ISA species are less dominant than in the case described above.

In the case of Cd, Pb and Sr, the low ISA concentration considered does not seem to have a significant influence on the speciation of those metals. However, results are only preliminary due to the scarce thermodynamic data available.

Table A1-4. Isosaccharinate speciation in the different cement porewaters studied in present work. $[ISA]_{aq}=4.5\cdot10^{-6}$ M.

Porewater	A	B	C	D
pH	13.06	12.60	11.60	9.66
$[Ca]_T$ (M)	$1.48\cdot10^{-3}$	$2.00\cdot10^{-2}$	$2.59\cdot10^{-3}$	$4.57\cdot10^{-5}$
ISA	$ISAH_2^-$ (91.5%) Ca(ISAH) (7.4%) $Ca(ISAH_2)^+$ (1.1%)	$ISAH_2^-$ (46.9%) Ca(ISAH) (38.1%) $Ca(ISAH_2)^+$ (15.1%)	$ISAH_2^-$ (91.7%) Ca(ISAH) (1.8%) $Ca(ISAH_2)^+$ (6.5%)	$ISAH_2^-$ (99.9%) Ca(ISAH) (0.0%) $Ca(ISAH_2)^+$ (0.1%)

Table A1-5. EDTA speciation in the different cement porewaters studied in present work. $[EDTA]_{aq}=3.8\cdot10^{-6}$ M.

Porewater	A	B	C	D
pH	13.06	12.60	11.60	9.66
$[Ca]_T$ (M)	$1.48\cdot10^{-3}$	$2.00\cdot10^{-2}$	$2.59\cdot10^{-3}$	$4.57\cdot10^{-5}$
EDTA	$Ca(EDTA)^{2-}$ (100.0%)	$Ca(EDTA)^{2-}$ (100.0%)	$Ca(EDTA)^{2-}$ (100.0%)	$Ca(EDTA)^{2-}$ (98.8%)

Table A1-6. Radionuclide speciation in the SILO. $[ISA]_{aq}=3.8\cdot10^{-5}$ M (considering ISA sorption). Only species with ≥10% are shown.

Porewater	A	B	C	D
pH	13.06	12.60	11.60	9.66
$[Ca]_T$ (M)	$1.48\cdot10^{-3}$	$2.00\cdot10^{-2}$	$2.59\cdot10^{-3}$	$4.57\cdot10^{-5}$
Am*	$Am(OH)_3$ (35.3%) $Am(OH)_3(ISAH_2)^-$ (62.4%)	$Am(OH)_3$ (50.4%) $Am(OH)_3(ISAH_2)^-$ (45.4%)	$Am(OH)_2^+$ (11.5%) $Am(OH)_3$ (32.1%) $Am(OH)_3(ISAH_2)^-$ (56.2%)	$Am(OH)_2^+$ (16.8%) $Am(CO_3)^+$ (10.3%) $Am(CO_3)_2^-$ (65.6%)
Eu	$Eu(OH)_3$ (12.4%) $Eu(OH)_3(ISAH_2)^-$ (87.0%)	$Eu(OH)_3$ (21.6%) $Eu(OH)_3(ISAH_2)^-$ (77.3%)	$Eu(OH)_3$ (12.4%) $Eu(OH)_3(ISAH_2)^-$ (86.4%)	$Eu(CO_3)_2^-$ (84.6%)
Th*	$Th(OH)_4$ (26.4%) $CaTh(OH)_4(ISAH_2)^+$ (56.4%) $Th(OH)_4(ISAH_2)^-$ (14.7%)	$CaTh(OH)_4(ISAH_2)^+$ (95.7%)	$CaTh(OH)_4(ISAH_2)^+$ (88.7%)	$Th(OH)_4$ (27.7%) $Th(OH)_4(ISAH_2)^-$ (16.7%) $Th(OH)_3(CO_3)^-$ (42.8%)
Pu*	$Pu(OH)_4$ (14.1%) $Pu(OH)_4(ISAH_2)^-$ (39.3%) $Pu(OH)_4(ISAH_2)_2^{2-}$ (46.6%)	$Pu(OH)_4$ (31.3%) $Pu(OH)_4(ISAH_2)^-$ (44.7%) $Pu(OH)_4(ISAH_2)_2^{2-}$ (24.0%)	$Pu(OH)_4$ (16.0%) $Pu(OH)_4(ISAH_2)^-$ (44.4%) $Pu(OH)_4(ISAH_2)_2^{2-}$ (39.6%)	$Pu(OH)_4$ (14.4%) $Pu(OH)_4(ISAH_2)^-$ (43.5%) $Pu(OH)_4(ISAH_2)_2^{2-}$ (39.9%)
U*	$UO_2(OH)_4^{2-}$ (32.0%) $UO_2(OH)_4(ISAH_2)^{3-}$ (66.3%)	$UO_2(OH)_4^{2-}$ (49.8%) $UO_2(OH)_4(ISAH_2)^{3-}$ (40.7%)	$UO_2(OH)_3^-$ (53.2%) $UO_2(OH)_4^{2-}$ (21.8%) $UO_2(OH)_4(ISAH_2)^{3-}$ (25.0%)	$CaUO_2(CO_3)_3^{2-}$ (60.7%) $UO_2(CO_3)_3^{4-}$ (35.0%)

* $[Am]_T=1.1\cdot10^{-7}$ M. Americium solid phases precipitate. Case A, $[Am]_{aq}= 1.4\cdot10^{-9}$ M; Case B, $[Am]_{aq}= 9.8\cdot10^{-10}$ M; Case C, $[Am]_{aq}= 1.6\cdot10^{-9}$ M; Case D, $[Am]_{aq}= 9.1\cdot10^{-8}$ M.

* $[Eu]_T=5.2\cdot10^{-11}$ M. Europium solid phases do not precipitate.

* $[Th]_T=6.5\cdot10^{-9}$ M. Thorium solid phases precipitate. Case A, $[Th]_{aq}= 4.6\cdot10^{-9}$ M; Case B, Thorium does not precipitate; Case C, Thorium does not precipitate; Case D, $[Th]_{aq}= 4.5\cdot10^{-9}$ M.

* $[Pu]_T=6.5\cdot10^{-9}$ M. Plutonium solid phases precipitate. Case A, $[Pu]_{aq}= 3.4\cdot10^{-9}$ M; Case B, $[Pu]_{aq}= 1.6\cdot10^{-9}$ M; Case C, $[Pu]_{aq}= 3.1\cdot10^{-9}$ M; Case D, $[Pu]_{aq}= 3.5\cdot10^{-9}$ M.

* $[U]_T=1.7\cdot10^{-6}$ M. Uranium solid phases precipitate. Case A, Uranium does not precipitate; Case B, $[U]_{aq}= 4.6\cdot10^{-7}$ M; Case C, $[U]_{aq}= 1.3\cdot10^{-7}$ M; Case D, Uranium does not precipitate.

Table A1-7. Preliminary results: Metal speciation in the SILO. $[ISA]_{aq}=3.8\cdot10^{-5}$ M (considering ISA sorption). $[Cd]_{aq}=1.4\cdot10^{-12}$ M, $[Pb]_{aq}=7.7\cdot10^{-15}$ M, $[Sr]_{aq}=1.1\cdot10^{-9}$. Only species with ≥10% are shown.

Porewater	A	B	C	D
pH	13.06	12.60	11.60	9.66
$[Ca]_T$ (M)	$1.48\cdot10^{-3}$	$2.00\cdot10^{-2}$	$2.59\cdot10^{-3}$	$4.57\cdot10^{-5}$
Cd	$Cd(OH)_2$ (12.0%) $Cd(OH)_3^-$ (74.7%) $Cd(OH)_4^{2-}$ (13.0%)	$Cd(OH)_2$ (32.3%) $Cd(OH)_3^-$ (63.8%)	$Cd(OH)^+$ (13.7%) $Cd(OH)_2$ (72.3%) $Cd(OH)_3^-$ (13.0%)	Cd^{2+} (16.3%) $Cd(CO_3)$ (70.9%)
Pb	$Pb(OH)_4^{2-}$ (98.1%)	$Pb(OH)_4^{2-}$ (93.6%)	$Pb(OH)_3^-$ (40.8%) $Pb(OH)_4^{2-}$ (47.1%) $Pb(OH)_2(ISAH_2)^-$ (10.4%)	$Pb(OH)_2(ISAH_2)^-$ (44.6%) $Pb(CO_3)$ (34.3%)
Sr	Sr^{2+} (75.1%) $Sr(OH)^+$ (19.0%)	Sr^{2+} (90.0%)	Sr^{2+} (92.5%)	Sr^{2+} (89.6%)

Table A1-8. Radionuclide speciation in the BTF. $[ISA]_{aq}=4.5\cdot10^{-6}$ M (considering ISA sorption). $[Am]_{aq}=2.0\cdot10^{-11}$ M, $[Eu]_{aq}=3.9\cdot10^{-13}$ M, $[Th]_{aq}=2.6\cdot10^{-10}$ M, $[Pu]_{aq}=2.6\cdot10^{-10}$ M. Only species with ≥10% are shown.

Porewater	A	B	C	D
pH	13.06	12.60	11.60	9.66
$[Ca]_T$ (M)	$1.48\cdot10^{-3}$	$2.00\cdot10^{-2}$	$2.59\cdot10^{-3}$	$4.57\cdot10^{-5}$
Am	$Am(OH)_3$ (80.8%) $Am(OH)_3(ISAH_2)^-$ (13.9%)	$Am(OH)_3$ (84.2%)	$Am(OH)_2^+$ (22.8%) $Am(OH)_3$ (63.8%) $Am(OH)_3(ISAH_2)^-$ (13.2%)	$Am(OH)_2^+$ (16.9%) $Am(CO_3)^+$ (10.4%) $Am(CO_3)_2^-$ (66.2%)
Eu	$Eu(OH)_3$ (57.5%) $Eu(OH)_3(ISAH_2)^-$ (39.4%)	$Eu(OH)_3$ (67.7%) $Eu(OH)_3(ISAH_2)^-$ (28.8%)	$Eu(OH)_3$ (52.1%) $Eu(OH)_3(ISAH_2)^-$ (43.0%)	$Eu(CO_3)_2^-$ (86.6%)
Th	$Th(OH)_4$ (74.9%) $CaTh(OH)_4(ISAH_2)^+$ (15.6%)	$Th(OH)_4$ (22.4%) $CaTh(OH)_4(ISAH_2)^+$ (76.8%)	$Th(OH)_4$ (39.5%) $CaTh(OH)_4(ISAH_2)^+$ (57.9%)	$Th(OH)_4$ (35.2%) $Th(OH)_3(CO_3)^-$ (54.5%)
Pu	$Pu(OH)_4$ (76.7%) $Pu(OH)_4(ISAH_2)^-$ (20.9%)	$Pu(OH)_4$ (84.7%) $Pu(OH)_4(ISAH_2)^-$ (14.3%)	$Pu(OH)_4$ (73.3%) $Pu(OH)_4(ISAH_2)^-$ (24.1%)	$Pu(OH)_4$ (69.7%) $Pu(OH)_4(ISAH_2)^-$ (25.0%)
U*	$UO_2(OH)_4^{2-}$ (79.6%) $UO_2(OH)_4(ISAH_2)^{3-}$ (16.1%)	$UO_2(OH)_3^-$ (14.7%) $UO_2(OH)_4^{2-}$ (77.7%)	$UO_2(OH)_3^-$ (68.1%) $UO_2(OH)_4^{2-}$ (28.1%)	$CaUO_2(CO_3)_3^{2-}$ (58.8%) $UO_2(CO_3)_3^{4-}$ (37.2%)

* $[U]_T=2.5\cdot10^{-5}$ M. Uranium solid phases precipitate. Case A, $[U]_{aq}= 5.6\cdot10^{-6}$ M; Case B, $[U]_{aq}= 2.9\cdot10^{-7}$ M; Case C, $[U]_{aq}= 1.0\cdot10^{-7}$ M; Case D, $[U]_{aq}= 2.1\cdot10^{-6}$ M.

Table A1-9. Preliminary results: Metal speciation in the BTF. $[ISA]_T=4.5\cdot10^{-6}$ M (considering ISA sorption). $[Cd]_{aq}=2.3\cdot10^{-14}$ M, $[Pb]_{aq}=1.1\cdot10^{-13}$ M, $[Sr]_{aq}=3.1\cdot10^{-11}$. Only species with ≥10% are shown.

Porewater	A	B	C	D
pH	13.06	12.60	11.60	9.66
$[Ca]_T$ (M)	$1.48\cdot10^{-3}$	$2.00\cdot10^{-2}$	$2.59\cdot10^{-3}$	$4.57\cdot10^{-5}$
Cd	$Cd(OH)_2$ (12.0%) $Cd(OH)_3^-$ (74.8%) $Cd(OH)_4^{2-}$ (13.1%)	$Cd(OH)_2$ (32.3%) $Cd(OH)_3^-$ (63.9%)	$Cd(OH)^+$ (13.6%) $Cd(OH)_2$ (72.4%) $Cd(OH)_3^-$ (13.1%)	Cd^{2+} (16.5%) $Cd(CO_3)$ (70.9%)
Pb	$Pb(OH)_4^{2-}$ (98.1%)	$Pb(OH)_4^{2-}$ (93.7%)	$Pb(OH)_3^-$ (44.8%) $Pb(OH)_4^{2-}$ (52.0%)	$Pb(OH)_2$ (10.3%) $Pb(CO_3)$ (56.8%) $Pb(CO_3)_2^{2-}$ (14.3%)
Sr	Sr^{2+} (75.1%) $Sr(OH)^+$ (19.0%)	Sr^{2+} (90.0%)	Sr^{2+} (92.5%)	Sr^{2+} (89.7%)

A1.3.4 Metal ion speciation in the 1BMA in the presence of EDTA

Metal ion speciation in the 1BMA in the presence of EDTA, with $[EDTA]_T=3.8\cdot10^{-6}$ M, are calculated in test cases 13, 14, 15 and 16. The results are summarized in Appendix 4 (Tables A4-13 to A4-16) and also in Table A1-10.

Except in the case of Cd, EDTA does not seem to play a key role on the speciation of those metals at high pH values due to the presence of calcium.

Table A1-10. Preliminary results: Metal speciation in the 1BMA. $[EDTA]_T$=$3.8\cdot10^{-6}$ M. $[Ag]_{aq}$=$1.4\cdot10^{-10}$ M, $[Cd]_{aq}$=$1.9\cdot10^{-13}$ M, $[Sr]_{aq}$=$2.7\cdot10^{-10}$. Only species with ≥10% are shown.

Porewater	A	B	C	D
pH	13.06	12.60	11.60	9.66
$[Ca]_T$ (M)	$1.48\cdot10^{-3}$	$2.00\cdot10^{-2}$	$2.59\cdot10^{-3}$	$4.57\cdot10^{-5}$
Ag	$Ag(OH)_2^-$ (92.0%)	$Ag(OH)$ (13.9%) $Ag(OH)_2^-$ (69.1%) $AgCl$ (10.5%)	$AgCl$ (57.6%) $AgCl_2^-$ (30.9%)	$AgCl$ (59.8%) $AgCl_2^-$ (32.1%)
Cd	$Cd(OH)_2$ (12.0%) $Cd(OH)_3^-$ (74.6%) $Cd(OH)_4^{2-}$ (13.0%)	$Cd(OH)_2$ (32.2%) $Cd(OH)_3^-$ (63.7%)	$Cd(OH)_2$ (20.5%) $Cd(EDTA)^{2-}$ (71.5%)	$Cd(EDTA)^{2-}$ (100.0%)
Sr	Sr^{2+} (75.1%) $Sr(OH)^+$ (19.0%)	Sr^{2+} (90.0%)	Sr^{2+} (92.5%)	Sr^{2+} (89.6%)

A1.3.5 Th-ISA system: Sensitivity analysis

According to the calculations performed above, aqueous speciation of tetravalent actinides appear to be significantly affected by the presence of ISA.

Most of the published data available regarding tetravalent elements complexation with organic ligands under cement conditions concerns Th(IV), due to the experimental difficulties associated with maintaining IV oxidation state for other actinide elements under alkaline pH values. In order to give some hints on the possible differences or discrepancies arisen from the use of different thermodynamic data, we have performed a sensitivity analysis in the Ca-Th-Isa system. This analysis aims at comparing calculated Th speciation in the presence of ISA using different sets of thermodynamic data available in the literature: Vercammen (2000), Vercammen et al. (2001), Wieland et al. (2002), Colàs et al. (2013) and Colàs (2014).

The complexation of Th(IV) by α-isosaccharinic acid (ISA) and the influence of calcium in the system was studied by Vercammen et al. (2001) by batch sorption experiments. Based on best-fit analysis of the sorption data, Vercammen et al. (2001) postulated that complexes involving Calcium, Thorium and ISA were formed in the presence of calcium. Wieland et al. (2002) justified the effect ISA on Th uptake by hardened cement paste by taking into account the formation of those complexes.

The stability constants used by Wieland and co-workers are not independent of the stability constants of Th hydrolysis reactions. i.e. the stability values depend on the $Th(OH)_4(aq)$ stability constant used in the calculations. Thus, the values reported by Wieland et al. (2002) have been recalculated taking into account the stability constant for $Th(OH)_4(aq)$ used in present work. The results are shown in Table A1-11.

Table A1-11. Thermodynamic data for Th-ISA system using as a basis the work by Wieland et al. (2002).

Th-ISA					
Reaction	**log *K***	***I*$_M$**	**T (°C)**	**Reference**	**Recalculated value$^{(a)}$ log K°**
$Ca^{2+} + Th^{4+} + 2\ ISAH_2^- = CaTh(OH)_4(ISAH_2)_2 + 4H^+$	–7.4	0.3	25	Wieland et al. (2002)	–4.0

(a) Recalculated taking into account stability constants for $Th(OH)_4(aq)$ used in present work and corrected to I=0.

As stated in Section A1.2, speciation calculations performed in present report have been done by using the recent published database ThermoChimie vs. 9 (www.thermochimie-tdb.fr). The data for Ca-Th-ISA system included in ThermoChimie vs. 9 come from Colàs et al. (2013) and Colàs (2014), who studied the solubility of thorium oxyhydroxide in the presence of ISA or gluconate at pH = 12. The results obtained by those authors are summarized in Table A1-12.

Both sets of data have been used to calculate the Th speciation under cement conditions (Figure A1-2) and to calculate thorium speciation under SILO conditions (Table A1-13).

As seen in Figure A1-2 and Table A1-13, calculated thorium chemical speciation with both data sets is different.

Independently of the thermodynamic data set used for calculations, one can conclude that complexation with ISA dominates thorium speciation in most cases (expect in carbonated cement porewaters at pH=9.66). The influence of the organic ligand is relevant especially at ISA concentrations higher than 10^{-5} M.

Thus, one can conclude that even if different data available in the literature result in different calculated Th speciation, the result is that thorium will be significantly affected by the presence of ISA in the system, which will in turn influence its retention onto cement phases, as shown in Section A1.2.10.

Table A1-12. Thermodynamic data for Th-ISA system using as a basis the work by Colàs et al. (2013) and Colàs (2014).

Th-ISA		
Reaction	**log *K*°**	**Reference**
$Th^{4+} + ISAH_2^- = Th(OH)_4(ISAH_2)^- + 4H^+$	–13.2	Colàs (2014)
$Th^{4+} + 2ISAH_2^- = Th(OH)_4(ISAH_2)_2^{2-} + 4H^+$	–10.4	Colàs (2014)
$Ca^{2+} + Th^{4+} + ISAH_2^- = CaTh(OH)_4(ISAH_2)^+ + 4H^+$	–9.0	Colàs (2014)[(a)]

(a) Analogy with gluconate.

Table A1-13. Sensitivity analysis: Radionuclide speciation in the SILO. $[ISA]_{aq}=3.8\cdot10^{-5}$ M (considering ISA sorption). Only species with ≥10% are shown.

Porewater	A	B	C	D
pH	13.06	12.60	11.60	9.66
$[Ca]_T$ (M)	$1.48\cdot10^{-3}$	$2.00\cdot10^{-2}$	$2.59\cdot10^{-3}$	$4.57\cdot10^{-5}$
$[Th]_T$ (M)	$6.54\cdot10^{-9}$	$6.54\cdot10^{-9}$	$6.54\cdot10^{-9}$	$6.54\cdot10^{-9}$
Th speciation. Dataset recalculated from Wieland et al. (2002)				
Th	$Th(OH)_4$ (19.7%) $CaTh(OH)_4(ISAH_2)_2$ (78.9%)	$CaTh(OH)_4(ISAH_2)_2$ (97.1%)	$CaTh(OH)_4(ISAH_2)_2$ (97.1%)	$Th(OH)_4$ (28.6%) $CaTh(OH)_4(ISAH_2)_2$ (21.6%) $Th(OH)_3(CO_3)^-$ (44.2%)
	Th solid phases precipitate. $[Th]_{(aq)}=6.09\cdot10^{-9}$ M	Th solid phases do not precipitate.	Th solid phases do not precipitate.	Th solid phases precipitate. $[Th]_{(aq)}=4.39\cdot10^{-9}$ M
Th speciation. Dataset from ThermoChimie database				
Th	$Th(OH)_4$ (26.4%) $CaTh(OH)_4(ISAH_2)^+$ (56.4%) $Th(OH)_4(ISAH_2)^-$ (14.7%)	$CaTh(OH)_4(ISAH_2)^+$ (95.7%)	$CaTh(OH)_4(ISAH_2)^+$ (88.7%)	$Th(OH)_4$ (27.7%) $Th(OH)_4(ISAH_2)^-$ (16.7%) $Th(OH)_3(CO_3)^-$ (42.8%)
	Th solid phases precipitate. $[Th]_{(aq)}=4.55\cdot10^{-9}$ M	Th solid phases do not precipitate.	Th solid phases do not precipitate.	Th solid phases precipitate. $[Th]_{(aq)}=4.53\cdot10^{-9}$ M

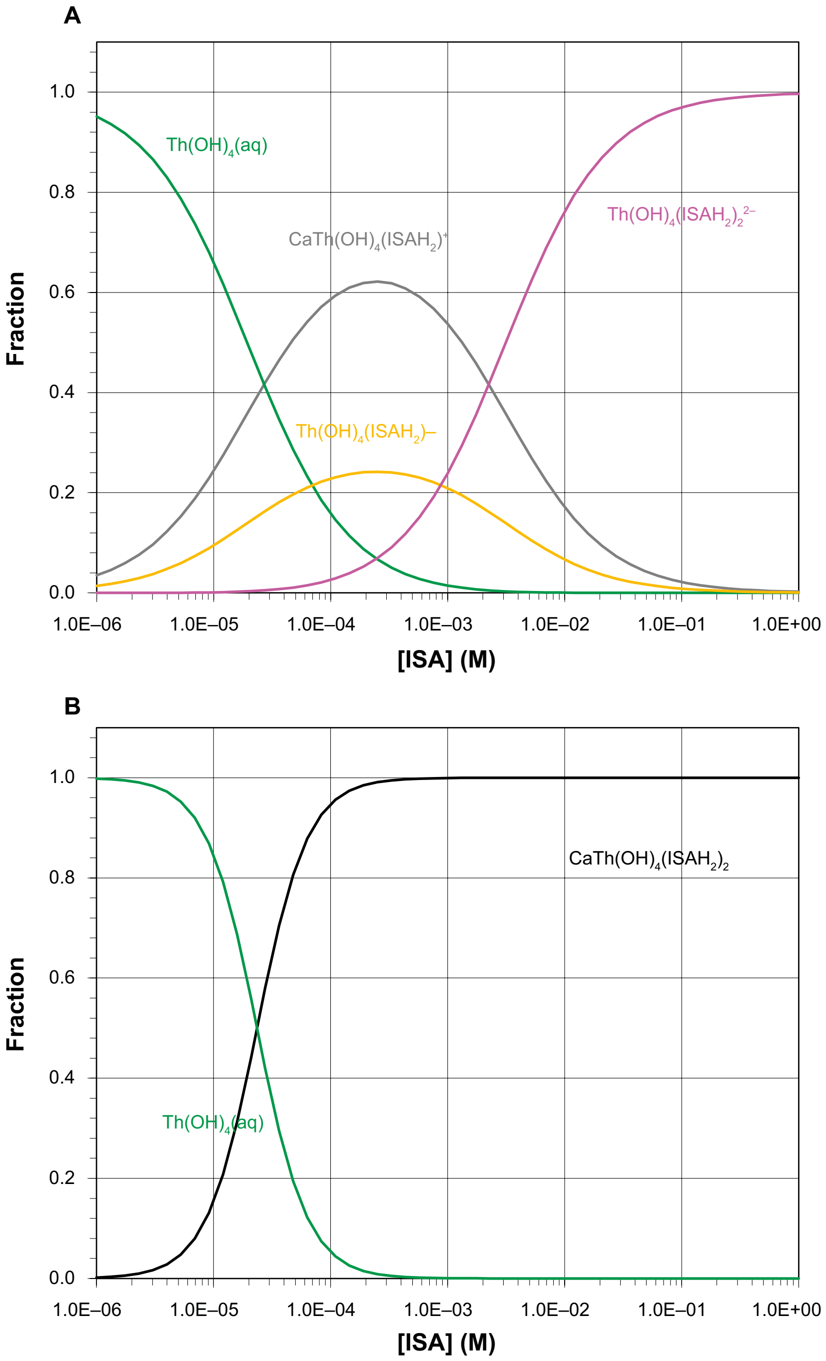


Figure A1-2. *Thorium speciation using different sets of thermodynamic data. A) Thermodynamic data from Colàs et al. (2013) and Colàs (2014). B) Thermodynamic data from Wieland et al. (2002).* $[Th]_T=1\cdot10^{-10}M$, *pH=13.3, I=0.3, calcium concentration in equilibrium with portlandite.*

A1.4 Conclusions

The influence of the organic ligands such as isosaccharinate and EDTA on the speciation of some trace elements of interest in SFR has been studied in present work.

Specifically, the following systems have been studied:

- Am-ISA.
- Eu-ISA.
- Th-ISA.
- Pu(IV)-ISA.
- U(VI)-ISA.

In addition, preliminary calculations have been carried out in the systems:

- Ag-EDTA.
- Cd-ISA and Cd-EDTA.
- Pb-ISA.
- Sr-ISA and Sr-EDTA.

The speciation calculations have been carried out with representative cement porewaters for four cement degradation states with the ThermoChimie database and modifications detailed in Section A1.6.

ISA is the ligand with higher complexation ability towards Am, Eu, Th, Pu(IV) and U(VI), with the exception of the more degraded cement porewaters, where the aqueous speciation is less affected by this ligand. In the case of Cd(II), Pb(II) and Sr(II), only preliminary results are discussed, as available thermodynamic data are scarce. According to the scarce available data results seem to indicate that ISA could affect the speciation of these metals although in a minor degree.

EDTA does not seem to play a key role on the speciation of Ag(I) or Sr(II) at high pH values in the presence of calcium. Nevertheless, calculations performed with the available data suggest that Cd-EDTA complexes could be quite stable under cement conditions.

Given the role of aqueous speciation on both, radionuclide sorption and mobility, this work aims at giving a general picture on the effect of organic ligands. The speciation calculations performed in present work could afterwards be used to evaluate radionuclide sorption behaviour in SFR.

Appendix 2

Thermodynamic data selection

Thermodynamic data for isosaccharinate and EDTA used in the calculations performed in present work are discussed in this section.

ThermoChimie database version 9 does include thermodynamic data relevant for the following systems in the alkaline pH range:

- ISA and EDTA hydrolysis.
- Ca-ISA and Ca-EDTA.
- Am-ISA.
- Eu-ISA.
- Th-ISA.
- Pu(IV)-ISA.
- U(VI)-ISA.

Thermodynamic data for the following systems (in the alkaline pH range) are not included in the database:

- Ag-EDTA.
- Cd-ISA and Cd-EDTA.
- Pb-ISA.
- Sr-ISA and Sr-EDTA.

A preliminary literature review has been performed in order to obtain thermodynamic data for those systems. The results of this review are reported below.

A2.1 Ag(I) – EDTA (preliminary selection)

Smith and Martell (2004) reported several values for the formation of Ag-EDTA complexes (Table A2-1). Those constants have been corrected in present work to zero ionic strength by using Davies equation (Table A2-2).

$AgEDTA^{3-}$ species may be formed under alkaline conditions and has been taken into account in the calculations performed in present work. $AgHEDTA^{2-}$and Ag_2EDTA^{2-} species were not taken into account in the calculations as the former only appears at pH < 9, and the latter only at very high Ag concentrations ($\geq 10^{-3}$ M).

Table A2-1. Thermodynamic data collected for Ag-EDTA system.

Ag-EDTA				
Reaction	**log *K***	***I***	**T (°C)**	**Reference**
$Ag^+ + EDTA^{4-} = AgEDTA^{3-}$	7.20 ± 0.03	0.1	25	Smith and Martell (2004)
$AgEDTA^{3-} + H^+ = AgHEDTA^{2-}$	6.04	0.1	25	Smith and Martell (2004)
$2Ag^+ + EDTA^{4-} = Ag_2EDTA^{2-}$	7.60	1.0	25	Smith and Martell (2004)

Table A2-2. Thermodynamic data extrapolated to infinite dilution for Ag-EDTA system.

Ag-EDTA (I_M = 0)		
Reaction	**log K^0**	**Reference**
$Ag^+ + EDTA^{4-} = AgEDTA^{3-}$	8.15 ± 0.03 (a)	Present work
$Ag^+ + EDTA^{4-} + H^+ = AgHEDTA^{2-}$	14.89 (a)	Present work
$2Ag^+ + EDTA^{4-} = Ag_2EDTA^{2-}$	10.56 (a)	Present work

(a) Original values from Smith and Martell (2004) extrapolated to I=0 in the present work.

A2.2 Cd(II) – EDTA (preliminary selection)

Smith and Martell (2004) reported thermodynamic data concerning Cd complexation with Ethylenediaminetetraacetic acid at 25°C (Table A2-3). Those constants have been corrected in present work to zero ionic strength by using Davies equation (Table A2-4).

The species $CdEDTA^{2-}$ and $Cd(OH)EDTA^{3-}$ may be relevant at alkaline pH values and have been taken into account in the calculations. Preliminary calculations have shown that the protonated species, $CdHEDTA^{-}$ and CdH_2EDTA, would only be formed at $pH < 6.0$ and thus they have not been taken into account.

A2.3 Cd(II) – ISA (preliminary selection)

Evans (2003) and Warwick et al. (2006) studied the formation of Cadmium-ISA soluble complexes using an ion exchange resin method (Schubert method) at different pH values. The authors also used other techniques as UV/Vis spectroscopy, conductometric Schubert and Lindenbaum (1952) titrations and potentiometry in order to investigate the system. Nevertheless, the authors reported different stability constants for the formation of the same species at different pH values, which is unlikely.

The results obtained by those authors in the alkaline pH range were revaluated by Grivé et al. (2011) (see Table A2-5). Those revaluated values have been used to perform the calculations reported in present work.

A2.4 Pb(II) – ISA (preliminary selection)

No thermodynamic data for Pb complexation with ISA have been found. Gluconate ($GLUH_4^{-}$) is an organic ligand with similar structure and chemical properties. Thus, Pb-GLU complexes have been used as analogues for Pb-ISA complexes.

Table A2-3. Thermodynamic data collected for Cd-EDTA system.

Cd-EDTA				
Reaction	**log *K***	***I*$_M$**	**T (°C)**	**Reference**
$Cd^{2+} + EDTA^{4-} = CdEDTA^{2-}$	18.10	0.0	25	Smith and Martell (2004)
$CdEDTA^{2-} + H^{+} = CdHEDTA^{-}$	2.90	0.1	25	Smith and Martell (2004)
$CdHEDTA^{-} + H^{+} = CdH_2EDTA$	1.60 ± 0.10	1.0	25	Smith and Martell (2004)
$Cd(OH)EDTA^{3-} + H^{+} = CdEDTA^{2-} + H_2O$	13.2	1.0	25	Smith and Martell (2004)

Table A2-4. Thermodynamic data extrapolated to infinite dilution for Cd-EDTA system.

Cd-EDTA (*I*$_M$ = 0)		
Reaction	**log *K*^{0}**	**Reference**
$Cd^{2+} + EDTA^{4-} = CdEDTA^{2-}$	18.10	Smith and Martell (2004)
$Cd^{2+} + EDTA^{4-} + H^{+} = CdHEDTA^{-}$	21.46 (a)	Present work
$Cd^{2+} + EDTA^{4-} + 2H^{+} = CdH_2EDTA$	22.97 ± 0.10 (a)	Present work
$Cd^{2+} + EDTA^{4-} + H_2O = Cd(OH)EDTA^{3-} + H^{+}$	3.67 (a)	Present work

(a) Original values from Smith and Martell (2004) extrapolated to I=0 in the present work.

Table A2-5. Thermodynamic data collected for Cd-ISA system.

Cd-ISA		
Reaction	**log *K*^{0}**	**Reference**
$Cd^{2+} + ISAH_2^{-} = CdISAH_2^{+}$	2.60	Grivé et al. (2011)
$6\ Cd^{2+} + ISAH_2^{-} + 3H_2O = Cd(OH)_3(ISAH_2)^{2-} + 3H^{+}$	–31.60	Grivé et al. (2011)

Table A2-6. Thermodynamic data collected for Pb-GLU system.

Pb-GLU				
Reaction	log *K*	I_M	T (°C)	Reference
$Pb^{2+} + GLUH_4^- = PbGLUH_4^+$	2.60	0.10	25	Sawyer (1964)
$Pb^{2+} + GLUH_4^- + 2OH^- = PbGLUH_2^- + 2H_2O$	15.70	0.15	25	Sawyer (1964)

Table A2-7. Thermodynamic data for Pb-ISA system.

Pb-ISA (I_M = 0)		
Reaction	log K^0	Reference
$Pb^{2+} + ISAH_2^- = PbISAH_2^+$	3.06 (a)	Present work
$Pb^{2+} + ISAH_2^- + 2H_2O = Pb(OH)_2(ISAH_2)^- + 2H^+$	–11.68 (a)	Present work

(a) Original values for Pb-gluconate complexes from Sawyer (1964) extrapolated to I=0 in the present work. Pb-GLU system was used as analogue for Pb-ISA system.

Results reported by Sawyer (1964) for the formation of lead-gluconate complexes are summarized in Table A2-6.

Values reported by Sawyer (1964) were extrapolated to zero ionic strength by using Davies equation and were used as analogues for the Pb-ISA system. The results of these calculations are shown in Table A2-7.

The formation of $Pb(OH)_2(ISAH_2)^-$ complex has been taken into account in the calculations. Preliminary studies have shown that the species $PbISAH_2^+$ is only formed at pH < 8.5; this species has not been included in the calculations performed in present work.

A2.5 Sr(II)-EDTA (preliminary selection)

Smith and Martell (2004) reported some stability formation constants from several data sources at different temperatures and ionic strengths; Hummel (1991) extrapolated those stability constants at infinite dilution. The results of these studies are summarized in Table A2-8.

Preliminary calculations have shown that the species $SrHEDTA^-$ will only appear at low pH values and thus has not been included in the calculations carried out in present work. The values used in the calculations performed in present work are shown in Table A2-9.

Table A2-8. Thermodynamic data collected for Sr-EDTA system.

Sr-EDTA				
Reaction	log *K*	I_M	T (°C)	Reference
$Sr^{2+} + EDTA^{4-} = SrEDTA^{2-}$	8.72 ± 0.04	0.10	25	Smith and Martell (2004)
$SrEDTA^{2-} + H^+ = SrHEDTA^-$	3.93	0.10	20	Smith and Martell (2004)
$Sr^{2+} + EDTA^{4-} = SrEDTA^{2-}$	10.40 ± 0.04 (a)	0.00	25	Hummel (1991)
$SrEDTA^{2-} + H^+ = SrHEDTA^-$	4.35 (a)	0.00	20	Hummel (1991)

(a) Original value from Smith and Martell (2004) extrapolated to infinite dilution by Hummel (1991).

Table A2-9. Thermodynamic data calculated to infinite dilution for Sr-EDTA system.

Sr-EDTA (I_M = 0)		
Reaction	log K^0	Reference
$Sr^{2+} + EDTA^{4-} = SrEDTA^{2-}$	10.40 ± 0.04	Hummel (1991)

A2.6 Sr(II) – ISA (preliminary selection)

As in the case of Pb(II), there is no thermodynamic data available for Strontium complexation with ISA; gluconate has been used as analogue.

Results reported by Sawyer (1964) for strontium-gluconate system are summarized in Table A2-10.

Values reported by Sawyer (1964) constant were extrapolated to zero ionic strength by using Davies equation and were used as analogues for the Sr-ISA system. The results of these calculations are shown in Table A2-11.

A2.7 Summary of thermodynamic data

Thermodynamic data for M-ISA and M-EDTA system used in the calculations in present work are summarized in Table A2-12.

Table A2-10. Thermodynamic data collected for Sr-GLU system.

Sr-GLU				
Reaction	**log *K***	**I_M**	**T (°C)**	**Reference**
$Sr^{2+} + GLUH_4^- = SrGLUH_4^+$	1.01	0.16	25	Sawyer (1964)

Table A2-11. Thermodynamic data calculated to infinite dilution for Sr-ISA system.

Sr-ISA ($I_M = 0$)		
Reaction	**log K^0**	**Reference**
$Sr^{2+} + ISAH_2^- = SrISAH_2^+$	1.54 [(a)]	Present work

(a) Original values for Sr-gluconate complexes from Sawyer (1964) extrapolated to I=0 in the present work. Sr-GLU system was used as analogue for Sr-ISA system.

Table A2-12. Thermodynamic data for the M-Ligand complexes used in the calculations in present work.

	ISA		
Metal	**Reaction**	**log K^0**	**Reference**
Calcium	$Ca^{2+} + ISAH_2^- = Ca(ISAH_2)^+$	1.70	ThermoChimie vs. 9
Calcium	$Ca^{2+} + ISAH_2^- = CaISAH(aq) + H^+$	–10.40	ThermoChimie vs. 9
Calcium	$Ca^{2+} + 2ISAH_2^- = Ca(ISAH_2)_2(s)$	6.40	ThermoChimie vs. 9
Americium	$Am^{3+} + ISAH_2^- + 3H_2O = Am(OH)_3(ISAH_2)^- + 3H^+$	–21.50	ThermoChimie vs. 9
Europium	$Eu^{3+} + ISAH_2^- + 3H_2O = Eu(OH)_3(ISAH_2)^- + 3H^+$	–20.90	ThermoChimie vs. 9
Thorium*	$Th^{4+} + ISAH_2^- + 4H_2O = Th(OH)_4(ISAH_2)^- + 4H^+$	–13.20	ThermoChimie vs. 9
Thorium*	$Th^{4+} + 2ISAH_2^- + 4H_2O = Th(OH)_4(ISAH_2)_2^{2-} + 4H^+$	–10.40	ThermoChimie vs. 9
Thorium*	$Th^{4+} + ISAH_2^- + Ca^{2+} + 4H_2O = CaTh(OH)_4(ISAH_2)^+ + 4H^+$	–9.00	ThermoChimie vs. 9
Plutonium	$Pu^{4+} + 4H_2O + ISAH_2– = Pu(OH)_4(ISAH_2)^- + 4H^+$	–3.60	ThermoChimie vs. 9
Plutonium	$Pu^{4+} + 4H_2O + 2ISAH_2^- = Pu(OH)_4(ISAH_2)_2^{2-} + 4H^+$	0.70	ThermoChimie vs. 9
Uranium	$UO_2^{2+} + ISAH_2^- + 4H_2O = UO_2(OH)_4(ISAH_2)^{3-} + 4H+$	–28.10	ThermoChimie vs. 9
Cadmium	$Cd^{2+} + ISAH_2^- = CdISAH_2^+$	2.60	Grivé et al. (2011)
Cadmium	$7\ Cd^{2+} + ISAH_2^- + 3H_2O = Cd(OH)_3(ISAH_2)^{2-} + 3H^+$	–31.60	Grivé et al. (2011)
Lead	$Pb^{2+} + ISAH_2^- + 2H_2O = Pb(OH)_2(ISAH_2)^- + 2H^+$	–11.68	Present work
Strontium	$Sr^{2+} + ISAH_2^- = SrISAH_2^+$	1.54	Present work
	EDTA		
Metal	**Reaction**	**log K^0**	**Reference**
Calcium	$Ca^{2+} + EDTA^{4-} = Ca(EDTA)^{2-}$	12.69	ThermoChimie vs. 9
Sodium	$Na^+ + EDTA^{4-} = Na(EDTA)^{3-}$	2.80	ThermoChimie vs. 9
Silver	$Ag^+ + EDTA^{4-} = AgEDTA^{3-}$	8.15	Present work
Cadmium	$Cd^{2+} + EDTA^{4-} = CdEDTA^{2-}$	18.10	Present work
Cadmium	$Cd^{2+} + EDTA^{4-} + H_2O = Cd(OH)EDTA^{3-} + H^+$	3.67	Present work
Strontium	$Sr^{2+} + EDTA^{4-} = SrEDTA^{2-}$	10.40	Hummel (1991)

* In the case of thorium, a sensitivity analysis with other data available from the literature has been carried out; see previous section for details.

Appendix 3

List of calculations

Table A3-1. List of calculations performed in present work.

	vault	pH	[Ca]	[ISA] sorption	[EDTA]	[Am]	[Eu]	[Th]	[Pu]	[U]	[Ag]	[Cd]	[Pb]	[Sr]
1	Silo	13.06	1.49E–03	3.80E–05	–	1.05E–07	5.23E–11	6.54E–09	6.54E–09	1.65E–06	1.06E–09	1.42E–12	7.67E–15	1.09E–09
2	Silo	12.6	2.00E–02	3.80E–05	–	1.05E–07	5.23E–11	6.54E–09	6.54E–09	1.65E–06	1.06E–09	1.42E–12	7.67E–15	1.09E–09
3	Silo	11.6	2.59E–03	3.80E–05	–	1.05E–07	5.23E–11	6.54E–09	6.54E–09	1.65E–06	1.06E–09	1.42E–12	7.67E–15	1.09E–09
4	Silo	9.66	4.57E–05	3.80E–05	–	1.05E–07	5.23E–11	6.54E–09	6.54E–09	1.65E–06	1.06E–09	1.42E–12	7.67E–15	1.09E–09
5	Silo	13.06	1.49E–03	–	5.20E–07	1.05E–07	5.23E–11	6.54E–09	6.54E–09	1.65E–06	1.06E–09	1.42E–12	7.67E–15	1.09E–09
6	Silo	12.6	2.00E–02	–	5.20E–07	1.05E–07	5.23E–11	6.54E–09	6.54E–09	1.65E–06	1.06E–09	1.42E–12	7.67E–15	1.09E–09
7	Silo	11.6	2.59E–03	–	5.20E–07	1.05E–07	5.23E–11	6.54E–09	6.54E–09	1.65E–06	1.06E–09	1.42E–12	7.67E–15	1.09E–09
8	Silo	9.66	4.57E–05	–	5.20E–07	1.05E–07	5.23E–11	6.54E–09	6.54E–09	1.65E–06	1.06E–09	1.42E–12	7.67E–15	1.09E–09
9	1BMA	13.06	1.49E–03	2.90E–04	–	1.44E–10	3.49E–12	1.67E–09	1.67E–09	4.82E–07	1.44E–10	1.90E–13	1.38E–15	2.67E–10
10	1BMA	12.6	2.00E–02	2.90E–04	–	1.44E–10	3.49E–12	1.67E–09	1.67E–09	4.82E–07	1.44E–10	1.90E–13	1.38E–15	2.67E–10
11	1BMA	11.6	2.59E–03	2.90E–04	–	1.44E–10	3.49E–12	1.67E–09	1.67E–09	4.82E–07	1.44E–10	1.90E–13	1.38E–15	2.67E–10
12	1BMA	9.66	4.57E–05	2.90E–04	–	1.44E–10	3.49E–12	1.67E–09	1.67E–09	4.82E–07	1.44E–10	1.90E–13	1.38E–15	2.67E–10
13	1BMA	13.06	1.49E–03	–	3.80E–06	1.44E–10	3.49E–12	1.67E–09	1.67E–09	4.82E–07	1.44E–10	1.90E–13	1.38E–15	2.67E–10
14	1BMA	12.6	2.00E–02	–	3.80E–06	1.44E–10	3.49E–12	1.67E–09	1.67E–09	4.82E–07	1.44E–10	1.90E–13	1.38E–15	2.67E–10
15	1BMA	11.6	2.59E–03	–	3.80E–06	1.44E–10	3.49E–12	1.67E–09	1.67E–09	4.82E–07	1.44E–10	1.90E–13	1.38E–15	2.67E–10
16	1BMA	9.66	4.57E–05	–	3.80E–06	1.44E–10	3.49E–12	1.67E–09	1.67E–09	4.82E–07	1.44E–10	1.90E–13	1.38E–15	2.67E–10
17	BTF	13.06	1.49E–03	4.50E–06	–	2.03E–11	3.91E–13	2.55E–10	2.55E–10	2.54E–05	1.88E–11	2.28E–14	1.14E–13	3.07E–11
18	BTF	12.6	2.00E–02	4.50E–06	–	2.03E–11	3.91E–13	2.55E–10	2.55E–10	2.54E–05	1.88E–11	2.28E–14	1.14E–13	3.07E–11
19	BTF	11.6	2.59E–03	4.50E–06	–	2.03E–11	3.91E–13	2.55E–10	2.55E–10	2.54E–05	1.88E–11	2.28E–14	1.14E–13	3.07E–11
20	BTF	9.66	4.57E–05	4.50E–06	–	2.03E–11	3.91E–13	2.55E–10	2.55E–10	2.54E–05	1.88E–11	2.28E–14	1.14E–13	3.07E–11
21	BTF	13.06	1.49E–03	–	1.30E–06	2.03E–11	3.91E–13	2.55E–10	2.55E–10	2.54E–05	1.88E–11	2.28E–14	1.14E–13	3.07E–11
22	BTF	12.6	2.00E–02	–	1.30E–06	2.03E–11	3.91E–13	2.55E–10	2.55E–10	2.54E–05	1.88E–11	2.28E–14	1.14E–13	3.07E–11
23	BTF	11.6	2.59E–03	–	1.30E–06	2.03E–11	3.91E–13	2.55E–10	2.55E–10	2.54E–05	1.88E–11	2.28E–14	1.14E–13	3.07E–11
24	BTF	9.66	4.57E–05	–	1.30E–06	2.03E–11	3.91E–13	2.55E–10	2.55E–10	2.54E–05	1.88E–11	2.28E–14	1.14E–13	3.07E–11

Appendix 4

Results

In this section the results obtained in the 24 calculations described in Table A3-1 are shown. Each table correspond to a different case; the full list of cases is reported in the previous section.

The concentrations provided in the table legend correspond to the aqueous ligand, metal or radionuclide concentration in solution. As described in the methodology section, in some cases metal/radionuclide solid phases (e.g. ThO_2(s), $Pu(OH)_4$(am)…) are slightly oversaturated. In those cases the oversaturated solid phases have been allowed to precipitate in the calculations; the aqueous concentration reported in the table legend does take into account the precipitation. Those cases are indicated by an "*" in the tables.

The percent values provided in the table correspond to the % of each species present in solution. Empty cells indicate that the concentration of the species in solution is < 1%.

Table A4-1. Speciation in the SILO. $[ISA]_{aq} = 3.8 \cdot 10^{-5}$ M (considering ISA sorption). Porewater A, pH = 13.06, $[Ca]_{aq} = 1.48 \cdot 10^{-3}$ M, $[Am]_{aq} = 1.4 \cdot 10^{-9}$ M, $[Eu]_{aq} = 5.2 \cdot 10^{-11}$ M, $[Th]_{aq} = 4.6 \cdot 10^{-9}$ M, $[U]_{aq} = 1.7 \cdot 10^{-6}$ M, $[Pu]_{aq} = 3.4 \cdot 10^{-9}$ M, $[Cd]_{aq} = 1.4 \cdot 10^{-12}$ M, $[Pb]_{aq} = 7.7 \cdot 10^{-15}$ M, $[Sr]_{aq} = 1.1 \cdot 10^{-9}$ M.

ISA	$ISAH_2^-$ 88.9%	$Ca(ISAH)$ 7.2%	$Ca(ISAH_2)^+$ 1.1%								
Am*	$Am(OH)_2^+$	$Am(OH)_3$ 35.3%	$Am(OH)_4^-$ 1.7%	$Am(OH)_3(ISAH_2)^-$ 62.4%	$Am(EDTA)^-$	$Am(CO_3)^+$	$Am(CO_3)_2^-$				
Eu	$Eu(OH)_2^+$	$Eu(OH)_3$ 12.4%	$Eu(OH)_4^-$	$Eu(OH)_3(ISAH_2)^-$ 87.0%	$Eu(CO_3)^+$	$Eu(CO_3)_2^-$					
Th*	$Th(OH)_4$ 26.4%	$Th(OH)_4(ISAH_2)^-$ 14.7%	$Th(OH)_4(ISAH_2)_2^{2-}$	$CaTh(OH)_4(ISAH_2)^+$ 56.4%	$Th(OH)_3(CO_3)^-$	$Th(OH)_2(CO_3)_2^{2-}$	$Th(OH)_4(CO_3)^{2-}$ 1.9%				
U	$UO_2(OH)_3^-$ 1.7%	$UO_2(OH)_4^{2-}$ 32.0%	$UO_2(OH)_4(ISAH_2)^{3-}$ 66.3%	$UO_2(CO_3)_3^{4-}$	$UO_2(CO_3)_2^{2-}$	$Ca_2UO_2(CO_3)_3$	$CaUO_2(CO_3)_3^{2-}$				
Pu*	$Pu(OH)_4$ 14.1%	$Pu(OH)_4(ISAH_2)^-$ 39.3%	$Pu(OH)_4(ISAH_2)_2^{2-}$ 46.6%	$Pu(OH)_3(ISAH_2)$	$Pu(OH)_3(ISAH_2)_2^-$	$Pu(CO_3)_2(OH)_2^{2-}$					
Cd	Cd^{2+}	$Cd(OH)^+$	$Cd(OH)_2$ 12.0%	$Cd(OH)_3^-$ 74.7%	$Cd(OH)_4^{2-}$ 13.0%	$Cd(OH)_3(ISAH_2)^{2-}$	$Cd(ISAH_2)^+$	$Cd(EDTA)^{2-}$	$Cd(OH)(EDTA)^{3-}$	$Cd(CO_3)$	$CdCl^+$
Pb	$Pb(OH)^+$	$Pb(OH)_2$	$Pb(OH)_3^-$ 1.9%	$Pb(OH)_4^{2-}$ 98.1%	$Pb(OH)_2(ISAH_2)^-$	$Pb(EDTA)^{2-}$	$Pb(CO_3)$	$Pb(CO_3)_2^{2-}$			
Sr	Sr^{2+} 75.1%	$Sr(OH)^+$ 19.0%	$Sr(ISAH_2)^+$	$Sr(EDTA)^{2-}$	$Sr(CO_3)$ 5.4%	$Sr(SO_4)$					

Table A4-2. Speciation in the SILO. $[ISA]_{aq} = 3.8 \cdot 10^{-5}$ M (considering ISA sorption). Porewater B, pH = 12.60, $[Ca]_{aq} = 2.00 \cdot 10^{-2}$ M, $[Am]_{aq} = 9.8 \cdot 10^{-10}$ M, $[Eu]_{aq} = 5.2 \cdot 10^{-11}$ M, $[Th]_{aq} = 6.5 \cdot 10^{-9}$ M, $[U]_{aq} = 4.6 \cdot 10^{-7}$ M, $[Pu]_{aq} = 1.6 \cdot 10^{-9}$ M, $[Cd]_{aq} = 1.4 \cdot 10^{-12}$ M, $[Pb]_{aq} = 7.7 \cdot 10^{-15}$ M, $[Sr]_{aq} = 1.1 \cdot 10^{-9}$ M.

ISA	$ISAH_2^-$ 46.6%	$Ca(ISAH)$ 37.9%	$Ca(ISAH_2)^+$ 15.0%								
Am*	$Am(OH)_2^+$ 2.0%	$Am(OH)_3$ 50.4%	$Am(OH)_4^-$	$Am(OH)_3(ISAH_2)^-$ 45.4%	$Am(EDTA)^-$	$Am(CO_3)^+$	$Am(CO_3)_2^-$				
Eu	$Eu(OH)_2^+$	$Eu(OH)_3$ 21.6%	$Eu(OH)_4^-$	$Eu(OH)_3(ISAH_2)^-$ 77.3%	$Eu(CO_3)^+$	$Eu(CO_3)_2^-$					
Th	$Th(OH)_4$ 3.3%	$Th(OH)_4(ISAH_2)^-$	$Th(OH)_4(ISAH_2)_2^{2-}$	$CaTh(OH)_4(ISAH_2)^+$ 95.7%	$Th(OH)_3(CO_3)^-$	$Th(OH)_2(CO_3)_2^{2-}$	$Th(OH)_4(CO_3)^{2-}$				
U*	$UO_2(OH)_3^-$ 9.5%	$UO_2(OH)_4^{2-}$ 49.8%	$UO_2(OH)_4(ISAH_2)^{3-}$ 40.7%	$UO_2(CO_3)_3^{4-}$	$UO_2(CO_3)_2^{2-}$	$Ca_2UO_2(CO_3)_3$	$CaUO_2(CO_3)_3^{2-}$				
Pu*	$Pu(OH)_4$ 31.3%	$Pu(OH)_4(ISAH_2)^-$ 44.7%	$Pu(OH)_4(ISAH_2)_2^{2-}$ 24.0%	$Pu(OH)_3(ISAH_2)$	$Pu(OH)_3(ISAH_2)_2^-$	$Pu(CO_3)_2(OH)_2^{2-}$					
Cd	Cd^{2+}	$Cd(OH)^+$	$Cd(OH)_2$ 32.3%	$Cd(OH)_3^-$ 63.8%	$Cd(OH)_4^{2-}$ 3.1%	$Cd(OH)_3(ISAH_2)^{2-}$	$Cd(ISAH_2)^+$	$Cd(EDTA)^{2-}$	$Cd(OH)(EDTA)^{3-}$	$Cd(CO_3)$	$CdCl^+$
Pb	$Pb(OH)^+$	$Pb(OH)_2$	$Pb(OH)_3^-$ 6.3%	$Pb(OH)_4^{2-}$ 93.6%	$Pb(OH)_2(ISAH_2)^-$	$Pb(EDTA)^{2-}$	$Pb(CO_3)$	$Pb(CO_3)_2^{2-}$			
Sr	Sr^{2+} 90.0%	$Sr(OH)^+$ 9.8%	$Sr(ISAH_2)^+$	$Sr(EDTA)^{2-}$	$Sr(CO_3)$	$Sr(SO_4)$					

Table A4-3. Speciation in the SILO. $[ISA]_{aq} = 3.8\cdot10^{-5}$ M (considering ISA sorption). Porewater C, pH = 11.60, $[Ca]_{aq} = 2.59\cdot10^{-3}$ M, $[Am]_{aq} = 1.6\cdot10^{-9}$ M, $[Eu]_{aq} = 5.2\cdot10^{-11}$ M, $[Th]_{aq} = 6.5\cdot10^{-9}$ M, $[U]_{aq} = 1.3\cdot10^{-7}$ M, $[Pu]_{aq} = 3.1\cdot10^{-9}$ M, $[Cd]_{aq} = 1.4\cdot10^{-12}$ M, $[Pb]_{aq} = 7.7\cdot10^{-15}$ M, $[Sr]_{aq} = 1.1\cdot10^{-9}$ M.

ISA	$ISAH_2^-$ 91.6%	$Ca(ISAH)$ 1.8%	$Ca(ISAH_2)^+$ 6.5%								
Am*	$Am(OH)_2^+$ 11.5%	$Am(OH)_3$ 32.1%	$Am(OH)_4^-$	$Am(OH)_3(ISAH_2)^-$ 56.2%	$Am(EDTA)^-$	$Am(CO_3)^+$	$Am(CO_3)_2^-$				
Eu	$Eu(OH)_2^+$ 1.1%	$Eu(OH)_3$ 12.4%	$Eu(OH)_4^-$	$Eu(OH)_3(ISAH_2)^-$ 86.4%	$Eu(CO_3)^+$	$Eu(CO_3)_2^-$					
Th	$Th(OH)_4$ 7.2%	$Th(OH)_4(ISAH_2)^-$ 4.0%	$Th(OH)_4(ISAH_2)_2^{2-}$	$CaTh(OH)_4(ISAH_2)^+$ 88.7%	$Th(OH)_3(CO_3)^-$	$Th(OH)_2(CO_3)_2^{2-}$	$Th(OH)_4(CO_3)^{2-}$				
U*	$UO_2(OH)_3^-$ 53.2%	$UO_2(OH)_4^{2-}$ 21.8%	$UO_2(OH)_4(ISAH_2)^{3-}$ 25.0%	$UO_2(CO_3)_3^{4-}$	$UO_2(CO_3)_2^{2-}$	$Ca_2UO_2(CO_3)_3$	$CaUO_2(CO_3)_3^{2-}$				
Pu*	$Pu(OH)_4$ 16.0%	$Pu(OH)_4(ISAH_2)^-$ 44.4%	$Pu(OH)_4(ISAH_2)_2^{2-}$ 39.6%	$Pu(OH)_3(ISAH_2)$	$Pu(OH)_3(ISAH_2)_2^-$	$Pu(CO_3)_2(OH)_2^{2-}$					
Cd	Cd^{2+}	$Cd(OH)^+$ 13.7%	$Cd(OH)_2$ 72.3%	$Cd(OH)_3^-$ 13.0%	$Cd(OH)_4^{2-}$	$Cd(OH)_3(ISAH_2)^{2-}$	$Cd(ISAH_2)^+$	$Cd(EDTA)^{2-}$	$Cd(OH)(EDTA)^{3-}$	$Cd(CO_3)$	$CdCl^+$
Pb	$Pb(OH)^+$	$Pb(OH)_2$ 1.6%	$Pb(OH)_3^-$ 40.8%	$Pb(OH)_4^{2-}$ 47.1%	$Pb(OH)_2(ISAH_2)^-$ 10.4%	$Pb(EDTA)^{2-}$	$Pb(CO_3)$	$Pb(CO_3)_2^{2-}$			
Sr	Sr^{2+} 92.5%	$Sr(OH)^+$ 1.3%	$Sr(ISAH_2)^+$	$Sr(EDTA)^{2-}$	$Sr(CO_3)$	$Sr(SO_4)$ 5.6%					

Table A4-4. Speciation in the SILO. $[\mathrm{ISA}]_{aq} = 3.8\cdot10^{-5}$ M (considering ISA sorption). Porewater D, pH = 9.66, $[\mathrm{Ca}]_{aq} = 4.57\cdot10^{-5}$ M, $[\mathrm{Am}]_{aq} = 9.1\cdot10^{-8}$ M, $[\mathrm{Eu}]_{aq} = 5.2\cdot10^{-11}$ M, $[\mathrm{Th}]_{aq} = 4.5\cdot10^{-9}$ M, $[\mathrm{U}]_{aq} = 1.7\cdot10^{-6}$ M, $[\mathrm{Pu}]_{aq} = 3.5\cdot10^{-9}$ M, $[\mathrm{Cd}]_{aq} = 1.4\cdot10^{-12}$ M, $[\mathrm{Pb}]_{aq} = 7.7\cdot10^{-15}$ M, $[\mathrm{Sr}]_{aq} = 1.1\cdot10^{-9}$ M.

ISA	$\mathrm{ISAH_2^-}$ 99.9%	Ca(ISAH)	$\mathrm{Ca(ISAH_2)^+}$								
Am*	$\mathrm{Am(OH)_2^+}$ 16.8%	$\mathrm{Am(OH)_3}$	$\mathrm{Am(OH)_4^-}$	$\mathrm{Am(OH)_3(ISAH_2)^-}$ 1.1%	$\mathrm{Am(EDTA)^-}$	$\mathrm{Am(CO_3)^+}$ 10.3%	$\mathrm{Am(CO_3)_2^-}$ 65.6%				
Eu	$\mathrm{Eu(OH)_2^+}$ 2.7%	$\mathrm{Eu(OH)_3}$	$\mathrm{Eu(OH)_4^-}$	$\mathrm{Eu(OH)_3(ISAH_2)^-}$ 2.7%	$\mathrm{Eu(CO_3)^+}$ 6.6%	$\mathrm{Eu(CO_3)_2^-}$ 84.6%					
Th*	$\mathrm{Th(OH)_4}$ 27.7%	$\mathrm{Th(OH)_4(ISAH_2)^-}$ 16.7%	$\mathrm{Th(OH)_4(ISAH_2)_2^{2-}}$	$\mathrm{CaTh(OH)_4(ISAH_2)^+}$ 6.7%	$\mathrm{Th(OH)_3(CO_3)^-}$ 42.8%	$\mathrm{Th(OH)_2(CO_3)_2^{2-}}$ 5.1%	$\mathrm{Th(OH)_4(CO_3)^{2-}}$				
U	$\mathrm{UO_2(OH)_3^-}$	$\mathrm{UO_2(OH)_4^{2-}}$	$\mathrm{UO_2(OH)_4(ISAH_2)^{3-}}$	$\mathrm{UO_2(CO_3)_3^{4-}}$ 35.0%	$\mathrm{UO_2(CO_3)_2^{2-}}$	$\mathrm{Ca_2UO_2(CO_3)_3}$ 3.4%	$\mathrm{CaUO_2(CO_3)_3^{2-}}$ 60.7%				
Pu*	$\mathrm{Pu(OH)_4}$ 14.4%	$\mathrm{Pu(OH)_4(ISAH_2)^-}$ 43.5%	$\mathrm{Pu(OH)_4(ISAH_2)_2^{2-}}$ 39.9%	$\mathrm{Pu(OH)_3(ISAH_2)}$ 1.9%	$\mathrm{Pu(OH)_3(ISAH_2)_2^-}$	$\mathrm{Pu(CO_3)_2(OH)_2^{2-}}$					
Cd	$\mathrm{Cd^{2+}}$ 16.3%	$\mathrm{Cd(OH)^+}$ 4.7%	$\mathrm{Cd(OH)_2}$	$\mathrm{Cd(OH)_3^-}$	$\mathrm{Cd(OH)_4^{2-}}$	$\mathrm{Cd(OH)_3(ISAH_2)^{2-}}$	$\mathrm{Cd(ISAH_2)^+}$	$\mathrm{Cd(EDTA)^{2-}}$	$\mathrm{Cd(OH)(EDTA)^{3-}}$	$\mathrm{Cd(CO_3)}$ 70.9%	$\mathrm{CdCl^+}$ 5.5%
Pb	$\mathrm{Pb(OH)^+}$ 4.2%	$\mathrm{Pb(OH)_2}$ 6.3%	$\mathrm{Pb(OH)_3^-}$ 1.8%	$\mathrm{Pb(OH)_4^{2-}}$	$\mathrm{Pb(OH)_2(ISAH_2)^-}$ 44.6%	$\mathrm{Pb(EDTA)^{2-}}$	$\mathrm{Pb(CO_3)}$ 34.3%	$\mathrm{Pb(CO_3)_2^{2-}}$ 8.7%			
Sr	$\mathrm{Sr^{2+}}$ 89.6%	$\mathrm{Sr(OH)^+}$	$\mathrm{Sr(ISAH_2)^+}$	$\mathrm{Sr(EDTA)^{2-}}$	$\mathrm{Sr(CO_3)}$ 5.0%	$\mathrm{Sr(SO_4)}$ 4.1%					

Table A4-5. Speciation in the SILO. $[EDTA]_{aq} = 5.2 \cdot 10^{-7}$ M. Porewater A, pH = 13.06, $[Ca]_{aq} = 1.48 \cdot 10^{-3}$ M, $[Ag]_{aq} = 1.1 \cdot 10^{-9}$ M, $[Cd]_{aq} = 1.4 \cdot 10^{-12}$ M, $[Sr]_{aq} = 1.1 \cdot 10^{-9}$ M.

EDTA	$EDTA^{4-}$	$Ca(EDTA)^{2-}$	$Mg(EDTA)^{2-}$	$Na(EDTA)^{3-}$							
		100.0%									
Ag	Ag^{+}	$Ag(OH)$	$Ag(OH)_2^{-}$	$Ag(EDTA)^{3-}$	$AgCl$	$AgCl_2^{-}$					
		5.9%	92.0%		1.1%						
Cd	Cd^{2+}	$Cd(OH)^{+}$	$Cd(OH)_2$	$Cd(OH)_3^{-}$	$Cd(OH)_4^{2-}$	$Cd(OH)_3(ISAH_2)^{2-}$	$Cd(ISAH_2)^{+}$	$Cd(EDTA)^{2-}$	$Cd(OH)(EDTA)^{3-}$	$Cd(CO_3)$	$CdCl^{+}$
			12.0%	74.8%	13.0%						
Sr	Sr^{2+}	$Sr(OH)^{+}$	$Sr(ISAH_2)^{+}$	$Sr(EDTA)^{2-}$	$Sr(CO_3)$	$Sr(SO_4)$					
	75.1%	19.0%			5.4%						

Table A4-6. Speciation in the SILO. $[EDTA]_{aq} = 5.2 \cdot 10^{-7}$ M. Porewater B, pH = 12.60, $[Ca]_{aq} = 2.00 \cdot 10^{-2}$ M, $[Ag]_{aq} = 1.1 \cdot 10^{-9}$ M, $[Cd]_{aq} = 1.4 \cdot 10^{-12}$ M, $[Sr]_{aq} = 1.1 \cdot 10^{-9}$ M.

EDTA	$EDTA^{4-}$	$Ca(EDTA)^{2-}$	$Mg(EDTA)^{2-}$	$Na(EDTA)^{3-}$							
		100.0%									
Ag	Ag^{+}	$Ag(OH)$	$Ag(OH)_2^{-}$	$Ag(EDTA)^{3-}$	$AgCl$	$AgCl_2^{-}$					
	4.4%	13.9%	69.1%		10.5%	2.1%					
Cd	Cd^{2+}	$Cd(OH)^{+}$	$Cd(OH)_2$	$Cd(OH)_3^{-}$	$Cd(OH)_4^{2-}$	$Cd(OH)_3(ISAH_2)^{2-}$	$Cd(ISAH_2)^{+}$	$Cd(EDTA)^{2-}$	$Cd(OH)(EDTA)^{3-}$	$Cd(CO_3)$	$CdCl^{+}$
			32.3%	63.9%	3.1%						
Sr	Sr^{2+}	$Sr(OH)^{+}$	$Sr(ISAH_2)^{+}$	$Sr(EDTA)^{2-}$	$Sr(CO_3)$	$Sr(SO_4)$					
	90.0%	9.8%									

Table A4-7. Speciation in the SILO. $[EDTA]_{aq} = 5.2 \cdot 10^{-7}$ M. Porewater C, pH = 11.60, $[Ca]_{aq} = 2.59 \cdot 10^{-3}$ M, $[Ag]_{aq} = 1.1 \cdot 10^{-9}$ M, $[Cd]_{aq} = 1.4 \cdot 10^{-12}$ M, $[Sr]_{aq} = 1.1 \cdot 10^{-9}$ M.

EDTA	$EDTA^{4-}$	$Ca(EDTA)^{2-}$	$Mg(EDTA)^{2-}$	$Na(EDTA)^{3-}$							
		100.0%									
Ag	Ag^{+}	Ag(OH)	$Ag(OH)_2^{-}$	$Ag(EDTA)^{3-}$	AgCl	$AgCl_2^{-}$					
	7.4%	2.6%	1.2%		57.6%	30.9%					
Cd	Cd^{2+}	$Cd(OH)^{+}$	$Cd(OH)_2$	$Cd(OH)_3^{-}$	$Cd(OH)_4^{2-}$	$Cd(OH)_3(ISAH_2)^{2-}$	$Cd(ISAH_2)^{+}$	$Cd(EDTA)^{2-}$	$Cd(OH)(EDTA)^{3-}$	$Cd(CO_3)$	$CdCl^{+}$
		10.1%	53.8%	9.7%				25.6%			
Sr	Sr^{2+}	$Sr(OH)^{+}$	$Sr(ISAH_2)^{+}$	$Sr(EDTA)^{2-}$	$Sr(CO_3)$	$Sr(SO_4)$					
	92.5%	1.3%				5.6%					

Table A4-8. Speciation in the SILO. $[EDTA]_{aq} = 5.2 \cdot 10^{-7}$ M. Porewater D, pH = 9.66, $[Ca]_{aq} = 4.57 \cdot 10^{-5}$ M, $[Ag]_{aq} = 1.1 \cdot 10^{-9}$ M, $[Cd]_{aq} = 1.4 \cdot 10^{-12}$ M, $[Sr]_{aq} = 1.1 \cdot 10^{-9}$ M.

EDTA	$EDTA^{4-}$	$Ca(EDTA)^{2-}$	$Mg(EDTA)^{2-}$	$Na(EDTA)^{3-}$							
		87.9%	1.0%								
Ag	Ag^{+}	Ag(OH)	$Ag(OH)_2^{-}$	$Ag(Edta)^{3-}$	AgCl	$AgCl_2^{-}$					
	7.3%				59.8%	32.1%					
Cd	Cd^{2+}	$Cd(OH)^{+}$	$Cd(OH)_2$	$Cd(OH)_3^{-}$	$Cd(OH)_4^{2-}$	$Cd(OH)_3(ISAH_2)^{2-}$	$Cd(ISAH_2)^{+}$	$Cd(EDTA)^{2-}$	$Cd(OH)(EDTA)^{3-}$	$Cd(CO_3)$	$CdCl^{+}$
								99.8%			
Sr	Sr^{2+}	$Sr(OH)^{+}$	$Sr(ISAH_2)^{+}$	$Sr(EDTA)^{2-}$	$Sr(CO_3)$	$Sr(SO_4)$					
	89.7%				5.0%	4.1%					

Table A4-9. Speciation in the 1BMA. $[ISA]_{aq} = 2.9\cdot10^{-4}$ M (considering ISA sorption). Porewater A, pH = 13.06, $[Ca]_{aq} = 1.48\cdot10^{-3}$ M, $[Am]_{aq} = 1.4\cdot10^{-10}$ M, $[Eu]_{aq} = 3.5\cdot10^{-12}$ M, $[Th]_{aq} = 1.7\cdot10^{-9}$ M, $[U]_{aq} = 4.8\cdot10^{-7}$ M, $[Pu]_{aq} = 1.7\cdot10^{-9}$ M, $[Cd]_{aq} = 1.9\cdot10^{-13}$ M, $[Pb]_{aq} = 1.4\cdot10^{-15}$ M, $[Sr]_{aq} = 2.7\cdot10^{-10}$ M.

ISA	$ISAH_2^-$ 91.5%	$Ca(ISAH)$ 7.3%	$Ca(ISAH_2)^+$ 1.1%								
Am	$Am(OH)_2^+$	$Am(OH)_3$ 6.7%	$Am(OH)_4^-$	$Am(OH)_3(ISAH_2)^-$ 92.9%	$Am(EDTA)^-$	$Am(CO_3)^+$	$Am(CO_3)_2^-$				
Eu	$Eu(OH)_2^+$	$Eu(OH)_3$ 1.8%	$Eu(OH)_4^-$	$Eu(OH)_3(ISAH_2)^-$ 98.1%	$Eu(CO_3)^+$	$Eu(CO_3)_2^-$					
Th	$Th(OH)_4$ 4.3%	$Th(OH)_4(ISAH_2)^-$ 18.8%	$Th(OH)_4(ISAH_2)_2^{2-}$ 5.5%	$CaTh(OH)_4(ISAH_2)^+$ 71.1%	$Th(OH)_3(CO_3)^-$	$Th(OH)_2(CO_3)_2^{2-}$	$Th(OH)_4(CO_3)^{2-}$				
U	$UO_2(OH)_3^-$	$UO_2(OH)_4^{2-}$ 5.8%	$UO_2(OH)_4(ISAH_2)^{3-}$ 93.9%	$UO_2(CO_3)_3^{4-}$	$UO_2(CO_3)_2^{2-}$	$Ca_2UO_2(CO_3)_3$	$CaUO_2(CO_3)_3^{2-}$				
Pu	$Pu(OH)_4$	$Pu(OH)_4(ISAH_2)^-$ 9.7%	$Pu(OH)_4(ISAH_2)_2^{2-}$ 89.9%	$Pu(OH)_3(ISAH_2)$	$Pu(OH)_3(ISAH_2)_2^-$	$Pu(CO_3)_2(OH)_2^{2-}$					
Cd	Cd^{2+}	$Cd(OH)^+$	$Cd(OH)_2$ 11.8%	$Cd(OH)_3^-$ 73.6%	$Cd(OH)_4^{2-}$ 12.8%	$Cd(OH)_3(ISAH_2)^{2-}$ 1.7%	$Cd(ISAH_2)^+$	$Cd(EDTA)^{2-}$	$Cd(OH)(EDTA)^{3-}$	$Cd(CO_3)$	$CdCl^+$
Pb	$Pb(OH)^+$	$Pb(OH)_2$	$Pb(OH)_3^-$ 1.9%	$Pb(OH)_4^{2-}$ 98.0%	$Pb(OH)_2(ISAH_2)^-$	$Pb(EDTA)^{2-}$	$Pb(CO_3)$	$Pb(CO_3)_2^{2-}$			
Sr	Sr^{2+} 75.0%	$Sr(OH)^+$ 19.0%	$Sr(ISAH_2)^+$	$Sr(EDTA)^{2-}$	$Sr(CO_3)$ 5.4%	$Sr(SO_4)$					

Table A4-10. Speciation in the 1BMA. $[ISA]_{aq} = 2.9 \cdot 10^{-4}$ M (considering ISA sorption). Porewater B, pH = 12.60, $[Ca]_{aq} = 2.00 \cdot 10^{-2}$ M, $[Am]_{aq} = 1.4 \cdot 10^{-10}$ M, $[Eu]_{aq} = 3.5 \cdot 10^{-12}$ M, $[Th]_{aq} = 1.7 \cdot 10^{-9}$ M, $[U]_{aq} = 4.8 \cdot 10^{-7}$ M, $[Pu]_{aq} = 1.7 \cdot 10^{-9}$ M, $[Cd]_{aq} = 1.9 \cdot 10^{-13}$ M, $[Pb]_{aq} = 1.4 \cdot 10^{-15}$ M, $[Sr]_{aq} = 2.7 \cdot 10^{-10}$ M.

ISA	$ISAH_2^-$ 47.0%	$Ca(ISAH)$ 37.9%	$Ca(ISAH_2)^+$ 15.0%								
Am	$Am(OH)_2^+$	$Am(OH)_3$ 12.5%	$Am(OH)_4^-$	$Am(OH)_3(ISAH_2)^-$ 86.5%	$Am(EDTA)^-$	$Am(CO_3)^+$	$Am(CO_3)_2^-$				
Eu	$Eu(OH)_2^+$	$Eu(OH)_3$ 3.5%	$Eu(OH)_4^-$	$Eu(OH)_3(ISAH_2)^-$ 96.3%	$Eu(CO_3)^+$	$Eu(CO_3)_2^-$					
Th	$Th(OH)_4$	$Th(OH)_4(ISAH_2)^-$	$Th(OH)_4(ISAH_2)_2^{2-}$	$CaTh(OH)_4(ISAH_2)^+$ 98.5%	$Th(OH)_3(CO_3)^-$	$Th(OH)_2(CO_3)_2^{2-}$	$Th(OH)_4(CO_3)^{2-}$				
U	$UO_2(OH)_3^-$ 2.5%	$UO_2(OH)_4^{2-}$ 13.4%	$UO_2(OH)_4(ISAH_2)^{3-}$ 84.1%	$UO_2(CO_3)_3^{4-}$	$UO_2(CO_3)_2^{2-}$	$Ca_2UO_2(CO_3)_3$	$CaUO_2(CO_3)_3^{2-}$				
Pu	$Pu(OH)_4$ 1.7%	$Pu(OH)_4(ISAH_2)^-$ 19.2%	$Pu(OH)_4(ISAH_2)_2^{2-}$ 79.1%	$Pu(OH)_3(ISAH_2)$	$Pu(OH)_3(ISAH_2)_2^-$	$Pu(CO_3)_2(OH)_2^{2-}$					
Cd	Cd^{2+}	$Cd(OH)^+$	$Cd(OH)_2$ 32.1%	$Cd(OH)_3^-$ 63.5%	$Cd(OH)_4^{2-}$ 3.1%	$Cd(OH)_3(ISAH_2)^{2-}$	$Cd(ISAH_2)^+$	$Cd(EDTA)^{2-}$	$Cd(OH)(EDTA)^{3-}$	$Cd(CO_3)$	$CdCl^+$
Pb	$Pb(OH)^+$	$Pb(OH)_2$	$Pb(OH)_3^-$ 6.3%	$Pb(OH)_4^{2-}$ 93.1%	$Pb(OH)_2(ISAH_2)^-$	$Pb(EDTA)^{2-}$	$Pb(CO_3)$	$Pb(CO_3)_2^{2-}$			
Sr	Sr^{2+} 89.8%	$Sr(OH)^+$ 9.8%	$Sr(ISAH_2)^+$	$Sr(EDTA)^{2-}$	$Sr(CO_3)$	$Sr(SO_4)$					

Table A4-11. Speciation in the 1BMA. $[ISA]_{aq} = 2.9·10^{–4}$ M (considering ISA sorption). Porewater C, pH = 11.60, $[Ca]_{aq} = 2.59·10^{–3}$ M, $[Am]_{aq} = 1.4·10^{–10}$ M, $[Eu]_{aq} = 3.5·10^{–12}$ M, $[Th]_{aq} = 1.7·10^{–9}$ M, $[U]_{aq} = 3.5·10^{–7}$ M, $[Pu]_{aq} = 1.7·10^{–9}$ M, $[Cd]_{aq} = 1.9·10^{–13}$ M, $[Pb]_{aq} = 1.4·10^{–15}$ M, $[Sr]_{aq} = 2.7·10^{–10}$ M.

ISA	$ISAH_2^–$ 91.7%	Ca(ISAH) 1.8%	$Ca(ISAH_2)^+$ 6.4%								
Am	$Am(OH)_2^+$ 2.4%	$Am(OH)_3$ 6.8%	$Am(OH)_4^–$	$Am(OH)_3(ISAH_2)^–$ 90.8%	$Am(EDTA)^–$	$Am(CO_3)^+$	$Am(CO_3)_2^–$				
Eu	$Eu(OH)_2^+$	$Eu(OH)_3$ 1.8%	$Eu(OH)_4^–$	$Eu(OH)_3(ISAH_2)^–$ 98.0%	$Eu(CO_3)^+$	$Eu(CO_3)_2^–$					
Th	$Th(OH)_4$ 1.0%	$Th(OH)_4(ISAH_2)^–$ 4.2%	$Th(OH)_4(ISAH_2)_2^{2–}$	$CaTh(OH)_4(ISAH_2)^+$ 93.8%	$Th(OH)_3(CO_3)^–$	$Th(OH)_2(CO_3)_2^{2–}$	$Th(OH)_4(CO_3)^{2–}$				
U*	$UO_2(OH)_3^–$ 20.0%	$UO_2(OH)_4^{2–}$ 8.2%	$UO_2(OH)_4(ISAH_2)^{3–}$ 71.8%	$UO_2(CO_3)_3^{4–}$	$UO_2(CO_3)_2^{2–}$	$Ca_2UO_2(CO_3)_3$	$CaUO_2(CO_3)_3^{2–}$				
Pu	$Pu(OH)_4$	$Pu(OH)_4(ISAH_2)^–$ 12.7%	$Pu(OH)_4(ISAH_2)_2^{2–}$ 86.7%	$Pu(OH)_3(ISAH_2)$	$Pu(OH)_3(ISAH_2)_2^–$	$Pu(CO_3)_2(OH)_2^{2–}$					
Cd	Cd^{2+}	$Cd(OH)^+$ 13.6%	$Cd(OH)_2$ 72.2%	$Cd(OH)_3^–$ 13.0%	$Cd(OH)_4^{2–}$	$Cd(OH)_3(ISAH_2)^{2–}$	$Cd(ISAH_2)^+$	$Cd(EDTA)^{2–}$	$Cd(OH)(EDTA)^{3–}$	$Cd(CO_3)$	$CdCl^+$
Pb	$Pb(OH)^+$	$Pb(OH)_2$	$Pb(OH)_3^–$ 24.1%	$Pb(OH)_4^{2–}$ 27.9%	$Pb(OH)_2(ISAH_2)^–$ 47.1%	$Pb(EDTA)^{2–}$	$Pb(CO_3)$	$Pb(CO_3)_2^{2–}$			
Sr	Sr^{2+} 92.1%	$Sr(OH)^+$ 1.3%	$Sr(ISAH_2)^+$	$Sr(EDTA)^{2–}$	$Sr(CO_3)$	$Sr(SO_4)$ 5.5%					

Table A4-12. Speciation in the 1BMA. $[ISA]_{aq} = 2.9 \cdot 10^{-4}$ M (considering ISA sorption). Porewater D, pH = 9.66, $[Ca]_{aq} = 4.57 \cdot 10^{-5}$ M, $[Am]_{aq} = 1.4 \cdot 10^{-10}$ M, $[Eu]_{aq} = 3.5 \cdot 10^{-12}$ M, $[Th]_{aq} = 1.7 \cdot 10^{-9}$ M, $[U]_{aq} = 4.8 \cdot 10^{-7}$ M, $[Pu]_{aq} = 1.7 \cdot 10^{-9}$ M, $[Cd]_{aq} = 1.9 \cdot 10^{-13}$ M, $[Pb]_{aq} = 1.4 \cdot 10^{-15}$ M, $[Sr]_{aq} = 2.7 \cdot 10^{-10}$ M.

ISA	$ISAH_2^-$ 99.9%	$Ca(ISAH)$	$Ca(ISAH_2)^+$								
Am	$Am(OH)_2^+$ 15.6%	$Am(OH)_3$	$Am(OH)_4^-$	$Am(OH)_3(ISAH_2)^-$ 7.5%	$Am(EDTA)^-$	$Am(CO_3)^+$ 9.6%	$Am(CO_3)_2^-$ 61.5%				
Eu	$Eu(OH)_2^+$ 2.3%	$Eu(OH)_3$	$Eu(OH)_4^-$	$Eu(OH)_3(ISAH_2)^-$ 17.4%	$Eu(CO_3)^+$ 5.6%	$Eu(CO_3)_2^-$ 71.8%					
Th	$Th(OH)_4$ 9.7%	$Th(OH)_4(ISAH_2)^-$ 44.8%	$Th(OH)_4(ISAH_2)_2^{2-}$ 10.0%	$CaTh(OH)_4(ISAH_2)^+$ 18.1%	$Th(OH)_3(CO_3)^-$ 15.1%	$Th(OH)_2(CO_3)_2^{2-}$ 1.8%	$Th(OH)_4(CO_3)^{2-}$				
U	$UO_2(OH)_3^-$	$UO_2(OH)_4^{2-}$	$UO_2(OH)_4(ISAH_2)^{3-}$	$UO_2(CO_3)_3^{4-}$ 35.0%	$UO_2(CO_3)_2^{2-}$	$Ca_2UO_2(CO_3)_3$ 3.5%	$CaUO_2(CO_3)_3^{2-}$ 60.7%				
Pu	$Pu(OH)_4$	$Pu(OH)_4(ISAH_2)^-$ 12.3%	$Pu(OH)_4(ISAH_2)_2^{2-}$ 86.6%	$Pu(OH)_3(ISAH_2)$	$Pu(OH)_3(ISAH_2)_2^-$	$Pu(CO_3)_2(OH)_2^{2-}$					
Cd	Cd^{2+} 16.2%	$Cd(OH)^+$ 4.6%	$Cd(OH)_2$	$Cd(OH)_3^-$	$Cd(OH)_4^{2-}$	$Cd(OH)_3(ISAH_2)^{2-}$	$Cd(ISAH_2)^+$ 1.3%	$Cd(EDTA)^{2-}$	$Cd(OH)(EDTA)^{3-}$	$Cd(CO_3)$ 70.2%	$CdCl^+$ 5.5%
Pb	$Pb(OH)^+$ 1.1%	$Pb(OH)_2$ 1.6%	$Pb(OH)_3^-$	$Pb(OH)_4^{2-}$	$Pb(OH)_2(ISAH_2)^-$ 86.0%	$Pb(EDTA)^{2-}$	$Pb(CO_3)$ 8.7%	$Pb(CO_3)_2^{2-}$ 2.2%			
Sr	Sr^{2+} 89.2%	$Sr(OH)^+$	$Sr(ISAH_2)^+$	$Sr(EDTA)^{2-}$	$Sr(CO_3)$ 5.0%	$Sr(SO_4)$ 4.0%					

Table A4-13. Speciation in the 1BMA. $[\mathrm{EDTA}]_{aq} = 3.8\cdot10^{-6}$ M. Porewater A, pH = 13.06, $[\mathrm{Ca}]_{aq} = 1.48\cdot10^{-3}$ M, $[\mathrm{Ag}]_{aq} = 1.4\cdot10^{-10}$ M, $[\mathrm{Cd}]_{aq} = 1.9\cdot10^{-13}$ M, $[\mathrm{Sr}]_{aq} = 2.7\cdot10^{-10}$ M.

EDTA	$EDTA^{4-}$	$Ca(EDTA)^{2-}$ 100.0%	$Mg(EDTA)^{2-}$	$Na(EDTA)^{3-}$							
Ag	Ag^{+}	$Ag(OH)$ 5.9%	$Ag(OH)_2^{-}$ 92.0%	$Ag(EDTA)^{3-}$	$AgCl$ 1.1%	$AgCl_2^{-}$					
Cd	Cd^{2+}	$Cd(OH)^{+}$	$Cd(OH)_2$ 12.0%	$Cd(OH)_3^{-}$ 74.6%	$Cd(OH)_4^{2-}$ 13.0%	$Cd(OH)_3(ISAH_2)^{2-}$	$Cd(ISAH_2)^{+}$	$Cd(EDTA)^{2-}$	$Cd(OH)(EDTA)^{3-}$	$Cd(CO_3)$	$CdCl^{+}$
Sr	Sr^{2+} 75.1%	$Sr(OH)^{+}$ 19.0%	$Sr(ISAH_2)^{+}$	$Sr(EDTA)^{2-}$	$Sr(CO_3)$ 5.4%	$Sr(SO_4)$					

Table A4-14. Speciation in the 1BMA. $[\mathrm{EDTA}]_{aq} = 3.8\cdot10^{-6}$ M. Porewater B, pH = 12.60, $[\mathrm{Ca}]_{aq} = 2.00\cdot10^{-2}$ M, $[\mathrm{Ag}]_{aq} = 1.4\cdot10^{-10}$ M, $[\mathrm{Cd}]_{aq} = 1.9\cdot10^{-13}$ M, $[\mathrm{Sr}]_{aq} = 2.7\cdot10^{-10}$ M.

EDTA	$EDTA^{4-}$	$Ca(EDTA)^{2-}$ 100.0%	$Mg(EDTA)^{2-}$	$Na(EDTA)^{3-}$							
Ag	Ag^{+} 4.4%	$Ag(OH)$ 13.9%	$Ag(OH)_2^{-}$ 69.1%	$Ag(EDTA)^{3-}$	$AgCl$ 10.5%	$AgCl_2^{-}$ 2.1%					
Cd	Cd^{2+}	$Cd(OH)^{+}$	$Cd(OH)_2$ 32.2%	$Cd(OH)_3^{-}$ 63.7%	$Cd(OH)_4^{2-}$ 3.1%	$Cd(OH)_3(ISAH_2)^{2-}$	$Cd(ISAH_2)^{+}$	$Cd(EDTA)^{2-}$	$Cd(OH)(EDTA)^{3-}$	$Cd(CO_3)$	$CdCl^{+}$
Sr	Sr^{2+} 90.0%	$Sr(OH)^{+}$ 9.8%	$Sr(ISAH_2)^{+}$	$Sr(EDTA)^{2-}$	$Sr(CO_3)$	$Sr(SO_4)$					

Table A4-15. Speciation in the 1BMA. $[EDTA]_{aq} = 3.8\cdot10^{-6}$ M. Porewater C, pH = 11.60, $[Ca]_{aq} = 2.59\cdot10^{-3}$ M, $[Ag]_{aq} = 1.4\cdot10^{-10}$ M, $[Cd]_{aq} = 1.9\cdot10^{-13}$ M, $[Sr]_{aq} = 2.7\cdot10^{-10}$ M.

EDTA	$EDTA^{4-}$	$Ca(EDTA)^{2-}$ 100.0%	$Mg(EDTA)^{2-}$	$Na(EDTA)^{3-}$							
Ag	Ag^{+} 7.4%	Ag(OH) 2.6%	$Ag(OH)_2^{-}$ 1.2%	$Ag(EDTA)^{3-}$	AgCl 57.6%	$AgCl_2^{-}$ 30.9%					
Cd	Cd^{2+}	$Cd(OH)^{+}$ 3.9%	$Cd(OH)_2$ 20.5%	$Cd(OH)_3^{-}$ 3.7%	$Cd(OH)_4^{2-}$	$Cd(OH)_3(ISAH_2)^{2-}$	$Cd(ISAH_2)^{+}$	$Cd(EDTA)^{2-}$ 71.5%	$Cd(OH)(EDTA)^{3-}$	$Cd(CO_3)$	$CdCl^{+}$
Sr	Sr^{2+} 92.5%	$Sr(OH)^{+}$ 1.3%	$Sr(ISAH_2)^{+}$	$Sr(EDTA)^{2-}$	$Sr(CO_3)$	$Sr(SO_4)$ 5.6%					

Table A4-16. Speciation in the 1BMA. $[EDTA]_{aq} = 3.8\cdot10^{-6}$ M. Porewater D, pH = 9.66, $[Ca]_{aq} = 4.57\cdot10^{-5}$ M, $[Ag]_{aq} = 1.4\cdot10^{-10}$ M, $[Cd]_{aq} = 1.9\cdot10^{-13}$ M, $[Sr]_{aq} = 2.7\cdot10^{-10}$ M.

EDTA	$EDTA^{4-}$	$Ca(EDTA)^{2-}$ 98.8%	$Mg(EDTA)^{2-}$ 1.2%	$Na(EDTA)^{3-}$							
Ag	Ag^{+} 7.3%	Ag(OH)	$Ag(OH)_2^{-}$	$Ag(EDTA)^{3-}$	AgCl 59.8%	$AgCl_2^{-}$ 32.1%					
Cd	Cd^{2+}	$Cd(OH)^{+}$	$Cd(OH)_2$	$Cd(OH)_3^{-}$	$Cd(OH)_4^{2-}$	$Cd(OH)_3(ISAH_2)^{2-}$	$Cd(ISAH_2)^{+}$	$Cd(EDTA)^{2-}$ 100.0%	$Cd(OH)(EDTA)^{3-}$	$Cd(CO_3)$	$CdCl^{+}$
Sr	Sr^{2+} 89.6%	$Sr(OH)^{+}$	$Sr(ISAH_2)^{+}$	$Sr(EDTA)^{2-}$	$Sr(CO_3)$ 5.0%	$Sr(SO_4)$ 4.1%					

Table A4-17. Speciation in the BTF. $[ISA]_{aq} = 4.5 \cdot 10^{-6}$ M (considering ISA sorption). Porewater A, pH = 13.06, $[Ca]_{aq} = 1.48 \cdot 10^{-3}$ M, $[Am]_{aq} = 2.0 \cdot 10^{-11}$ M, $[Eu]_{aq} = 3.9 \cdot 10^{-13}$ M, $[Th]_{aq} = 2.6 \cdot 10^{-10}$ M, $[U]_{aq} = 5.6 \cdot 10^{-6}$ M, $[Pu]_{aq} = 2.6 \cdot 10^{-10}$ M, $[Cd]_{aq} = 2.3 \cdot 10^{-14}$ M, $[Pb]_{aq} = 1.1 \cdot 10^{-13}$ M, $[Sr]_{aq} = 3.1 \cdot 10^{-11}$ M.

ISA	$ISAH_2^-$ 73.2%	$Ca(ISAH)$ 5.9%	$Ca(ISAH_2)^+$								
Am	$Am(OH)_2^+$ 1.2%	$Am(OH)_3$ 80.8%	$Am(OH)_4^-$ 4.0%	$Am(OH)_3(ISAH_2)^-$ 13.9%	$Am(EDTA)^-$	$Am(CO_3)^+$	$Am(CO_3)_2^-$				
Eu	$Eu(OH)_2^+$	$Eu(OH)_3$ 57.5%	$Eu(OH)_4^-$ 2.8%	$Eu(OH)_3(ISAH_2)^-$ 39.4%	$Eu(CO_3)^+$	$Eu(CO_3)_2^-$					
Th	$Th(OH)_4$ 74.9%	$Th(OH)_4(ISAH_2)^-$ 4.1%	$Th(OH)_4(ISAH_2)_2^{2-}$	$CaTh(OH)_4(ISAH_2)^+$ 15.6%	$Th(OH)_3(CO_3)^-$	$Th(OH)_2(CO_3)_2^{2-}$	$Th(OH)_4(CO_3)^{2-}$ 5.3%				
U*	$UO_2(OH)_3^-$ 4.3%	$UO_2(OH)_4^{2-}$ 79.6%	$UO_2(OH)_4(ISAH_2)^{3-}$ 16.1%	$UO_2(CO_3)_3^{4-}$	$UO_2(CO_3)_2^{2-}$	$Ca_2UO_2(CO_3)_3$	$CaUO_2(CO_3)_3^{2-}$				
Pu	$Pu(OH)_4$ 76.7%	$Pu(OH)_4(ISAH_2)^-$ 20.9%	$Pu(OH)_4(ISAH_2)_2^{2-}$ 2.4%	$Pu(OH)_3(ISAH_2)$	$Pu(OH)_3(ISAH_2)_2^-$	$Pu(CO_3)_2(OH)_2^{2-}$					
Cd	Cd^{2+}	$Cd(OH)^+$	$Cd(OH)_2$ 12.0%	$Cd(OH)_3^-$ 74.8%	$Cd(OH)_4^{2-}$ 13.1%	$Cd(OH)_3(ISAH_2)^{2-}$	$Cd(ISAH_2)^+$	$Cd(EDTA)^{2-}$	$Cd(OH)(EDTA)^{3-}$	$Cd(CO_3)$	$CdCl^+$
Pb	$Pb(OH)^+$	$Pb(OH)_2$	$Pb(OH)_3^-$ 1.9%	$Pb(OH)_4^{2-}$ 98.1%	$Pb(OH)_2(ISAH_2)^-$	$Pb(EDTA)^{2-}$	$Pb(CO_3)$	$Pb(CO_3)_2^{2-}$			
Sr	Sr^{2+} 75.1%	$Sr(OH)^+$ 19.0%	$Sr(ISAH_2)^+$	$Sr(EDTA)^{2-}$	$Sr(CO_3)$ 5.4%	$Sr(SO_4)$					

Table A4-18. Speciation in the BTF. $[\mathrm{ISA}]_{aq} = 4.5\cdot10^{-6}$ M (considering ISA sorption). Porewater B, pH = 12.60, $[\mathrm{Ca}]_{aq} = 2.00\cdot10^{-2}$ M, $[\mathrm{Am}]_{aq} = 2.0\cdot10^{-11}$ M, $[\mathrm{Eu}]_{aq} = 3.9\cdot10^{-13}$ M, $[\mathrm{Th}]_{aq} = 2.6\cdot10^{-10}$ M, $[\mathrm{U}]_{aq} = 2.9\cdot10^{-7}$ M, $[\mathrm{Pu}]_{aq} = 2.6\cdot10^{-10}$ M, $[\mathrm{Cd}]_{aq} = 2.3\cdot10^{-14}$ M, $[\mathrm{Pb}]_{aq} = 1.1\cdot10^{-13}$ M, $[\mathrm{Sr}]_{aq} = 3.1\cdot10^{-11}$ M.

ISA	$\mathrm{ISAH_2^-}$ 46.6%	Ca(ISAH) 37.9%	$\mathrm{Ca(ISAH_2)^+}$ 15.0%								
Am	$\mathrm{Am(OH)_2^+}$ 3.3%	$\mathrm{Am(OH)_3}$ 84.2%	$\mathrm{Am(OH)_4^-}$ 1.3%	$\mathrm{Am(OH)_3(ISAH_2)^-}$ 9.0%	$\mathrm{Am(EDTA)^-}$	$\mathrm{Am(CO_3)^+}$	$\mathrm{Am(CO_3)_2^-}$				
Eu	$\mathrm{Eu(OH)_2^+}$	$\mathrm{Eu(OH)_3}$ 67.7%	$\mathrm{Eu(OH)_4^-}$ 1.1%	$\mathrm{Eu(OH)_3(ISAH_2)^-}$ 28.8%	$\mathrm{Eu(CO_3)^+}$	$\mathrm{Eu(CO_3)_2^-}$					
Th	$\mathrm{Th(OH)_4}$ 22.4%	$\mathrm{Th(OH)_4(ISAH_2)^-}$	$\mathrm{Th(OH)_4(ISAH_2)_2^{2-}}$	$\mathrm{CaTh(OH)_4(ISAH_2)^+}$ 76.8%	$\mathrm{Th(OH)_3(CO_3)^-}$	$\mathrm{Th(OH)_2(CO_3)_2^{2-}}$	$\mathrm{Th(OH)_4(CO_3)^{2-}}$				
U*	$\mathrm{UO_2(OH)_3^-}$ 14.7%	$\mathrm{UO_2(OH)_4^{2-}}$ 77.7%	$\mathrm{UO_2(OH)_4(ISAH_2)^{3-}}$ 7.5%	$\mathrm{UO_2(CO_3)_3^{4-}}$	$\mathrm{UO_2(CO_3)_2^{2-}}$	$\mathrm{Ca_2UO_2(CO_3)_3}$	$\mathrm{CaUO_2(CO_3)_3^{2-}}$				
Pu	$\mathrm{Pu(OH)_4}$ 84.7%	$\mathrm{Pu(OH)_4(ISAH_2)^-}$ 14.3%	$\mathrm{Pu(OH)_4(ISAH_2)_2^{2-}}$	$\mathrm{Pu(OH)_3(ISAH_2)}$	$\mathrm{Pu(OH)_3(ISAH_2)_2^-}$	$\mathrm{Pu(CO_3)_2(OH)_2^{2-}}$					
Cd	$\mathrm{Cd^{2+}}$	$\mathrm{Cd(OH)^+}$	$\mathrm{Cd(OH)_2}$ 32.3%	$\mathrm{Cd(OH)_3^-}$ 63.9%	$\mathrm{Cd(OH)_4^{2-}}$ 3.1%	$\mathrm{Cd(OH)_3(ISAH_2)^{2-}}$	$\mathrm{Cd(ISAH_2)^+}$	$\mathrm{Cd(EDTA)^{2-}}$	$\mathrm{Cd(OH)(EDTA)^{3-}}$	$\mathrm{Cd(CO_3)}$	$\mathrm{CdCl^+}$
Pb	$\mathrm{Pb(OH)^+}$	$\mathrm{Pb(OH)_2}$	$\mathrm{Pb(OH)_3^-}$ 6.3%	$\mathrm{Pb(OH)_4^{2-}}$ 93.7%	$\mathrm{Pb(OH)_2(ISAH_2)^-}$	$\mathrm{Pb(EDTA)^{2-}}$	$\mathrm{Pb(CO_3)}$	$\mathrm{Pb(CO_3)_2^{2-}}$			
Sr	$\mathrm{Sr^{2+}}$ 90.0%	$\mathrm{Sr(OH)^+}$ 9.8%	$\mathrm{Sr(ISAH_2)^+}$	$\mathrm{Sr(EDTA)^{2-}}$	$\mathrm{Sr(CO_3)}$	$\mathrm{Sr(SO_4)}$					

Table A4-19. Speciation in the BTF. $[ISA]_{aq} = 4.5 \cdot 10^{-6}$ M (considering ISA sorption). Porewater C, pH = 11.60, $[Ca]_{aq} = 2.59 \cdot 10^{-3}$ M, $[Am]_{aq} = 2.0 \cdot 10^{-11}$ M, $[Eu]_{aq} = 3.9 \cdot 10^{-13}$ M, $[Th]_{aq} = 2.6 \cdot 10^{-10}$ M, $[U]_{aq} = 1.0 \cdot 10^{-7}$ M, $[Pu]_{aq} = 2.6 \cdot 10^{-10}$ M, $[Cd]_{aq} = 2.3 \cdot 10^{-14}$ M, $[Pb]_{aq} = 1.1 \cdot 10^{-13}$ M, $[Sr]_{aq} = 3.1 \cdot 10^{-11}$ M.

ISA	$ISAH_2^-$	$Ca(ISAH)$	$Ca(ISAH_2)^+$								
	91.6%	1.8%	6.5%								
Am	$Am(OH)_2^+$	$Am(OH)_3$	$Am(OH)_4^-$	$Am(OH)_3(ISAH_2)^-$	$Am(EDTA)^-$	$Am(CO_3)^+$	$Am(CO_3)_2^-$				
	22.8%	63.8%		13.2%							
Eu	$Eu(OH)_2^+$	$Eu(OH)_3$	$Eu(OH)_4^-$	$Eu(OH)_3(ISAH_2)^-$	$Eu(CO_3)^+$	$Eu(CO_3)_2^-$					
	4.7%	52.1%		43.0%							
Th	$Th(OH)_4$	$Th(OH)_4(ISAH_2)^-$	$Th(OH)_4(ISAH_2)_2^{2-}$	$CaTh(OH)_4(ISAH_2)^+$	$Th(OH)_3(CO_3)^-$	$Th(OH)_2(CO_3)_2^{2-}$	$Th(OH)_4(CO_3)^{2-}$				
	39.5%	2.6%		57.9%							
U*	$UO_2(OH)_3^-$	$UO_2(OH)_4^{2-}$	$UO_2(OH)_4(ISAH_2)^{3-}$	$UO_2(CO_3)_3^{4-}$	$UO_2(CO_3)_2^{2-}$	$Ca_2UO_2(CO_3)_3$	$CaUO_2(CO_3)_3^{2-}$				
	68.1%	28.1%	3.8%								
Pu	$Pu(OH)_4$	$Pu(OH)_4(ISAH_2)^-$	$Pu(OH)_4(ISAH_2)_2^{2-}$	$Pu(OH)_3(ISAH_2)$	$Pu(OH)_3(ISAH_2)_2^-$	$Pu(CO_3)_2(OH)_2^{2-}$					
	73.3%	24.1%	2.5%								
Cd	Cd^{2+}	$Cd(OH)^+$	$Cd(OH)_2$	$Cd(OH)_3^-$	$Cd(OH)_4^{2-}$	$Cd(OH)_3(ISAH_2)^{2-}$	$Cd(ISAH_2)^+$	$Cd(EDTA)^{2-}$	$Cd(OH)(EDTA)^{3-}$	$Cd(CO_3)$	$CdCl^+$
		13.6%	72.4%	13.1%							
Pb	$Pb(OH)^+$	$Pb(OH)_2$	$Pb(OH)_3^-$	$Pb(OH)_4^{2-}$	$Pb(OH)_2(ISAH_2)^-$	$Pb(EDTA)^{2-}$	$Pb(CO_3)$	$Pb(CO_3)_2^{2-}$			
		1.8%	44.8%	52.0%	1.4%						
Sr	Sr^{2+}	$Sr(OH)^+$	$Sr(ISAH_2)^+$	$Sr(EDTA)^{2-}$	$Sr(CO_3)$	$Sr(SO_4)$					
	92.5%	1.3%				5.6%					

Table A4-20. Speciation in the BTF. $[ISA]_{aq} = 4.5 \cdot 10^{-6}$ M (considering ISA sorption). Porewater D, pH = 9.66, $[Ca]_{aq} = 4.57 \cdot 10^{-5}$ M, $[Am]_{aq} = 2.0 \cdot 10^{-11}$ M, $[Eu]_{aq} = 3.9 \cdot 10^{-13}$ M, $[Th]_{aq} = 2.6 \cdot 10^{-10}$ M, $[U]_{aq} = 2.1 \cdot 10^{-6}$ M, $[Pu]_{aq} = 2.6 \cdot 10^{-10}$ M, $[Cd]_{aq} = 2.3 \cdot 10^{-14}$ M, $[Pb]_{aq} = 1.1 \cdot 10^{-13}$ M, $[Sr]_{aq} = 3.1 \cdot 10^{-11}$ M.

ISA	$ISAH_2^-$ 99.9%	$Ca(ISAH)$	$Ca(ISAH_2)^+$								
Am	$Am(OH)_2^+$ 16.9%	$Am(OH)_3$	$Am(OH)_4^-$	$Am(OH)_3(ISAH_2)^-$	$Am(EDTA)^-$	$Am(CO_3)^+$ 10.4%	$Am(CO_3)_2^-$ 66.2%				
Eu	$Eu(OH)_2^+$ 2.8%	$Eu(OH)_3$	$Eu(OH)_4^-$	$Eu(OH)_3(ISAH_2)^-$	$Eu(CO_3)^+$ 6.8%	$Eu(CO_3)_2^-$ 86.6%					
Th	$Th(OH)_4$ 35.2%	$Th(OH)_4(ISAH_2)^-$ 2.5%	$Th(OH)_4(ISAH_2)_2^{2-}$	$CaTh(OH)_4(ISAH_2)^+$	$Th(OH)_3(CO_3)^-$ 54.5%	$Th(OH)_2(CO_3)_2^{2-}$ 6.4%	$Th(OH)_4(CO_3)^{2-}$				
U*	$UO_2(OH)_3^-$	$UO_2(OH)_4^{2-}$	$UO_2(OH)_4(ISAH_2)^{3-}$	$UO_2(CO_3)_3^{4-}$ 37.2%	$UO_2(CO_3)_2^{2-}$	$Ca_2UO_2(CO_3)_3$ 3.0%	$CaUO_2(CO_3)_3^{2-}$ 58.8%				
Pu	$Pu(OH)_4$ 69.7%	$Pu(OH)_4(ISAH_2)^-$ 25.0%	$Pu(OH)_4(ISAH_2)_2^{2-}$ 2.7%	$Pu(OH)_3(ISAH_2)$ 1.1%	$Pu(OH)_3(ISAH_2)_2^-$	$Pu(CO_3)_2(OH)_2^{2-}$ 1.5%					
Cd	Cd^{2+} 16.5%	$Cd(OH)^+$ 4.6%	$Cd(OH)_2$	$Cd(OH)_3^-$	$Cd(OH)_4^{2-}$	$Cd(OH)_3(ISAH_2)^{2-}$	$Cd(ISAH_2)^+$	$Cd(EDTA)^{2-}$	$Cd(OH)(EDTA)^{3-}$	$Cd(CO_3)$ 70.9%	$CdCl^+$ 5.6%
Pb	$Pb(OH)^+$ 6.9%	$Pb(OH)_2$ 10.3%	$Pb(OH)_3^-$ 2.9%	$Pb(OH)_4^{2-}$	$Pb(OH)_2(ISAH_2)^-$ 8.7%	$Pb(EDTA)^{2-}$	$Pb(CO_3)$ 56.8%	$Pb(CO_3)_2^{2-}$ 14.3%			
Sr	Sr^{2+} 89.7%	$Sr(OH)^+$	$Sr(ISAH_2)^+$	$Sr(EDTA)^{2-}$	$Sr(CO_3)$ 5.0%	$Sr(SO_4)$ 4.1%					

Table A4-21. Speciation in the BTF. $[\mathrm{EDTA}]_{aq} = 1.3 \cdot 10^{-6}$ M. Porewater A, pH = 13.06, $[\mathrm{Ca}]_{aq} = 1.48 \cdot 10^{-3}$ M, $[\mathrm{Ag}]_{aq} = 1.9 \cdot 10^{-11}$ M, $[\mathrm{Cd}]_{aq} = 2.3 \cdot 10^{-14}$ M, $[\mathrm{Sr}]_{aq} = 3.1 \cdot 10^{-11}$ M.

EDTA	EDTA^{4-}	$\mathrm{Ca(EDTA)}^{2-}$	$\mathrm{Mg(EDTA)}^{2-}$	$\mathrm{Na(EDTA)}^{3-}$							
		100.0%									
Ag	Ag^{+}	$\mathrm{Ag(OH)}$	$\mathrm{Ag(OH)}_2^{-}$	$\mathrm{Ag(EDTA)}^{3-}$	AgCl	AgCl_2^{-}					
		5.9%	92.0%		1.1%						
Cd	Cd^{2+}	$\mathrm{Cd(OH)}^{+}$	$\mathrm{Cd(OH)}_2$	$\mathrm{Cd(OH)}_3^{-}$	$\mathrm{Cd(OH)}_4^{2-}$	$\mathrm{Cd(OH)}_3\mathrm{(ISAH}_2)^{2-}$	$\mathrm{Cd(ISAH}_2)^{+}$	$\mathrm{Cd(EDTA)}^{2-}$	$\mathrm{Cd(OH)(EDTA)}^{3-}$	$\mathrm{Cd(CO}_3)$	CdCl^{+}
			12.0%	74.8%	13.0%						
Sr	Sr^{2+}	$\mathrm{Sr(OH)}^{+}$	$\mathrm{Sr(ISAH}_2)^{+}$	$\mathrm{Sr(EDTA)}^{2-}$	$\mathrm{Sr(CO}_3)$	$\mathrm{Sr(SO}_4)$					
	75.1%	19.0%			5.4%						

Table A4-22. Speciation in the BTF. $[\mathrm{EDTA}]_{aq} = 1.3 \cdot 10^{-6}$ M. Porewater B, pH = 12.60, $[\mathrm{Ca}]_{aq} = 2.00 \cdot 10^{-6}$ M, $[\mathrm{Ag}]_{aq} = 1.9 \cdot 10^{-11}$ M, $[\mathrm{Cd}]_{aq} = 2.3 \cdot 10^{-14}$ M, $[\mathrm{Sr}]_{aq} = 3.1 \cdot 10^{-11}$ M.

EDTA	EDTA^{4-}	$\mathrm{Ca(EDTA)}^{2-}$	$\mathrm{Mg(EDTA)}^{2-}$	$\mathrm{Na(EDTA)}^{3-}$							
		100.0%									
Ag	Ag^{+}	$\mathrm{Ag(OH)}$	$\mathrm{Ag(OH)}_2^{-}$	$\mathrm{Ag(EDTA)}^{3-}$	AgCl	AgCl_2^{-}					
	4.4%	13.9%	69.1%		10.5%	2.1%					
Cd	Cd^{2+}	$\mathrm{Cd(OH)}^{+}$	$\mathrm{Cd(OH)}_2$	$\mathrm{Cd(OH)}_3^{-}$	$\mathrm{Cd(OH)}_4^{2-}$	$\mathrm{Cd(OH)}_3\mathrm{(ISAH}_2)^{2-}$	$\mathrm{Cd(ISAH}_2)^{+}$	$\mathrm{Cd(EDTA)}^{2-}$	$\mathrm{Cd(OH)(EDTA)}^{3-}$	$\mathrm{Cd(CO}_3)$	CdCl^{+}
			32.3%	63.8%	3.1%						
Sr	Sr^{2+}	$\mathrm{Sr(OH)}^{+}$	$\mathrm{Sr(ISAH}_2)^{+}$	$\mathrm{Sr(EDTA)}^{2-}$	$\mathrm{Sr(CO}_3)$	$\mathrm{Sr(SO}_4)$					
	90.0%	9.8%									

Table A4-23. Speciation in the BTF. $[EDTA]_{aq} = 1.3 \cdot 10^{-6}$ M. Porewater C, pH = 11.60, $[Ca]_{aq} = 2.59 \cdot 10^{-3}$ M, $[Ag]_{aq} = 1.9 \cdot 10^{-11}$ M, $[Cd]_{aq} = 2.3 \cdot 10^{-14}$ M, $[Sr]_{aq} = 3.1 \cdot 10^{-11}$ M.

EDTA	$EDTA^{4-}$	$Ca(EDTA)^{2-}$ 100.0%	$Mg(EDTA)^{2-}$	$Na(EDTA)^{3-}$							
Ag	Ag^{+} 7.4%	$Ag(OH)$ 2.6%	$Ag(OH)_2^{-}$ 1.2%	$Ag(EDTA)^{3-}$	$AgCl$ 57.5%	$AgCl_2^{-}$ 30.9%					
Cd	Cd^{2+}	$Cd(OH)^{+}$ 7.3%	$Cd(OH)_2$ 39.0%	$Cd(OH)_3^{-}$ 7.1%	$Cd(OH)_4^{2-}$	$Cd(OH)_3(ISAH_2)^{2-}$	$Cd(ISAH_2)^{+}$	$Cd(EDTA)^{2-}$ 46.1%	$Cd(OH)(EDTA)^{3-}$	$Cd(CO_3)$	$CdCl^{+}$
Sr	Sr^{2+} 92.5%	$Sr(OH)^{+}$ 1.3%	$Sr(ISAH_2)^{+}$	$Sr(EDTA)^{2-}$	$Sr(CO_3)$	$Sr(SO_4)$ 5.6%					

Table A4-24. Speciation in the BTF. $[EDTA]_{aq} = 1.3 \cdot 10^{-6}$ M. Porewater D, pH = 9.66, $[Ca]_{aq} = 4.57 \cdot 10^{-5}$ M, $[Ag]_{aq} = 1.9 \cdot 10^{-11}$ M, $[Cd]_{aq} = 2.3 \cdot 10^{-14}$ M, $[Sr]_{aq} = 3.1 \cdot 10^{-11}$ M.

EDTA	$EDTA^{4-}$	$Ca(EDTA)^{2-}$ 98.7%	$Mg(EDTA)^{2-}$ 1.3%	$Na(EDTA)^{3-}$							
Ag	Ag^{+} 7.3%	$Ag(OH)$	$Ag(OH)_2^{-}$	$Ag(EDTA)^{3-}$	$AgCl$ 59.8%	$AgCl_2^{-}$ 32.1%					
Cd	Cd^{2+}	$Cd(OH)^{+}$	$Cd(OH)_2$	$Cd(OH)_3^{-}$	$Cd(OH)_4^{2-}$	$Cd(OH)_3(ISAH_2)^{2-}$	$Cd(ISAH_2)^{+}$	$Cd(EDTA)^{2-}$ 99.9%	$Cd(OH)(EDTA)^{3-}$	$Cd(CO_3)$	$CdCl^{+}$
Sr	Sr^{2+} 89.7%	$Sr(OH)^{+}$	$Sr(ISAH_2)^{+}$	$Sr(EDTA)^{2-}$	$Sr(CO_3)$ 5.0%	$Sr(SO_4)$ 4.1%					